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Syntheses and Studies of Acetylenic Polymers

by

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Syntheses and studies of acetylenic polymers

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A series of new diiodo aryl compounds have been conveniently synthesized. Based on these diiodo compounds, a series of novel soluble polymers, poly(2,5-dialkoxy-1,4-phenyleneethynylene)s (**PPE** polymers) have been synthesized by using a palladium-catalyzed polymerization. These **PPE** polymers have been well characterized by routine methods. The molecular weights range from 8,000 to 40,000.

The properties of these **PPE** polymers such as absorption, fluorescence, and conductivity have been studied. A **PPE** polymer with the butoxy side chain exhibits a weak electrical conductivity ($\sigma = 10^{-3}$ S/cm) after doping with AsF_5. The absorption spectra of **PPE** polymers in THF solution at room temperature show an absorption maximum at $\lambda = 440$ nm. However, the absorption spectra of **PPE** polymers in the film state at room temperature show an absorption maximum at $\lambda = 480$ nm. **PPE** polymer-based light emitting diode (**LED**) devices have been prepared and studied. Greenish light from these **LED** devices can be observed.

Furthermore, poly(ethynylene-*p*-arylene-ethynylene-silylene)s have been synthesized through the same palladium-catalyzed polymerization. These polymers have also been characterized by routine methods. The molecular weights of these polymers are between 6,000 and 82,000. Their absorption and fluorescence have been studied. Some of these polymers exhibit thermotropic liquid crystalline properties. In addition, the nonlinear optical properties of these polymers have been briefly examined.

Poly(silylene-ethynylene) homopolymers as well as alternating copolymers have been synthesized through a novel palladium-catalyzed polymerization. The molecular weights of these polymers range from $56x10^3$ to $5.3x10^3$. The thermal stability of these polymers has also been investigated and the char yields range from 51% to 83%. One of these polymers exhibits thermotropic liquid crystalline properties.

DEDICATION

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GENERAL INTRODUCTION

Acetylenic polymers have been a focus of synthesis and study in Barton's group since 1985. Poly(*p*-phenyleneethynylene), an acetylenic polymer, has been of great interest to the group because of its π conjugated backbone. Previously, however, this polymer and its derivatives have not been well studied because of synthetic difficulties. In section one of this dissertation, the synthesis and study of derivatives of poly(*p*-phenyleneethynylene) are discussed and their application in polymeric-based light emitting diode devices are explored.

Poly(ethynylene-phenylene-ethynylene-silylene)s, which are also acetylenic polymers, have both silylene and ethyne in their polymer main chain. However, π conjugation along the polymer main chain does not exist because of the introduction of silylene. These polymers have also not been studied. In section two and three, the synthesis of these polymers and the studies of their properties such as liquid crystalline properties and fluorescence are discussed.

Silylene acetylene polymers or poly(silylene-ethynylene)s, which are precursors to silicon carbide, have been previously synthesized through a condensation reaction between dichlorosilane and dianion. However, this route cannot afford silylene acetylene copolymers. In section four, the convenient synthesis of these silylene acetylene polymers as well as copolymers through a novel palladium-catalyzed polymerization is discussed.

SECTION ONE: CONJUGATED ACETYLENIC POLYMERS

INTRODUCTION

Conjugated polymers[1] have been attracting chemists' attention for more than two decades because these polymers exhibit some unique properties such as conductivity, non-linear optical properties and fluorescence. Among these conjugated polymers, poly(*p*-phenylenevinylene), hereafter referred to as **PPV**, is one of the most interesting. From the polymer structure shown in Figure 1 one can see that **PPV** has π-π conjugation along the polymer backbone and the π electrons can delocalize in the conjugated polymer main chain. **PPV** can be regarded as a regular alternating copolymer of *p*-phenylene and vinylene.

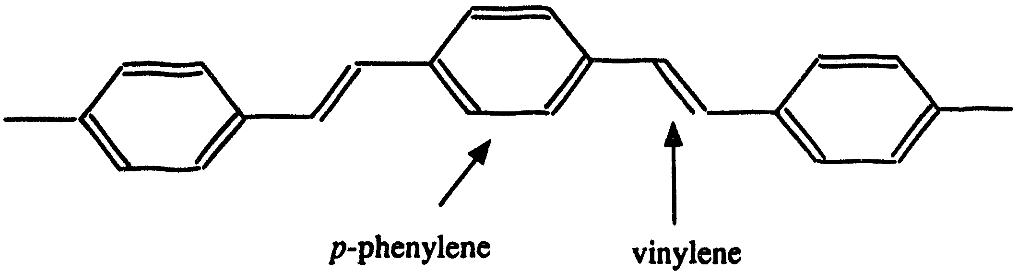


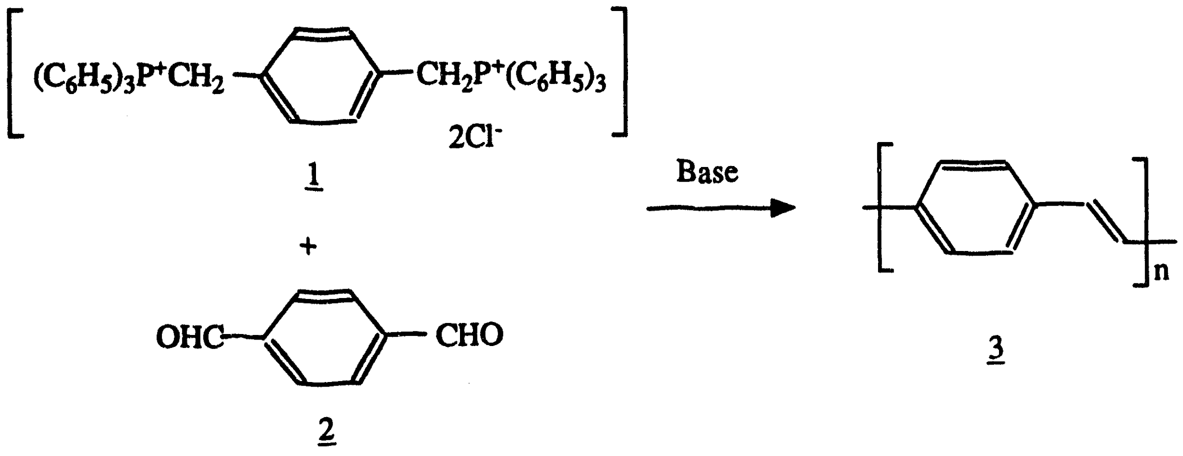
Figure 1. The structure of **PPV** polymer

PPV and its derivatives have been extensively studied because they can be synthesized by several different routes.

Direct syntheses of **PPV** and its derivatives

Poly(*p*-phenylene vinylene) 3 was first synthesized via a Wittig reaction of *p*-xylene bis(triphenylphosphonium chloride) 1 with terephthalaldehyde 2 described by

McDonald and Campbell[2], as shown in Scheme 1. The product, PPV polymer 3, is insoluble and infusible. Other groups[3] also reported the synthesis of PPV polymer through this method. However, this synthetic method can only provide an insoluble PPV powder.

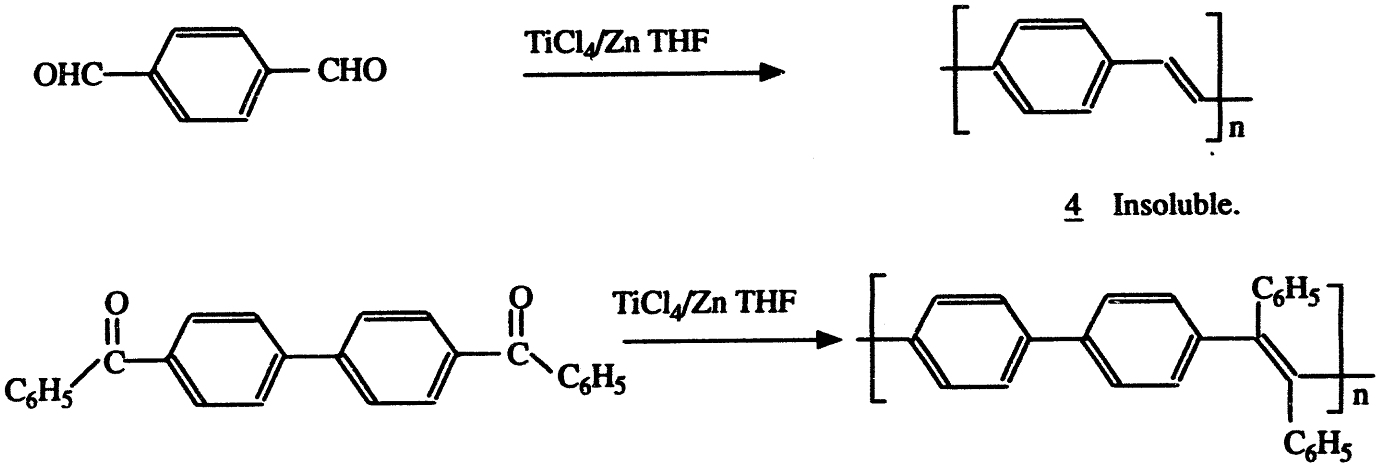


Scheme 1. Preparation of PPV via Witting reaction[2]

Later, the syntheses of PPV and its derivatives via the McMurry reaction as shown in Scheme 2 were reported by several different groups[4]. The product, PPV polymer 4, is also insoluble. However, with the side chains attached to the PPV polymer main chains, the PPV derivative 4a is soluble in a number of organic solvents[4]. Synthesis via the McMurry reaction gave the polymers 4 and 4a mainly with the entgegen (E) configuration.

The syntheses of PPV and its derivatives via precursor routes

Although the McMurry reaction can afford soluble and high molecular weight PPV derivatives, these direct attempts to synthesize high molecular weight PPV have



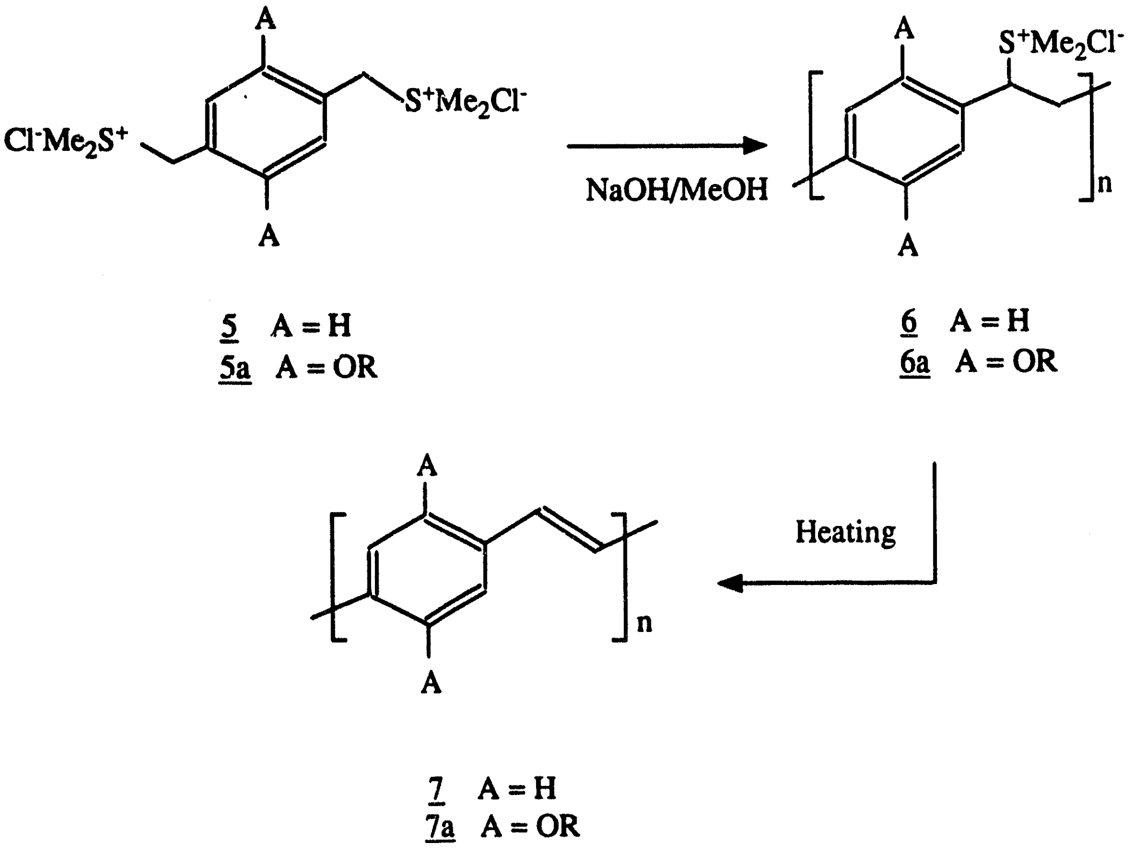
4 Insoluble.

4a Mw = 126,000
Mn = 36,000

Scheme 2. Synthesis of **PPV** via McMurry reaction[4] resulted only in the formation of oligomers because **PPV** oligomers were insoluble in the reaction media. Since **PPV** is not soluble in organic solvents, solution cast films can not be made. In order to overcome this problem the so-called "soluble precursor" synthesis, first discovered by Wessling and Zimmerman[5], was later developed by a number of groups[6] to prepare **PPV** and its derivatives. This method is illustrated in Scheme 3. The idea is that a soluble polymeric precursor can be cast into film and then converted to a conjugated **PPV** film by thermal elimination of small molecules.

The monomers, bis-sulphonium salts 5 or 5a, can be conveniently synthesized according to the literature[5]. In the first step, polymerization of a bis-sulphonium salt 5 yields a high molecular weight and water-soluble precursor polymer 6. In the second step, the precursor polymer 6 is directly converted to conjugated **PPV** polymer 7 with good mechanical properties through the thermal elimination of the sulfonium groups. Through this route, several groups have synthesized and studied **PPV** and its soluble dialkoxy[6] and dialkyl[7] derivatives.

Recently, it was reported by Grubbs[8] that **PPV** polymer can be prepared by a new precursor route shown in Scheme 4. The new precursor 9 was prepared by the living ring-opening metathesis polymerization (**ROMP**) of bis(carboxylic ester) derivatives of bicyclo [2.2.2] octa-5,8-diene-cis-2,3-diol 8. One advantage of this method is that the precursor polymer obtained has narrow molecular weight distributions (**PD** = 1.2-1.3), which is consistent with a living polymerization with slow initiation. The degree of polymerization can also be controlled. The precursor polymer 9 can be converted to **PPV** 10 upon heating. Since the conversion to **PPV** polymer 10 would not change the polymer chain length, **PPV** polymer 10 obtained from this route also has a narrow molecular weight distribution. Although the precursor polymer 9 consists of both *cis* and *trans*-vinylene units, only the *trans* isomer can be detected in the IR spectra. This fact



<u>5</u> A = H
<u>5a</u> A = OR

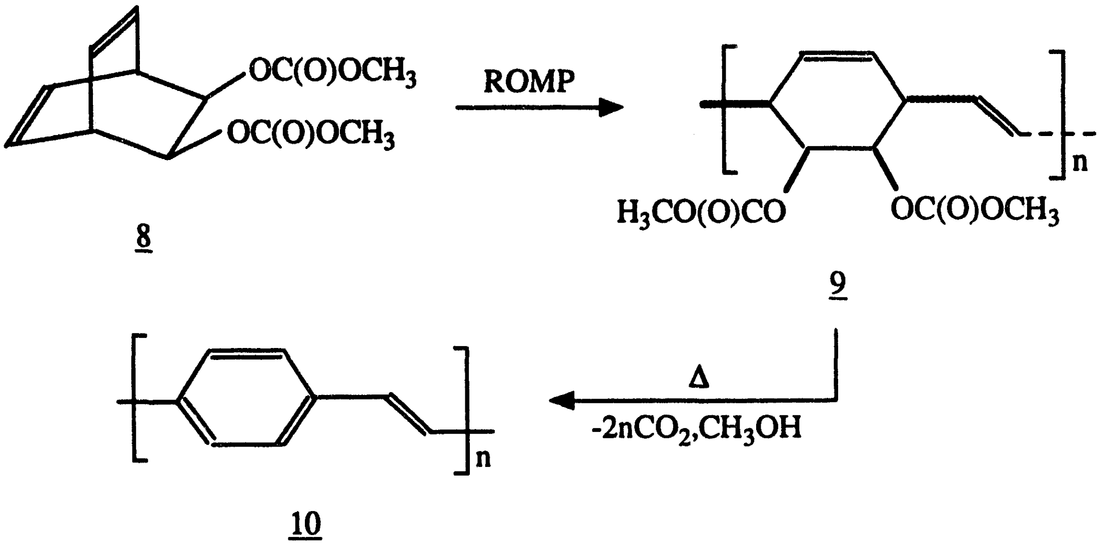
<u>6</u> A = H
<u>6a</u> A = OR

<u>7</u> A = H
<u>7a</u> A = OR

Scheme 3. Synthesis of **PPV** and its derivatives via soluble precursors[5,6]

indicates that a thermal *cis* to *trans* isomerization occurs during the elimination. The synthesis of the monomer <u>8</u> is also given therein[8]. Although precursor routes can provide good films of **PPV** and its derivatives with strong mechanical properties, there are still saturated carbons in the polymer main chain due to incomplete elimination.

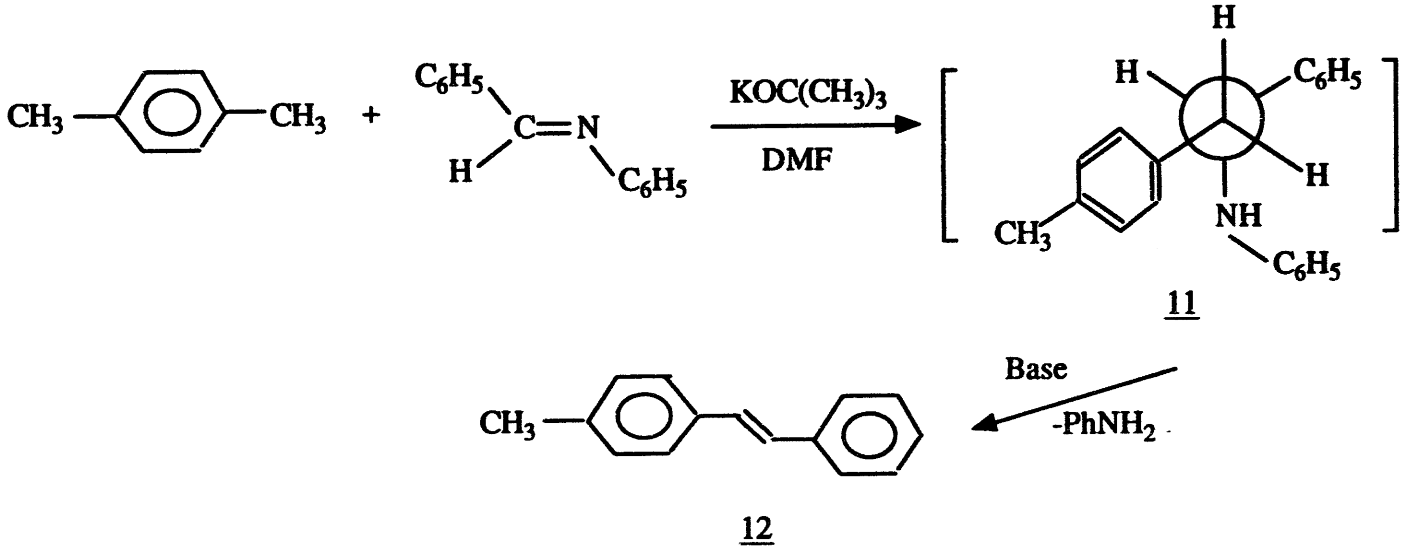
Very recently, it was reported that a **PPV** derivative <u>14</u> can also be directly synthesized via Siegrist method[9] (Scheme 5) with excellent yield. Since the selectivity in the model reaction is more than 1000:1 in favor of the **E** configuration, this method afforded a **PPV** derivative <u>14</u> with a high content of *trans*-vinylene as proved by NMR.



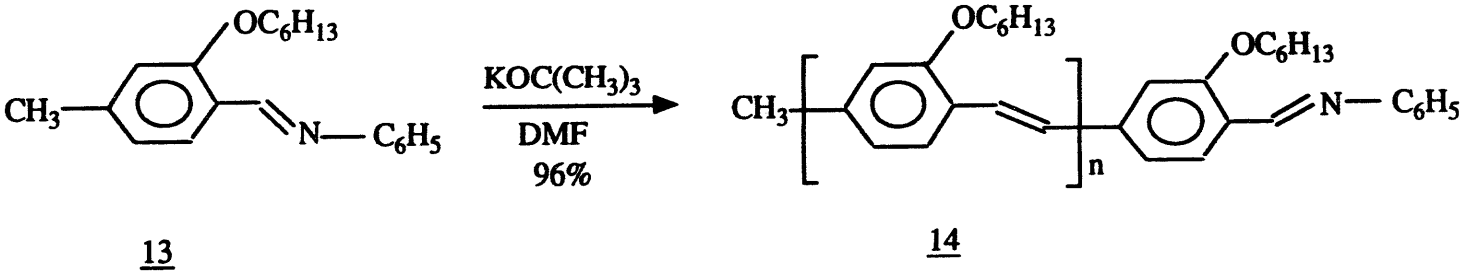
Scheme 4. Synthesis of PPV precursor through ROMP[8]

Electroconductivity

The established syntheses of PPV polymers have made the study of PPV and its derivatives possible. Since PPV polymers have a linear π-conjugated backbone, their electroconductivity has been extensively studied by a number of groups[3a,10-12]. Wnek[3a] reported that PPV, which was prepared via a Wittig reaction, had a conductivity of 3 S/cm after doping with AsF_5. He also reported that exposure of PPV to either I_2 or NH_3 vapor for several hours produced no dramatic change in electrical conductivity. Later, Murase[10] reported that stretched PPV films show extremely high conductivity of 3000 S/cm and 500 S/cm after doping with AsF_5 and SO_3, respectively. Interestingly he found that I_2 doped PPV has a low conductivity of 10^{-2} S/cm. However, these PPV films were prepared via Wessling's precursor method and the PPV had a higher molecular weight.



Model reaction



Scheme 5. Siegrist polymerization[9]

Light emitting diodes

Light-emitting diodes (LEDs) are rectifying semiconductor devices that convert electrical energy into electromagnetic radiation. They are typically inorganic solid-state devices that emit radiation in the visible region to the near infrared, i.e., in a region of about 400-1300 nm. For example, a red LED can be made of a gallium arsenide (GaAs) semiconductor. Although inorganic materials are very stable, they are not easily or economically used in large-area displays. This is because of the difficulty in scaling the fabrication to a large area. Thus LEDs for large screens can't be made of these inorganic materials.

Organic-based LEDs have been studied since 1963[13]. Although the efficiencies and selection of emission color are very good for organic material-based LEDs, there are still problems associated with the long-term stability of the sublimed organic film against crystallization and other structural changes. One way to improve the stability of these organic layers is to replace these organic monomers with polymeric materials since polymeric materials can be easily manipulated and can form amorphous layers.

Conjugated polymers are good choices for light- emitting diode devices in that they can, in principle, provide good charge transport. There is a strong possibility that these polymeric materials will find commercial use in a variety of display applications. The first conjugated polymer LED device was reported by Friend[14] in 1990. Since then, there has been a rapidly increasing number of publications[15,16] demonstrating the applications of these conjugated polymers in LED devices. Among them are PPV derivatives[15] and poly(p-phenylene)[16] (PPP) based LED devices. The color range accessible already includes the three colors (red, green and blue) required for full-color displays. These devices can be operated at low direct current drive voltages with brightness and good efficiency.

However, a lot of problems still remain before these polymeric LED devices can be commercialized. For instance, the lifetimes of polymeric LED devices for continuous operations at room temperature are not long enough and the brightness needs to be improved. In order to overcome these problems it is necessary to develop new polymers for LED devices and study the emitting mechanism.

The LED device shown in Figure 2 can be considered as a sandwich. The first layer is the hole injection layer made of ITO (indium and tin oxide). The second layer is the emissive layer made of polymeric material. The third layer is the electron injection layer made of metal with a low work function. When the electric voltage is applied to the LED device light is emitted.

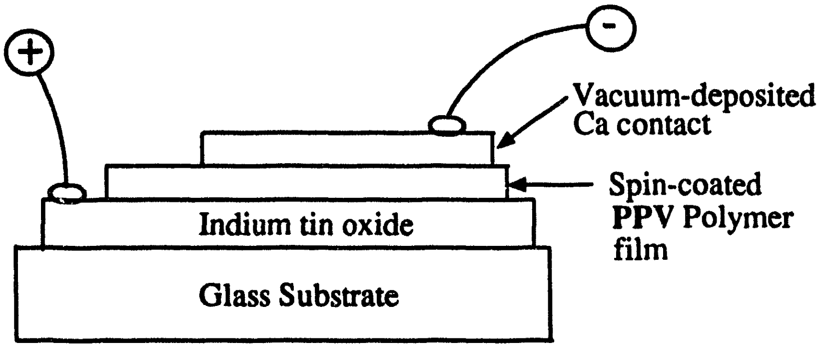


Figure 2. LED device

The proposed emitting mechanism[17] for the polymeric LED devices is explained in Figures 3 and 4. In Figure 3 ϕ_{Ito} and ϕ_{ca} are the work functions of ITO and calcium metal, respectively. Both E_a and $E_{a'}$ represent the energy needed to raise an electron from the LUMO or the HOMO to the vacuum level.

When voltage is applied to this device, holes (positive charges) from the ITO

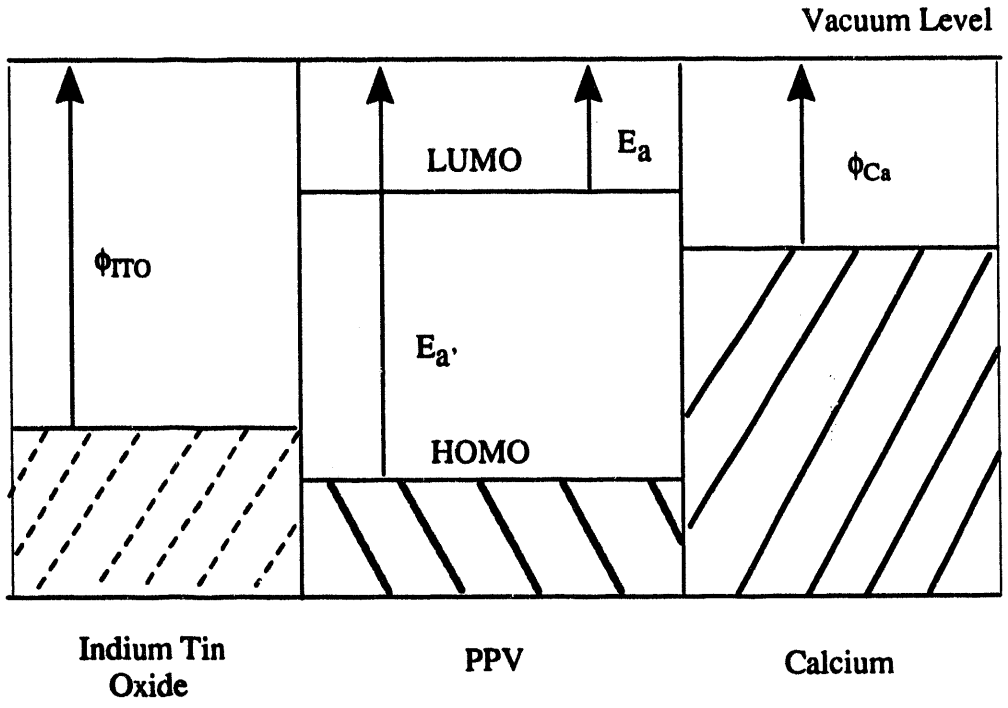


Figure 3. LED device (open circuit)

layer, as well as electrons, from the calcium layer are injected into the polymer layer. Both holes and electrons move through the conjugated polymer under the influence of the applied electric field. The charges either annihilate one another to form a triplet or a singlet exciton, as shown in Figure 4, of which only the singlet may decay radiatively; or the charges pass through the conjugated polymer layer to the electrode of opposite charge.

Polymeric LEDs are likely to replace the inorganic LEDs in the future because of their advantages. First, the cost of polymeric LEDs are very low compared with that of the inorganic LEDs. Second, polymeric films can be easily fabricated and large films can be easily made and patterned. Third, different polymers can emit different colors which can cover the color range. Fourth, flexible LEDs can be fabricated since conducting polymers such as polyaniline can be used as the substrates. If the light intensity of polymeric LEDs can be improved and the lifetime of polymeric LEDs can be made to match that of commercial LEDs it's very difficult to predict what kind of impact these polymeric LEDs will have commercially.

Non-linear optical properties

Conjugated organic polymers are emerging as an important class of third-order nonlinear optical materials for photonics applications in the form of integrated optical devices. The third harmonic generation (THG) of PPV and its derivatives has been studied because good optical-quality films of the polymer can be prepared through the precursor route. Kaino[18] et al. (1987) reported a $\chi^{(3)}$ value of 10^{-11}esu for PPV at a fundamental wavelength of 1.85 µm. For the 2,5-dimethoxy PPV derivative, which has a smaller band gap, a four-wave mixing experiment[19] yielded a $\chi^{(3)}$ value of 4×10^{-9} esu (at $\lambda = 602$ nm).

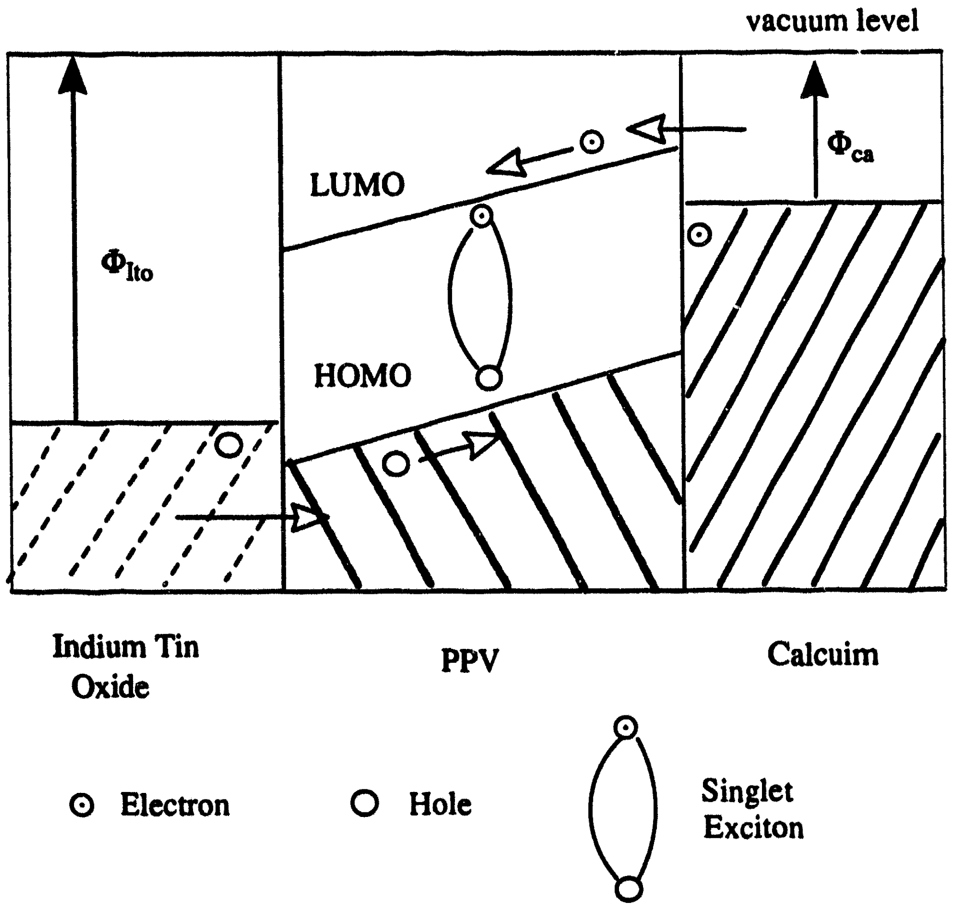


Figure 4. LED device with applied bias

Laser dyes

In recent years dye lasers based on organic chromophores have been widely used[20]. The main advantage of dye lasers is the possibility of frequency tuning in a broad range of wavelengths. Materials available for use as chromophores in dye lasers have been conjugated organic molecules which exhibit strong fluorescence, used either in solution or in blends with various host materials.

Conjugated polymers such as **PPV**, its derivatives, and poly(*p*-phenylene) (**PPP**) have exhibited both photoluminescence and electroluminescence. However, they have not been studied for use as laser dyes. Very recently, Moses[21] reported that one of the soluble **PPV** derivatives, poly[2-methoxy, 5-(2'-ethyl-hexoxy)-p-phenylenevinylene], can be used as a laser dye. This was the first report that a laser can be made from a conjugated polymer. The performance of this **PPV** derivative in solution as a laser dye was compared to that of rhodamine 6G, a very popular laser dye, in solution under identical conditions. The results indicate that the quantum yield of this **PPV** derivative laser is comparable to that of a rhodamine 6G laser. A natural extension of this work would be the construction of an efficient solid state polymer laser.

LITERATURE SURVEY

Poly(*p*-phenyleneethynylene), hereafter referred to as PPE, and its derivatives have conjugated backbones along the polymer main chains along which the π electrons can delocalize. Like PPV, PPE (Figure 5) can also be regarded as a regular alternating copolymer of *p*-phenylene and ethyne or acetylene. The main chain or backbone of PPE has a perfect linear rigid-rod structure which is similar to "uncooked spaghetti."

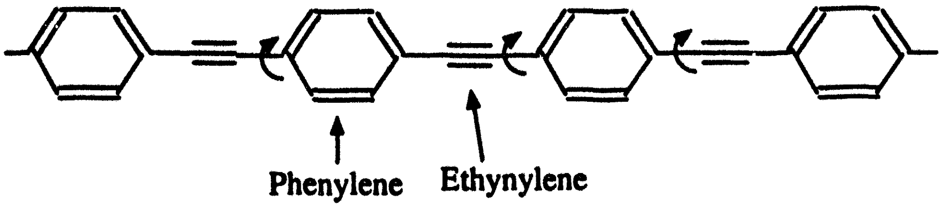


Figure 5. Poly(*p*-phenyleneethynylene)

The structural difference between PPV and PPE is that PPE has acetylene units instead of vinylene units in its polymer main chain. Therefore, PPE has no *cis* or *trans* configurational options as does PPV.

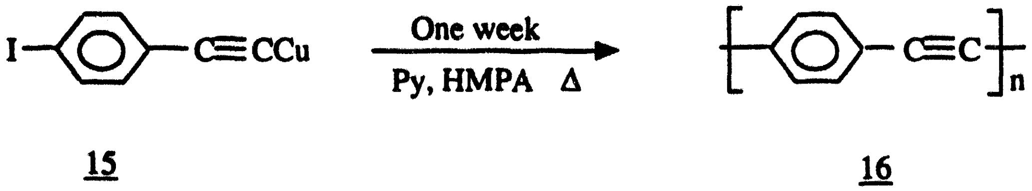
The major motion of the PPE polymer sequences is phenyl rotation in the polymer main chain as shown in Figure 5. This rotation can break the π-conjugation along the polymer main chain. Recent neutron diffraction measurements[22] on oriented PPV at room temperature have shown that the ring torsion angles, i.e., the twist of the phenyl rings out of the vinylene plane, are on the order 7°±6°. Such small torsion angles should result in negligible effects on the electronic band structure compared with that for the fully coplanar conformation. The torsion angles for PPE should be comparable to that of PPV.

Although PPV and its derivatives have been extensively studied, the properties of

PPE and its derivatives have remained unexplored due to synthetic difficulties. Few syntheses of PPE and its derivatives have been reported.

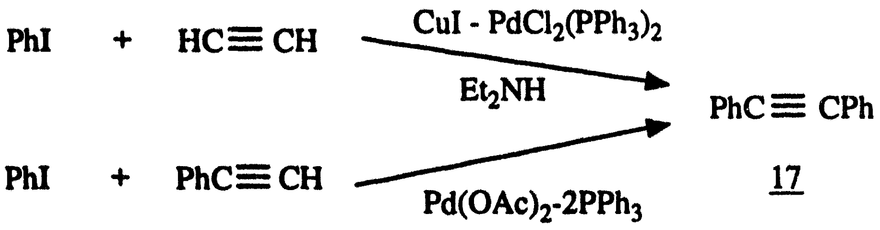
Direct synthesis of PPE polymers

In 1983 Jen[23] first reported the synthesis of PPE via a coupling reaction as shown in Scheme 6. PPE, the insoluble product 16, showed weak electrical conductivity, $\sigma = 10^{-3}$ S/cm after doping with AsF_5.



Scheme 6. Synthesis of PPE via coupling reaction[23]

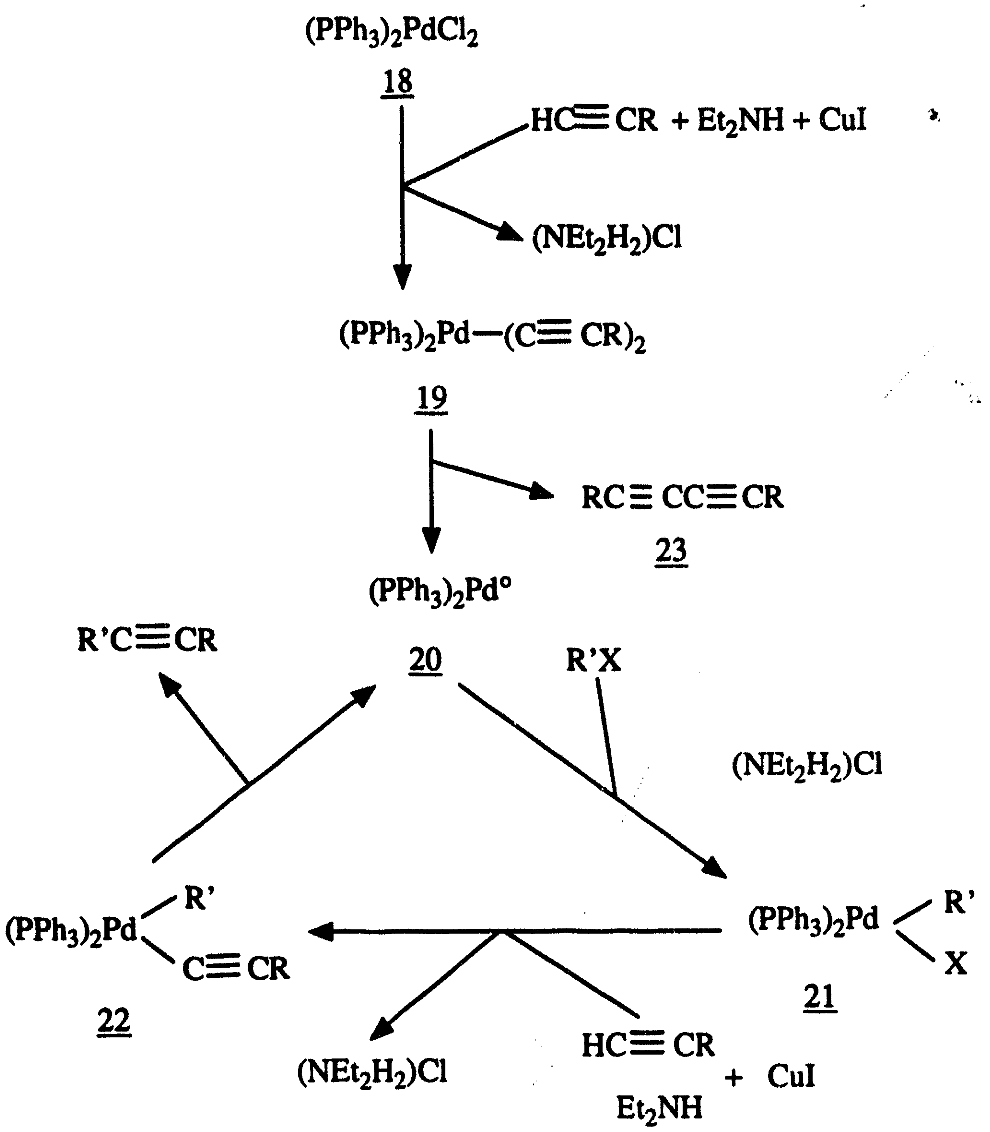
Diphenylacetylene, a compound related to PPE polymer, has been conveniently synthesized[24,25] through a palladium-catalyzed coupling as shown in Scheme 6 with excellent yield. The palladium-catalyzed coupling reaction between a terminal acetylene compound and an aryl halide has been well established[24-26]. The proposed mechanism[24] is given in Scheme 7. It seems likely that the substitution occurs through an initial formation of bis(triphenylphosphine) dialkynylpalladium(II) 19, which gives a catalytic species, bis(triphenylphosphine)palladium(0) 20, through a reductive elimination of a butadiyne compound. Subsequent oxidative addition of an aryl halide to 20, is followed by an alkynylation of the adduct 21, to give an aryl derivative of palladium 22, which easily regenerates the original intermediate 20 through the reductive elimination of the



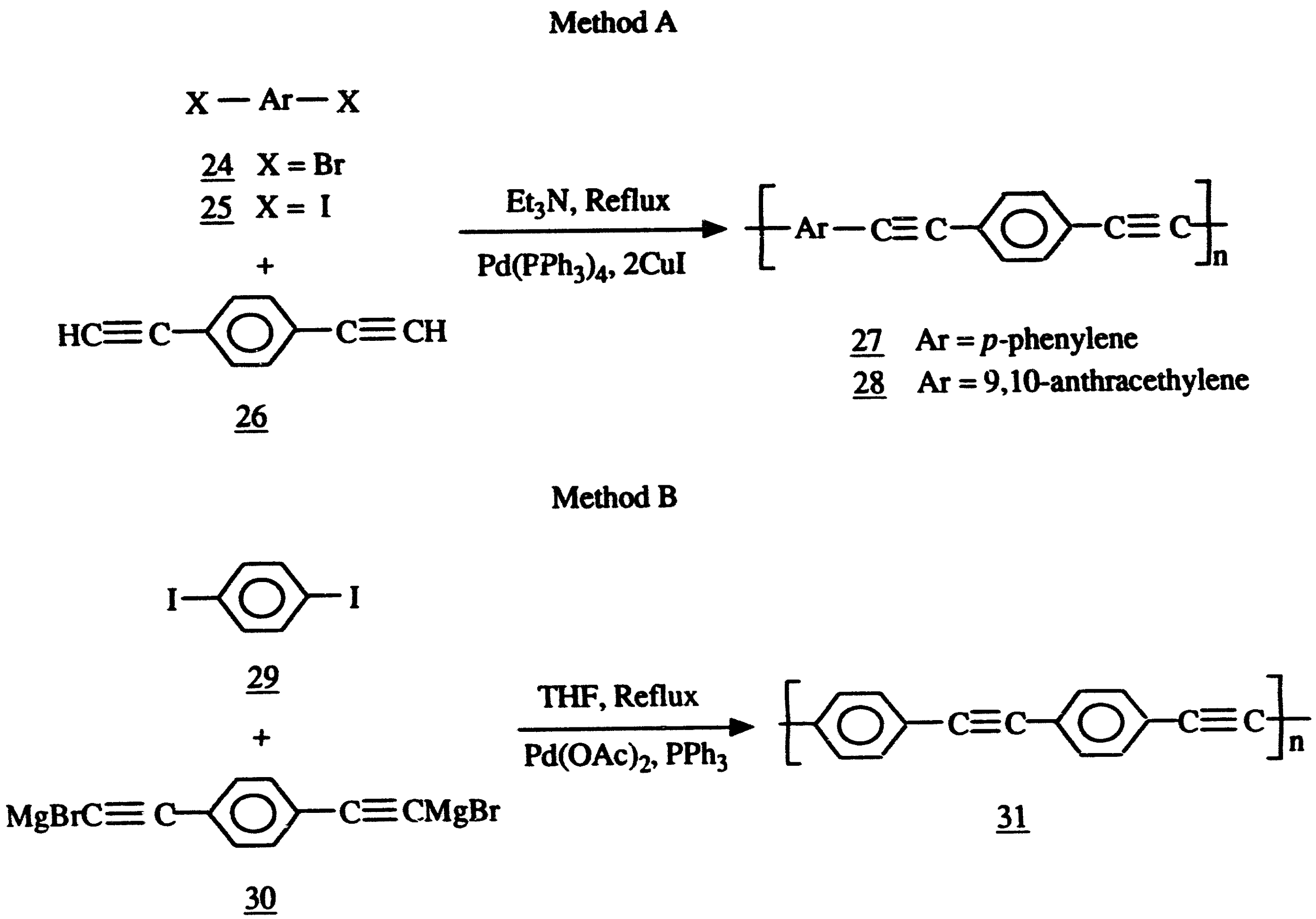
Scheme 7. Pd-coupling reaction[24,25]

substitution product.

Based on this palladium-coupling reaction, Yamamoto[27] reported the synthesis of **PPE** in 1984 as demonstrated in Scheme 9. In method A, diethynylbenzene 26 and dihalo aryl compounds 24 or 25 were used and the solvent was triethylamine. Both $Pd(PPh_3)_4$ and CuI were used as catalysts. In method B, a diGrignard reagent 30 was used instead of diethynylbenzene and the reaction was performed in THF. However, since it's difficult to control the concentration of 30, the second method cannot provide polymer 31 with high molecular weights. Without any side groups attached to the polymer main chain the **PPE** polymer, like **PPV**, is completely insoluble, does not melt and thus cannot be well characterized by routine methods. The halogen content in polymers was between 4% and 11% from elemental analysis. The molecular weights of these **PPE** polymers ranged from 1500 to 4000 as calculated from the elemental analysis by assuming two terminal halogens per chain. Powder X-ray diffraction patterns of the polymers show sharp diffraction bands indicating the high degree of crystallinity of the polymers. Polymer 28 showed electric conductivity of $\sigma = 4\times10^{-5}$ S/cm after exposure to I_2 vapor for 18 hours at room temperature. Polymer 28 also showed very weak electrical conductivity, $\sigma = 6.6\times10^{-8}$ S/cm at 247 K after exposure to AsF_5 vapor; yet, it did not interact with tetracyanoethylene (TCNE) and tetracyanoquinodimethane, as proved by no change in the IR spectrum of



Scheme 8. Proposed mechanism of Pd-coupling reaction[24]



Scheme 9. Palladium-catalyzed polymerization[27]

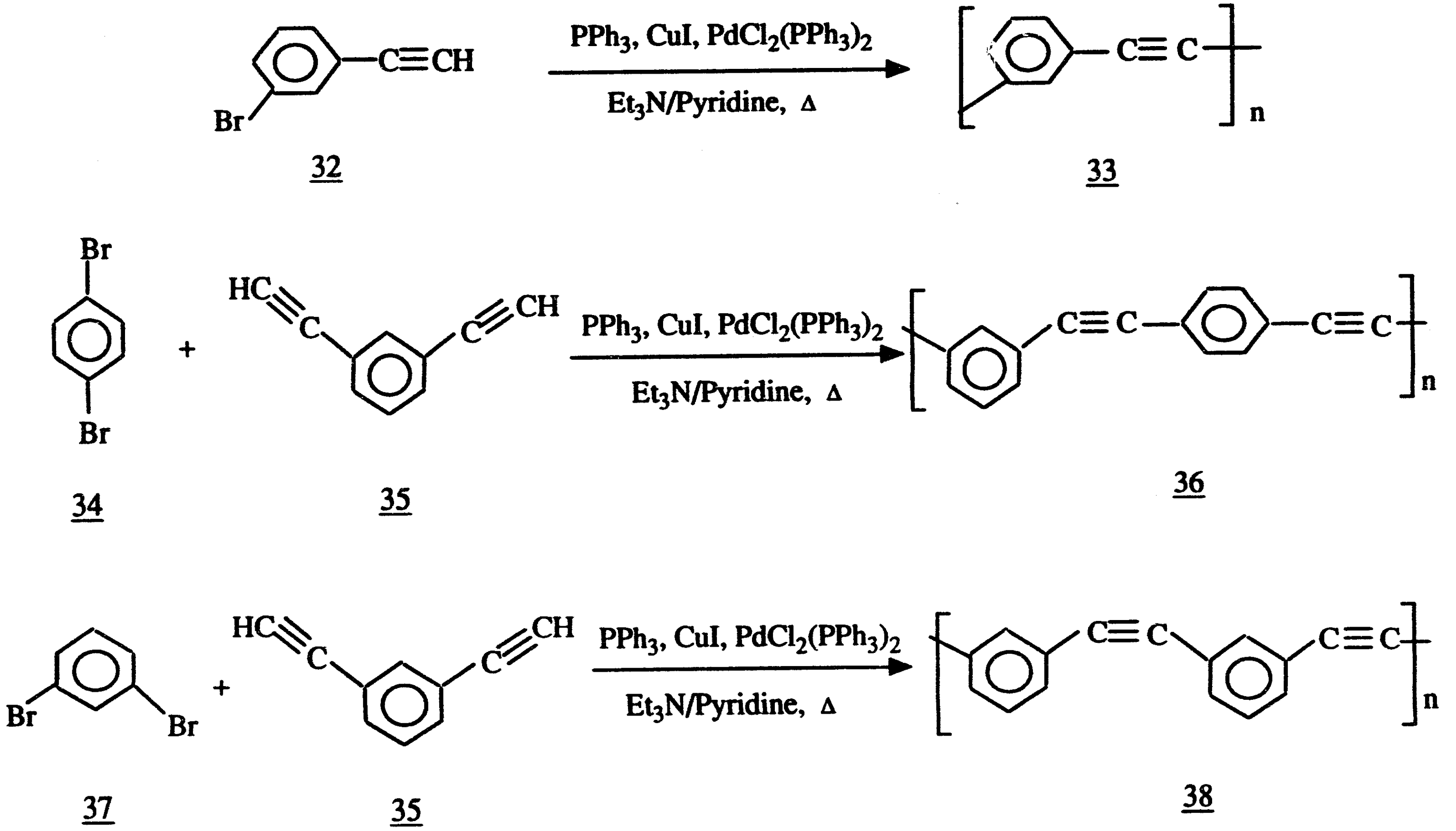
polymer 28 after dipping polymer 28 in solutions of these electron acceptors.

In 1986 Trumbo[28] reported the synthesis of m-**PPE** polymer 33 and copolymers 36 and 38 by using a similar Pd-coupling reaction as shown in Scheme 10. Both CuI and $PdCl_2(PPh_3)_2$ were used as the catalysts. Both triethylamine and pyridine were used as the base and solvent. All the polymerizations were performed at 90°C. The molecular weights of the soluble part of the polymers ranged from 1200 to 1500. Because the polymerization was limited by the poor solubility of **PPE** in the reaction media, high molecular weight **PPE** could not be synthesized by this method.

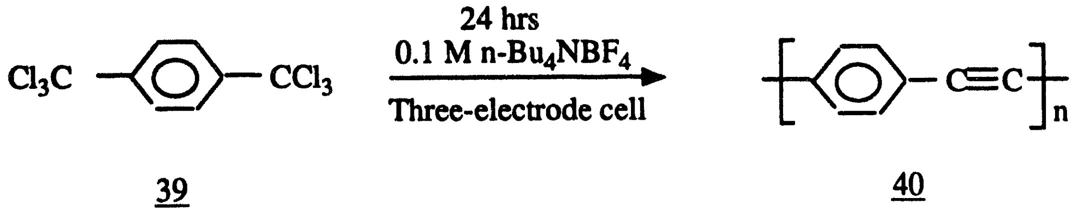
In 1987 Tateishi[29] reported an electrochemical synthesis of a **PPE** polymer film 40 as shown in Scheme 11. The polymer film can be produced on the electrode. However, elemental analysis indicated that there was a considerable amount of chlorine (8.7%) and copper (7.6%) in the polymer 40. The SO_3-doped film of 40 exhibited a high conductivity, 70 S/cm at 25°C, whereas the I_2-doped film only had a conductivity of $3x10^{-7}$ S/cm under the same conditions.

In 1989 Wright[30] reported the synthesis of metal-complexed **PPE** polymers through the Pd-coupling reaction shown in Scheme 12. 1,4-Bis[(trimethylstannyl) ethynyl]benzene 42 or 4,4'-bis[(trimethylstannyl)ethynyl] biphenyl 43 instead of diethynyl arenes was used as one of the monomers. The other monomer 41 was $\{h^6\text{-}1,4\text{-}C_6H_4Cl_2\}Cr(CO)_3$. This polymerization afforded metal-complexed **PPE** polymer 44 or 45 in excellent yields. However, even with $Cr(CO)_3$ attached to the polymer main chain, these polymers still exhibited low solubility in all organic solvents. The polymers, 44 and 45, were not characterized by NMR.

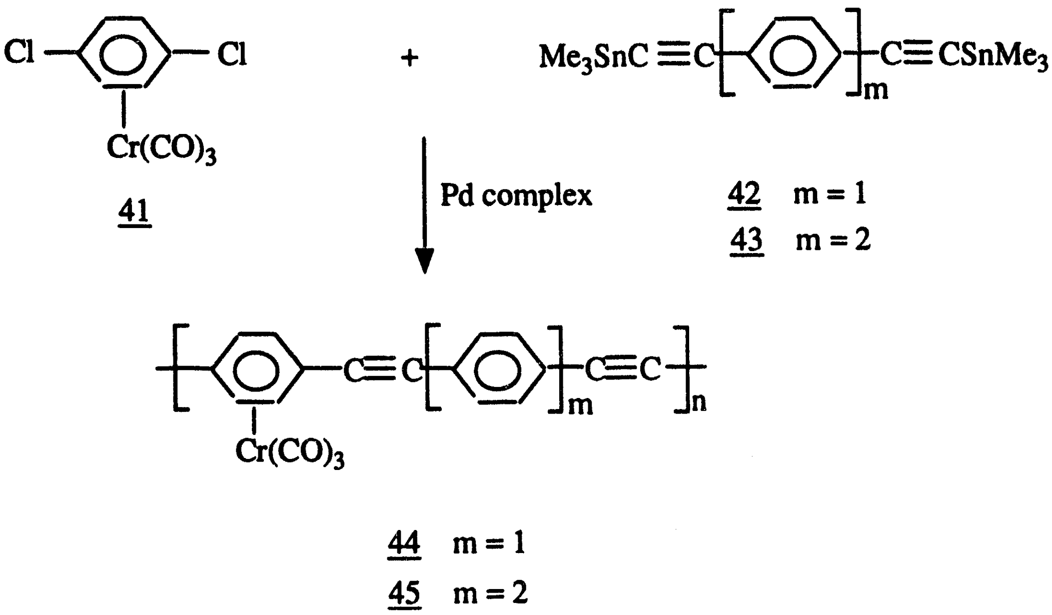
In 1989 Cernia[31] reported the synthesis of poly((2,5-thiophenedyl)ethynylene) (**PThE**) 46 via the same Pd-catalyzed polymerization (Scheme 13). **PThE** is partially soluble in hot nitrobenzene. It did not exhibit high conductivity after exposure to I_2.



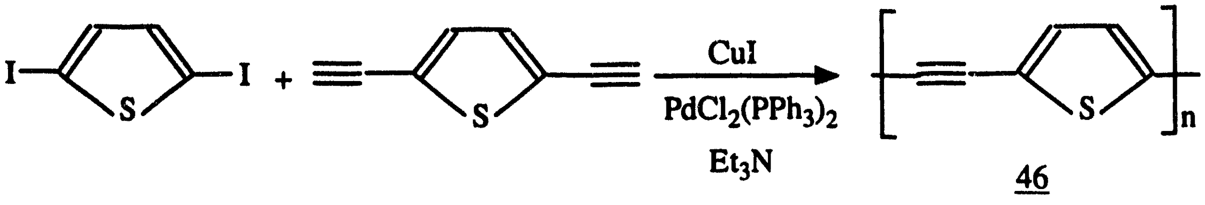
Scheme 10. Synthesis of m-PPE homopolymers and copolymers[28]



Scheme 11. Electrochemical synthesis of PPE[29]



Scheme 12. Synthesis of metal-complexed PPE polymers[30]



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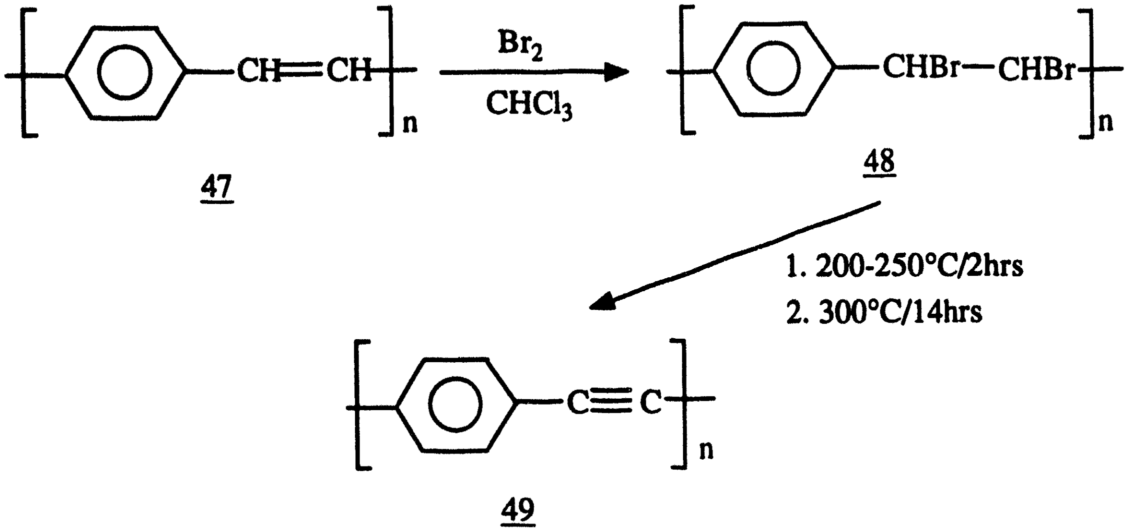
Scheme 13. Synthesis of poly((2,5-thiophenedyl)ethynylene)[31]

Precursor route to PPE polymers

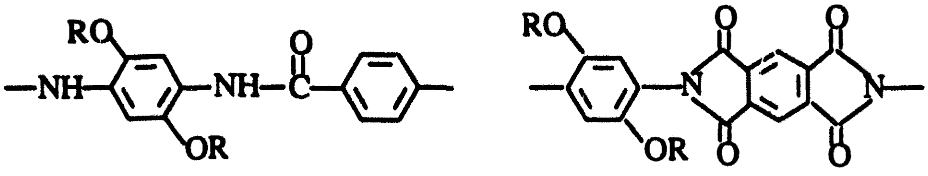
So far, only the direct syntheses of **PPE** polymers have been discussed. The palladium catalyzed polymerization can afford **PPE** polymers with excellent yields. However, these **PPE** polymers are not soluble in organic solvents. Recently, Hsieh[32] reported that **PPE** polymer film 49 was prepared through a precursor route as shown in Scheme 14. **PPV** polymer, the starting material 47 prepared from Wessling's method, was first brominated to give a precursor polymer, poly(α,dibromoxylylene) 48, and then this precursor polymer 48 was converted to **PPE** 49 by dehydrobromination. Bromination of **PPV** films in bromine/chloroform solution was found to be very effective. IR spectroscopy was used to monitor the conversion of 47 to 48. The disappearance of vinylene groups with time was reflected by the diminishing IR signals associated with *trans*-vinylene C-H, the stretching and out-of-plane deformation peaks at 3024 and 966 cm^{-1} respectively. Since dehydrobromination was incomplete as indicated by the high weight% (12%-22%) of bromine, well-defined **PPE** polymer cannot be synthesized by using this method. Further study of precursor routes to synthesize **PPE** polymers is necessary.



Scheme 14. Precursor route to PPE[32]

The synthesis of soluble PPE polymers

Since unsubstituted PPE is insoluble in all organic solvents and not meltable, the molecular weight of PPE made by palladium-catalyzed polymerization was limited by solubility and only PPE oligomers were prepared. The precursor route also did not afford well defined PPE. In order to fully study PPE polymers it is necessary to synthesize soluble PPE polymers which can be characterized and processed into films. One method to accomplish this is to append the flexible side chains onto the stiff main chain of PPE. The side chains act like a bound solvent, which lowers the interaction between the main chains, and leads to a large increase in entropy when dissolving[33]. Therefore, the polymers would have better solubility in reaction media and high molecular weight polymers can be synthesized. This method has already been demonstrated in the synthesis of other "rigid-rod" polymers such as polyimide[34] and polyamide[33] shown in Figure 6.



Polyamide

Polyimide

R = -$(CH_2)_nH$.

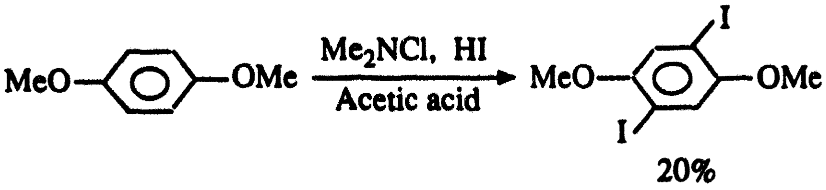
Figure 6. Stiff polymers with flexible side chains

Since the Pd-catalyzed polymerization has been used to make unsubstituted PPE polymer in excellent yield, it might also be used to make substituted PPE polymers. The next problem was that what kind of side chains or substituted groups would be chosen to meet this requirement. For synthetic convenience alkoxy side chains were chosen. Thus one of the monomers would be either 1,4-dibromo or -diiodo- 2,5-dialkoxybenzene and the other would be 1,4-dialkoxy-2,5-diethynylbenzene.

From the literature it is known[24,26] that ethynyl compounds react with aryl iodides much faster than do aryl bromides at the same temperature. Some of these coupling reactions using iodo compounds can even be performed at room temperature. The polymerization probably can be carried out at room temperature which will reduce the chance of undesirable side reactions.

The synthesis of diiodobenzene compounds

Although synthesis of aryl iodides has long been studied[35], the direct synthetic methods leading to diiodo-dialkoxybenzenes are relatively few. In 1953 Jones reported[36] the synthesis of 1,4-diiodo-2,5-dimethoxybenzene as shown in Scheme 15. This method afforded the product with only 20% yield.

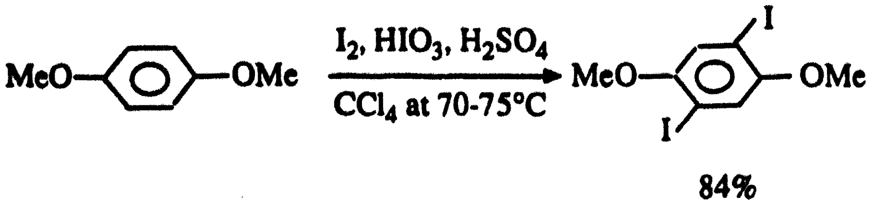


Scheme 15. Preparation of diiodo dimethoxybenzene[36]

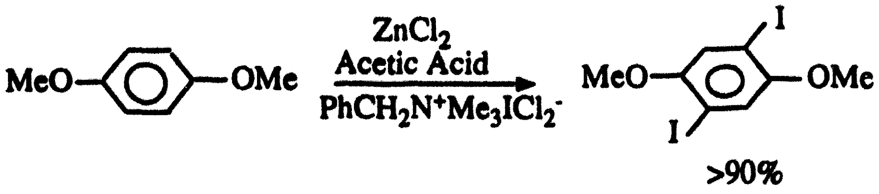
In 1980 Shvartzberg[37a] reported the synthesis of 1,4-diiodo-2,5-dimethoxybenzene, as shown in Scheme 16, with 84% yield. Very recently, Yu[37b] extended this method to prepare a series of dialkoxy-diiodobenzenes with good yield. However, strong oxidant and acid which may not be compatible with certain functional groups were used in this synthesis which will limit the applicability of this method.

In 1988 Kajigaeshi[38] reported the new method shown in Scheme 17 to prepare 1,4-diiodo-2,5-dimethoxybenzene. In this synthesis a weak acid and a weak oxidant were used to synthesize a variety of diiodo compounds bearing a variety of functional groups with excellent yield[38-41].

Therefore, a series of diiodo-dialkoxylbenzenes as well as other diiodo compounds might be synthesized by extrapolation of this method. The starting materials, 1,4-dialkoxybenzenes, can be easily synthesized[42] by the alkylation reaction between n-alkyl bromides and hydroquinone with good yields.

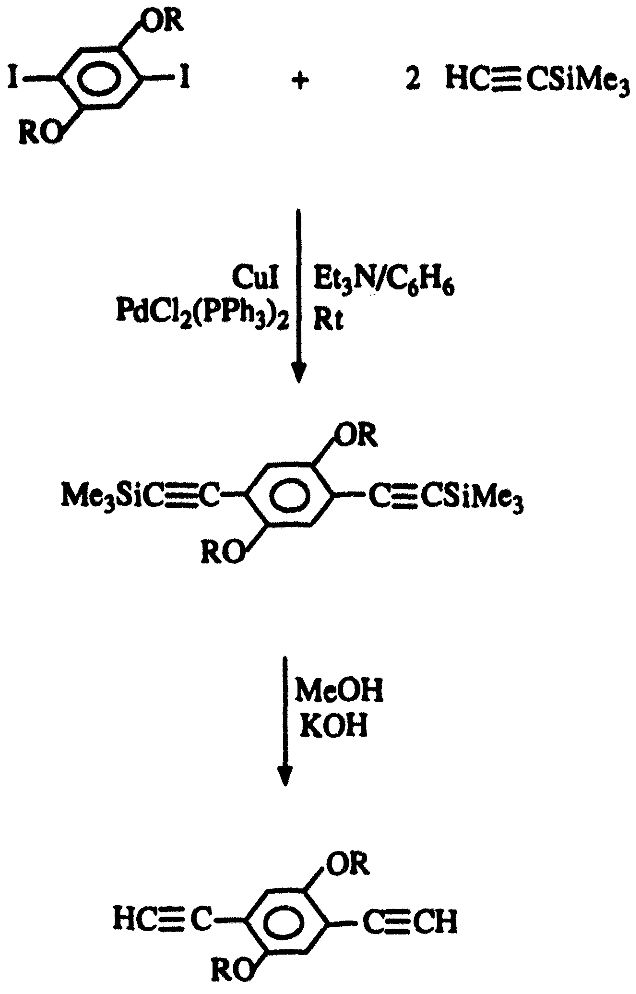


Scheme 16. Preparation of diiodo dimethoxybenzene[37a]



Scheme 17. Preparation of diiodo dimethoxybenzene[38]

The other monomer, 1,4-diethynyl-2,5-dialkoxylbenzene, might be conveniently synthesized through two simple reactions as shown in Scheme 18. Palladium coupling between a diiodo aryl compound and two equivalents of trimethylsilylacetylene should afford a bis(trimethylsilylethynyl)-dialkoxybenzene. Then desilylation of these bissilyl compounds should give 1,4-diethynyl-2,5-dialkoxybenzene.

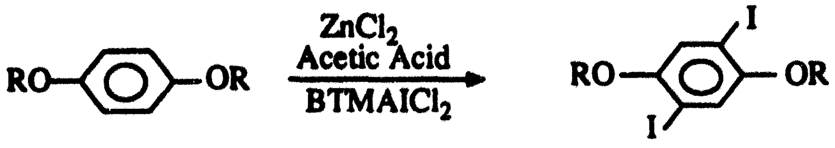


Scheme 18. Synthesis of diethynyl monomers

RESULTS AND DISCUSSION

The synthesis of the monomers

1,4-dimethoxy-2,5-diiodobenzene 55 has been synthesized in excellent yield according to the literature[38]. The iodination reaction for preparation of other diiodo compounds is shown in Scheme 19. The iodination reagent, benzyltrimethylammonium dichloroiodate ($BTMAICl_2$), can be either conveniently synthesized[39] from the reaction shown in Scheme 20 with excellent yield or ordered from Aldrich.

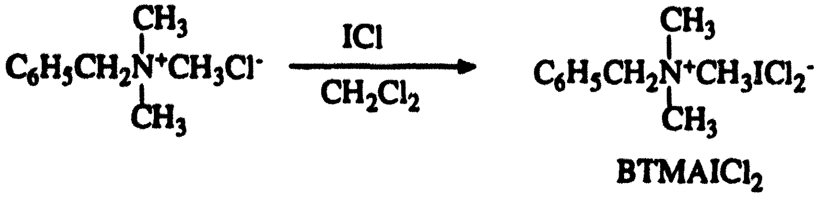


Diiodo compounds

No	50	51	52	53	54
R	n-C_4H_9	n-C_5H_{11}	n-C_6H_{13}	n-C_8H_{17}	n-$C_{10}H_{21}$

Scheme 19. Synthesis of diiodo compounds

The iodination reaction times depended on the specific dialkoxybenzenes and were between 12 and 48 hours at room temperature to 70°C. From GC and GC-MS analysis it was found that diiodo-compounds were formed even when starting materials still existed. Even when a 5-fold excess $BTMAICl_2$ was used with a reaction time over 72 hours between 50-70°C mono-iodo compounds still existed. The diiodo products can be conveniently isolated. Recrystallization of crude products in methanol or isopropanol afforded pure diiodo products. The isolated product yield ranged from 40% to 70%. These diiodo compounds form white crystals with the melting points between 56°C and 86°C. They are stable in the air and soluble in a variety of organic solvents such as benzene, tetrahydrofuran, and chloroform. These diiodo compounds 50-54 have been characterized by ^1H and ^{13}C-NMR, FT-IR, exact mass and elemental analysis. Some physical properties are summarized in Table 1.



$$C_6H_5CH_2\overset{CH_3}{\underset{CH_3}{N^+}}CH_3Cl^- \xrightarrow[CH_2Cl_2]{ICl} C_6H_5CH_2\overset{CH_3}{\underset{CH_3}{N^+}}CH_3ICl_2^-$$

BTMAICl$_2$

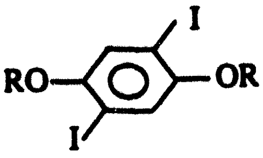
56a 56b

Scheme 20. Synthesis of an iodination reagent

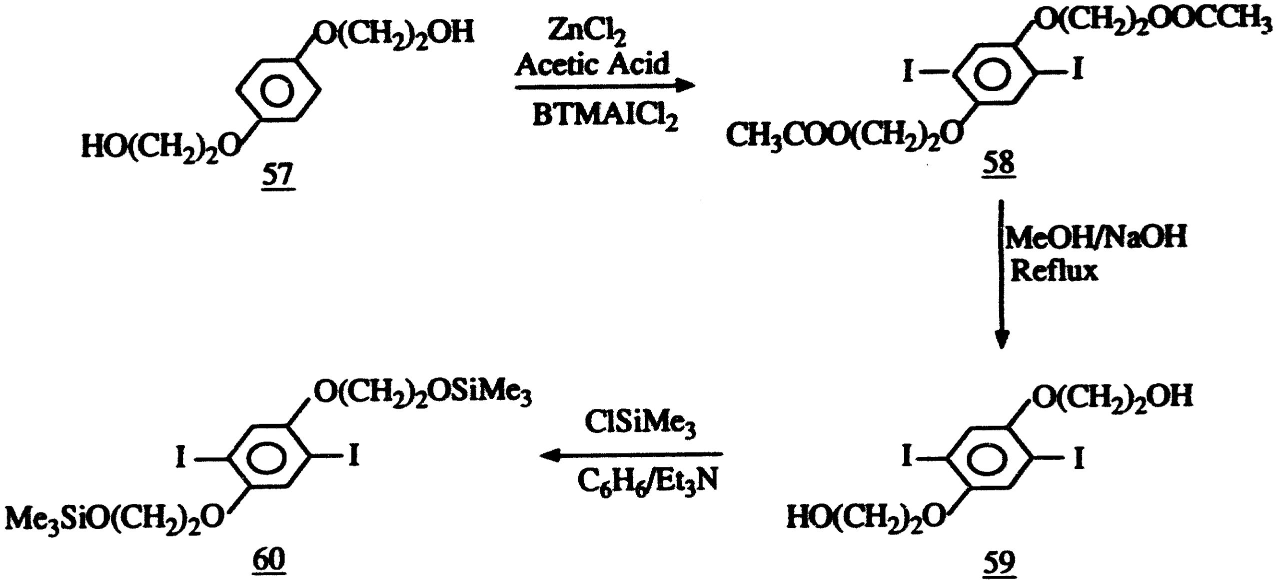
Other diiodo-compounds, 58-60, which have reactive functionalities were also synthesized with good yield (Scheme 21). Therefore, PPE polymers with different functionalities might also be synthesized. The synthesis of a PPE polymer with 2-hydroxyethoxy as the side chain will be discussed later.

The synthesis of diethynyl monomers is described in Scheme 22. The palladium-coupling reaction was performed under an argon atmosphere at room temperature with 70%-90% yield. However, 1%-5% of the oxidative side product, bis(trimethylsilyl)butadiyne, formed when either $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$ was used in the reaction. The products, 61-65, appear as yellow or greenish crystals. They are stable in the air. The desilylation was carried out in methanol containing a catalytic amount of potassium hydroxide under an argon atmosphere at room temperature to 50°C. However, if an unpurified starting material is used for desilylation the product yield will be low due

Table 1. Summary of diiodo compounds



No	Monomer	Yield	Mp°C	Exact Ms.	Reaction times
50	R= $-C_4H_9$	52%	86-88	473.955 cal 473.956 exp	24hrs
51	R= $-C_5H_{11}$	55%	73-75	501.987 cal 501.987 exp	12hrs
52	R= $-C_6H_{13}$	57%	58-59	530.018 cal 530.018 exp	12hrs
53	R= $-C_8H_{17}$	69%	56-57	586.080 cal 586.080 exp	12hrs
54	R= $-C_{10}H_{21}$	45%	59-61	642.143 cal 642.144 exp	48hrs



Scheme 21. Synthesis of functional monomers

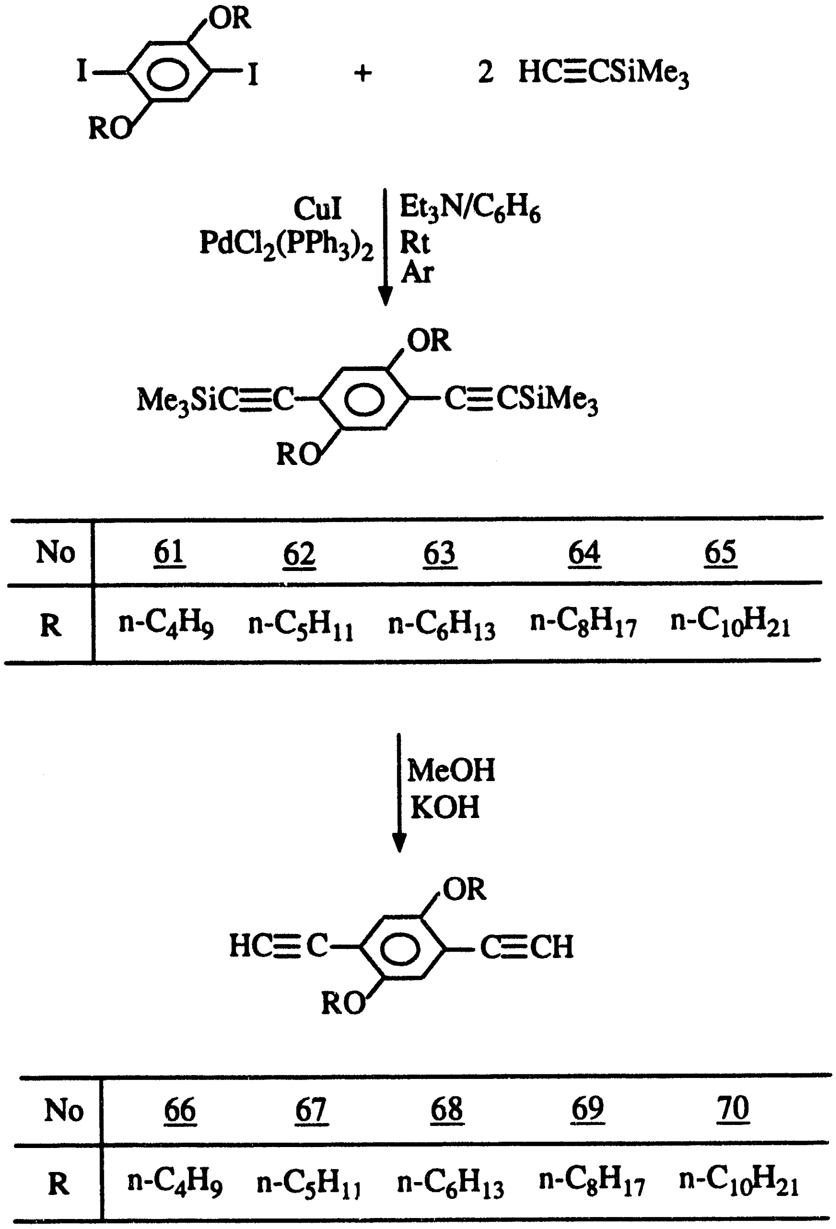
presumably to the coupling reaction catalyzed by the trace of CuI in the starting material. The desilylated diethynyl monomers also appear as greenish crystals. They were slowly oxidized upon air contact. These monomers were characterized by NMR, FT-IR and exact mass.

Palladium-catalyzed polymerization

The synthesis of **PPE** polymers 71-75 and 75a by the Pd-coupling reaction between diiodo aryl compounds and ethynyl compounds can be performed at room temperature in a few hours with excellent yields (Scheme 23). However, the solubilities of these **PPE** polymers are limited. So after the yellow polymer and amine salt precipitated from the toluene solution the reaction temperature was increased to 50-70°C and the polymer redissolved in the solution to continue the polymerization. When the polymerization was performed at 90-120°C, thermal crosslinking resulted in an insoluble product.

It is necessary to provide continuous stirring during the polymerization. Otherwise partial crosslinking will occur and the polymer will not dissolve in any solvent. Since **PPE** polymers had better solubility in toluene than in benzene toluene was used for the polymerization. The catalysts were $PdCl_2(PPh_3)_2$ and CuI in about a 1:1 ratio in most polymerizations. $Pd(PPh_3)_4$ was also successfully used in a few polymerizations. The reaction times were between 24 hours to 48 hours. After the polymerization was complete the amine salt was removed by the filtration. The polymers were purified by precipitation twice from excess methanol. The isolated polymer yields ranged from 70% to 95%.

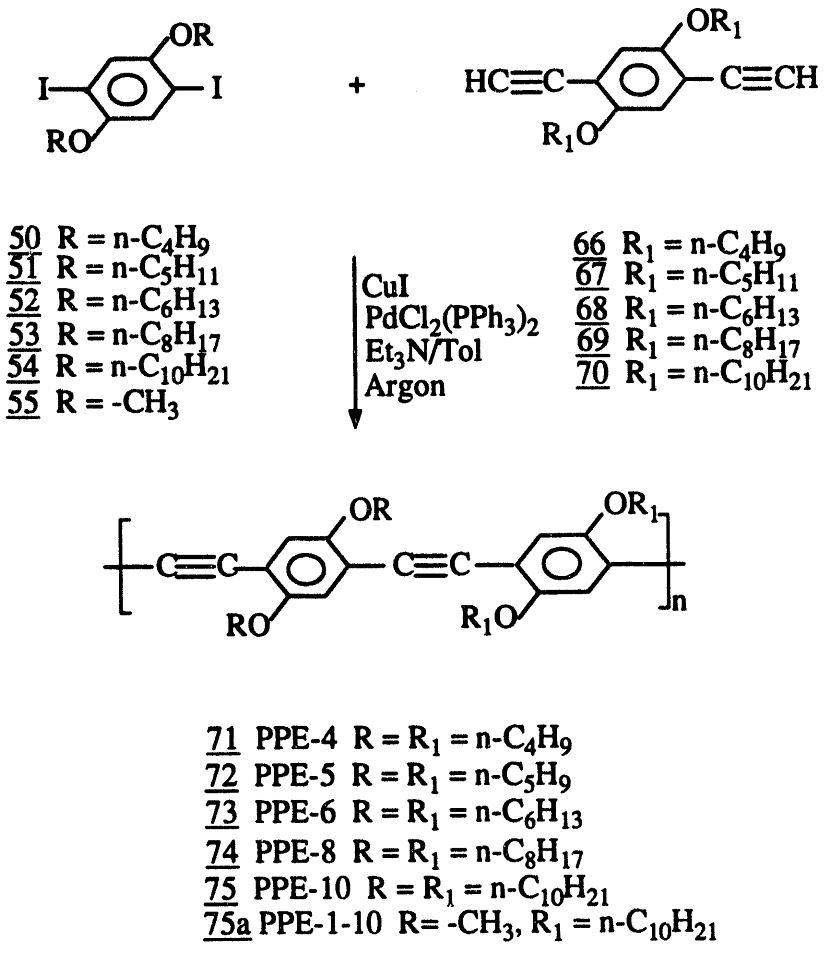
These **PPE** polymers 71-75a appear as yellow, orange or red powders. Even after being dried in vacuum they are still soluble in a variety of solvents such as THF,



No	<u>61</u>	<u>62</u>	<u>63</u>	<u>64</u>	<u>65</u>
R	n-C_4H_9	n-C_5H_{11}	n-C_6H_{13}	n-C_8H_{17}	n-$C_{10}H_{21}$

No	<u>66</u>	<u>67</u>	<u>68</u>	<u>69</u>	<u>70</u>
R	n-C_4H_9	n-C_5H_{11}	n-C_6H_{13}	n-C_8H_{17}	n-$C_{10}H_{21}$

Scheme 22. Synthesis of diethynyl monomers



<u>50</u> R = n-C_4H_9
<u>51</u> R = n-C_5H_{11}
<u>52</u> R = n-C_6H_{13}
<u>53</u> R = n-C_8H_{17}
<u>54</u> R = n-$C_{10}H_{21}$
<u>55</u> R = -CH_3

CuI
$PdCl_2(PPh_3)_2$
Et_3N/Tol
Argon

<u>66</u> R_1 = n-C_4H_9
<u>67</u> R_1 = n-C_5H_{11}
<u>68</u> R_1 = n-C_6H_{13}
<u>69</u> R_1 = n-C_8H_{17}
<u>70</u> R_1 = n-$C_{10}H_{21}$

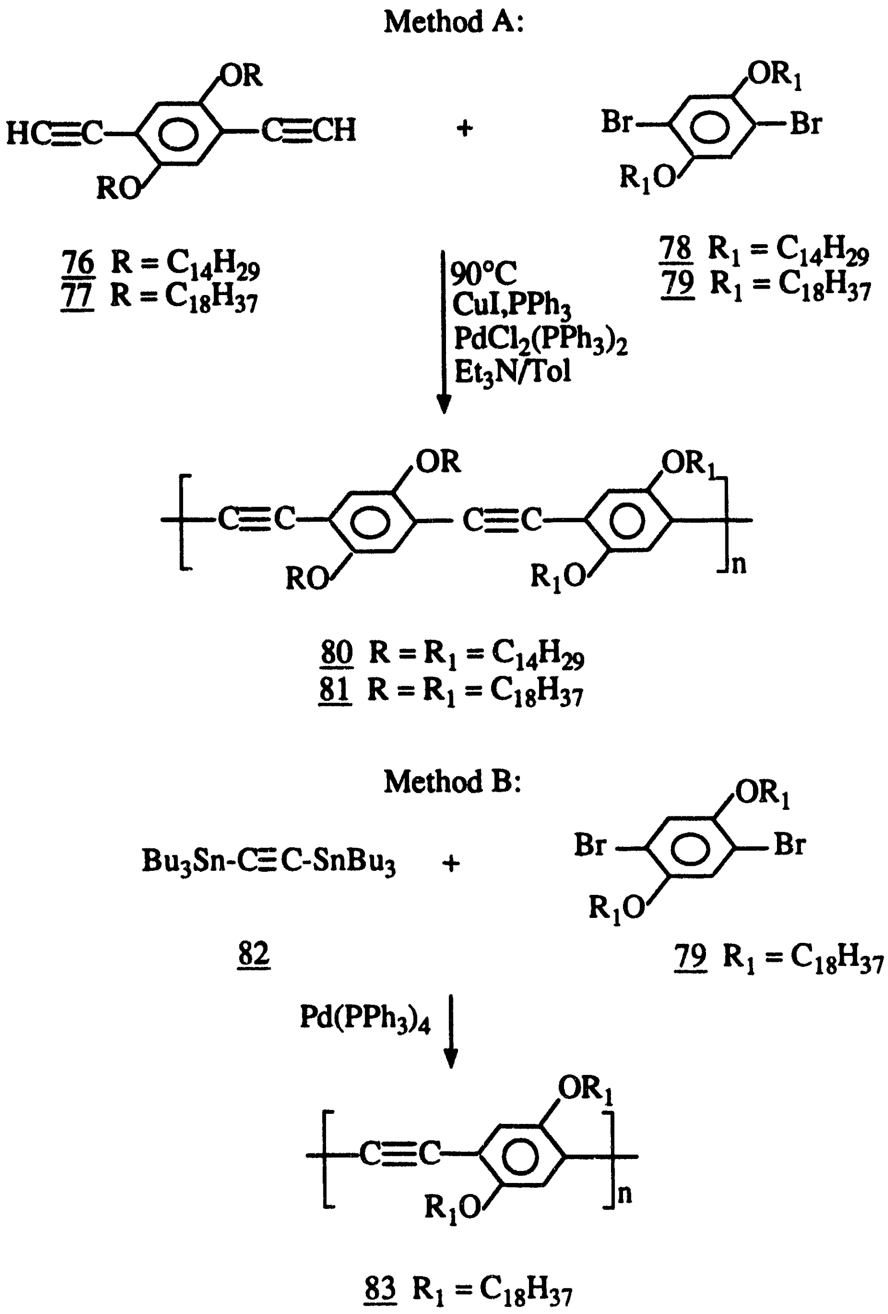
<u>71</u> PPE-4 R = R_1 = n-C_4H_9
<u>72</u> PPE-5 R = R_1 = n-C_5H_9
<u>73</u> PPE-6 R = R_1 = n-C_6H_{13}
<u>74</u> PPE-8 R = R_1 = n-C_8H_{17}
<u>75</u> PPE-10 R = R_1 = n-$C_{10}H_{21}$
<u>75a</u> PPE-1-10 R= -CH_3, R_1 = n-$C_{10}H_{21}$

Scheme 23. The synthesis of PPE derivatives by using Palladium-catalyzed polymerization

toluene and chloroform. For example, 16 g of **PPE-4** 71 can be dissolved in 1L toluene. Therefore, the **PPE** cast film can be made from this solution. Apparently the longer side chain the polymer has, the better the solubility in organic solvents. Also the **PPE** polymers with longer side chains form better films. However, the polymer with the longer side chain has a slower dissolution rate than one with the shorter side chains. The reason might be that the longer side chains are more entangled in each other than are the shorter ones. So it is difficult for the solvents to untangle the longer side chains and the polymer will dissolve in the solvent slowly. Dissolving these **PPE** polymers in organic solvents has to be done very carefully. First the polymer has to be ground into a fine powder. An ultrasonic bath is used to help dissolution. Second once only fine polymer particles are suspended in solution, the solution is slowly heated to the boiling point to completely dissolve the polymer. If large polymer particles exist and the solution is heated surface crosslinking renders the polymer insoluble.

Interestingly, Schultz[43,44] reported the synthesis of similar **PPE** polymers by using the same polymerization as shown in Scheme 24 when this work was being done. However, there are major differences between their work and this one. The major difference was that dibromoaryl compounds instead of diiodoaryl compounds were used in their polymerization which resulted in the necessity for a higher reaction temperature (90°) and subsequent lower purified polymer yield (30-80%). In their method B bis(tributylstannyl)acetylene was used in the polymerization and this route did not provide any better results. Most of these polymers were not soluble in toluene after being dried in vacuum. Only polymers with extremely long side chains such as tetradecoxy or longer were soluble in toluene. Why the polymers with short side chains cannot dissolve in solvent remains unknown.

The molecular weight of Schultz's polymer 81 was found to be above 10,000.



Scheme 24. Schultz's polymerization[43,44]

However, this polymer 81 has the octadecoxy side chain and the degree of polymerization is above 15. Acetylenic carbons in these polymers were not observed in ^{13}C-NMR, which Schultz explained was due to the fact that the rodlike and extremely stiff polymer backbone increases the relaxation times of the sp- and sp^2-carbons greatly which further lowers the known low intensity of the acetylenic carbon peak in ^{13}C-NMR.

The **PPE** polymers 71-75 prepared through our method have been well characterized by NMR, FTIR, UV in both solution and film, GPC and elemental analysis. Some of the data are summarized in Table 2. Other data are given in the experimental section.

Molecular weights of **PPE** polymers

The molecular weights of the **PPE** polymers 71-75 were measured by both GPC and viscometry in THF solution at room temperature. Polystyrenes were used as the standards. The number average molecular weights (Mn) ranged from 6.7×10^3 to 22×10^3 depending on the polymer side groups. The repeat units (DP) of **PPE** polymers were between 25 and 53. The polydispersities were between 2.4 and 5.1. The molecular weight distributions indicated that the polymerization is unimodal. However, the molecular weight distributions of Schultz's polymers shows that his polymerization is multimodal. This might be because several different polymerizations proceeded at high temperature when dibromo-aryl monomers were used.

Since **PPE** polymers have rigid-rod main chains, the GPC-derived molecular weights do not reflect the sizes of the polymers as well as they do for the random-coil variety[45a,45b]. The intrinsic viscosity [η], which depended on both polymer side and main chains, ranged from 0.30 to 1.32 dl/g in THF solution at room temperature. The elemental analysis data summarized in Table 3 indicated that the repeat units of **PPE** polymers presumably with one iodo end group ranged from 14 to 21 except **PPE-10**. Obviously, the GPC analysis using polystyrene standards has overestimated the molecular weight of **PPE** polymers, as has also been observed for polythiophenes[45c].

From the elemental analysis it was found these **PPE** polymers contained small amounts of iodine. NMR measurement didn't indicate any triethylamine salt existed in the polymers. It is reasonable to presume that the iodine came from the end group of polymer chains and one way to prove this was to react these polymers with terminal ethynyl compounds such as phenylacetylene to remove the iodine. The reaction is shown in Scheme 25. For example the content of iodine in one of **PPE-4** polymers was reduced from 5.38% to 0.5% after this treatment. In the second example polymer 86 reacted with trimethylsilylacetylene to afford polymer 87 and the content of iodine was reduced from 3.02% to 0.45%.

Since **PPE** polymers are insoluble in triethylamine, decreasing the triethylamine content in reaction media will increase the solubility as well as the molecular weights of these polymers. However, the polymerization rate will be decreased if the concentration of base is decreased. 1,8-diazabicyclo-[5.4.0]-undec- 7-ene (**DBU**) is a much stronger base than triethylamine. Therefore, by replacement of triethylamine with **DBU** should help solve this problem. The polymerization as shown in Scheme 26 was performed as before with the exception that a stoichiometric amount of **DBU** was used. The polymerization was quenched after 7 hours at room temperature to afford the **PPE-4** polymer 88 in 97% yield. The advantage of this new polymerization method is that the polymerization can be completed in a shorter time period and only a stoichiometric amount of DBU base need be used. However, **DBU** is more expensive than triethylamine.

Table 2. Summary of **PPE**-polymers

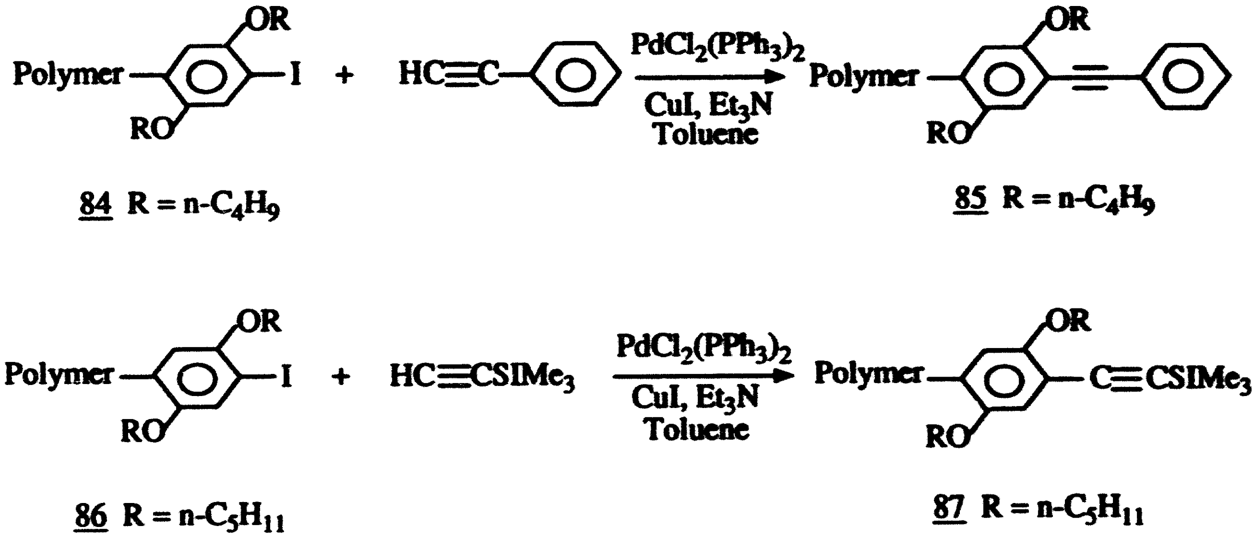
No	Polymers	Yields	Mn	PD	DP	Vis	Reaction Times
<u>71</u>	PPE-4	92%	7.9×10^3	3.1	33	0.34	15hrs
<u>72</u>	PPE-5	94%	6.7×10^3	4.5	25	0.40	16hrs
<u>73</u>	PPE-6	95%	10×10^3	2.4	30	0.30	16hrs
<u>74</u>	PPE-8	94%	12.4×10^3	3.7	35	0.49	24hrs
<u>75</u>	PPE-10	93%	22×10^3	3.1	53	1.32	24hrs

PD= Polydispersity, DP=The Degree of Polymerization,
Vis= Intrinsic Viscosity

Table 3. Summary of elemental analysis

No	Polymers	C%	H%	I%	DP
<u>71</u>	PPE-4	76.43(Cal.) 76.05(Exp.)	8.04(Cal.) 7.86(Exp.)	2.80(Cal.) 2.73(Exp.)	18
<u>72</u>	PPE-5	76.79(Cal.) 75.86(Exp.)	8.62(Cal.) 8.25(Exp.)	3.22(Cal.) 3.02(Exp.)	14
<u>73</u>	PPE-6	77.61(Cal.) 77.05(Exp.)	9.14(Cal.) 8.90(Exp.)	2.93(Cal.) 2.60(Exp.)	14
<u>74</u>	PPE-8	79.50(Cal.) 78.95(Exp.)	10.02(Cal.) 9.81(Exp.)	1.67(Cal.) 1.52(Exp.)	21
<u>75</u>	PPE-10	80.45(Exp.)	10.56(Exp.)	0(Exp.)	>21

*Calculation was based on the DP given in the table with one iodo end group.



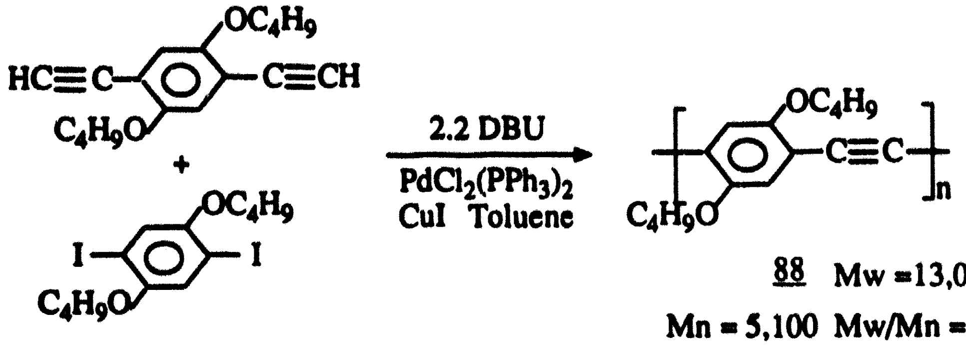
84 $R = n\text{-}C_4H_9$

85 $R = n\text{-}C_4H_9$

86 $R = n\text{-}C_5H_{11}$

87 $R = n\text{-}C_5H_{11}$

Scheme 25. Reaction of removing the iodine



<u>88</u> Mw =13,000
Mn = 5,100 Mw/Mn = 2.5

Scheme 26. Synthesis of PPE by using DBU as the base

Characterization of both monomers and PPE polymers

The FT-IR spectra of both diiodoaryl monomers and diethynylaryl monomers show absorption bands for certain functionalities. The data are given in the experimental section. ^{1}H and ^{13}C-NMR were used to characterize both monomers. Figure 7 shows a typical ^{1}H-NMR spectrum of 1,4-dialkoxy-2,5-diiodobenzene. The assignment of the peaks is also given in the spectrum. The ^{13}C-NMR spectrum for 1,4-dipentoxy-2,5-diiodobenzene is shown in Figure 8. Five peaks between 14.05 ppm and 70.36 ppm are assigned as the pentoxy carbons and the peaks at 80.31 ppm, 122.80 ppm, and 152.86 ppm are attributed to the aromatic carbons. The NMR data for all diiodoaryl compounds and diethynylaryl compounds are given in the experimental section.

PPE polymers <u>71</u>-<u>75</u> were also well characterized by routine methods. It is well known[46] that symmetrically substituted acetylenes have extremely weak or nonexistent absorbances in the IR spectrum and as expected the FT-IR spectra of PPE polymers did not exhibit any absorbances for CC triple bond stretching frequency. Neither absorbances for the C-H stretching or the CC-H stretching frequency in terminal acetylenes were observed.

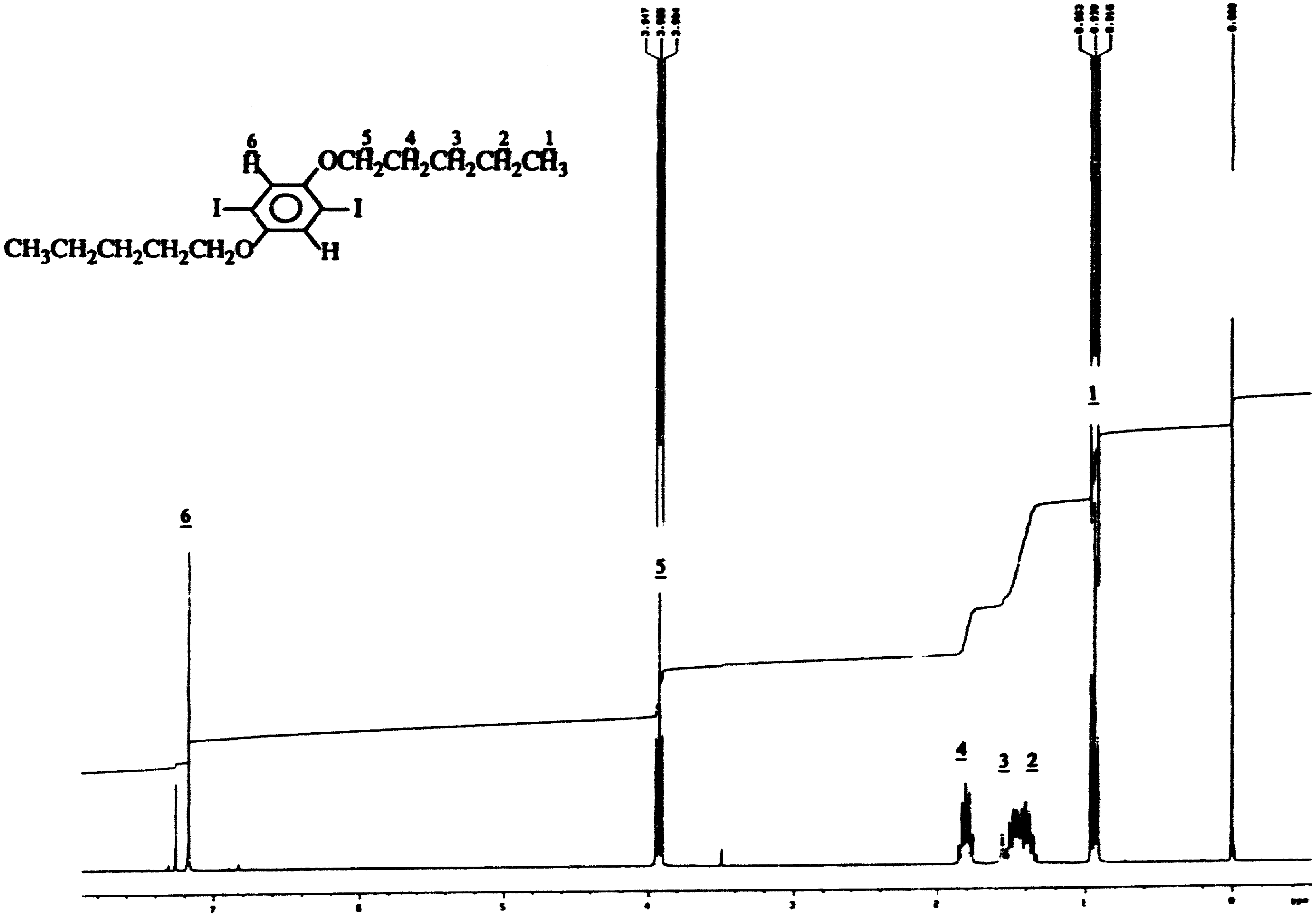


Figure 7. ^{1}H-NMR spectrum of 1,4-dipentoxy-2,5-diiodobenzene

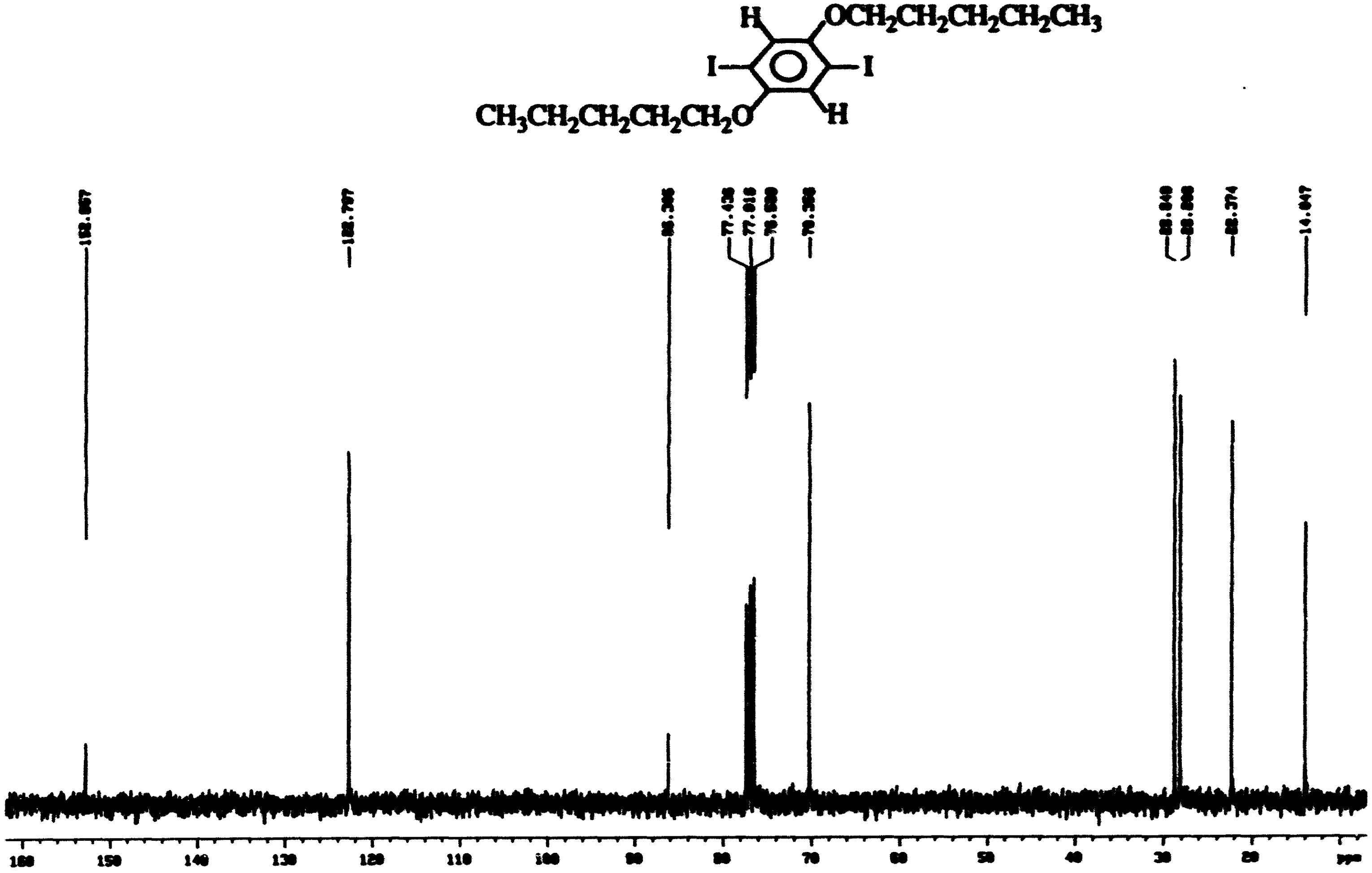
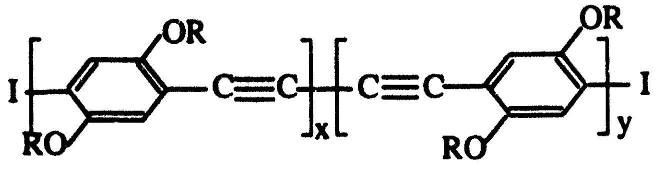


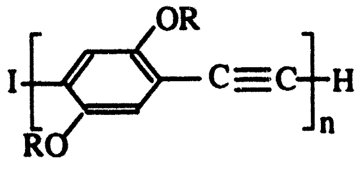
Figure 8. ^{13}C-NMR spectrum of 1,4-dipentoxy-2,5-diiodobenzene

PPE polymers 71-75 were completely characterized by solution phase NMR. The ^{1}H-NMR and ^{13}C-NMR spectrum of PPE-6 73 in $CDCl_3$ are shown in Figures 9 and 10. The peak at 7.02 ppm in Figure 9 is assigned to the aromatic protons in the PPE-6 73 main chain and the other labeled peaks are assigned to the alkoxy protons in the PPE-6 73 side chains.

In Figure 10 six peaks between 14.05 ppm and 69.70 ppm are assigned to the alkoxy side chain carbons and three peaks between 114.3 ppm and 153.51 ppm are assigned to the aryl carbons. The peak at 91.6 ppm, which was not observed by Schultz[36], is assigned to the ethynyl carbon in the PPE-6 73 main chain. The spectra of quantitative ^{13}C-NMR for PPE polymers further proved the PPE polymer structure. The peaks for the 1,3-butadiyne moiety were not observed in the ^{13}C-NMR spectra. However, they could be observed in the polymer main chain and ^{13}C-NMR may not be sensitive enough to observe the weak signals for 1,3-butadiyne. Therefore, these substituted PPE polymers should have the following structures (either polymer I or polymer II).



PPE polymers I



PPE polymers II

Other derivatized PPE polymers had similar ^{1}H-NMR and ^{13}C-NMR spectra to that of PPE-6 73, except for their different side chains, and the NMR as well as FTIR data are given in the experimental section.

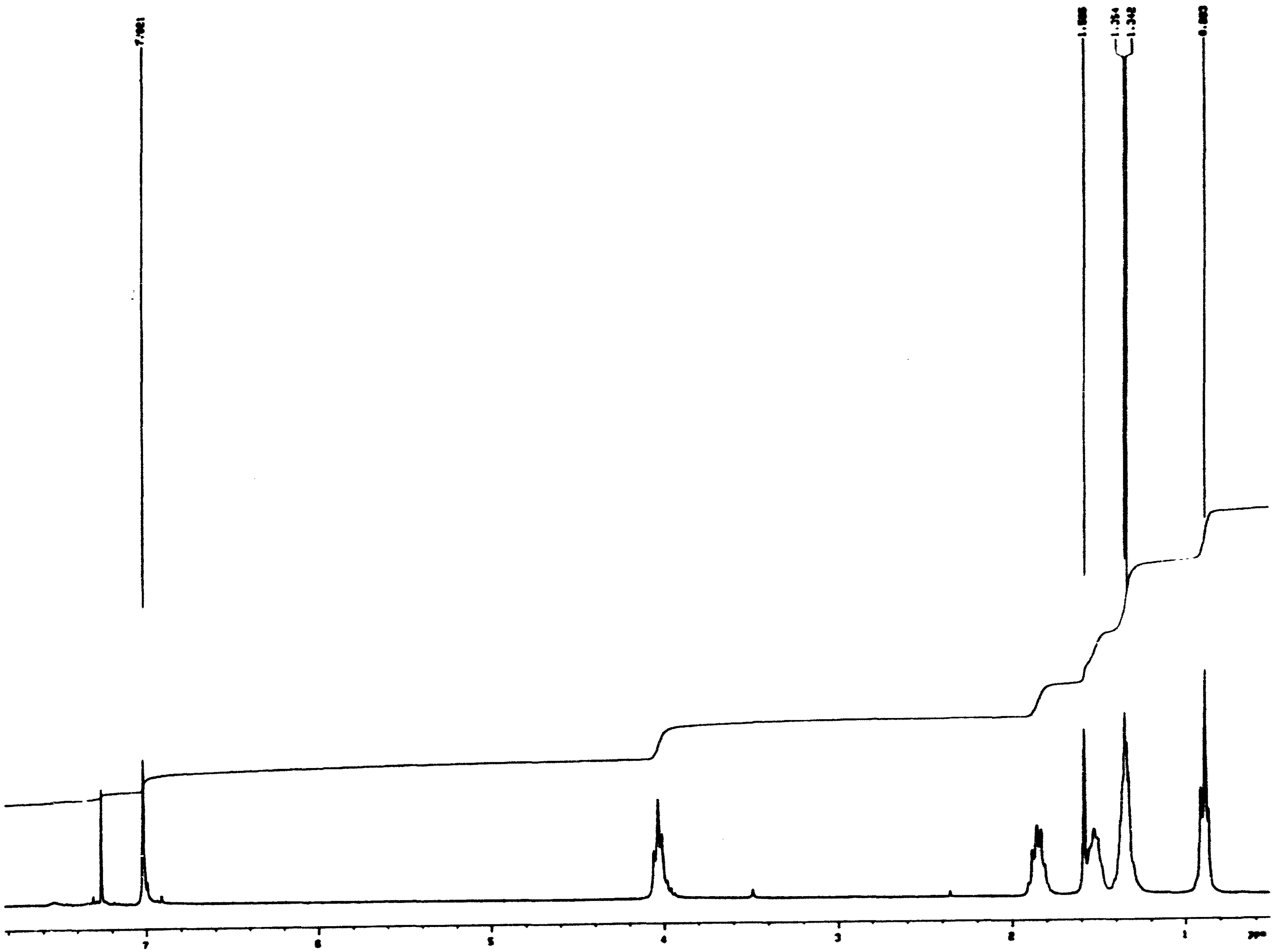


Figure 9. ^{1}H-NMR spectrum of **PPE polymer** 73

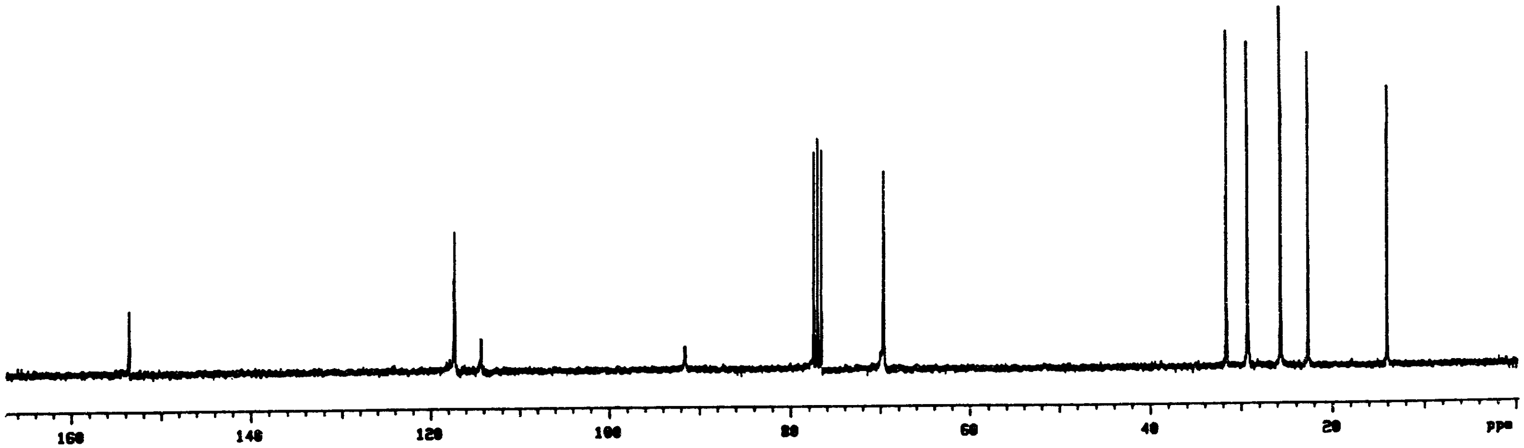


Figure 10. ^{13}C-NMR spectrum of **PPE** polymer <u>73</u>

Thermal behaviors of PPE polymers

The thermal stability of **PPE**-polymers 71-75 was analyzed by a thermogravimetric analyzer (TGA) under a helium atmosphere at a heating rate of 20°C/min. TGA results in Figure 11 show that **PPE** polymers start to lose weight rapidly around 360°C and after 500°C they slowly lose weight. The total weight loss of **PPE** polymers depend on the side chain length. The polymer with longer side chains loses more weight than the one with shorter side chains.

During the pyrolysis of **PPE**-4 (71) a butyl fragment was observed by mass spectrometer as the major volatile product. The TGA results are summarized in Table 4. The char yields of these **PPE** polymers after heating to 1100°C range from 43% of **PPE**-4 (71) to 25% of **PPE**-10 (75).

Table 4. TGA results of **PPE** polymers

Polymers	PPE-4 71	PPE-5 72	PPE-6 73	PPE-8 74	PPE-10 75
Char Yields	43%	39%	35%	31%	25%

A differential scanning calorimeter (DSC) was used to study the phase transition behavior of **PPE** polymers 71-75. One example is shown in Figure 12 in which **PPE** 71 was examined. An endothermal peak appears at 139°C and this indicates that **PPE** 71 melts at this temperature. An exothermal peak is observed at 175°C and this indicates that decomposition or thermal crosslinking occur at about this temperature. The endothermal

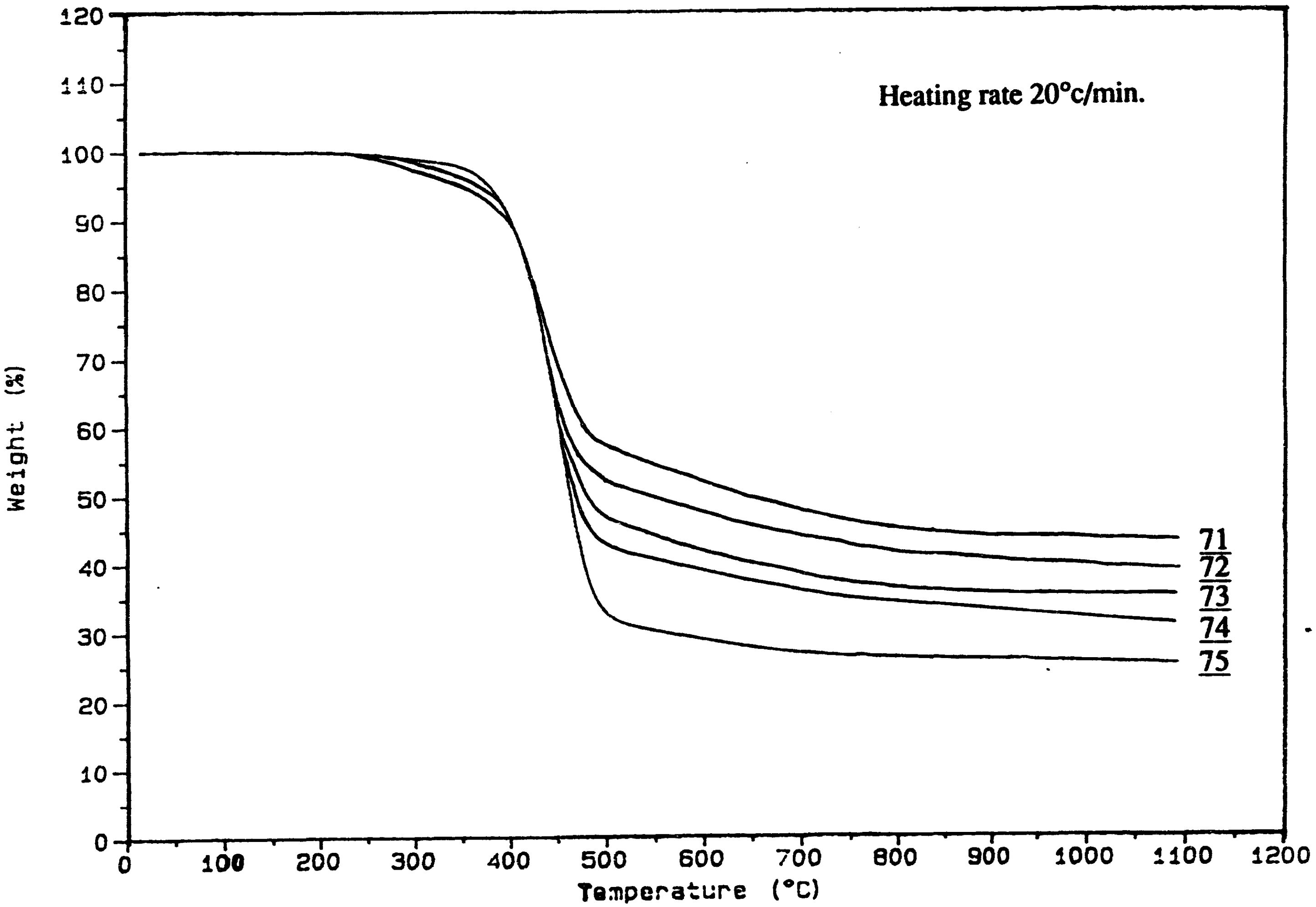


Figure 11. TGA results of PPE polymers

and exothermal peaks are overlapped and therefore **PPE** 71 starts to decompose during melting. No endothermal peaks are observed before the exothermal peaks appear or the endothermal and exothermal peaks overlap each other in DSC experiments for other **PPE** polymers. These results indicate that these **PPE** polymers 71-75 decomposed either before or during the melting. Therefore, it is impossible to study the thermotropic liquid crystalline properties of **PPE** polymers 71-75 due to the decomposition before or during the melting.

Figure 13 shows a pattern of powder X-ray diffraction for **PPE-4** (71) and the pattern for **PPE-5** (72) shows similar sharp peaks. The sharp peaks in powder X-ray diffraction patterns indicate that both **PPE-4** (71) and **PPE-5** (72) have crystallinity which agreed with Yamamoto's result for unsubstituted **PPE** polymer[27].

UV-spectroscopic study

Since both silyl compounds ($Me_3SiCCArCCSiMe_3$) 61-65 and diethynyl monomers (HCCArCCH) 66-70 have conjugated functionalities their spectroscopic properties have been studied. Compounds 61-65 as well as 66-70 exhibit strong UV absorption in organic solvents. The absorption spectra for compounds 65 and 70 are shown in Figure 14. Diethynyl monomer 70 has an absorption maximum at λ= 345 nm and three bands at λ= 334 nm, 270 nm and 261 nm in THF solution. Compared with that of diethynyl compound 70 the absorption spectrum of silyl compound 65 shows similiar absorptions in which there are three peaks at 344 nm, 285 nm and 273 nm and an absorption maximum at 357 nm. The absorption spectrum of compound 65 has a red shift of about 11 nm which possibly is due to σ-π conjugation between silicon-carbon σ-bonds and conjugated ethynyl π-bonds. Other monomers have similar absorption spectra.

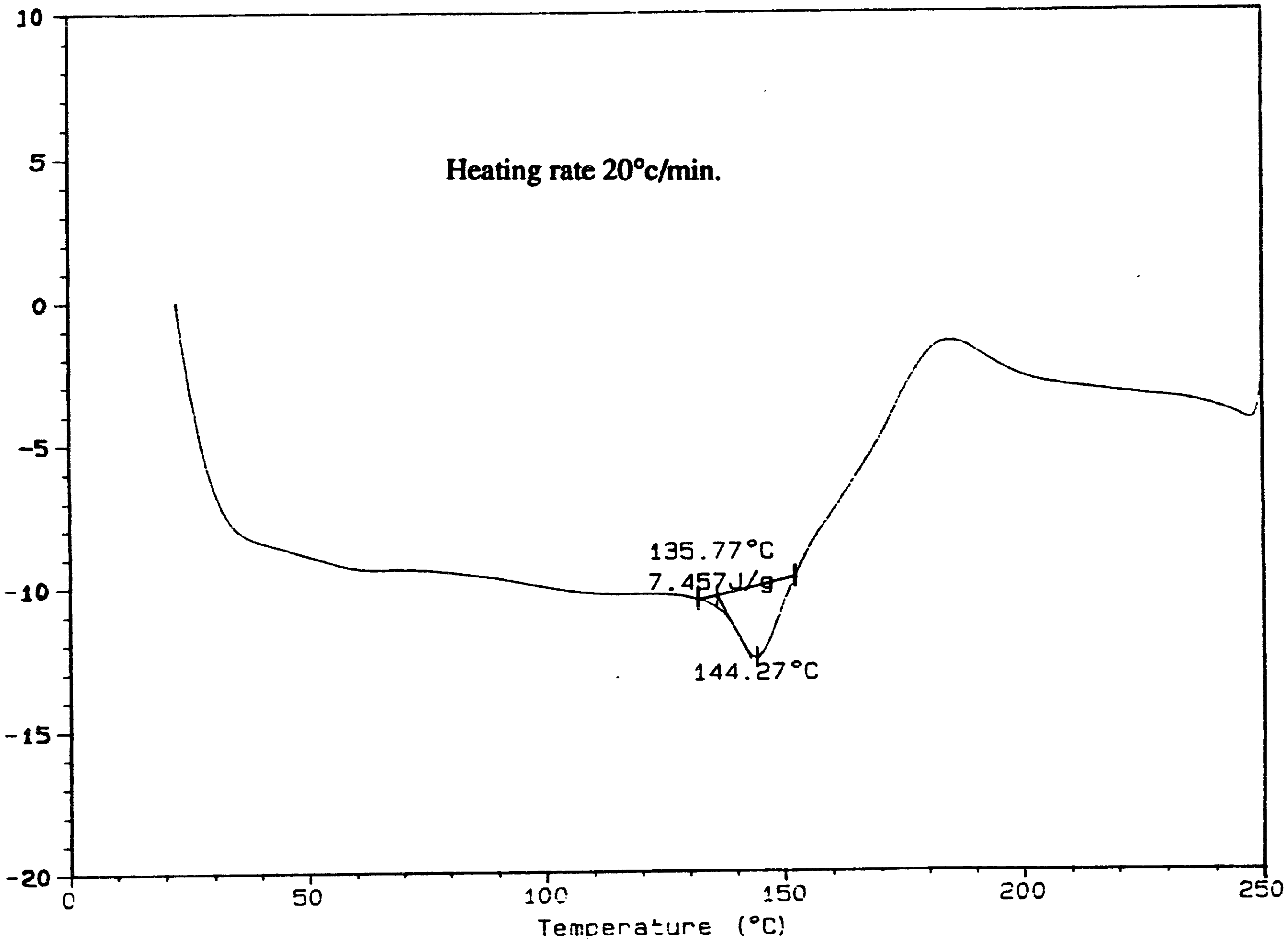


Figure 12. DSC thermogram of **PPE** polymer <u>71</u>

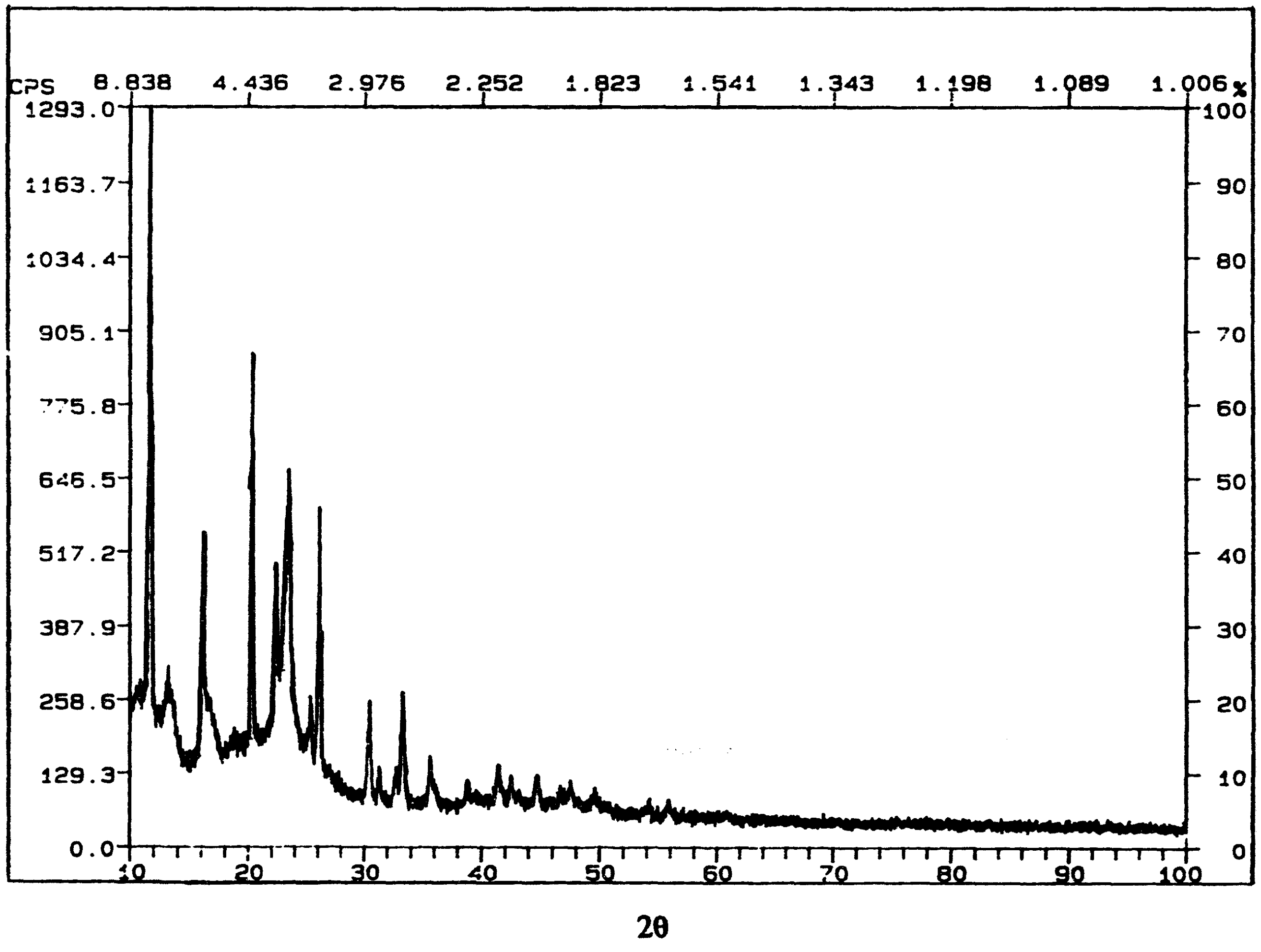


Figure 13. Pattern of powder X-ray diffraction for PPE polymer 71

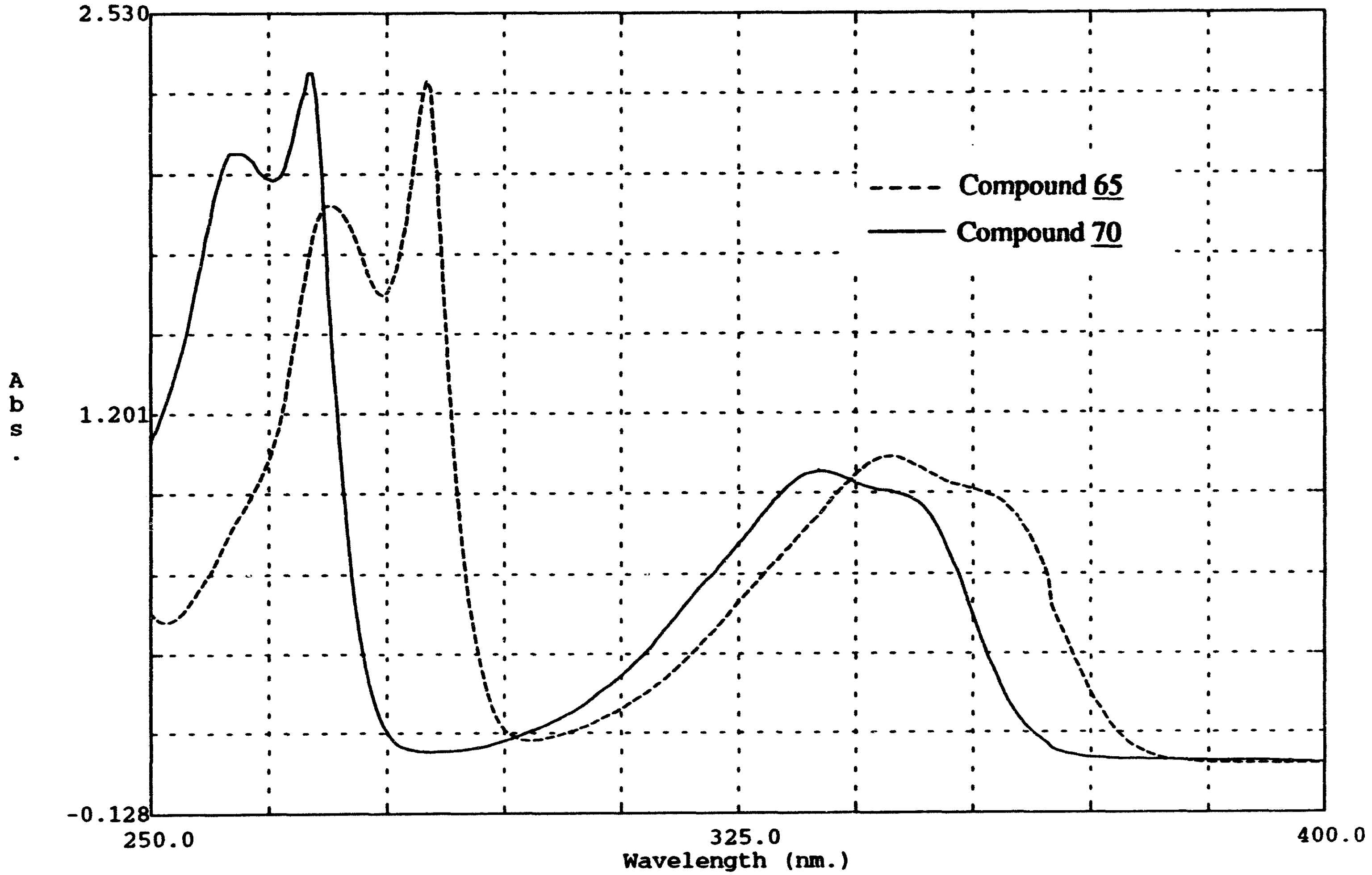


Figure 14. The absorption spectra for compounds 65 and 70 in THF solution

The absorption spectra of PPE polymers 71-75 depend on the physical state. In both dilute THF and toluene solutions the absorption spectra of PPE polymers show two broad and structureless absorption bands at appropriately λ= 440 nm and λ= 316 nm. Figure 15 shows the absorption spectrum of PPE-6 73 in THF solution at room temperature. There is an absorption maximum at λ= 442 nm, an onset at ca. 490 nm, and a second absorption peak at λ= 316 nm.

The absorption spectrum of PPE-6 73 as a film at room temperature is shown in Figure 15 and also shows two absorption peaks at λ= 442 nm and 326 nm. An absorption maximum at λ= 486 nm and an absorption tail to almost 700 nm appear. Other spectra of PPE polymers in the film state show similar absorptions.

Figure 16A shows the absorption spectra for PPE polymer 71 in 2-methyltetrahydrofuran (MTHF) at room temperature. Because it is impossible to find exact molecular weights of polymers, the molecular weight of the repeat units of polymer 71 is used to calculate the concentration of polymer 71 in MTHF solution. With increasing concentration from 10^{-7}M to 10^{-4}M a new band grows in at 480 nm which resemble the lowest energy feature of the solid film (Figure 16B). One possible explanation for the new band at 480 nm is that the PPE polymers in the solid state or concentrated solution have a special aggregation structure which helps the polymer main chains form a coplanar conformation with better π conjugation along the polymer main chain. So the absorption spectra of PPE polymers in the film state or concentrated solution exhibits a new band at ~ 480 nm. Another possible explanation is that inter-chain excitonic interactions are sufficiently strong to create a new state at ~ 480 nm.

The molar extinction coefficients of PPE polymers 71-75 in toluene solution are summarized in Table 5. The molecular weights of the structural units of PPE polymers 71-75 are also used to calculate molar extinction coefficients. The molar extinction

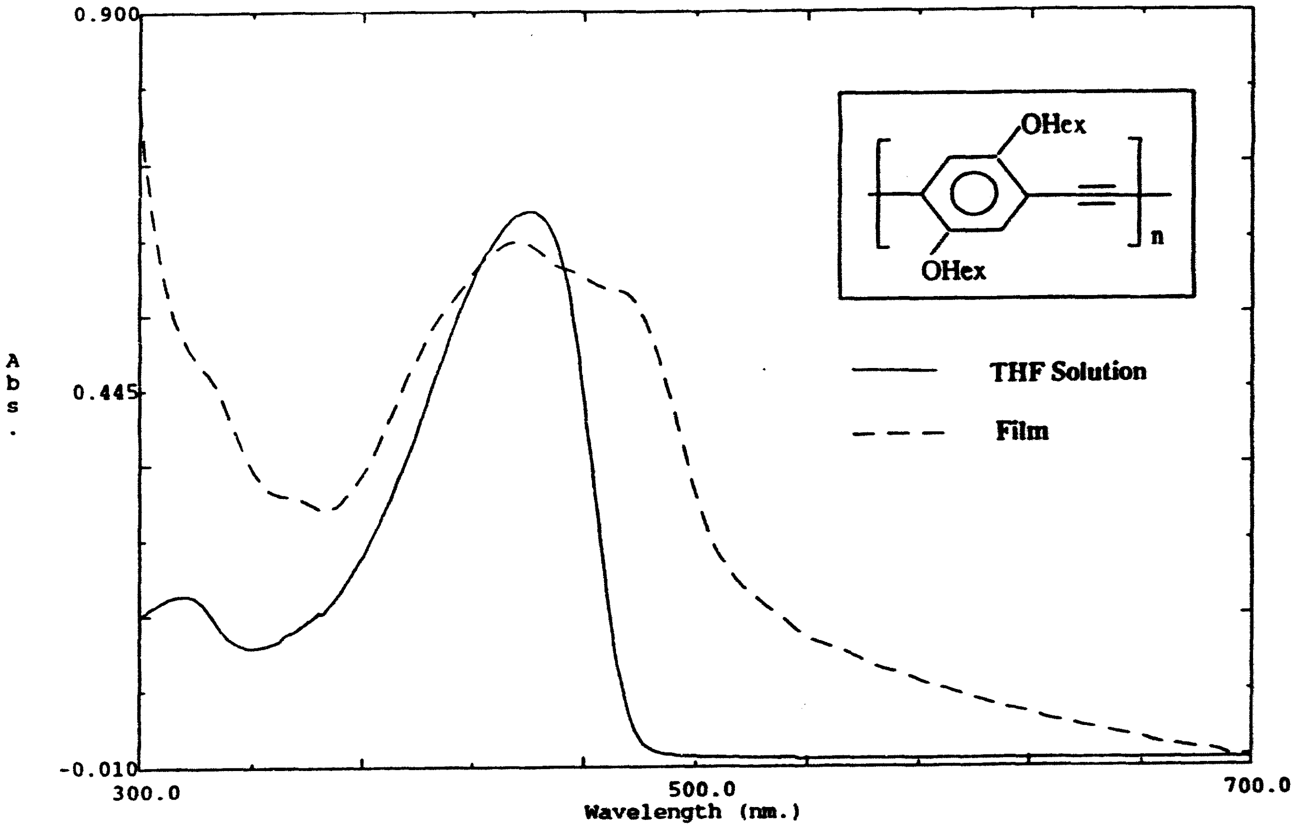


Figure 15. The absorption spectrum for polymer 73 in THF and the film state

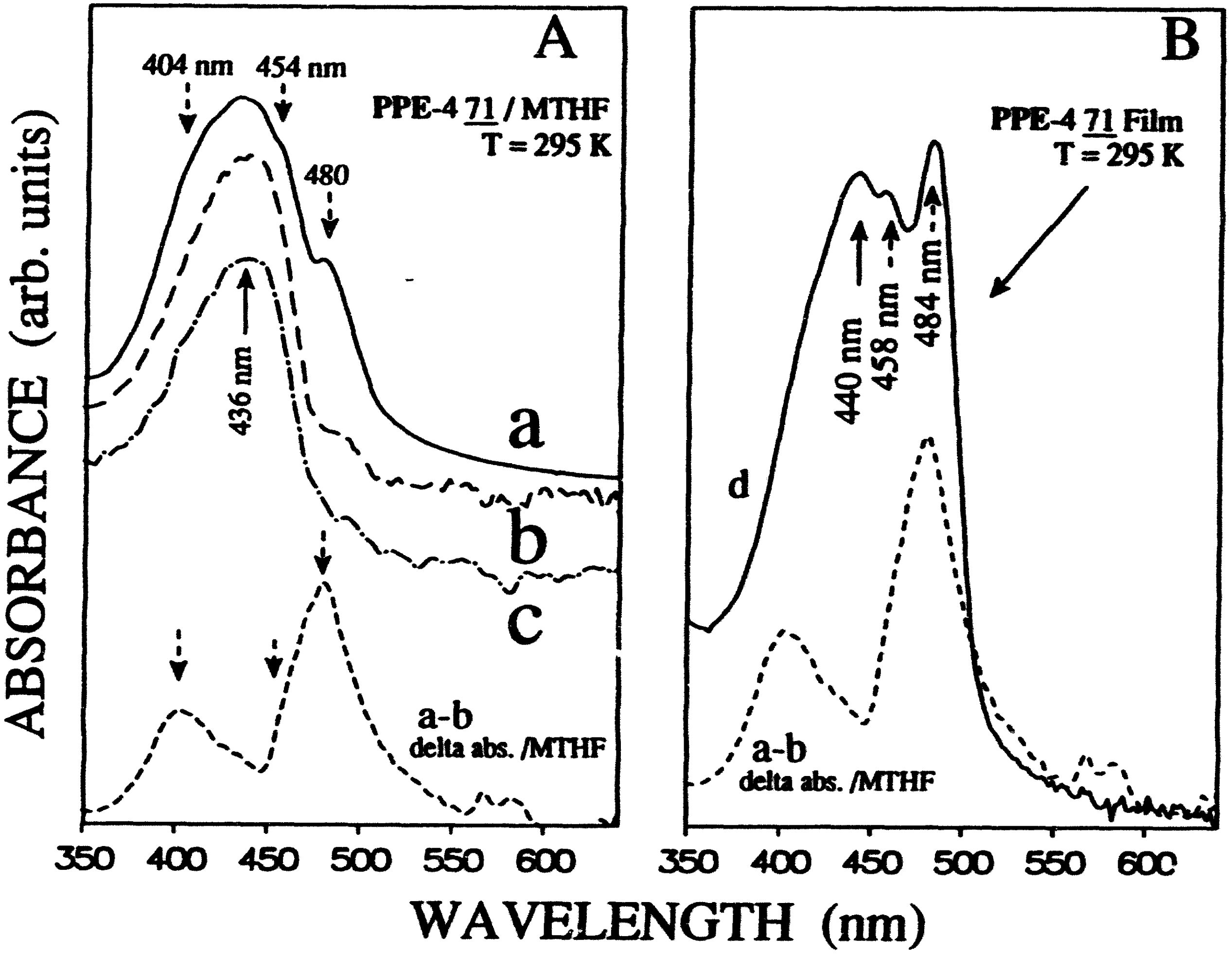


Figure 16. (A) The absorption spectra for polymer 71 in MTHF at 295K
(B) The absorption spectra for polymer 71 in the film state at 295K

coefficients range from ca ~ $9x10^4$ at 440 nm to ~$3x10^4$ at 315 nm. PPE polymers have much stronger absorption at 440 nm than 315 nm.

Table 6 summarizes the absorption bands of PPE polymers 71-75 in different solvents such as toluene, THF, chloroform, and benzonitrile. PPE polymers 71-75 have similar absorption features in these solvents except for benzonitrile. Compared with the λ_{max} of PPE polymers in toluene, the λ_{max} in $CHCl_3$ exhibits a 10 nm red shift. Interestingly, the absorption spectra of PPE polymers 71-75 in PhCN solution depend on the polymer side chain length. The spectra for both polymers 71 and 72 show an absorption maximum at $\lambda = 452$ nm. However, the spectra for polymers 73-75 show a maximum around 490 nm accompanied with an absorption band at 450 nm. The reason for forming this new band in PhCN solution for polymers 73-75 is probably due to an unique aggregation state formed in PhCN.

The absorption spectra of similar PPE-polymers reported by Schultz[43] show a broad structureless absorption with a maximum in the range of $\lambda = 400$-440 nm accompanied by a less intense absorption at shorter wavelengths ($\lambda = 310$-320 nm). For example, the absorption spectrum of one of his polymers with the octadecoxy side chain in chloroform shows a maximum at $\lambda = 410$ nm. In comparison, our PPE polymers have an approximately 40 nm red shift which indicates that Schultz's polymers have very short main chains. Schultz's PPE polymers clearly have different structures from ours as is also revealed by NMR experiments.

A chloroform solution containing both PPE-6 73 and TCNE was refluxed for 20 hours, but no charge transfer complex bands were observed in UV absorption spectra and the solution kept its fluorescence.

Table 5. Summary extinction constants

No	Polymers	Peak 1.	Peak 2.	DP
71	PPE-4	$8.6\text{x}10^4$ (439nm)	$3.0\text{x}10^4$ (315nm)	18
72	PPE-5	$9.5\text{x}10^4$ (438nm)	$3.4\text{x}10^4$ (314nm)	14
73	PPE-6	$8.9\text{x}10^4$ (438nm)	$3.1\text{x}10^4$ (314nm)	14
74	PPE-8	$11\text{x}10^4$ (440nm)	$3.4\text{x}10^4$ (316nm)	21
75	PPE-10	$8.5\text{x}10^4$ (442nm)	$2.8\text{x}10^4$ (317nm)	>21

Study of fluorescence of PPE polymers

The PPE polymers in organic solutions upon excitation emit a strong greenish fluorescence. The emission spectrum of PPE-6 (73) in THF solution at room temperature in Figure 17 shows a strong emission at λ= 470 nm and a broad and structureless emission at λ= 501 nm with a tail ending at λ= 690 nm. In a collaboration with Prof. G.J. Small, laser-excited fluorescence of PPE polymer 71 was studied. Figure 18A shows both absorption and fluorescence (λ_{ex} = 360 nm) spectra for PPE 71 in the film state at low temperature (4.2 K). Figure 18B shows fluorescence spectra of PPE 71 at different concentrations in MTHF solution at room temperature and 4.2 K. The fluorescence spectrum at high concentrations bears a striking resemblance to that of the solid film. From Figure 18A it is clear that the fluorescence spectrum is significantly sharper than the absorption spectrum and that the origin band at 512.2 nm is located in the tail region.

Table 6. Summary of UV absorption of PPE polymers in different solvents

No	Polymers	Toluene	THF	$CHCl_3$	PhCN	DP
<u>71</u>	PPE-4	315nm 438nm	316nm 442nm	317nm 449nm	452nm	18
<u>72</u>	PPE-5	314nm 438nm	315nm 440nm	318nm 448nm	452nm	14
<u>73</u>	PPE-6	314nm 439nm	316nm 441nm	320nm 448nm	452nm 490nm	14
<u>74</u>	PPE-8	316nm 440nm	316nm 442nm	318nm 450nm	446nm 486nm	21
<u>75</u>	PPE-10	317nm 442nm	317nm 443nm	318nm 453nm	446nm 493nm	>21

All measurements were done at room temperature.

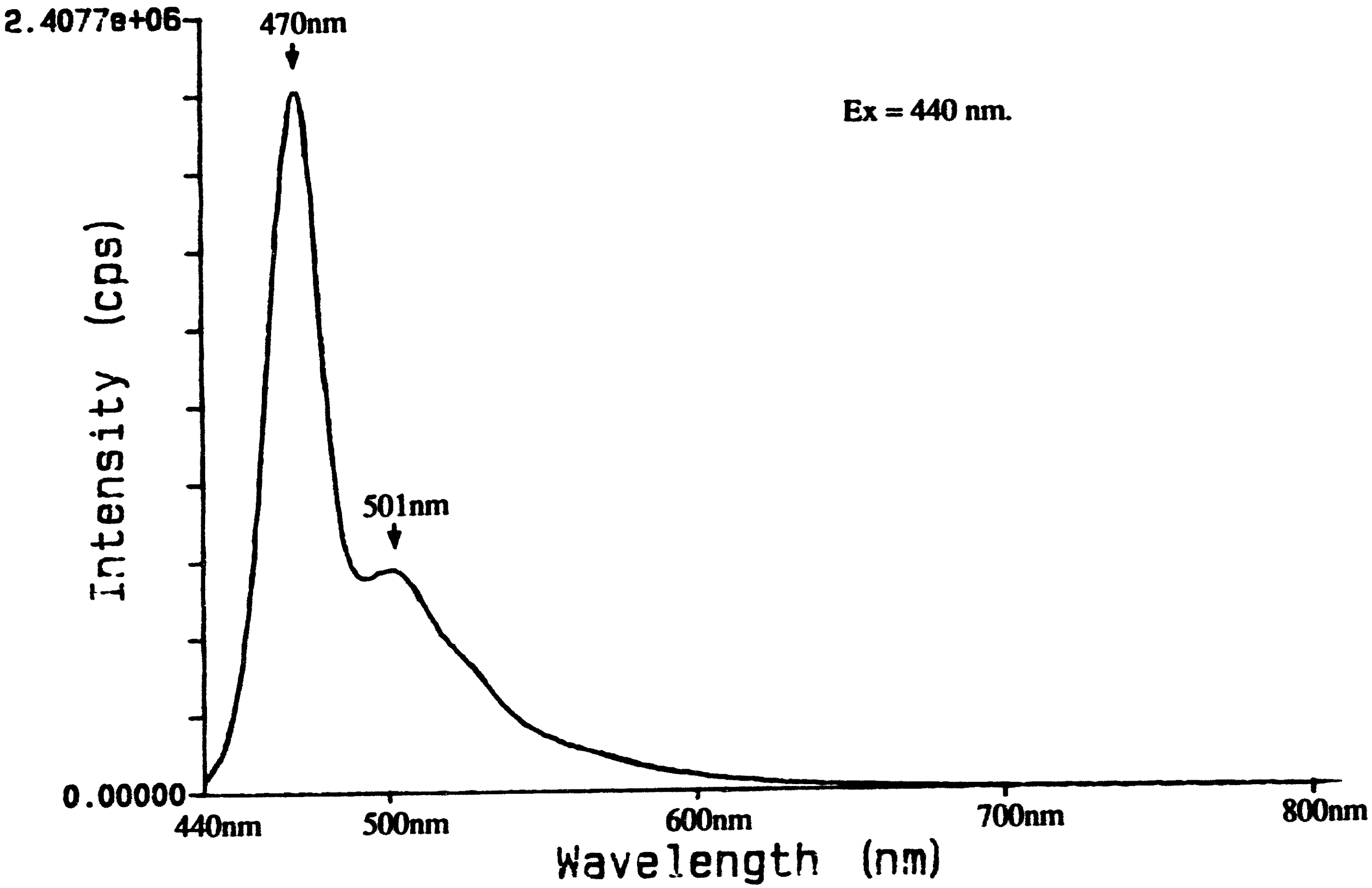


Figure 17. The emission spectrum for polymer 73 in THF at room temperature

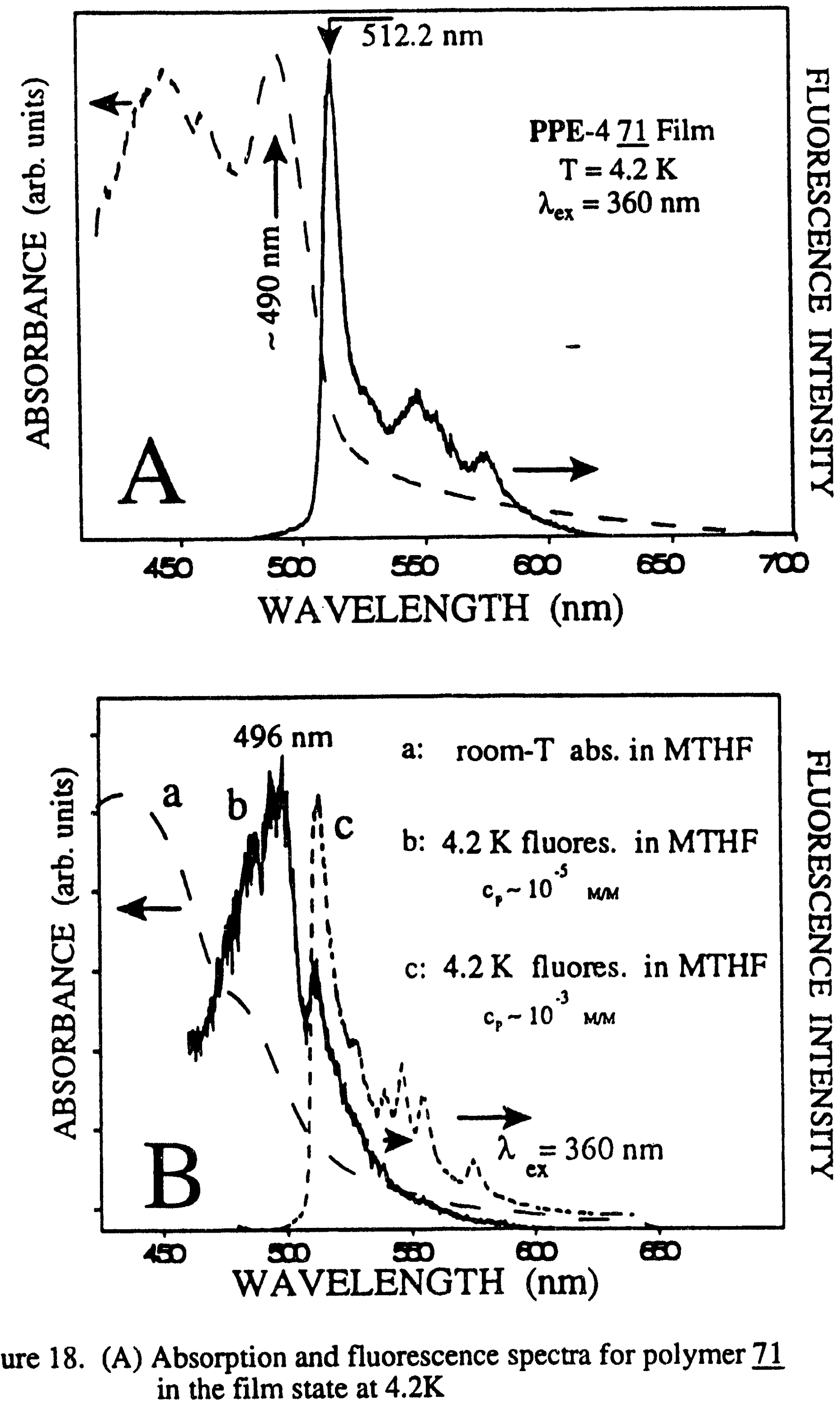


Figure 18. (A) Absorption and fluorescence spectra for polymer 71 in the film state at 4.2K

(B) Fluorescence spectra for polymer 71 in MTHF solution at room temperature and 4.2K

These results prove that ultra-fast downward energy cascading in the film and in the glass (at least for sufficiently high concentration) occurs to "localized" tail states which are emissive. However, these data are not sufficient to understand the polymer excited state electronic and vibrational structures. Further experiments are required to solve this problem.

Light Emitting Diodes (LEDs)

Because **PPE** polymers emit strong fluorescence upon excitation, the films of **PPE** polymers 71-75 could be used as the emissive layer in **LED** devices. In a collaboration with Prof. Shinar of Department of Physics **PPE** polymer-based **LED** devices have been made and studied. The **LED** device structure[47] is shown in Figure 19. The glass substrate is covered by the indium tin oxide (ITO) layer which was transparent and conductive. **PPE**-polymer is coated onto the ITO layer. Calcium or aluminum metal is deposited on the **PPE** surface by a metal vaporization apparatus or an electron beam apparatus. The device is placed either in vacuum or covered by aluminum oxide. A yellow light is emitted at low applied voltages.

Both the current-voltage (**I-V**) curve and the emission intensity-voltage curve of a **LED** using **PPE-6** 73 as emissive layer and calcium as the electron injection layer measured at 20 K is shown in Figure 20. Both current and emission intensities start to increase drastically above 40 volts.

The dependence of the total **EL** intensity on injected current **I** for the same diode used to produce the data shown in Figure 20 is plotted in Figure 21. Although the emission intensity appears to be directly proportional to **I**, its behavior is slightly nonlinear with a slope that increases with **I** at low values of the injected current. This dependence is

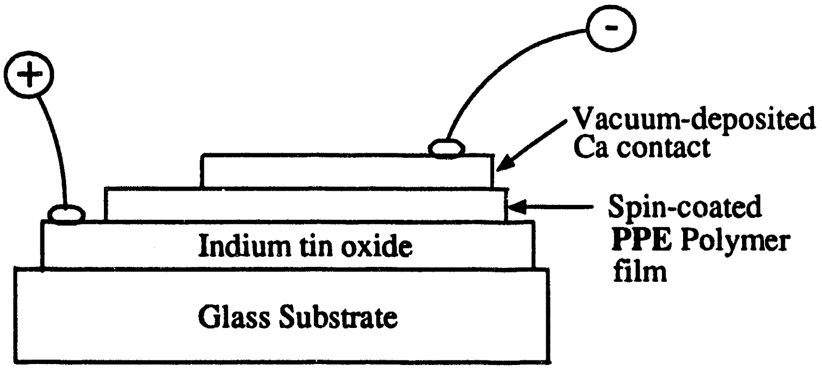


Figure 19. **LED** device

quite anomalous in comparison to inorganic **LEDs** such as GaAs in which **EL** intensity tends to saturate at high injection current.[47b]

The absorption, **PL**, and **EL** emission spectra of a typical **LED** using the **PPE-6** 73 as the emissive layer and Ca/Al as the electron injection layer is shown in Figure 22. The **EL** spectra is clearly slightly red-shifted with respect to the **PL** spectra with an overall emission in the yellow region of the visible spectrum.

Significant improvement in the performance of the **ITO/PPA-4** (71)/Al and **ITO/PPA-6** (73)/Al diodes was observed following annealing for 2-6 hours at about 150°C. That is the emission became much more homogeneous. Whereas the initial active area was typically about 20% it increased to about 80% following annealing. Some of the diodes were operable continuously for about 18 hours at a bias voltage of about 10V and injected current of about 0.5 mA despite exposure to air without a heat-sink. The **EL** threshold voltage typically decreased by about 30% following annealing. Some of the annealed **LEDs** were operable at temperature in excess of 75°C in most cases and up to

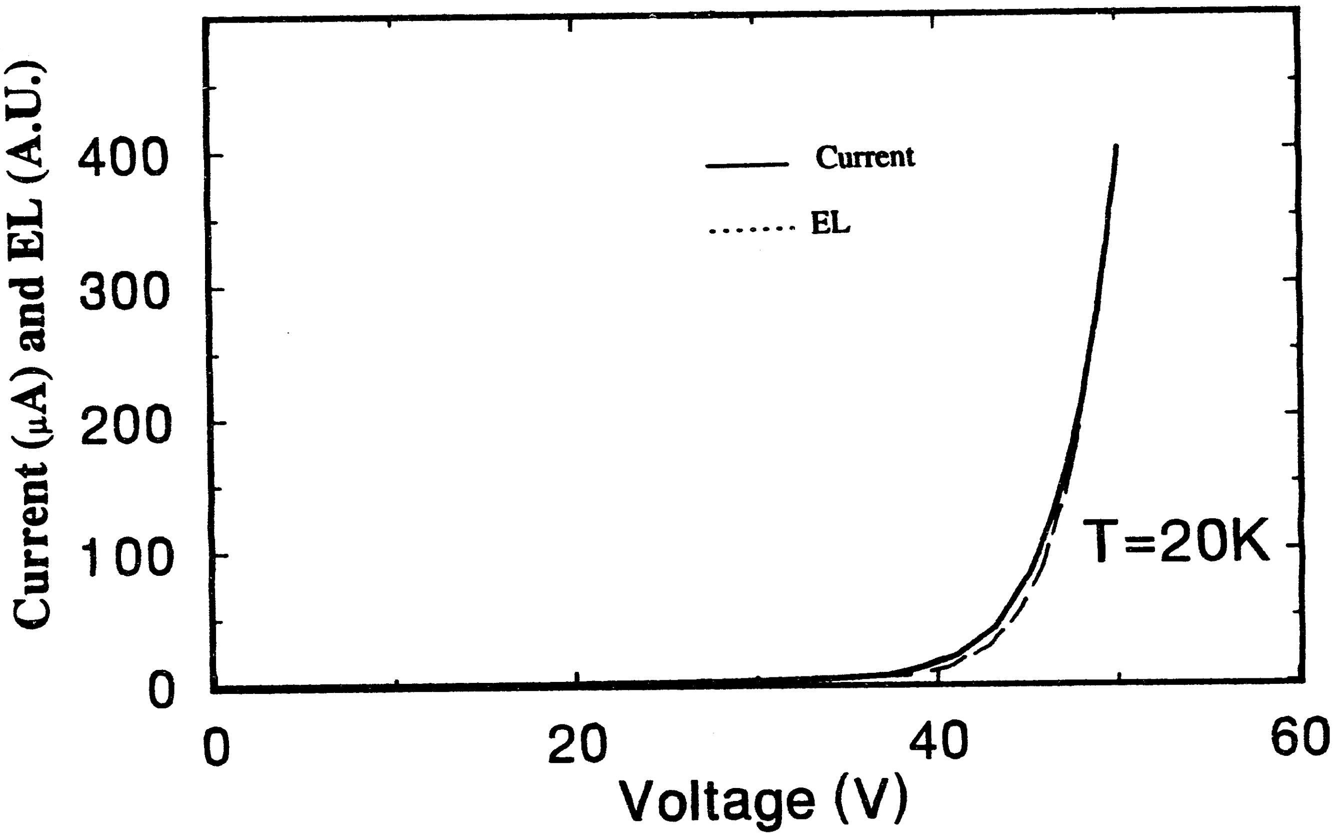


Figure 20. The current-voltage (I-V) curve and the emission intensity-voltage curve of a **LED** using **PPE-6** 73 as emissive layer is measured at 20K

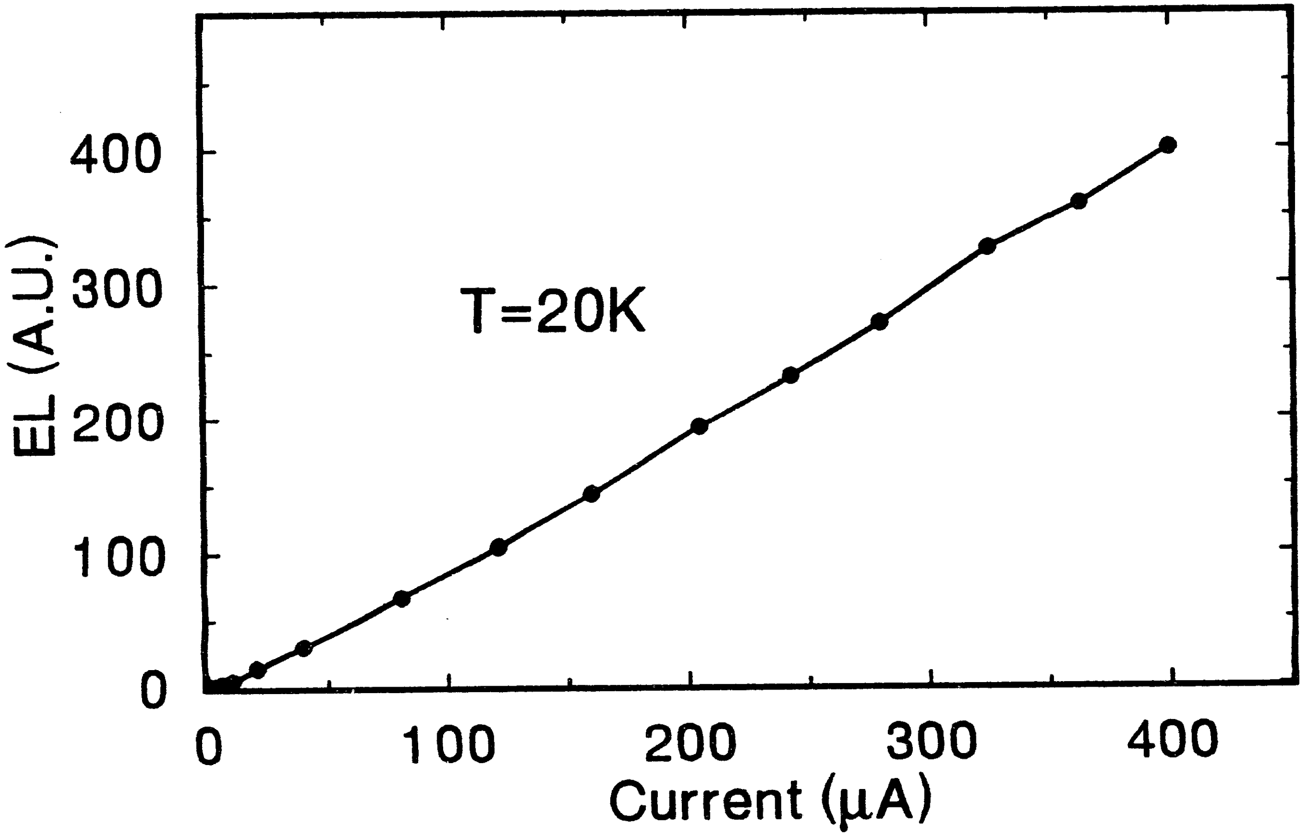


Figure 21. The dependence of the total EL intensity vs injected current I

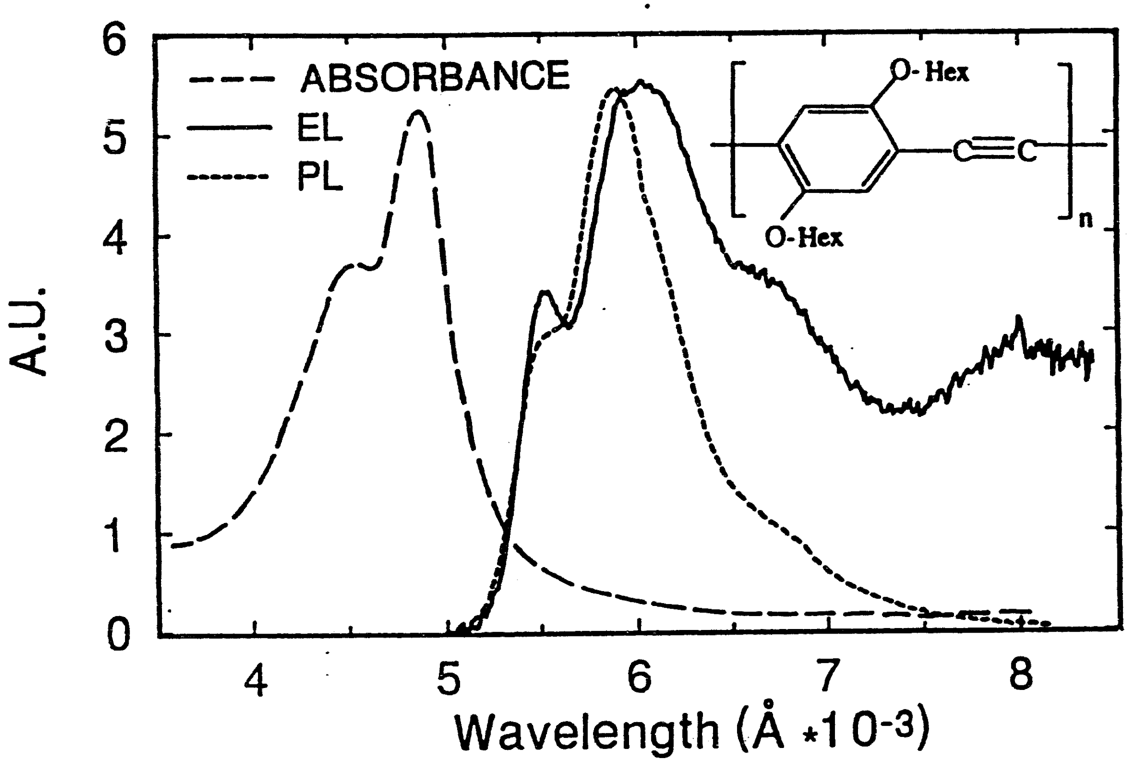


Figure 22. The EL spectrum of an ITO/PPE-6/Ca LED at 20 K

100° in some of the diodes. However, they failed above 100°C due to short circuits.

The quality of **LED** devices also depends on the homogeneity of the **PPE** film, which is mainly determined by polymer structure and molecular weight. Crystallization will occur if the polymer has low molecular weight, as was observed in our experiments. For example, the **LED** device made of **PPE-4** 71 with Mn of 3000 failed but succeeded with Mn above 8000. This crystallization will result in pinholes in the film which can be observed by microscope and the **LED** device will fail due to short circuits.

The yellow or greenish light can be observed by the human eye from this **PPE**-based **LED** only under weak light conditions which means the light intensity of this **LED** is not strong enough to compete with that of **inorganic material**-based **LEDs**. Also this **LED** can continuously emit light for only 24 hours in a dry box. Consequently, increasing the light intensity and improving the stability will be the next challenge.

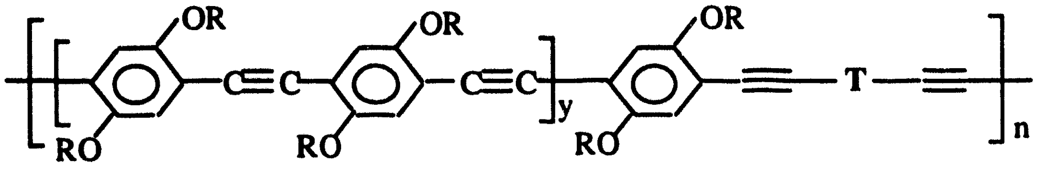
Conductivity

In a collaboration with Shinar's group the conductivity of **PPE-4** 71 was measured[48] by using a two probe technique. After doping with I_2 at 80°C, **PPE-4** 71 has a conductivity of $\sigma = 10^{-3}$ S/cm. However, **PPE-4** 71 shows a higher conductivity ($\sigma = 3\text{x}10^{-3}$ S/cm) after doping with AsF_5 at room temperature.

Block copolymers and color tuning of **LED** devices

PPE block copolymer 89 as shown in Scheme 27 can also be conveniently synthesized by using palladium-catalyzed polymerization. Tether **T** can be either a flexible sequence such as ethylene or a rigid-rod one such as phenylene. If the copolymer

89 has a flexible tether π-π conjugation along the polymer main chain will be broken. Since the bandgap of a **PPE** polymer will increase by decreasing the length of the π-π conjugated main chain both absorption and emission maximums will have a blue shift. Thus the emission range of **PPE** polymer 89 should be controllable by the length of polymer sequence.



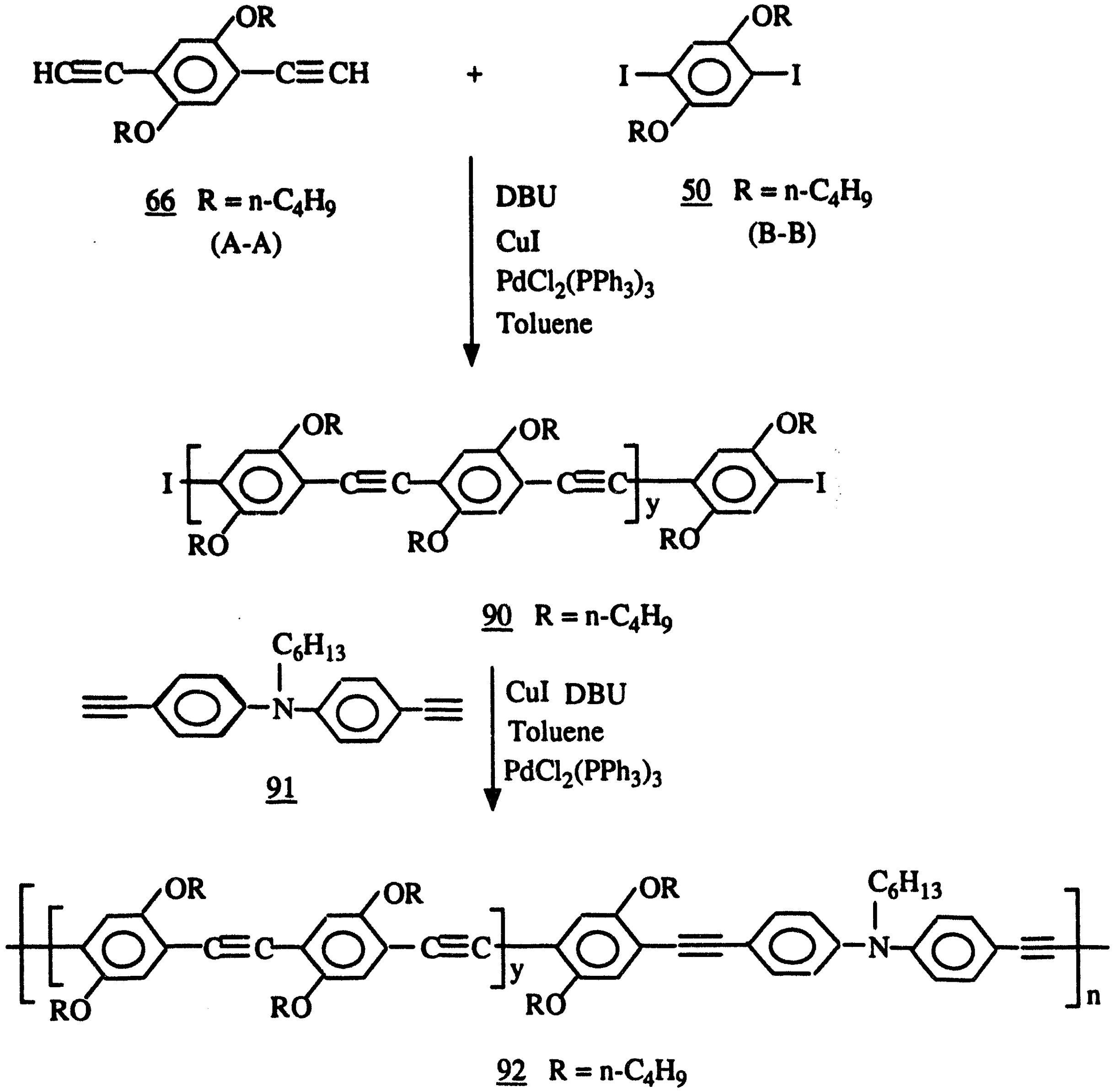
89

RO = alkoxy groups **T** = methylene, silylene

Scheme 27. **PPE** block copolymers

The length of the rigid-rod sequence in **PPE** block copolymer 89 can also be controlled by the polymer synthesis. The reactions in Scheme 28 demonstrate a synthetic example. The diiodo monomer 50 reacted with diethynyl monomer 66 in a ratio higher than 1:1. Therefore, in the first stage the macromer 90 formed with iodo as the end group if the diiodo monomer was in excess. In the second stage the second monomer 91 was then reacted with the macromer 90 to afford the block copolymer 92. The block copolymer was characterized by NMR, FT-IR, GPC and elemental analysis.

The length of macromer 90 can be controlled by varying the ratio between monomers 46 and 56[49]. For the polymerization of the bifunctional monomers A-A (66) and B-B (50) (diethynyl compound and diiodo compound) where B-B is present in excess the numbers of A and B functional groups are given by NA and NB respectively. NA and NB are equal to twice the number of A-A and B-B molecules respectively that are present.



Scheme 28. Synthesis of a block copolymer

The stoichiometric imbalance r of the two functional groups is given by r= NA/NB. The total number of monomer molecules is given by (NA + NB)/2 or NA(1 + 1/r)/2.

The extent of reaction p is defined as the fraction of A groups that have reacted at a particular time. The fraction of B groups that have reacted is given by rp. The fractions of unreacted A and B groups are (1-p) and (1-rp), respectively. The total numbers of unreacted A and B groups are NA(1-p) and NB(1-rp) respectively. The total number of polymer chain ends is given by the sum of total number of unreacted A and B groups. Since each polymer chain has two chain ends the total number of polymer molecules is one half the total number of chain ends or [NA(1-p) + NB(1-rp)]/2.

The number-average degree of polymerization Xn shown in Equation 1 is the total number of A-A and B-B molecules initially present divided by the total number of polymer molecules. When the polymerization is 100% complete (that is, p = 1.000), Equation 1 becomes Xn = (1+r)/(1-r). In actual practice p may approach, but never become equal to, unity.

$$Xn = \frac{N_A(1+1/r)/2}{[N_A(1-p) + N_B(1-rp)]/2} = \frac{1+r}{1+r-2rp}$$

Equation 1. Degree of polymerization[50]

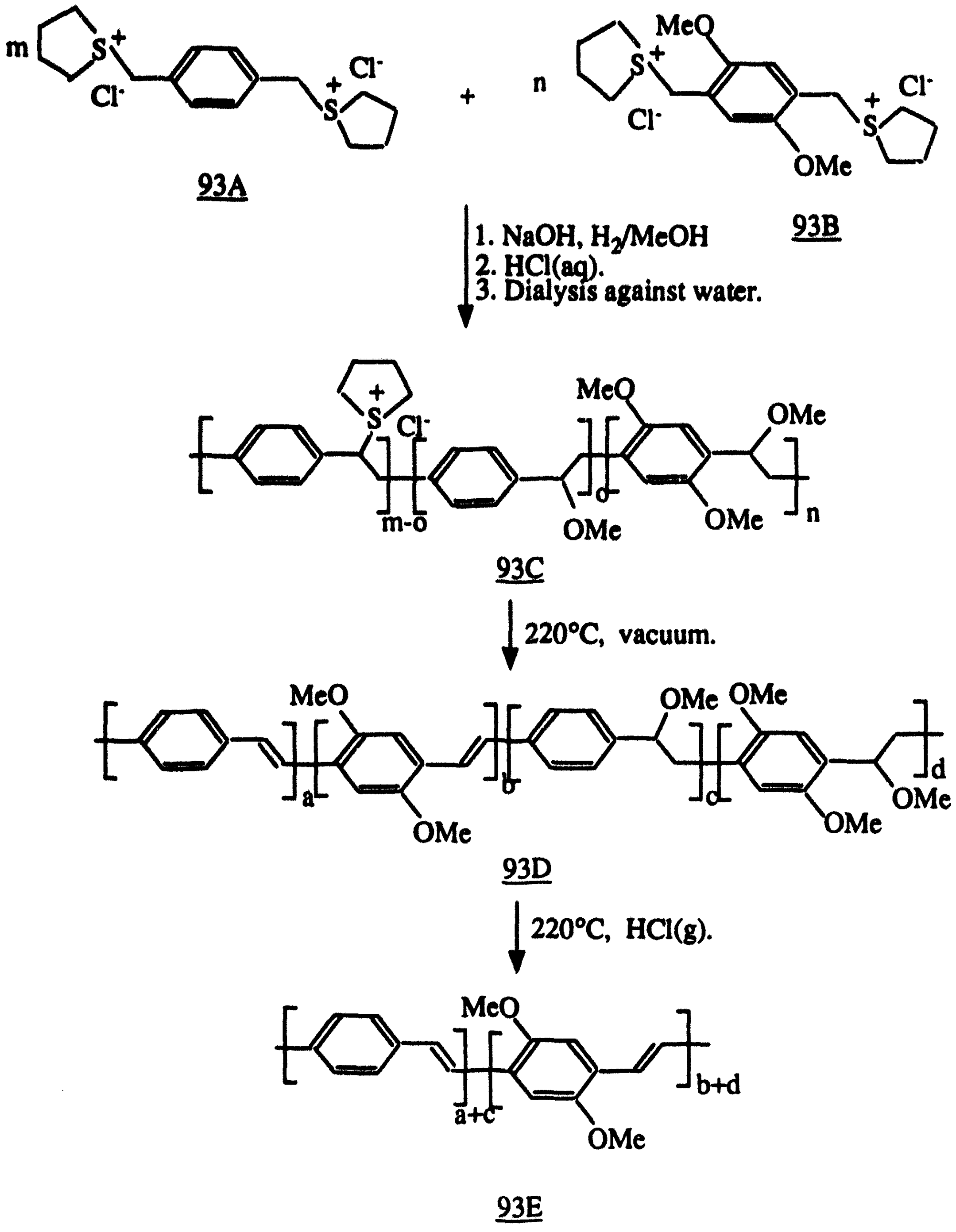
For block copolymer 92 r (the ratio between diethynyl monomer and diiodo monomer) is equal to 0.87. After the first stage of the polymerization shown in Scheme 28, Xn is 13 according to equation 1 (p = 1). After the second stage the PPE macromer 90 was connected by the second monomer 91. (Mn= 8.6×10^3. Mw= 2.1×10^4. Mw/Mn = 2.4.)

Control of the emission color is a requirement for the achievement of full-color displays. Fortunately, copolymers offer considerable flexibility for fine-tuning the emission color. Friend's group[50-52] has studied copolymers of PPV and its derivatives and has seen a linear shift in the emission spectra with varying composition. The synthetic pathway is illustrated in Scheme 29. Both monomers 93A and 93B copolymerized to form copolymer 93C which was then converted to copolymers 93D or 93E by heat treatment under different conditions. For example, a copolymer 93D thermally prepared from a precursor 93C which was synthesized from a 4:1 feed ratio of 93A to 93B had an absorption maximum at 376 nm and a copolymer 93E also thermally prepared from the same precursor 93C in HCl gas instead of vacuum had an absorption maximum at 427 nm. The LED devices made from 93D and 93E emitted different colors. Therefore, the emission color of the LED devices can be varied by controlling the copolymerization and the degree of conversion to the conjugated form.

Because the conjugation length of PPE copolymers can be controlled by the ratio between the monomers, the tuning of λ_{max} of UV absorption spectra can also be achieved. Figure 23 shows the UV absorption spectra of both PPE-4 71 and its copolymer 92. Compared with homopolymer PPE-4 71 the copolymer 92 has a 15 nm blue shift in the absorption maximum. The LED device made of 92 emitted a green color while others emitted a yellow or a yellow green color.

Laser dyes

Another feature of PPE polymers related to fluorescence is that they might be good laser dyes. Ethylene glycol[20] is a popular solvent for laser dyes, however PPE polymers are not soluble in this solvent. In order to make ethylene glycol-soluble PPE polymers one obvious method is to synthesize PPE polymers with hydroxyl functionality in the side chains. In principle PPE polymers 93 (Figure 25) should be soluble in



Scheme 29. Synthesis of an electroluminescent copolymer[51]

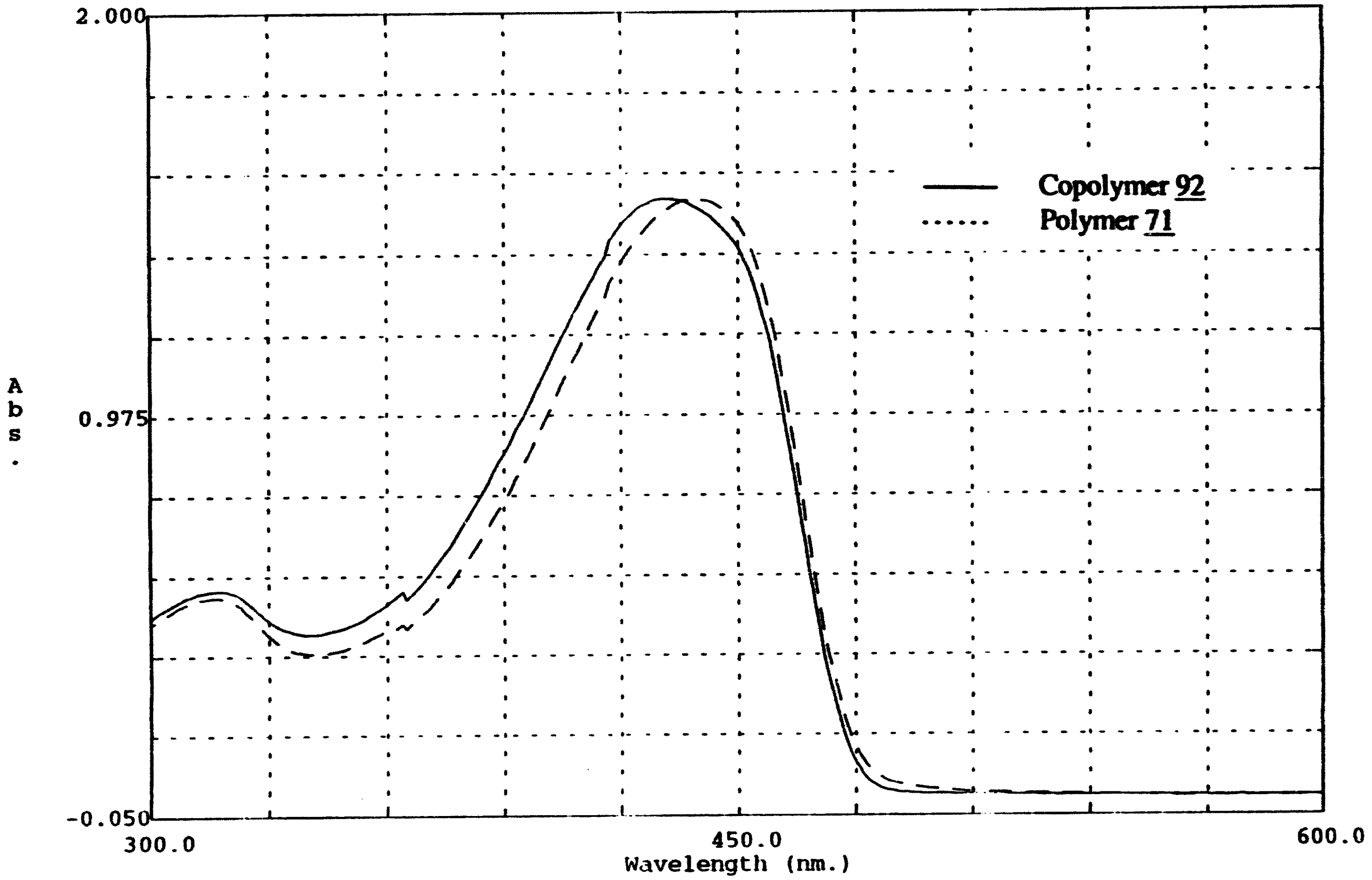
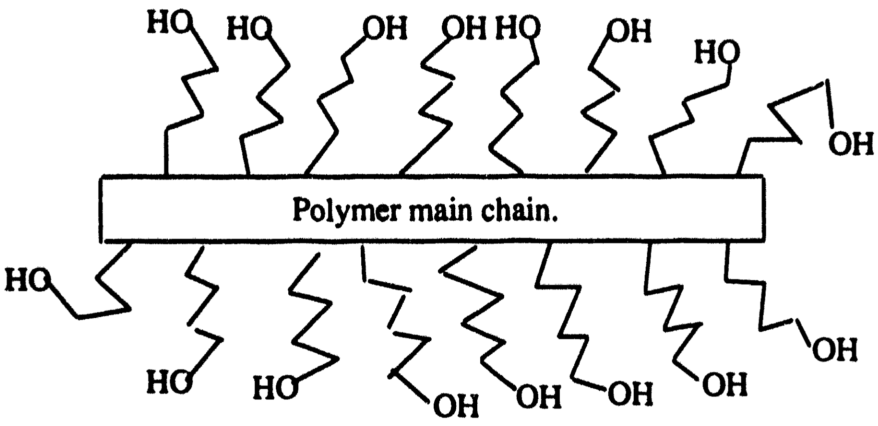


Figure 23. The absorption spectra for polymer 71 and copolymer 92 in THF at room temperature



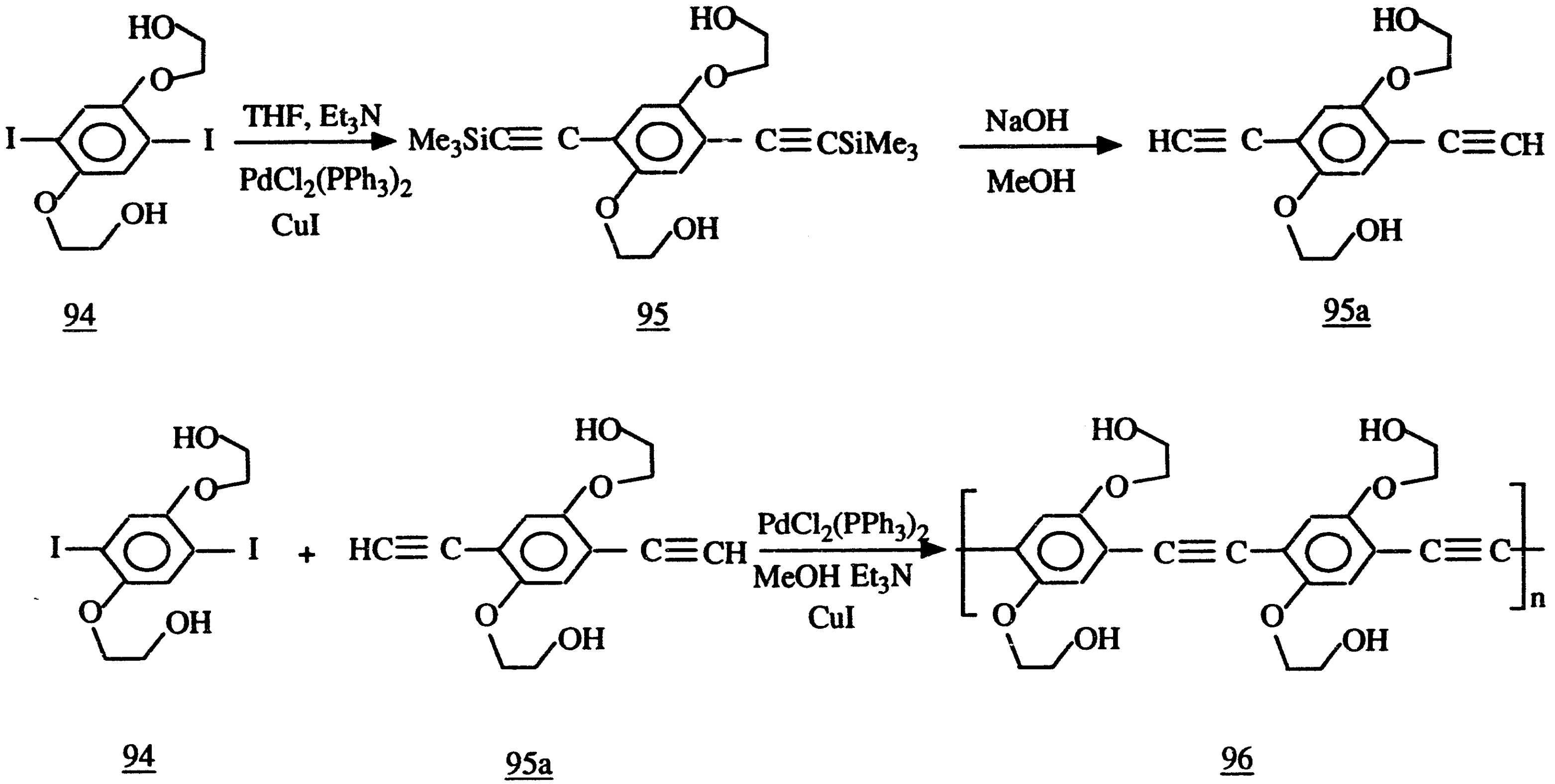
93

Figure 25. Model of an alcohol soluble **PPE** polymer

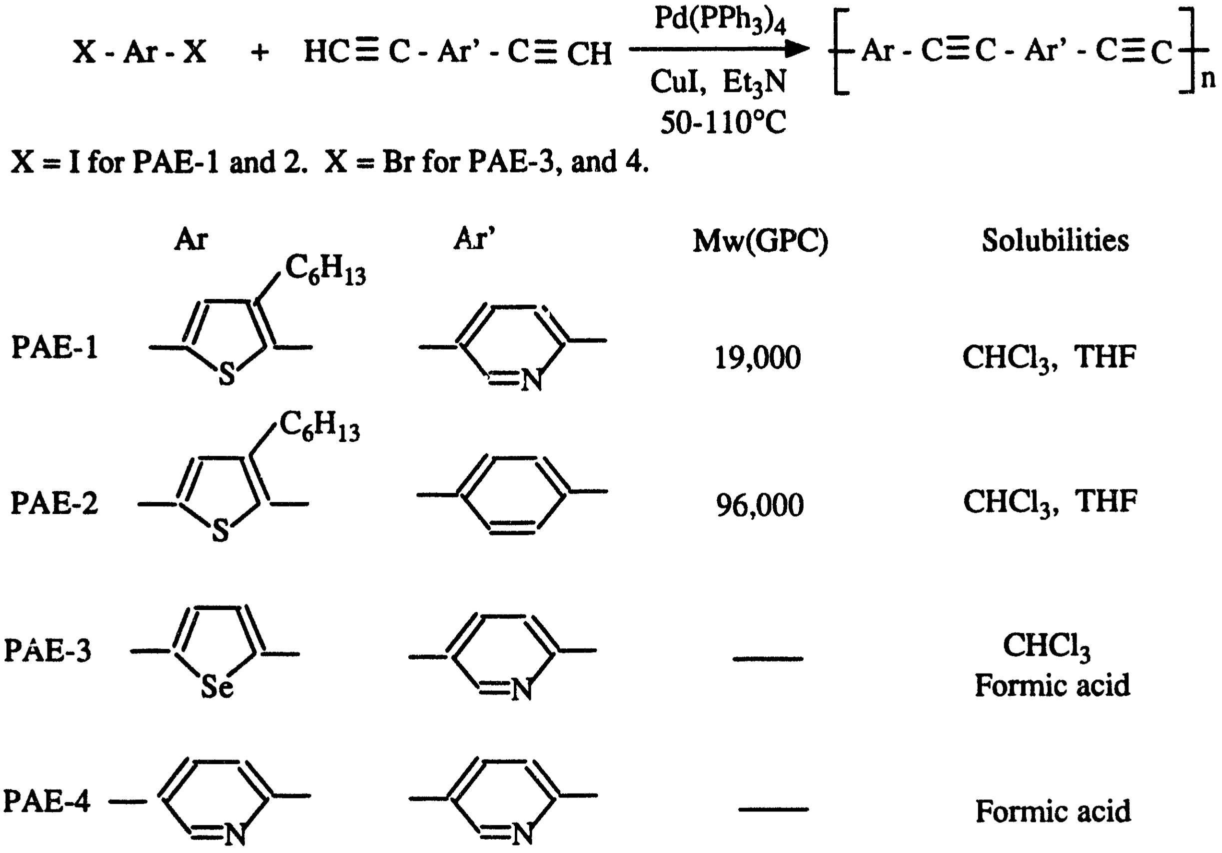
alcohols.

PPE polymer 96 (Scheme 30) is conveniently synthesized by Pd-catalyzed polymerization. Both monomers 94 and 95a are soluble in methanol. During the polymerization both an amine salt and a polymer precipitated from the solution simultaneously. Unfortunately, polymer 96 (λ_{max}= 424 nm in THF) had very low solubility in ethylene glycol or other organic solvents after purification and drying. Further modification of the **PPE** polymer structures is required to make them dissolve in ethylene glycol.

When this work was finished Yamamoto[53,54] reported the preparation and optical properties of soluble **PPE** polymers ([-Ar-CC-Ar'-CC-]n (Scheme 31). Both PAE-1 and 2 were characterized by ^{1}H-NMR, FT-IR and GPC. All of these polymers emit visible light when irradiated with UV or visible light (340-440 nm) and they are potentially useful electroluminescent materials. The film of PAE-2 exhibited a fairly strong THG with the $\chi^{(3)}$ value of about 10^{-10} esu as measured at 1.9 μm as the fundamental wavelength. PAE-1 is amorphous as judged from its powder X-ray diffraction pattern.



Scheme 30. Synthesis of alcohol soluble **PPE** polymer



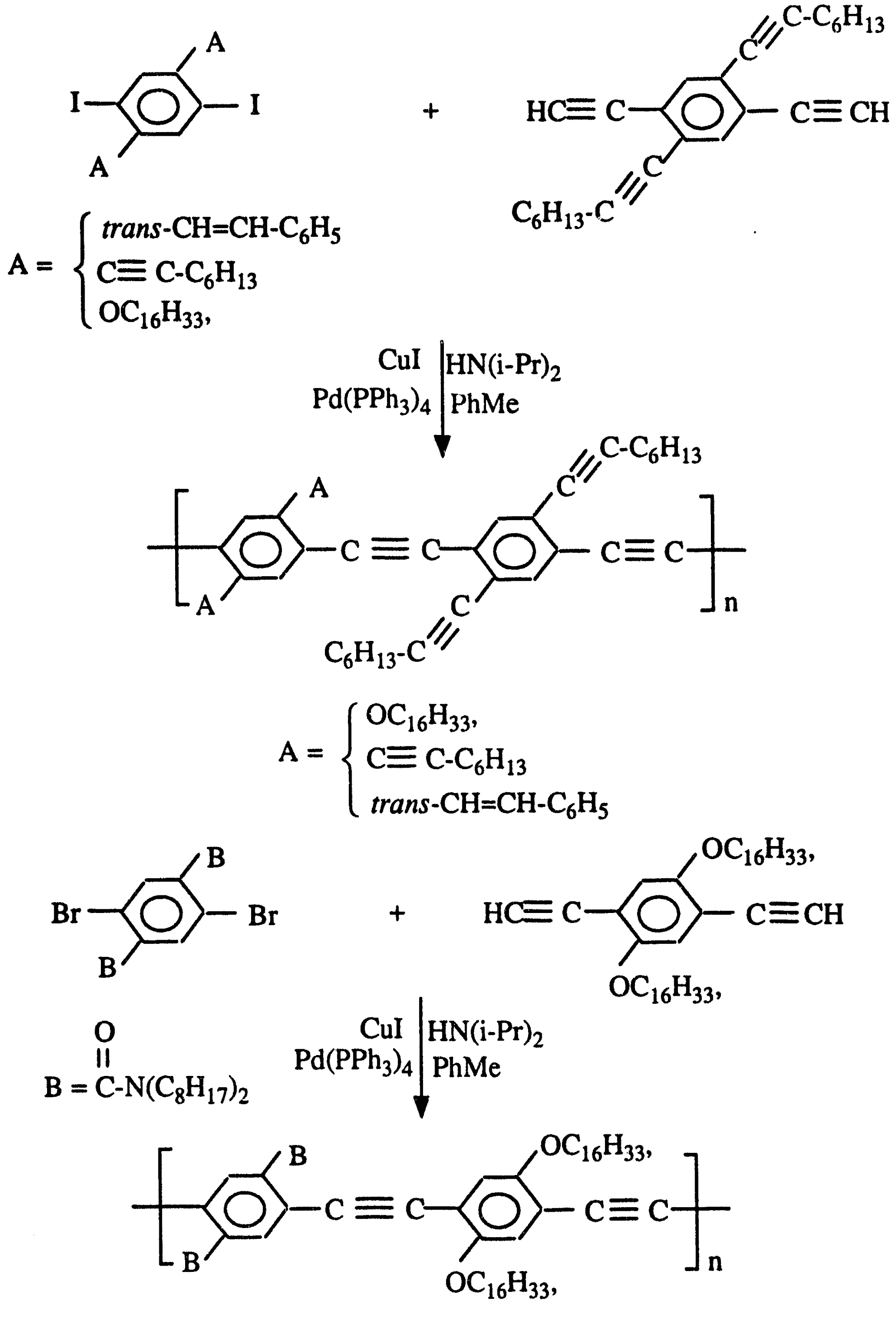
$$\mathrm{X - Ar - X} \quad + \quad \mathrm{HC{\equiv}C - Ar' - C{\equiv}CH} \xrightarrow[\substack{\mathrm{CuI,\ Et_3N} \\ 50\text{-}110^{\circ}\mathrm{C}}]{\mathrm{Pd(PPh_3)_4}} \left[\mathrm{Ar - C{\equiv}C - Ar' - C{\equiv}C}\right]_n$$

X = I for PAE-1 and 2. X = Br for PAE-3, and 4.

	Mw(GPC)	Solubilities
PAE-1	19,000	$CHCl_3$, THF
PAE-2	96,000	$CHCl_3$, THF
PAE-3	—	$CHCl_3$ Formic acid
PAE-4	—	Formic acid

Scheme 31. Synthesis of soluble **PAE** polymers[53,54]

As part of an effort to achieve liquid crystalline materials with extended conjugation Swager[55] reported the synthesis of the following functionalized **PPE** polymers (Scheme 32). However, these polymers, except the one with amide as the side chain, are only partially soluble and no characterizations were given in his paper[55].



Mn = 43,000 (GPC)

Scheme 32. Synthesis of functionalized **PPE** polymers[55]

CONCLUSIONS

A series of diiodo monomers as well as diethynyl monomers were synthesized. Based on these diiodo and diethynyl monomers, a series of soluble rigid-rod **PPE** derivative polymers, poly(2,5-dialkoxy-1,4-phenyleneethynylene)s, and one **PPE** block copolymer were synthesized by using a palladium-catalyzed polymerization. **PPE** polymers were well characterized by FT-IR, NMR and GPC since they were soluble in some organic solvents. As expected, these **PPE** polymers exhibited conductivity after doping with iodine and AsF_5.

These polymers showed a strong UV absorption between 350 nm and 500 nm. The absorption maximum for these **PPE** polymers appeared at 440 nm in a THF solution. Compared with the UV aborption in a THF solution, the absorption of these **PPE** in the film state showed a new peak at 480 nm and this new peak is presumably due to the better conjugation of these polymer in the solid state. These **PPE** polymers emit strong greenish or yellowish fluorescence upon excitation and a **PPE polymer-based LED** device was successfully prepared and studied. Unfortunately, this **LED** device had a short lifetime and low brightness. Improving both the light intensity and the stability of a **PPE-based LED** devices still remains a big challenge.

Some of these polymers did exhibit crystallinity as proved by powder X-ray diffraction patterns. However, attempts to study the thermotropic liquid crystalline properties of these **PPE** polymers failed due to their decomposition before melting.

SECTION TWO:

POLY(ETHYNYLENE-PHENYLENE-ETHYNYLENE-SILYLENE)S

INTRODUCTION

In order to introduce flexibility into the **PPE** polymer main chain for studying liquid crystalline properties and examining the effects of silicon in the polymer main chain of **PPE** polymers, poly(ethynylene-phenylene-ethynylene-silylene), a silicon containing polymer, hereafter referred to as **PEPESi$_m$** (Figure 26), was investigated. A **PEPESi$_m$** polymer can be regarded as a regular alternating copolymer of *p*-ethynylenephenyleneethynylene and silylene.

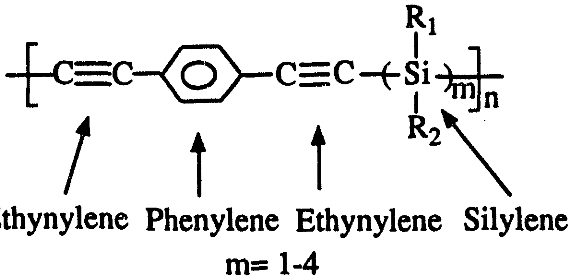


Figure 26. **PEPESi$_m$** polymers

Since silylene is one of major components along the polymer main chain, π-π extended conjugation does not exist as it does in both **PPV** and **PPE** polymers. The **PEPESi$_m$** polymer main chain is much less stiff than that of **PPE** polymers, therefore they should have better solubilities in organic solvents and lower melting points.

It is worthwhile to mention the transition metal analogues[56] of **PEPESi$_1$** polymers (Figure 27) since they have been studied. These transition metal poly-ynes represent an interesting class of linear organometallic polymers in which the transition metal is in the polymer main chain. These transition metal fragments with 6-8 d-electrons form very strong σ-bonds to acetylide ligands resulting in complexes with significant thermodynamic stability[56].

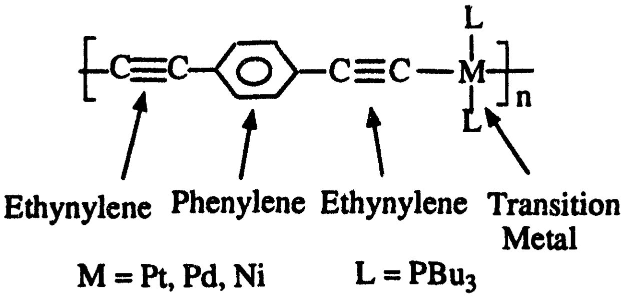
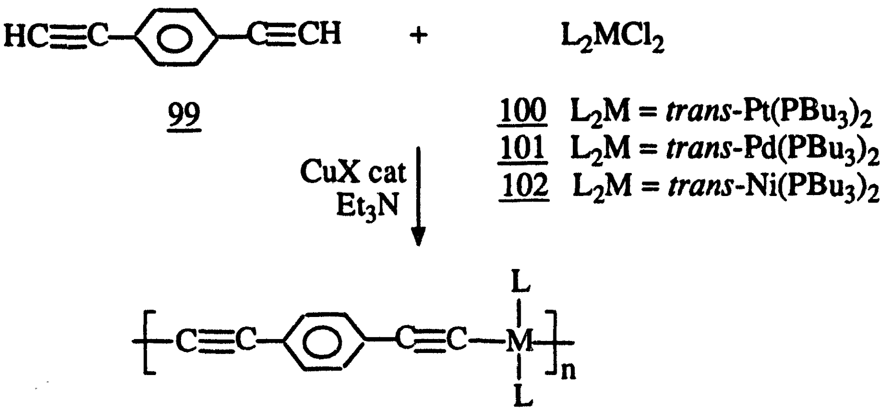


Figure 27. Analogues of **PEPESi1** polymers

They were conveniently synthesized by using a cuprous catalyst in the dehydrohalogenation between 1,4- diethynylbenzene 99 and transition metal halides 100-102 (Scheme 33). This polymerization afforded polymers 103-105 with high molecular weights (~30,000) and excellent yields.

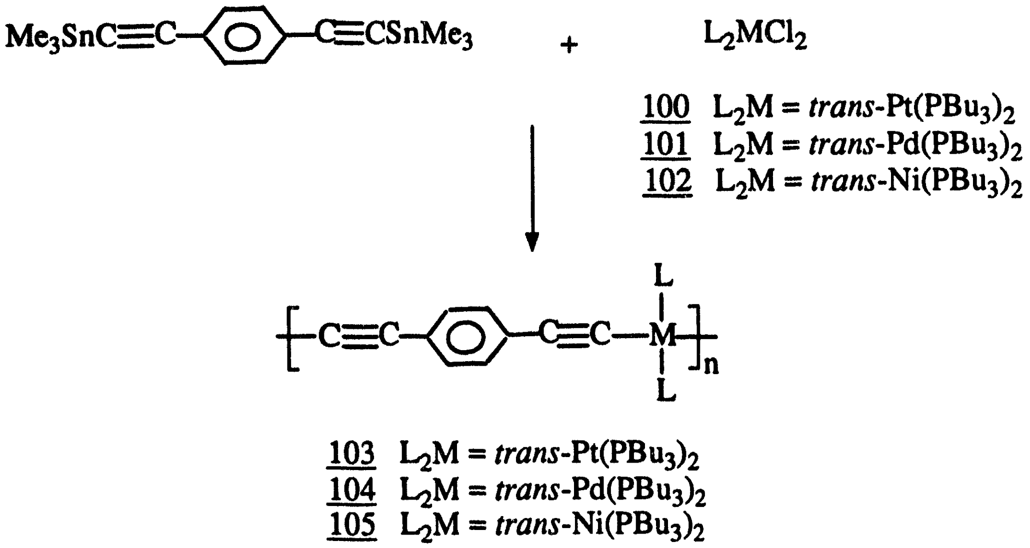
Recently, Friend[57a] reported another route to metal poly-ynes 103-105 (Scheme 34) in high yield (>96%) and with higher molecular weights (~70,000).



100 L_2M = *trans*-$Pt(PBu_3)_2$
101 L_2M = *trans*-$Pd(PBu_3)_2$
102 L_2M = *trans*-$Ni(PBu_3)_2$

103 L_2M = *trans*-$Pt(PBu_3)_2$
104 L_2M = *trans*-$Pd(PBu_3)_2$
105 L_2M = *trans*-$Ni(PBu_3)_2$

Scheme 33. Synthesis of metal-poly-ynes[56]



100 L_2M = *trans*-$Pt(PBu_3)_2$
101 L_2M = *trans*-$Pd(PBu_3)_2$
102 L_2M = *trans*-$Ni(PBu_3)_2$

103 L_2M = *trans*-$Pt(PBu_3)_2$
104 L_2M = *trans*-$Pd(PBu_3)_2$
105 L_2M = *trans*-$Ni(PBu_3)_2$

Scheme 34. Synthesis of metal-poly-ynes[57a]

These metal-polyynes are soluble in a variety of organic solvents such as benzene, THF and methylene chloride. In the solid state they are fairly stable to air and showed considerably good thermal stability. NMR[56], X-ray diffraction[56] and high-resolution electron microscopy[57b] studies indicated these metal poly-ynes had a linear rigid-rod structure. These metal poly-ynes also exhibited lyotropic liquid crystalline properties[56,57c].

UV absorption studies of both monomers and polymers provided clear evidence for d-π conjugation in the polymers[56,57a]. However, these metal poly-ynes did not exhibit high conductivity upon doping with iodine[57a]. Polymer 103 showed a strong absorption at about 388 nm (3.2 ev), and a much smaller peak at 400 nm (3.1 ev)[58]. However, the photoluminescence had its strongest emission at 517 nm (2.4 ev), and a small peak at 400 nm (3.1 ev). These results were interpreted in terms of a simple model (Figure 28) in which the large spin orbit coupling caused intersystem crossing. The weak peak at 400nm (3.1 ev) was assigned to singlet exciton decay. However, it was expected that the majority of singlets would decay to a lower energy triplet state. The strong peak at 517 nm (2.4 ev) was then assigned as the lowest triplet to ground state transition.

Frazier[59] studied the nonlinearity of these metal poly-ynes in THF solution by using a four-wave mixing method and found that these polymers had large third-order optical susceptibilities (1.45×10^{-33} esu). He also found that two-photon absorptions in these polymers make significant contributions to the nonlinearity. Very recently, devices employing these metal poly-ynes for optical switching have been reported[60].

Horn et al studied[61,62] the photochemical properties of the small molecules as shown in Figure 29. It was found that these compounds also possessed unique emission characteristics. At 77K normal $^1(\pi,\pi^*)$ fluorescence and $^3(\pi,\pi^*)$ phosphorescence were observed for those (phenylethynyl) pentamethyldisilanes bearing electron-donating substituents such as compound 106. At 77K those (phenylethynyl)pentamethyldisilanes bearing electron-withdrawing substituents such as compound 107 showed only a unique intramolecular $^1(\sigma\text{-}\pi^*)$ charge-transfer (CT) fluorescence in addition to the $^3(\pi,\pi^*)$ state phosphorescence. A proposed mechanism for the formation of the intramolecular CT fluorescent states is shown in Figure 29. Excitation of the localized $^1(\pi,\pi^*)$ state of the aromatic acetylene leaves a half-filled HOMO. If this orbital lies lower in energy than the Si-Si σ bond HOMO then exothermic $\sigma\rightarrow\pi^*$ charge transfer can occur from the Si-Si σ bond to the aromatic $^1(\pi,\pi^*)$ state. This energetic positioning of the aromatic HOMO and the Si-Si σ-bond occurs for those (phenylethynyl)pentamethyldisilanes bearing electron-withdrawing substituents or hydrogen such as compounds 107 and 108. In contrast, the lowest energy singly occupied orbital (SOMO) of the π,π^* state lies above that of the Si-Si σ bond HOMO for compound 106 bearing an electron-donating substituent. The CT is therefore endothermic and not as facile as other excited-state decay processes such as emission from the localized $^1(\pi,\pi^*)$ state.

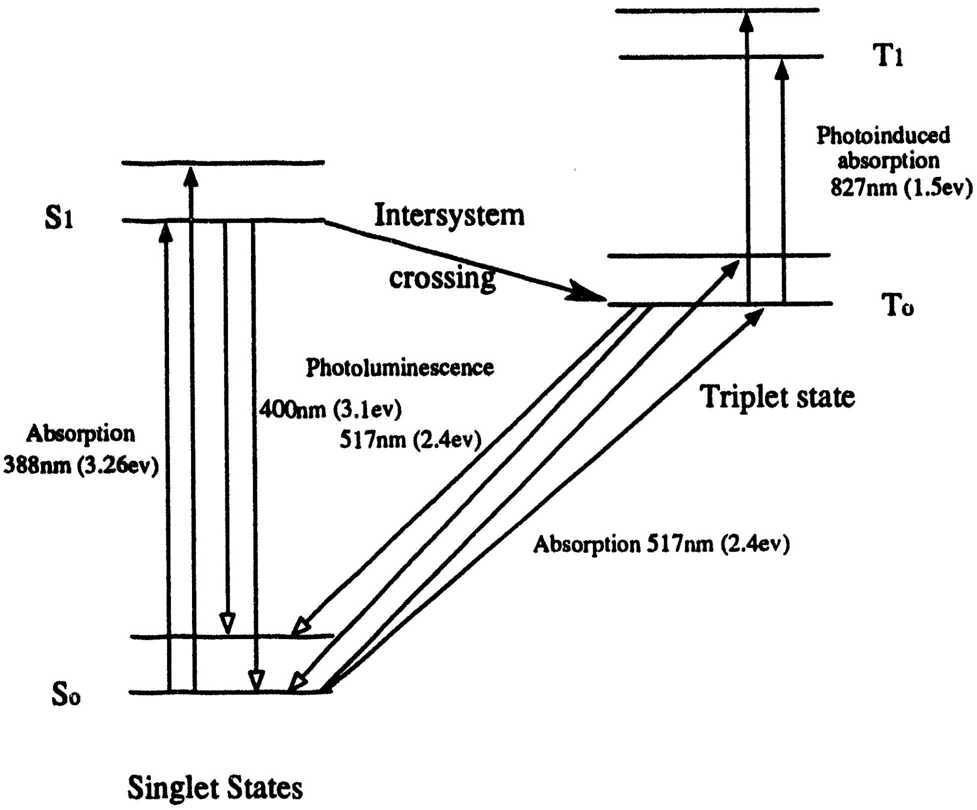


Figure 28. Simple model of explaining the optical properties of 103[58]

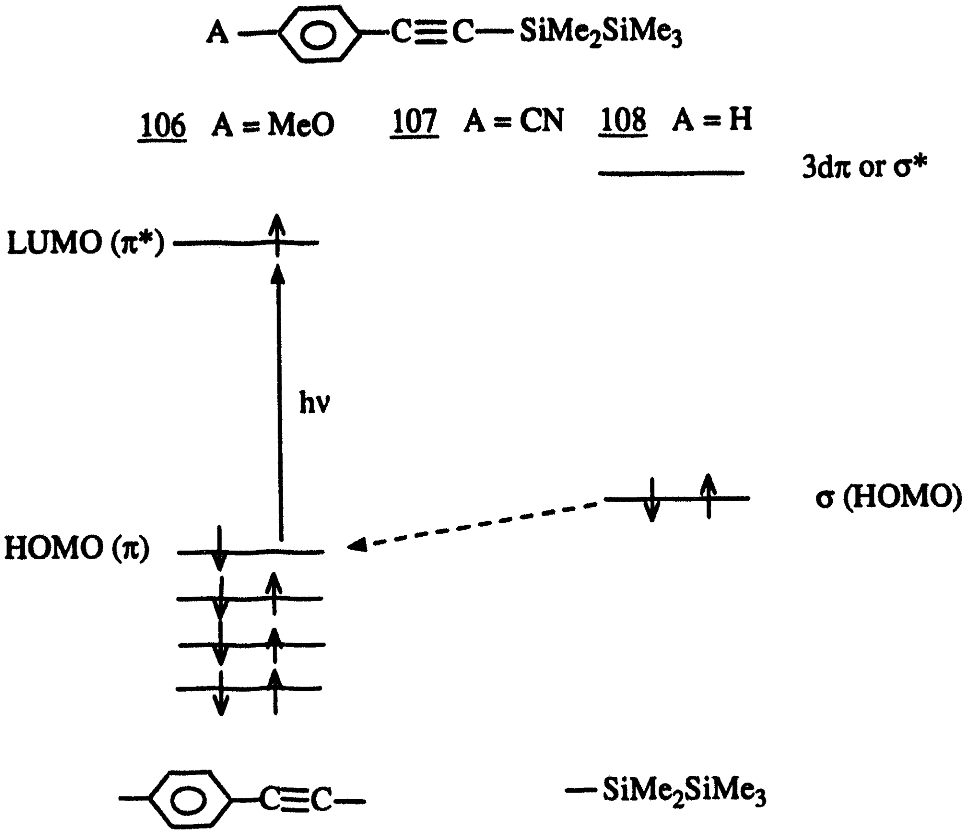
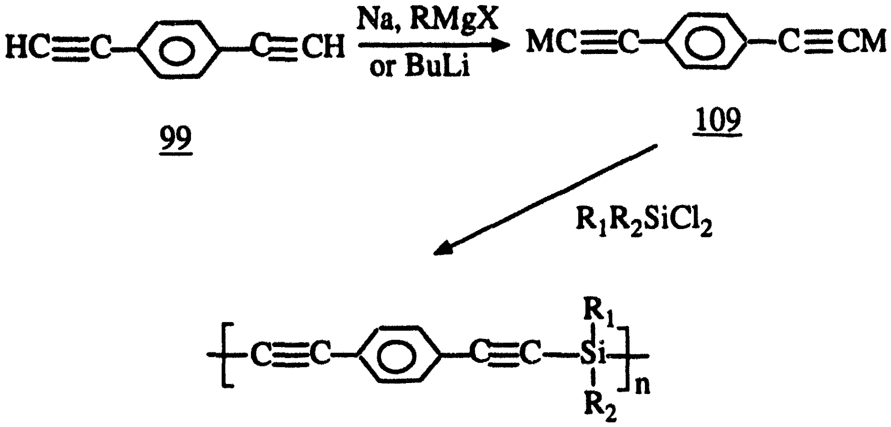


Figure 29. Proposed mechanism of charge transfer in arylethynylpentamethyldisilanes[62]

LITERATURE SURVEY

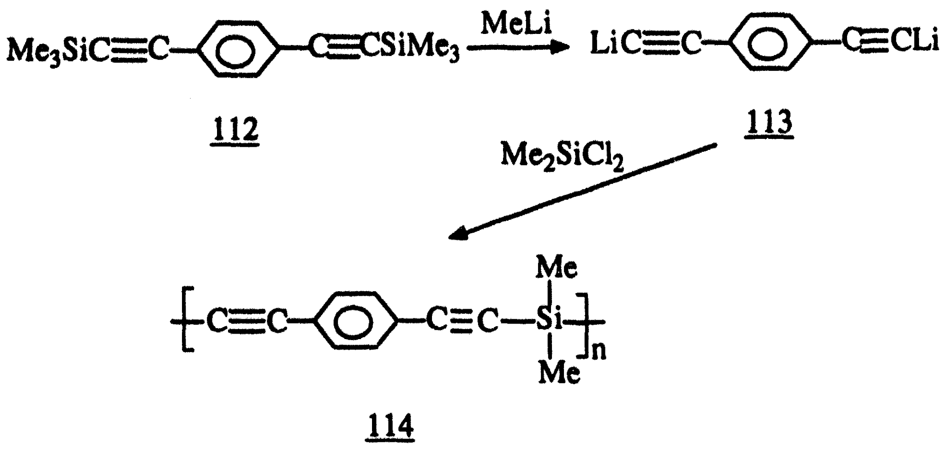
The synthesis of **PEPESi1** polymers has been attempted before[63,64]. The first synthetic approach[63] to them is shown in Scheme 35. 1,4-diethynylbenzene 99 reacted with Grignard or n-butyl lithium to form dianion 109 first, and then the dianion 109 was quenched by dialkyldichlorosilane to give the **PEPESi1** polymers 110-111. Since it was very difficult to control the stoichiometry, this route gave low molecular weight polymers or oligomers.



110 $R_1 = R_2 = Me$
111 $R_1 = C_6H_5$, $R_2 = Me$

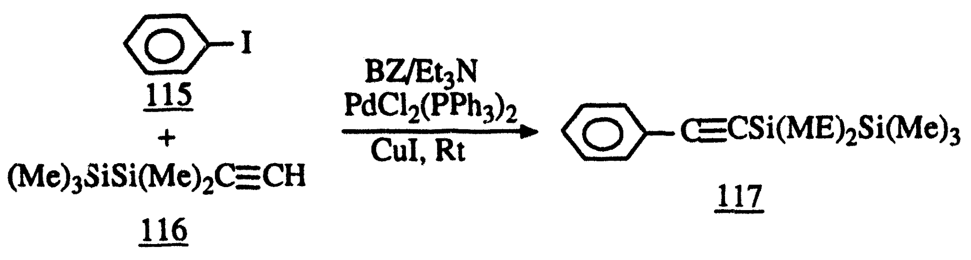
Scheme 35. Synthesis of **PEPESi1** polymers through dianions[63]

In the second approach[64], illustrated in Scheme 36, 1,4-bis(trimethylsilylethynyl) benzene 112 reacted with methyl lithium to form dianion 113, and quenching of dianion 113 with dialkyldichlorosilane gave the similar polymer 114. But the stoichiometric problem still existed and the molecular weights of these polymers ranged only from 1000 to 5000.



Scheme 36. Synthesis of a **PEPESi**$_1$ polymer through dianion[64]

In order to prepare **PEPESi**$_m$ polymers with higher molecular weights, the palladium-catalyzed polymerization of diiodobenzenes and diethynyl silanes was proposed. Whether this palladium catalyzed polymerization could be applied to the synthesis of **PEPESi**$_m$ polymers would depend on the stability of silicon carbon bonds under the reaction conditions. Fortunately, the palladium coupling[26b] shown in Scheme 37 gave good yields, and demonstrated that the cleavage of chemical bonds between silicon and ethynylcarbon, as well as between silicons, was not caused by the catalysts and the weak base at room temperature. Even though **PEPESi**$_m$ polymers have both or one of these bonds along the polymer main chains, these bonds will not be affected during the polymerization.



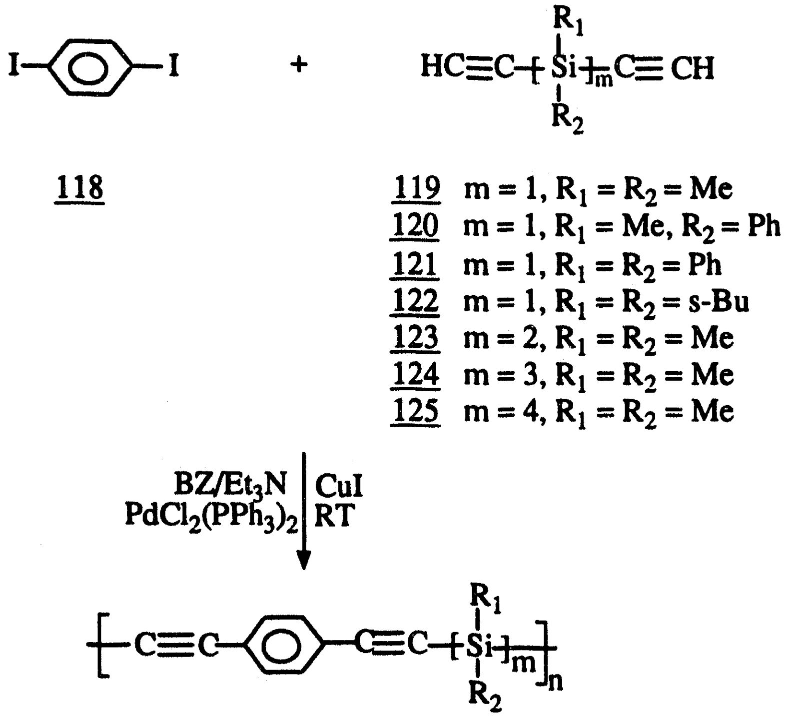
Scheme 37. The model reaction[26b]

RESULTS AND DISCUSSION

Palladium-catalyzed polymerization

The polymerization is illustrated in Scheme 38. 1,4-Diiodobenzene and diethynylsilane were used in a 1:1 ratio and the polymerization was performed under argon at room temperature. The solvents were benzene or toluene, and triethylamine in a definite volume ratio. As discussed before, diethylamine, a stronger and cheaper base, was not used in this polymerization because its HCl salt has good solubility in the polymerization media and this could cause a purification problem. The catalysts were $PdCl_2(PPh_3)_2$ and CuI in about a 1:1 ratio. The silane monomers <u>119</u>-<u>125</u> were synthesized by the reaction[65] between ethynyl Grignard and dichlorosilane compounds. The polymerization proceeded smoothly at room temperature, triethylamine salt gradually precipitated from the solution and the solution turned viscose. The polymerization was monitored by the precipitation of the amine salt. The polymerization times were between 10 minutes and 24 hours. In the case where the concentrations of both monomers were high, the polymerization was complete in short periods such as 10 minutes. However, the polymer precipitated from the solution due to the limitation of the solubility and the molecular weight of polymer was limited. Table 7 shows the time dependence of the molecular weight of polymer <u>128</u> as traced by gel permeation chromatography.

Purification was accomplished by removal of the salts by filtration and precipitating the polymers by pouring the solution into excess methanol. The yellow or grey polymers were collected by filtration and dried in vacuum. Table 8 shows some polymerization data. The polymerization yields ranged from 76% to 97%. Since polymers <u>126</u> and <u>130</u> have low solubility in toluene at room temperature, the molecular



118

119 m = 1, $R_1 = R_2 =$ Me
120 m = 1, $R_1 =$ Me, $R_2 =$ Ph
121 m = 1, $R_1 = R_2 =$ Ph
122 m = 1, $R_1 = R_2 =$ s-Bu
123 m = 2, $R_1 = R_2 =$ Me
124 m = 3, $R_1 = R_2 =$ Me
125 m = 4, $R_1 = R_2 =$ Me

126 m = 1, $R_1 = R_2 =$ Me
127 m = 1, $R_1 =$ Me, $R_2 =$ Ph
128 m = 1, $R_1 = R_2 =$ Ph
129 m = 1, $R_1 = R_2 =$ s-Bu
130 m = 2, $R_1 = R_2 =$ Me
131 m = 3, $R_1 = R_2 =$ Me
132 m = 4, $R_1 = R_2 =$ Me

Scheme 38. Synthesis of **PEPESim** polymers by Pd-catalyzed polymerization

Table 7

Time dependence of molecular weight (Mw) and degree of polymerization (DP)

Time	$Mw \times 10^{-3}$(GPC)	DP[a]
10 mins	2.0	8
1hr	6.3	21
6hrs	7.5	25
18hrs	13.6	44
32hrs	18.8	61

[a] Calculated using DP = Mw/306.4

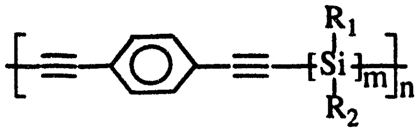
weight of 126 and 130 was measured at 60°C.

Characterization of **PEPESim** polymers

PEPESim polymers are obtained as yellow or grey solids. These polymers, except 126 and 130, are well soluble in a variety of organic solvents such as benzene, toluene, chloroform, tetrahydrofuran, and methylenechloride. The high solubility of the polymers can be attributed to the bulky substituents on the silicon, or more silylenes in the polymer backbone. They form good films.

There seemed to be no reports on clear characterization of **PEPESim** polymers as NMR techniques were unsophisticated at the time they were prepared. The good solubility of these polymers allowed us to investigate their spectroscopic properties and polymer structure. The FT-IR spectra of **PEPESim** polymers exhibited intense bands in the region (2160 cm^{-1}) attributed to stretching frequencies of the acetylenic bonds. A

Table 8. Summary of **PEPESim** polymers



No	Polymer Structure	Reaction Time	Yield	Mwx10^{-3}	PD	Solubilities
126	m= 1 R_1=R_2=Me	2 hrs	97%	4.7*	2.9	hot Tol&Chf
127	m= 1 R_1=Me R_2=Ph	10 min	76%	10	1.6	THF, C_6H_6 $CHCl_3$
128	m= 1 R_1=R_2=Ph	10 min	89%	16	2.3	THF, C_6H_6 $CHCl_3$
129	m= 1 R_1=R_2=s-Bu	24 hrs	86%	82	1.7	THF, C_6H_6 $CHCl_3$
130	m= 2 R_1=R_2=Me	1hr	90%	27*	4.6	hot Tol&Chf
131	m= 3 R_1=R_2=Me	48hrs	80%	20	2.1	THF, C_6H_6 $CHCl_3$
132	m= 4 R_1=R_2=Me	120hrs	87%	22	1.2	THF, C_6H_6 $CHCl_3$

* Molecular weights measured at 60°C in toluene; rest at 20°C.

small band in the region (2070 cm^{-1}) was attributed to stretching frequencies of the 1,3-butadiyne since the FT-IR spectra of polymers [-SiR_2-CC-CC-] exhibited similar absorption bands[66] in that region. This 1,3-butadiyne functionality in the polymer probably results from the oxidative-coupling side reaction as shown in Scheme 39. The rest of the data are given in experimental section.

$$\text{Polymer-SiR}_2\text{-C}{\equiv}\text{CH} \ + \ \text{HC}{\equiv}\text{C-SiR}_2\text{-Polymer}$$

$$\Big\downarrow \begin{array}{l}\text{CuI/O}_2\\ \text{Et}_3\text{N}\end{array}$$

$$\text{Polymer-SiR}_2\text{-C}{\equiv}\text{C-C}{\equiv}\text{C-SiR}_2\text{-Polymer}$$

Scheme 39. The oxidative coupling reaction

^{1}H-NMR spectrum (Figure 30) of polymer <u>129</u> shows a triplet at 0.95 ppm and doublet at 1.1 ppm for the two methyl groups, and a singlet at 7.36 ppm for the phenyl group. The resonance signals at ca. 0.9 ppm are assigned to the methine proton, while other resonance signals at ca. 1.35 ppm and 1.75 ppm belong to the methylene protons. Figure 31 shows a ^{13}C-NMR spectrum of polymer <u>129</u>. The peaks at 131.93 ppm and 123.17 ppm are assigned as the resonance signals of aromatic carbons and the resonance at 106.60 ppm is assigned to the carbon adjacent to phenyl. The peaks at 24.87 ppm, 19.78 ppm, 13.28 ppm are attributed to the two methyl carbons and one methylene carbon on the iso-butyl group. The doublet resonance signals at 13.87 ppm and 13.85 ppm are assigned to the methine carbon and the the triplet resonance signals at 90.58 ppm, 90.52 ppm, and 90.46 ppm are assigned to the ethynyl carbon adjacent to the silicon. Both doublet and triplet splittings result from the methine carbon, the stereogenic center, which attaches to the silicon. A detailed discussion of these splittings is given in Yi Pang's thesis[65]. Figure 32 shows a ^{29}Si-NMR spectrum of polymer <u>128</u>. One peak at -47.99 ppm is observed,

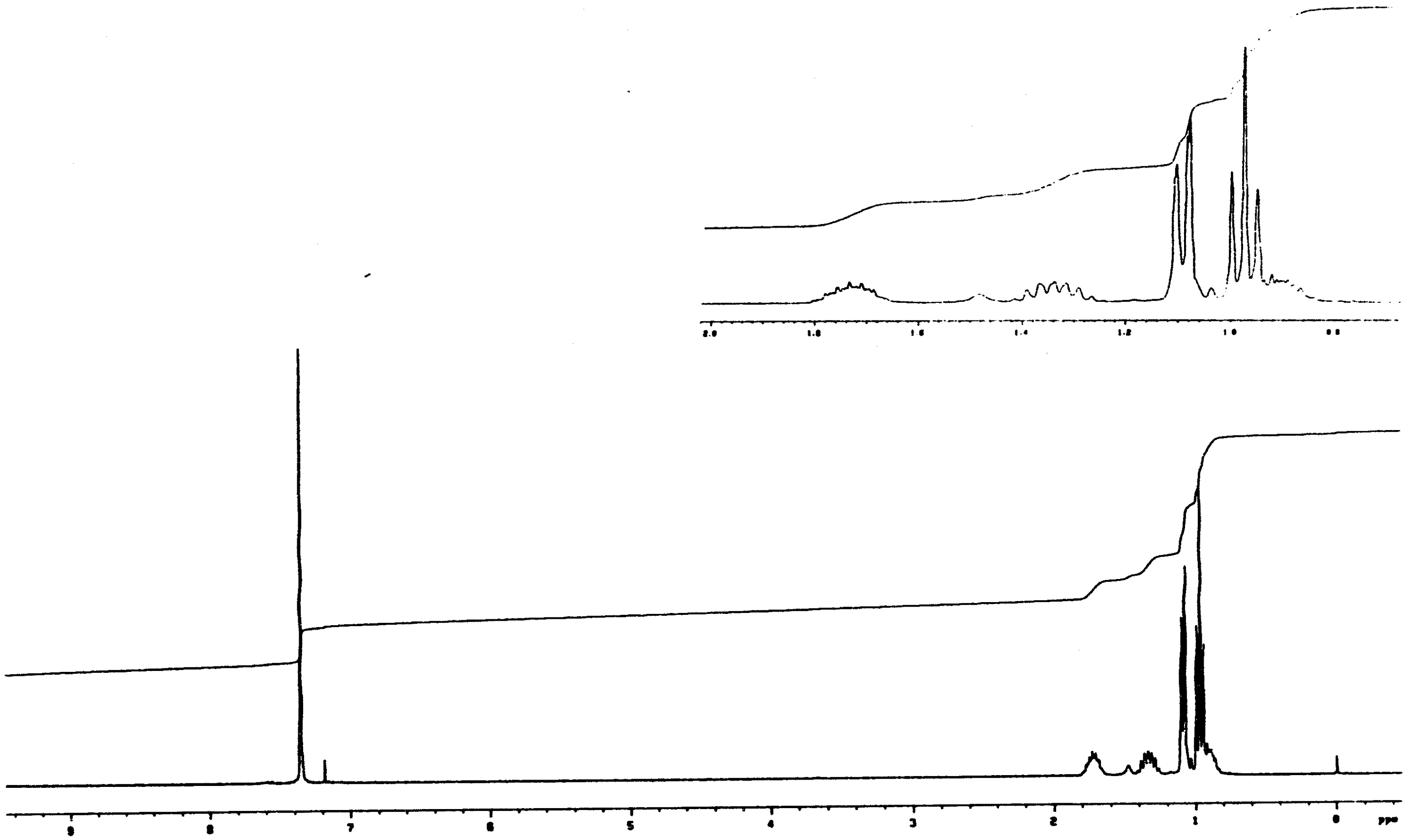


Figure 30. ¹H-NMR spectrum of polymer 129

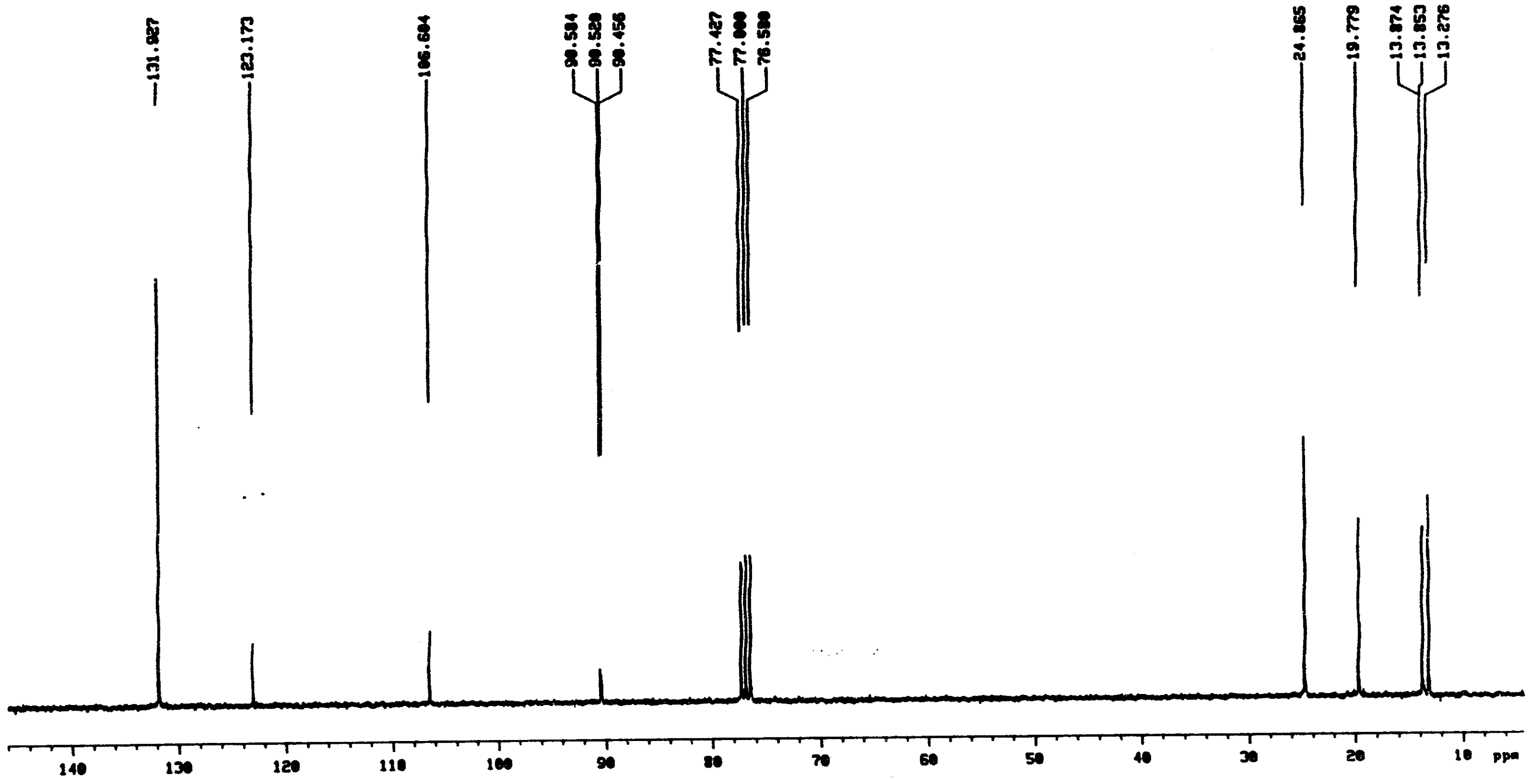


Figure 31. ^{13}C-NMR spectrum of polymer 129

which agrees with the proposed polymer structure. Table 9 summaries both ^{13}C-NMR and ^{29}Si-NMR data. The chemical shifts in ^{29}Si-NMR spectra for these polymers range from -25 ppm to -48 ppm. Since only one or two different silylenes are in the polymer main chain, one or two peaks were observed in ^{29}Si-NMR. The ^{13}C-chemical shifts for the ethynyl carbon adjacent to silylene in ^{13}C-NMR spectra are between 105 ppm and 108 ppm. The chemical shifts for the other ethynyl carbon are between 90 ppm and 96 ppm. However, no peaks for the 1,3-butadiyne moiety in ^{13}C-NMR experiments were observed even though the band for the 1,3-butadiyne moiety appeared in FT-IR spectra.

After these syntheses were completed, Corriu[67] et al. reported the preparation of similar polymers, as shown in Scheme 37, by the same method used above. Both dibromo and diiodo aryl compounds were used in their syntheses. Diphenyldiethynylsilane was used as the second monomer. Therefore, only polymers (**PEPESi1**) with one silicon in the repeat unit were prepared in Corriu's syntheses. The polymerization temperature was maintained at 90°C. After the polymerization was completed, the solvent was removed under vacuum and the polymer was extracted with THF and the THF solution then filtered through silica gel. Addition of pentane resulted in precipitation of the polymer. However, the amine salt Et_3NHX, which is also a product during the polymerization, cannot be completely removed in some cases.

In order to establish the stability of the ethynyl-silicon bonds in the workup media, **PEPESi1** 128 was put into a mixture of methanol and triethylamine (8:1 in volume) and the suspension solution was stirred at room temperature for 2 hours. However, the molecular weight of polymer 128 remained unchanged after above treatment. Thus, the cleavage of the silicon-alkylnyl bonds does not occur during purification.

The thermal stability of these **PEPESim** polymers, studied by thermogravimetric

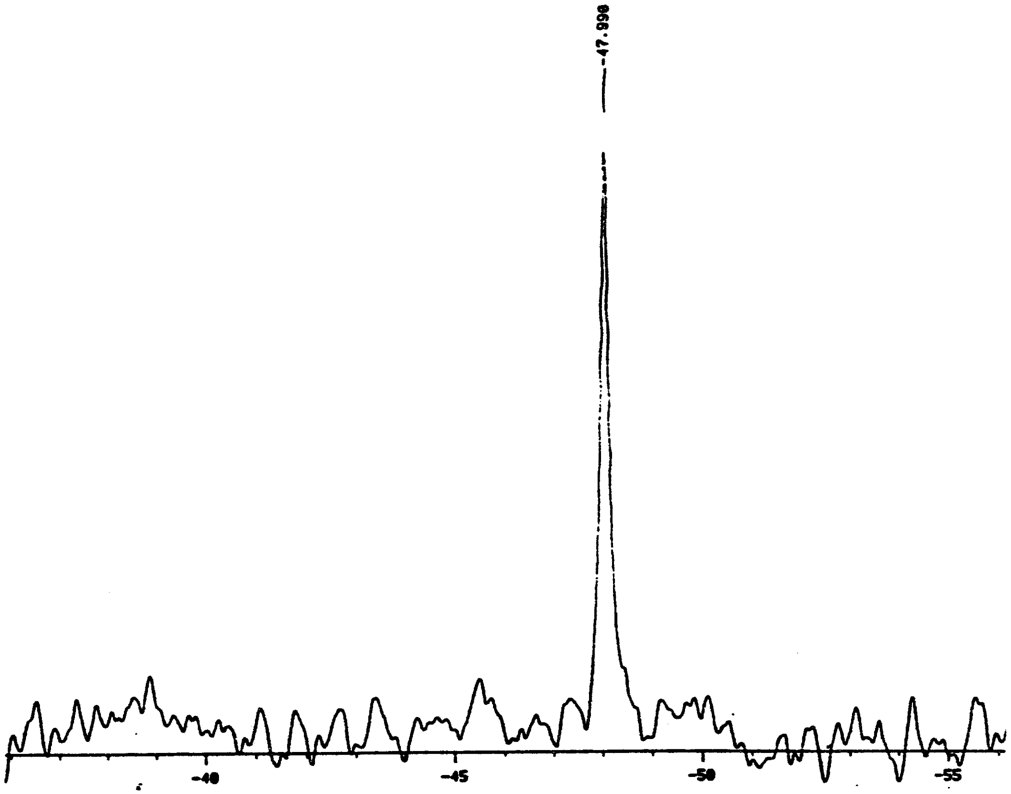


Figure 32. ^{29}Si-NMR spectrum of polymer <u>128</u>

Table 9.

^{13}C- and ^{29}Si-NMR data of **PEPESi$_m$** polymers

Polymers	^{29}Si δ(ppm)	^{13}C-NMR δ(ppm)	
		C_1	C_2
126	-39.66(1Si)	105.09	93.61
127	-43.44(1Si)	106.70	92.28
128	-47.99(1Si)	108.01	90.03
129	-25.62(1Si)	106.51	91.41
130	-37.33(2Si)	107.16	95.30
131	-33.92(2Si), -46.13(1Si)	107.25	95.42
132	-33.41(2Si), -43.36(2Si)	107.17	95.76

$-Si - C_2 \equiv C_1 - Ph -$ Si(Me)$_4$ was used as the reference.

analysis (TGA) (Table 10), indicated that these **PEPESi$_m$** polymers started to lose weight around 380°C under a helium atmosphere. Presumably, the alkyl or phenyl groups on the silicon were released during the heating.

Differential scanning calorimeter (DSC) results indicated that these polymers, with the exception of 131 and 132, did not melt before decomposition. For 131, the melting and decomposition occurred at almost the same temperature region. For 132, two exothermal peaks in Figure 33 were observed at 68.4°C and 76.1°C, which indicated that there would be a mesophase between this temperature region. The liquid crystalline properties will be discussed in section three.

Table 10. TGA results of **PEPESim** polymers

Polymer	126	127	128	129	130	131	132
Char yield	93%	88%	82%	66%	86%	79%	74%

TGA experiments were performed under Ar.

UV-spectroscopic study

Figure 34 shows absorption spectra of **PEPESi1**. Polymers with one silicon in the polymer main chain in dilute THF solution at room temperature show a strong absorption maximum at λ= 305 nm, similar to that of 1,4-bis(trimethylsilylethynyl)-benzene, which has a λ_{max} at 293 nm.

The spectra data of both metal-poly-ynes[58] and **PEPESi1** polymers are summarized in Table 11. As can be seen, the substituents on silicon do not affect λ_{max} (305 nm) or ϵ (10^5). The absorption bands for **PEPESi1** polymers are mainly determined by the polymer main chain structure unit.

Compared with compound 133, the λ_{max} of **PEPESi1** polymers only show a 10 nm red shift. However, the data of λ_{max} of metal-poly-ynes do exhibit a considerable red shift, compared with that of monomers. This is due to d-π conjugation along the polymer main chain.

Compared with that of monomer 133, these **PEPESi1** polymers do not exhibit a considerable red shift (10 nm). This means that no comparably significant d-π conjugation exists in this silicon polymer system.

The absorption spectrum (Figure 35) of polymer 132 in the film state shows

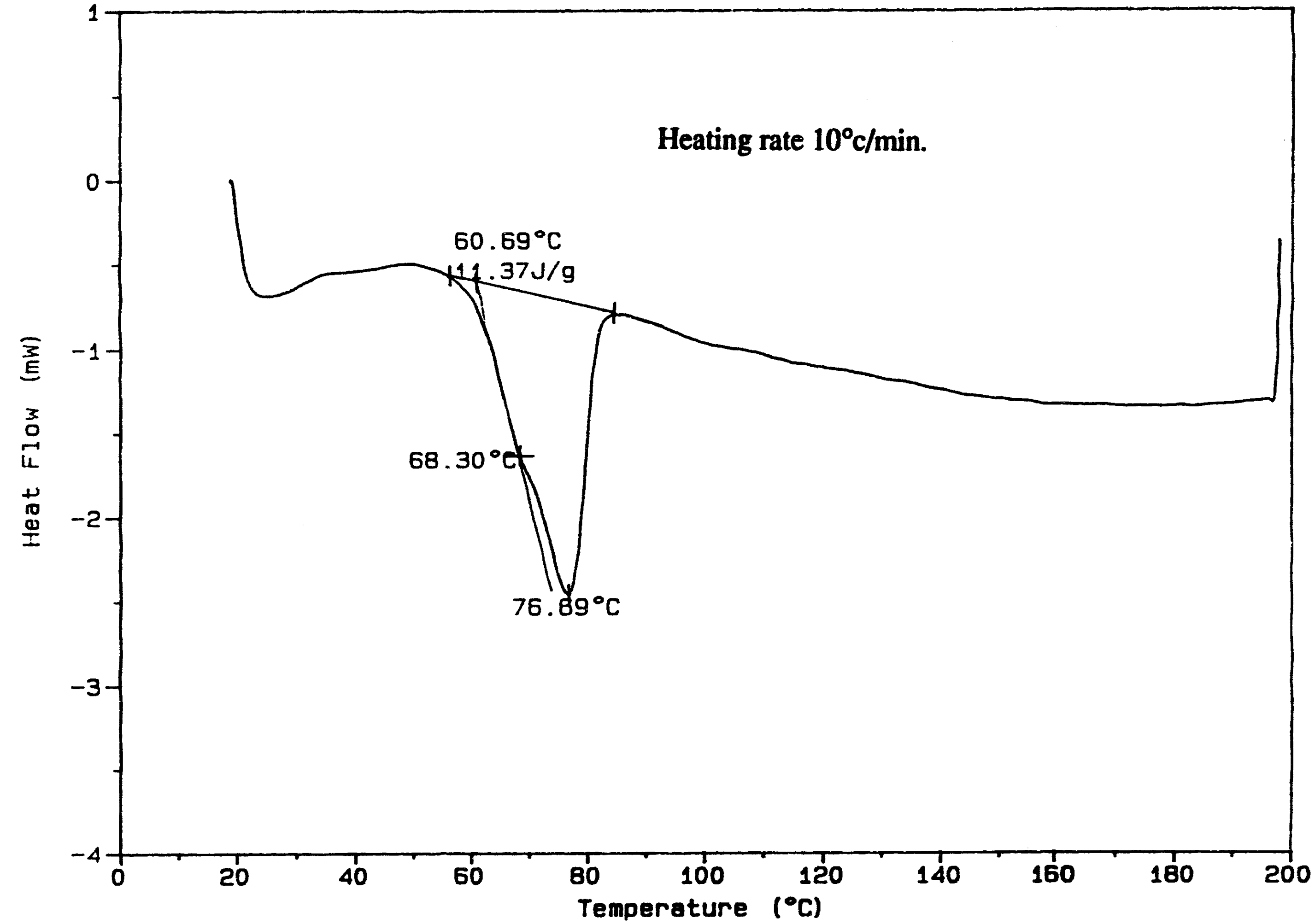


Figure 33. DSC thermogram of polymer 132

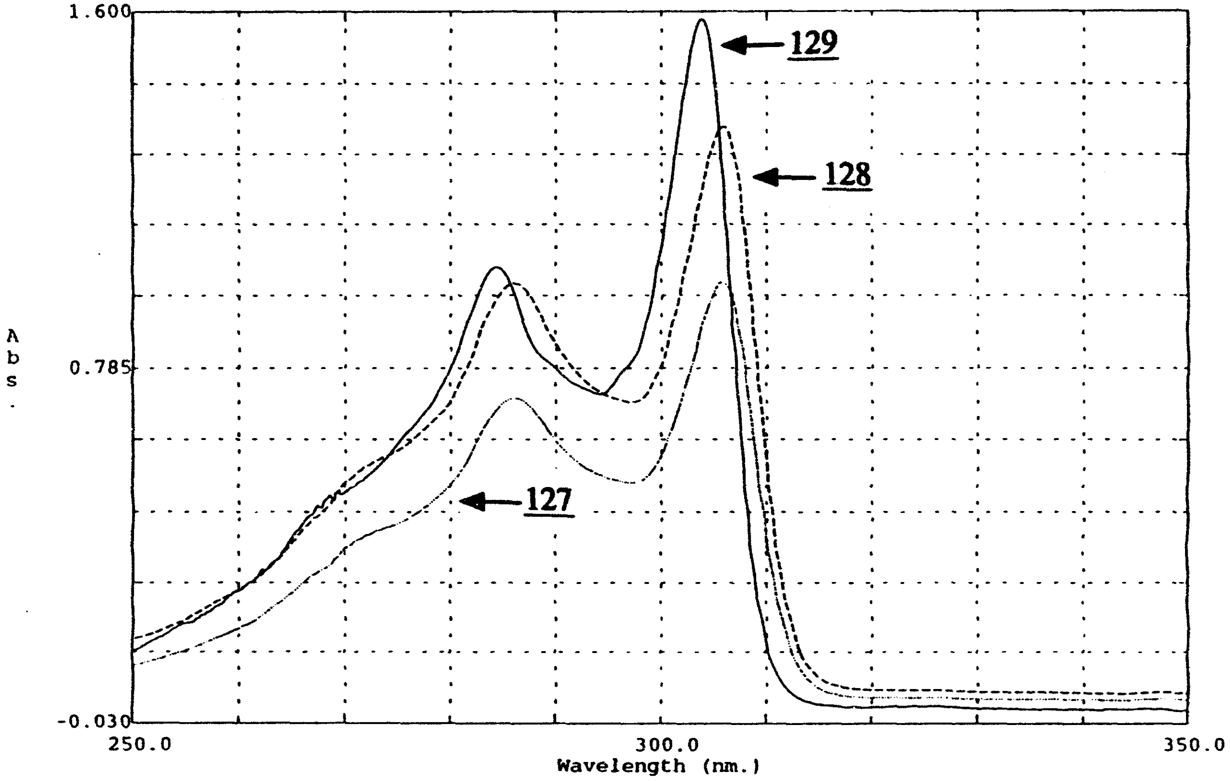
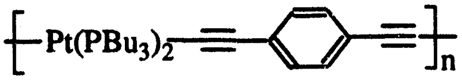
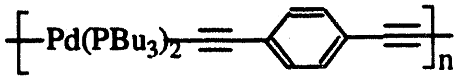
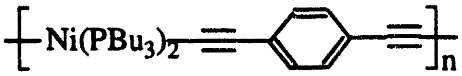
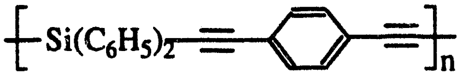
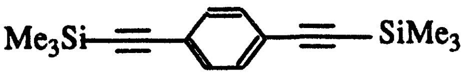


Figure 34. UV absorption spectra of polymers 127-129 in THF solution

Table 11. Spectra data of both metal and silicon poly-yne polymers

No	Polymer structure	IR (υ_{CC})	UV (λ_{max}, logϵ)
103		2095	380(4.80)
104		2095	349(4.80)
105		2075	402(4.50)
127		2160	306(5.01)
128		2160	306(4.89)
129		2158	304(4.93)
133		2156	293(4.78)

similar absorption peaks to itself in THF solution with a red shift. Since polymer 132 has Si-Si bonds in the polymer main chain, the red shift is presumably due to the σ-π conjugation enhanced between Si-Si σ-bonds and aromatic ethynyl π-bonds by the frozen or oriented conformation of the polymer main chain in the solid state.

Like metal poly-ynes, **PEPESim** polymers in solution also emitted strong purple fluorescence upon excitation. The emission spectrum (see Figure 36) of polymer 129 excited at 300 nm in THF solution at room temperature shows a very strong emission at 380 nm with a long tail.

The conductivity of **PEPESim** polymers has also been studied. They did not exhibit good conductivity upon being doped by iodine or AsF_5. This result agreed with Corriu's work[68].

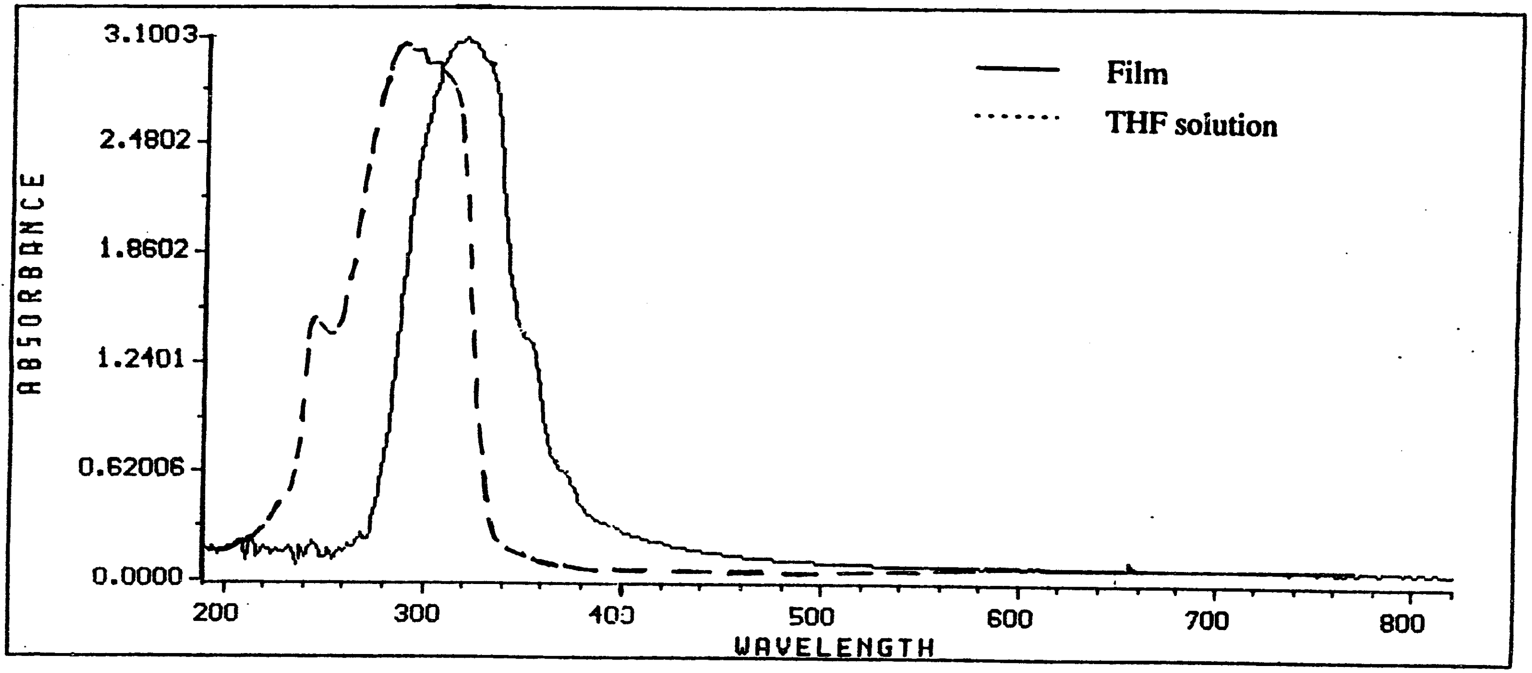


Figure 35. UV absorption spectrum of polymer 132 in the film state

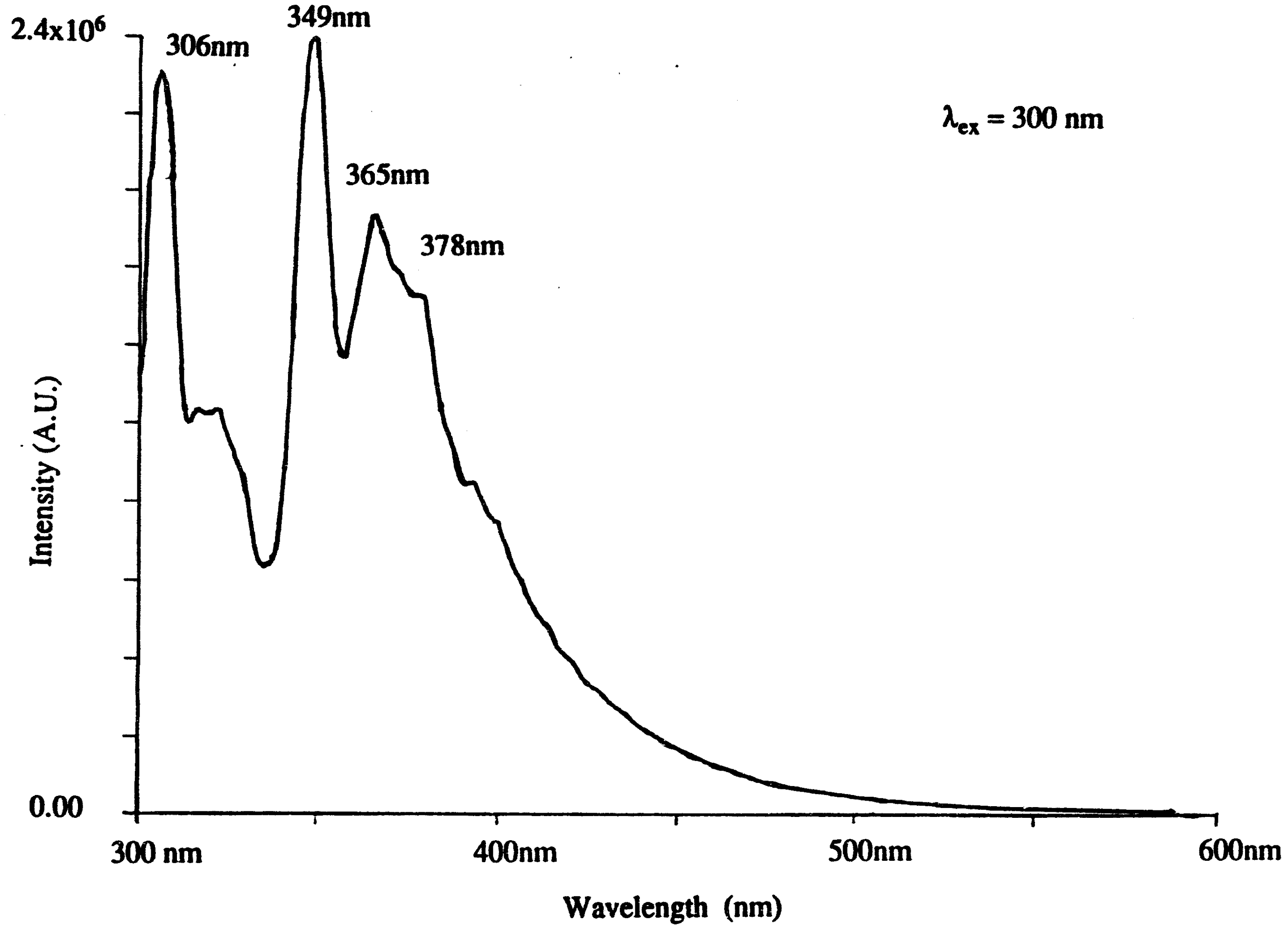


Figure 36. Emission spectrum of polymer 129 in THF solution

CONCLUSIONS

In this section, the syntheses of poly(silyleneethynylenephenyleneethynylene)s (**PEPESim**) are discussed. They were conveniently synthesized in excellent yield and with reasonable molecular weights via a palladium-catalyzed polymerization. These polymers were well characterized by routine methods since they are soluble in some organic solvents.

Spectroscopic studies indicated these polymers had a strong UV absorption at 305 nm as well as emission at 380 nm. Compared with metal analogues, they do not have comparable d-π conjugation along the polymer main chains. These polymers also did not show conductivity upon doping with iodine or AsF_5. Attempts to study the thermotropic liquid crystalline properties of **PEPESi1** polymers failed due to decomposition or crosslinking before the melting. The next section will focus on the synthesis and study of substituted **PEPESim** polymers, which should have lower melting points.

SECTION THREE:

SOLUBLE POLY(ETHYNYLENE-ARYLENE-ETHYNYLENE-SILYLENE)S

INTRODUCTION

Liquid crystals have attracted much interest and considerable progress in their development has been made over the past 20 years. They are extensively used in electrooptic devices.

Liquid crystals of low molecular weight compounds have been known for more than a centry[69]. Their properties have also been studied[70-73]. A crystal phase is characterized by a three-dimensional, long-range positional order of the molecule's center of mass in the crystalline lattice. Furthermore, in non-spherically symmetric molecules the superior molecular axes, which are usually the longest axes, are oriented with respect to each other.

For most organic molecules, the long-range orientational order is lost at the melting point T_m, and the melting solution is isotopic. For liquid crystalline molecules, the phase sequence is given in Figure 37. With increasing temperature, a step-wise melting occurred. First the smectic phase formed, which still retained anisotropic properties. Then, the nematic phase formed, which has a lower ordered structure. Further heating turned the nematic phase into an isotropic liquid. Both smectic and nematic phases are considered as the liquid crystalline (LC) phase. Sometimes, the crystals would not show or have a smectic phase and turned directly into the nematic phase during the heating. Normally, differential scanning colorimetry (DSC), polarized microscope and x-ray diffraction are used to study properties of liquid crystalline materials.

The properties of polymeric liquid crystals have also been extensively studied[74]. The existence of the LC state for polymers requires rigid and anisometric molecules. With the knowledge of these structural principles, the construction of polymers with potential LC properties is immediately obvious. The macromolecule as a whole must

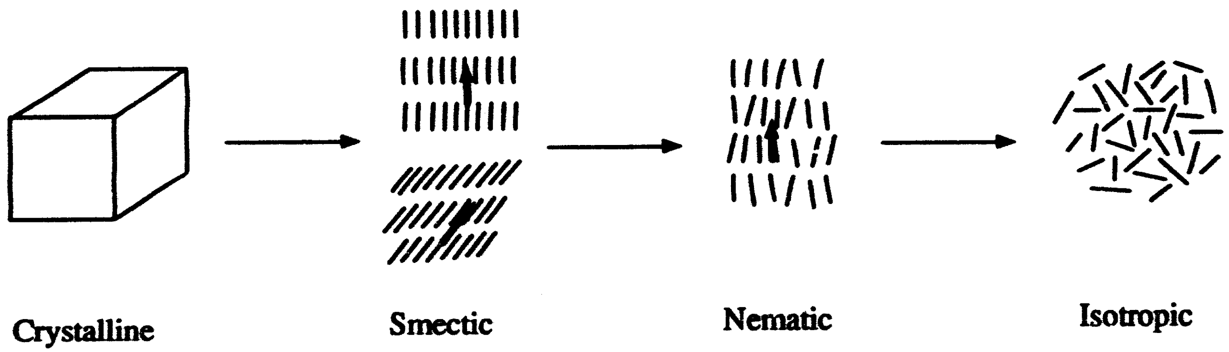


Figure 37. Phase sequence of a liquid crystalline substance

either have a rigid rod-like or disk-like structure or contain mesogenic groups as monomer units. Polymers whose total structures are mesogenic are only achievable when the polymer itself is rod shaped, for example via a rigid, helical secondary structure.

Normally, there are two fundamentally different types of LC polymers. The polymers in which the mesogenic groups are located in the polymer main chain are known as LC main chain polymers (see Figure 38). The polymers in which the mesogenic groups are attached to the polymer main chain in a side-chain-like manner are known as LC side chain polymers (also see Figure 38).

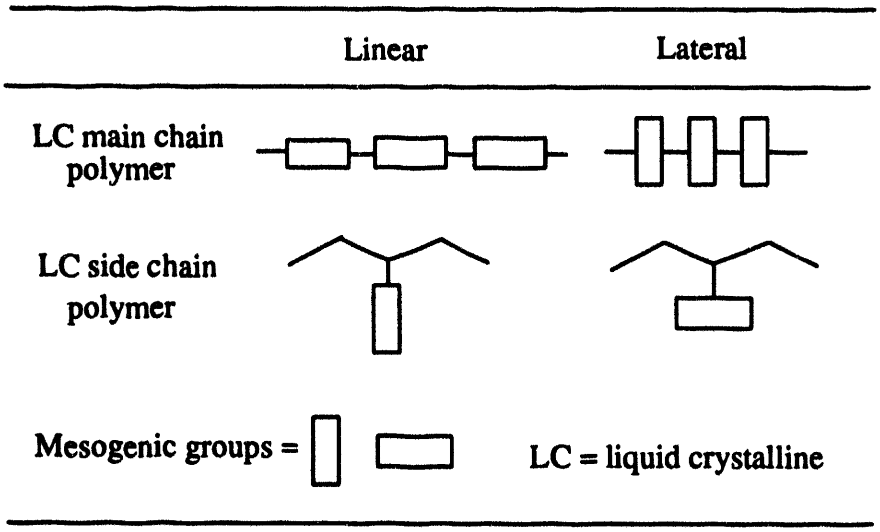


Figure 38. Types of liquid crystalline polymers

In comparison to low molecular weight liquid crystals, attachment of the mesogenic groups to the polymer generally restricts the translational and rotational motions of the mesogenic groups. Also, the molecular weight of a polymer has a certain distribution. Therefore, an influence on the temperature range of existence and a change in the physical properties of the LC phase is to be expected.

Silicon containing polymers, such as siloxane polymers, with the side chains as the mesogenic groups have also been studied. However, few silicon containing polymers with both silicon and the mesogenic groups in the main chain have been studied. Poly(ethynylene-1,4-phenylene-ethynylene-dialkylsilylene)s (**PEPESi**) have been synthesized by using palladium-catalyzed polymerization. However, as discussed before, these **PEPESi1** polymers decompose before melting. In order to study the thermotropic liquid crystalline properties of these silicon containing polymers, it is necessary to decrease the melting points of these polymers by modifying the polymer structure. It is well known that by attaching alkyl groups as the side chains on a rigid polymer main chain, the solid state properties of these polymers, such as solubility and melting point, can be significantly manipulated.

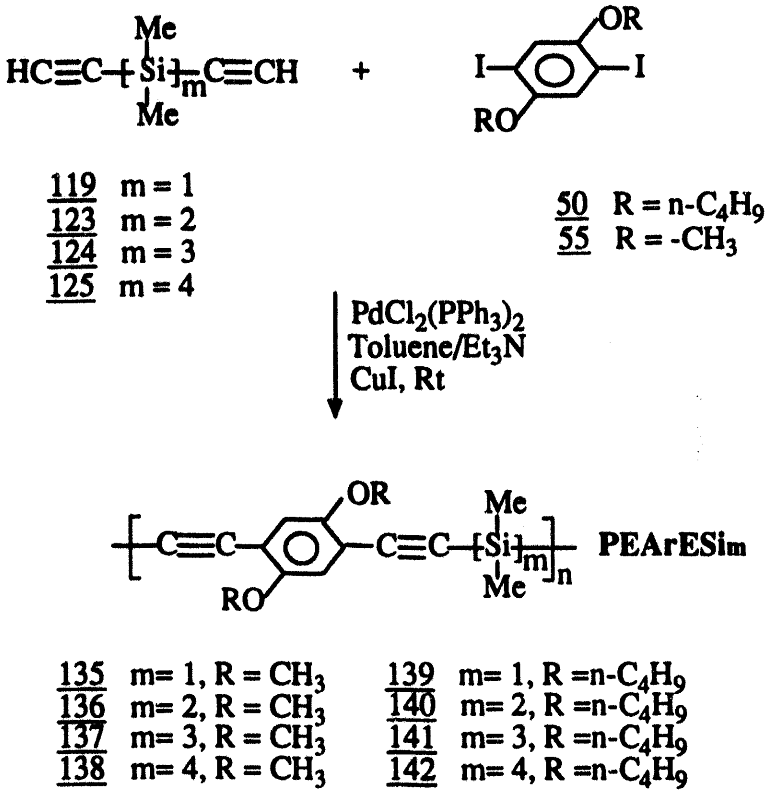
RESULTS AND DISCUSSION

Palladium-catalyzed polymerization

The polymerizations described in Scheme 40 were performed at room temperature. The solvents were toluene and triethylamine in about a 1:1 ratio. The diethynylsilane compounds were synthesized by the reaction between ethynyl Grignard reagents and dichlorosilane. 1,4-dimethoxy-2,5-diiodobenzene and 1,4-dibutoxy-2,5-diiodobenzene were conveniently synthesized according to the method discussed in section one. $PdCl_2(PPh_3)_2$ and CuI were used as the catalysts.

The alkoxy groups on the phenyl produce both steric hindrance and electronic donating effects which decrease the rate of the palladium coupling reactions, the polymerization times, which ranged from 16 to 100 hours, were much longer than that of the polymerization in which 1,4-diiodobenzene was used. During the polymerization, the amine salt precipitated from the solution and blue fluorescence was observed. The polymerization was followed by the amount of the amine salt precipitated. The purification procedure was similar to that for **PEPESim** polymers.

Some of the polymerization data are given in both Tables 12 and 13. The polymerization yields were between 50% and 88%. The molecular weights of these polymers, except 135, ranged from $9x10^3$ to $36x10^3$. The polydispersities of these polymers, except 135, were close to 2. The molecular weights of these polymers have unimodal distributions. Since polymer 135 has limited solubility in the reaction media, the molecular weight is smaller than that of the rest of the polymers. Those polymers with butoxy side chains have a much better solubility in organic solvents than the polymers with methoxy ones. These polymers normally appear as yellow or gray powders and form



$\underline{119}$ m = 1
$\underline{123}$ m = 2
$\underline{124}$ m = 3
$\underline{125}$ m = 4

$\underline{50}$ R = n-C_4H_9
$\underline{55}$ R = -CH_3

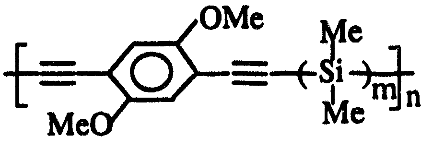
$PdCl_2(PPh_3)_2$
Toluene/Et_3N
CuI, Rt

$\underline{135}$ m= 1, R = CH_3
$\underline{136}$ m= 2, R = CH_3
$\underline{137}$ m= 3, R = CH_3
$\underline{138}$ m= 4, R = CH_3

$\underline{139}$ m= 1, R =n-C_4H_9
$\underline{140}$ m= 2, R =n-C_4H_9
$\underline{141}$ m= 3, R =n-C_4H_9
$\underline{142}$ m= 4, R =n-C_4H_9

Scheme 40. Palladium-catalyzed polymerization

Table 12. Summary of **PEArEm** polymers



No	Polymer Structure	Reaction Time (h)	Yield	Mwx10^{-3}	PD	Solubility
135	m= 1	55	88%	5.0	1.20	C_6H_6, THF $CHCl_3$
136	m= 2	16	50%	9.1	2.20	C_6H_6, THF $CHCl_3$
137	m= 3	96	60%	19.7	2.10	C_6H_6, THF $CHCl_3$
138	m= 4	96	53%	12.5	1.90	C_6H_6, THF $CHCl_3$

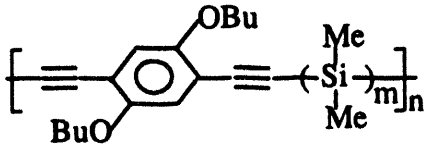
* Molecular weights measured at 20°C in THF.

good cast films.

Polymers 145 and 146, with silylene and methylene in the polymer main chain, as well as polymer 147 with germylene in the polymer main chain, have been synthesized with excellent yield by using the same polymerization as described in Scheme 41. Polymers 145, 146 and 147 also have good solubility in organic solvents and form good films.

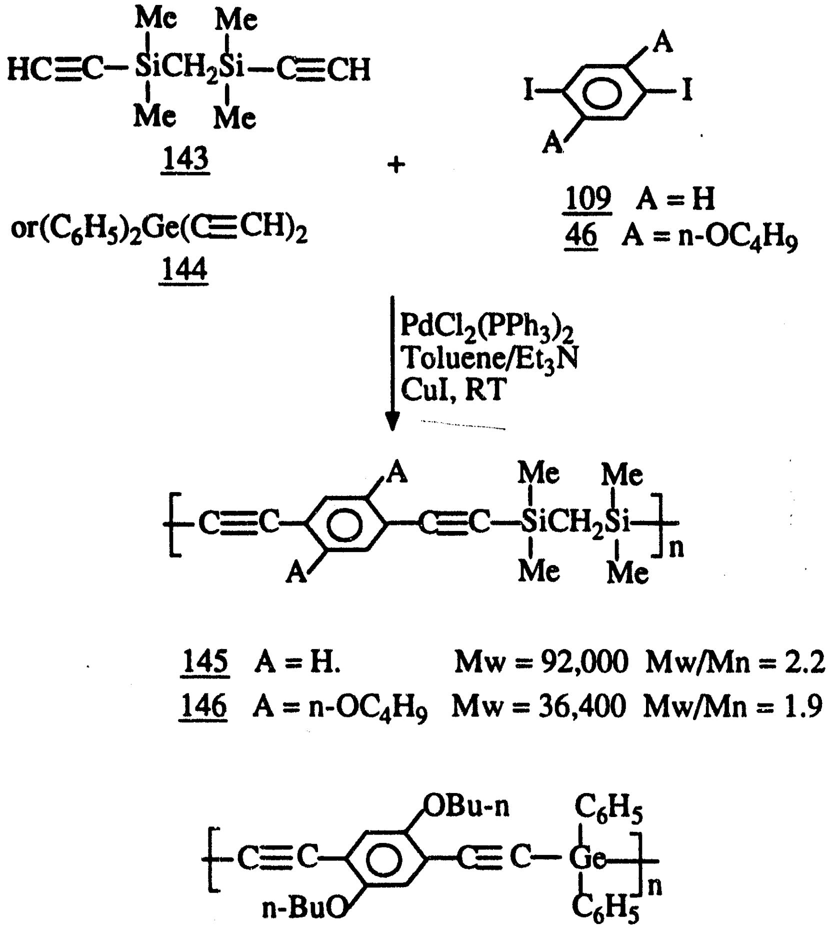
The silicon containing block copolymer 148 was also conveniently synthesized by using the same palladium-catalyzed polymerization.

Table 13. Summary of **PEArESim** polymers



No	Polymer Structure	Reaction Time (h)	Yield	$Mw \times 10^{-3}$	PD	Solubility
<u>139</u>	m= 1	24	71%	10.7	1.85	C_6H_6, THF $CHCl_3$
<u>140</u>	m= 2	24	88%	36.0	2.10	C_6H_6, THF $CHCl_3$
<u>141</u>	m= 3	66	70%	18.0	3.10	C_6H_6, THF $CHCl_3$
<u>142</u>	m= 4	72	70%	40.5	2.00	C_6H_6, THF $CHCl_3$

* Molecular weights measured at 20°C in THF.

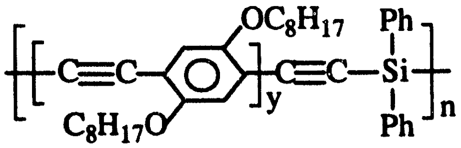


145 A = H. Mw = 92,000 Mw/Mn = 2.2

146 A = n-OC_4H_9 Mw = 36,400 Mw/Mn = 1.9

147 Mw = 15,200 Mw/Mn = 1.9

Scheme 41. Pd-catalyzed polymerization



148

Mw = 70,000 Mn = 11,000 Mw/Mn = 6.6

A silicon-containing block copolymer

Characterization of **PEArESim** polymers

None of these **PEArESi** polymers have ever been synthesized before. Good solubilities of these polymers in a variety of organic solvents such as benzene, tetrahydrofuran, and chloroform allowed us to characterize these **PEArESim** polymers by using FTIR and NMR techniques. The FTIR spectra of **PEArESim** polymers showed intense CC stretching bands in the region (2150 cm^{-1}).

The ^{1}H-NMR spectrum (Figure 39) of polymer 141 shows three singlets at 6.850 ppm, 0.34 ppm and 0.28 ppm for protons on the aryl group and the two different methyl group on the silylene respectively, two triplets at 3.90 ppm and 0.94 ppm for methylene-oxy group and methyl on the butoxy group respectively and two multiplets at 1.7 ppm and 1.5 ppm for the two butoxy methylenes. Figure 40 shows a ^{13}C-NMR spectrum of polymer 141. The resonance signals at 153.81 ppm, 117.25 and 114.11 ppm are assigned to the phenyl carbons. Other signals at 69.11 ppm, 31.37 ppm, 19.26 ppm and 13.88 ppm are attributed to the butoxy group. Signals at -1.98 ppm and -6.92 ppm are assigned to the methyl groups on the silylene and peaks at 103.71 ppm and 99.01 ppm are assigned to the ethynyl carbon adjacent to the aryl group and the ethynyl carbon attached to the silylene group respectively. No resonance signals for the 1,3-butadiyne group were observed in ^{13}C-NMR. ^{29}Si-NMR spectra of these polymers showed only one or two peaks, which correlated to both ^{1}H-NMR and ^{13}C-NMR spectra. Table 14 summarizes both ^{13}C-NMR and ^{29}Si-NMR data. The chemical shifts in ^{29}Si-NMR spectra range from -18 ppm to -46 ppm. The chemical shifts for the ethynyl carbon adjacent to silylene group in ^{13}C-NMR spectra are between 101 ppm and 104 ppm. The chemical shifts for the other ethynyl carbon are between 96 ppm and 100 ppm, except for 147. Other NMR data are given in the experimental part.

Thermotropic liquid crystalline properties of **PEArESi$_m$** polymers

DSC was used to study the phase transition behaviors of these **PEArESi$_m$** polymers. Unlike the polymers without alkoxy side chains, these polymers could melt when heated. The melting points depended on both the side chains and the flexible spacers (silylenes in the polymer main chain). Figures 41 and 42 are the DSC thermograms for polymers 138 and 142 (m = 4). Two endothermal peaks appear at 90°C and 110°C for 138 and 86°C 110°C for 142 respectively. The first endothermal peak indicate both polymers 138 and 142 start to melt at 90° and 86° and are thermally converted to a mesophase or liquid crystalline phase. The second thermal peak demonstrates that the liquid crystalline phase is converted to an isotropic liquid phase at 110°C (clearing point) for both polymers 138 and 142 upon further heating. A liquid crystalline phase exists between the melting point and the clearing point. Polarized microscopy observations, as shown in figure 43, also support this result. Both polymers 138 and 142 have a crystalline phase at room temperature, which was observed by polarized microscope. Since polymers 138 and 142 have similar melting points and clearing points, the melting points and clearing points for polymer 138 and 142 are mainly determined by the polymer main chain segments.

Table 14.

^{13}C- and ^{29}Si-NMR data of **PEArESim** polymers

Polymers	^{29}Si-NMR δ(ppm)	^{13}C-NMR δ(ppm)	
		C_1	C_2
135	-38.99(1Si)	101.66	96.86
136	-36.65(2Si)	103.54	98.63
137	-33.81(2Si), -45.93(1Si)	103.51	99.51
138	-33.42(2Si), -43.42(2Si)	103.50	99.71
139	-39.33(1Si)	101.82	96.51
140	-37.03(2Si)	103.68	98.03
141	-33.94(2Si), -46.33(1Si)	103.65	99.00
142	-33.43(2Si), -43.57(2Si)	103.66	99.20
145	-17.99(2Si)	104.96	96.86
146	-18.07(2Si)	101.44	100.64
147	———	103.19	92.69

-Si - $C_2 \equiv C_1$-Ar- Si(Me)$_4$ was used as the reference.

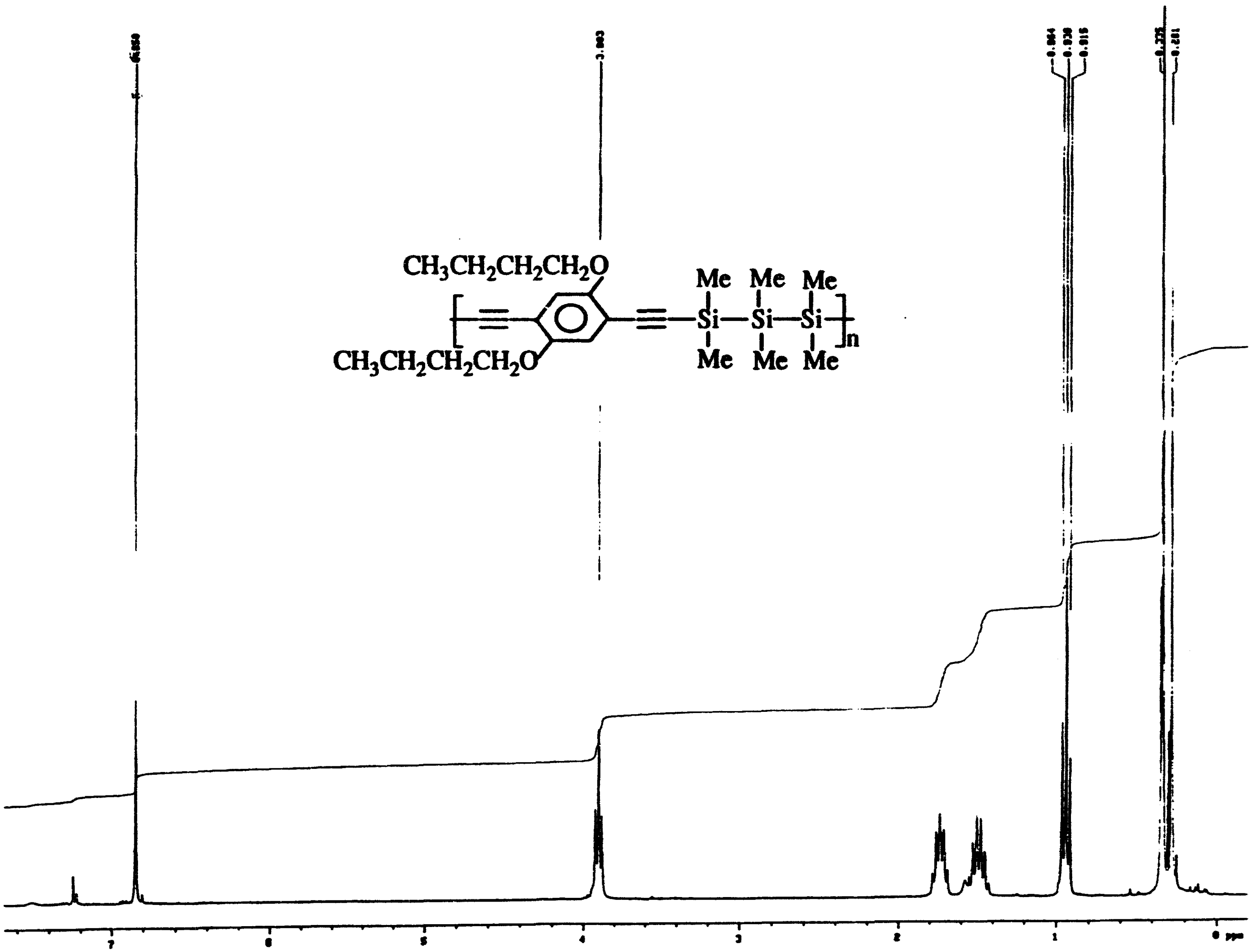


Figure 39. ^{1}H- NMR spectrum of polymer <u>141</u>

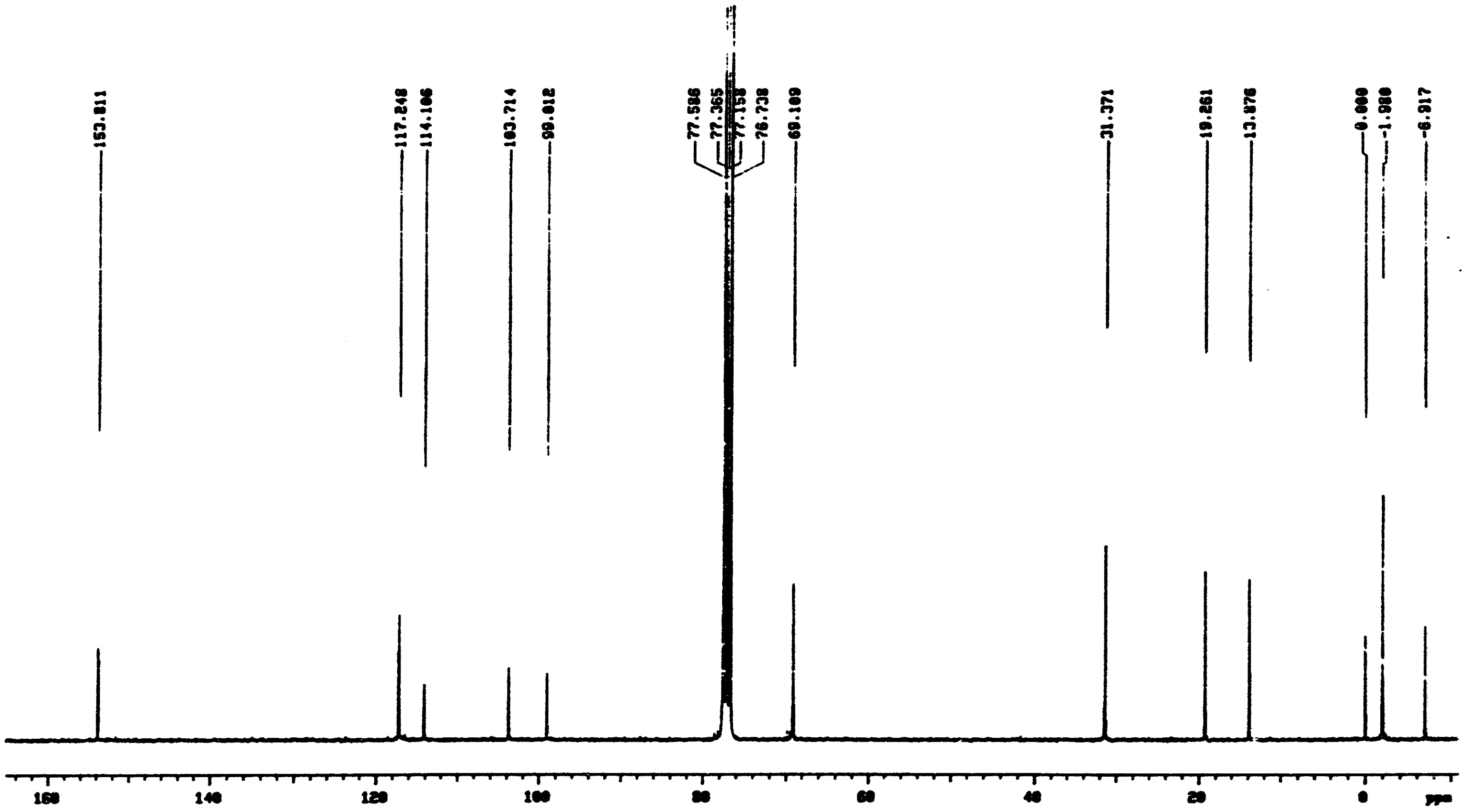


Figure 40. ^{13}C-NMR spectrum of polymer <u>141</u>

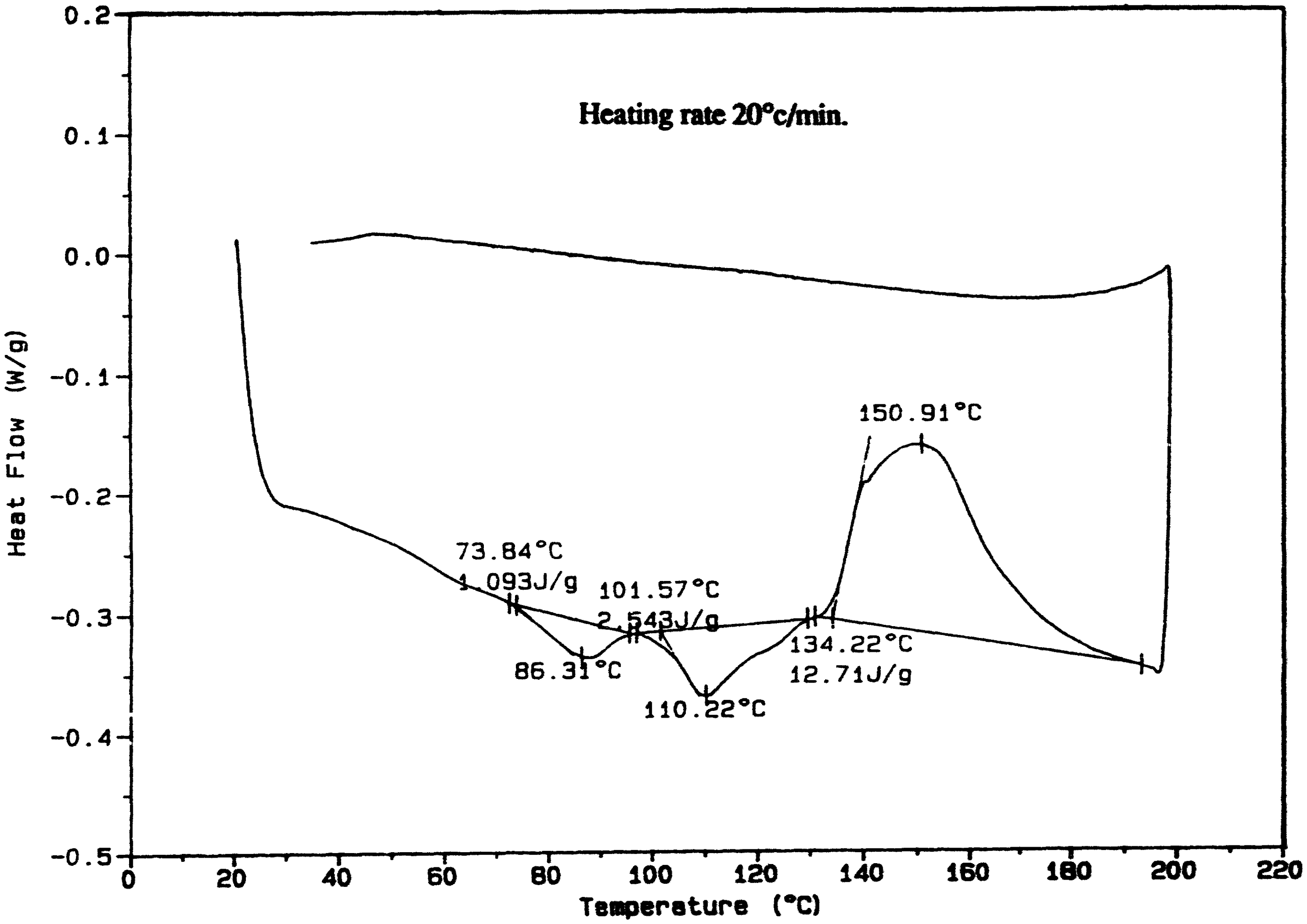


Figure 41. DSC thermogram of polymer <u>138</u>

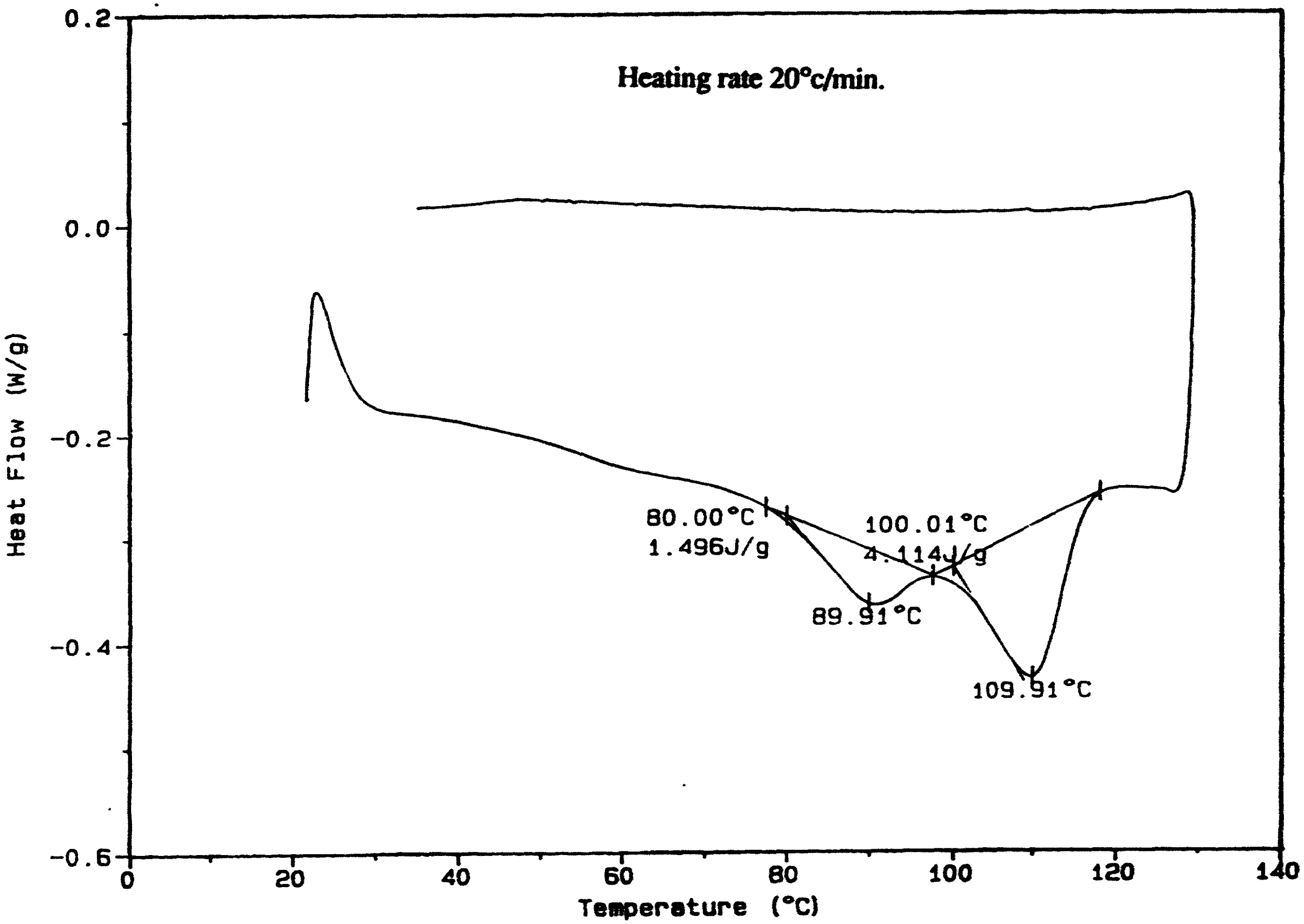
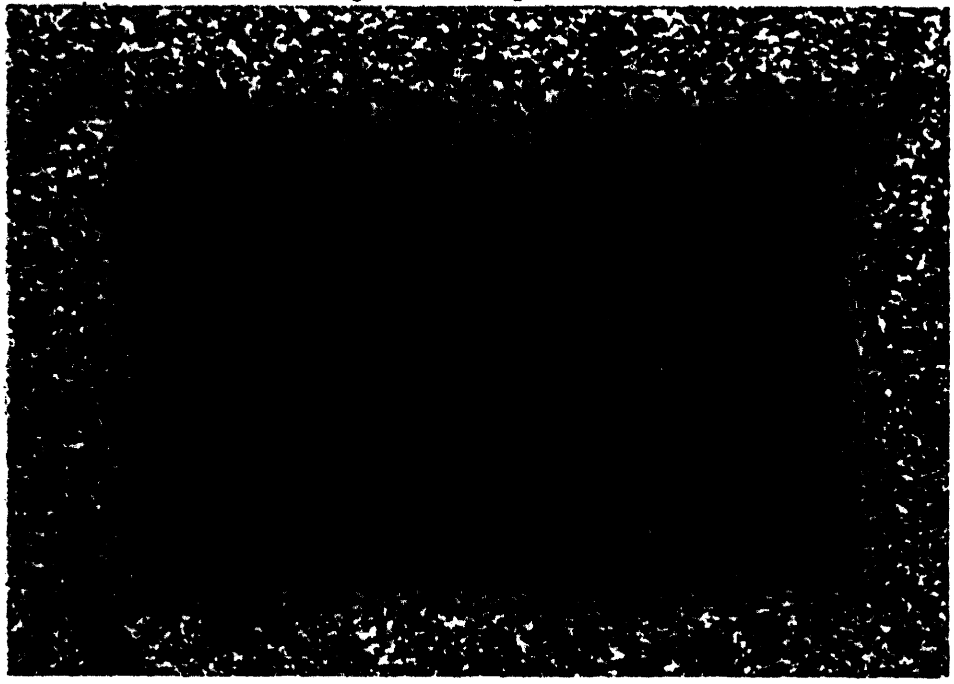
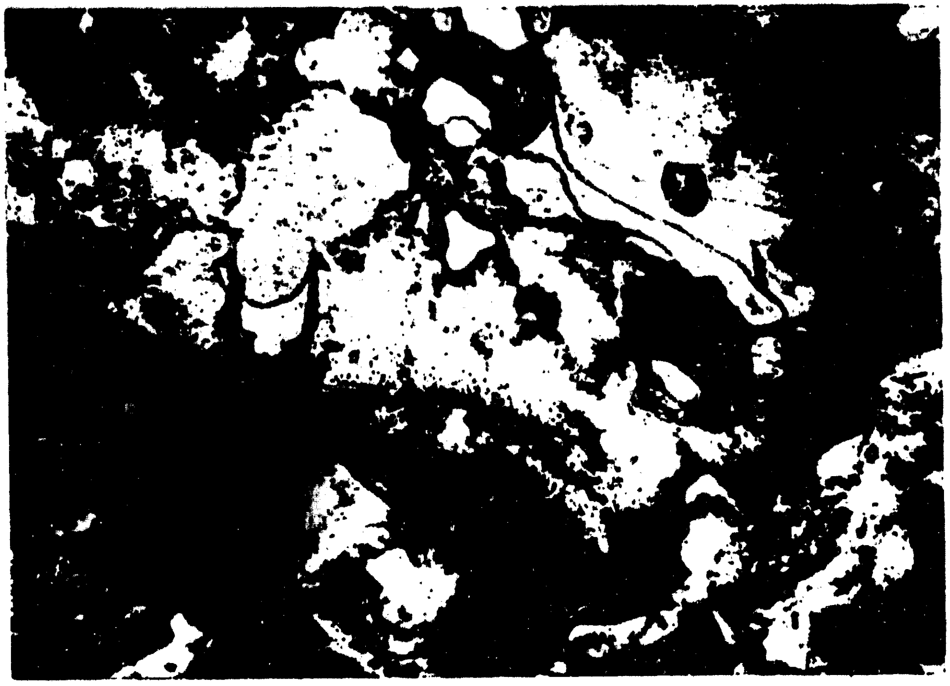


Figure 42. DSC thermogram of polymer 142

Observed under crossed-polarizers
cooling after isotropic melt



Cooled to 90°C, x125, LC phase



Cooled to 85°C, x400, LC phase

Figure 43. Polarized microscopic observation of polymer <u>142</u>

However, there is an exothermal peak right after the second endothermal peak only for 138, which implies that the decomposition or thermal crosslinking occurred after melting for 138, which has short side chains. Since this exothermal peak was not observed for 142, which has n-butoxy side chain longer than methoxy side chain of 138, the long side chain will help to prevent the thermal crosslinking between the polymer chains by increasing the distance between the polymer chains which contain reactive ethynyl groups. The X-ray experiment is needed to identify the mesophase.

Figure 44 shows the DSC thermogram for polymer 140. Two endothermal peaks are also observed at 157°C and 162°C for 140. Thus, a mesophase or liquid crystalline phase exists between 157°C (the melting point) and 162°C (the clearing point). This result also demonstrates that polymer 140 has higher melting point and clearing point than that of 142. Polarized microscope observation shown in Figure 45a and 45b also supports the existence of a mesophase for polymer 140. Due to decomposition or thermal crosslinking before the melting, it's impossible to study the thermal property of 136. Also, decomposition or crosslinking occurred to polymer 135 and 137 before melting.

Two exothermal peaks in DSC thermogram (Figure 46) are also observed at 56.5°C and 68°C for polymer 141, which implies that a mesophase also exists for 141 between this temperature range. Like 138, an endothermal peak appear after the clearing temperature, which also indicates that decomposition occurs at that temperature. A part of the DSC data are summarized in Table 15.

Thermal analysis results under a helium atmosphere for 135-138 as shown in Figure 47 indicated that these polymers started to loss the weight slowly at 200°C and that the weight losses were accelerated over 400°C. The char yields are between 63% and 75%. Other TGA data are given in Table 15.

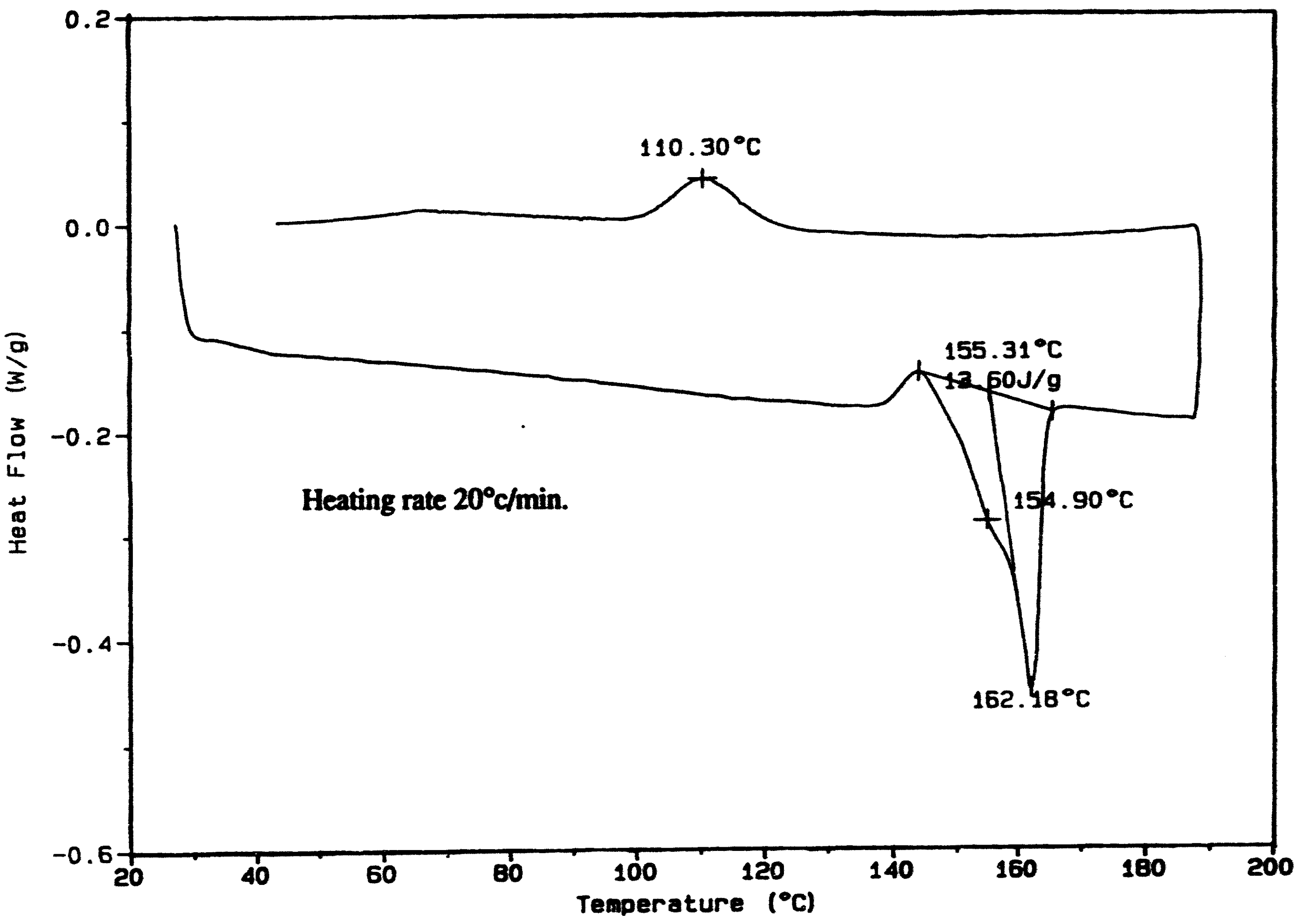
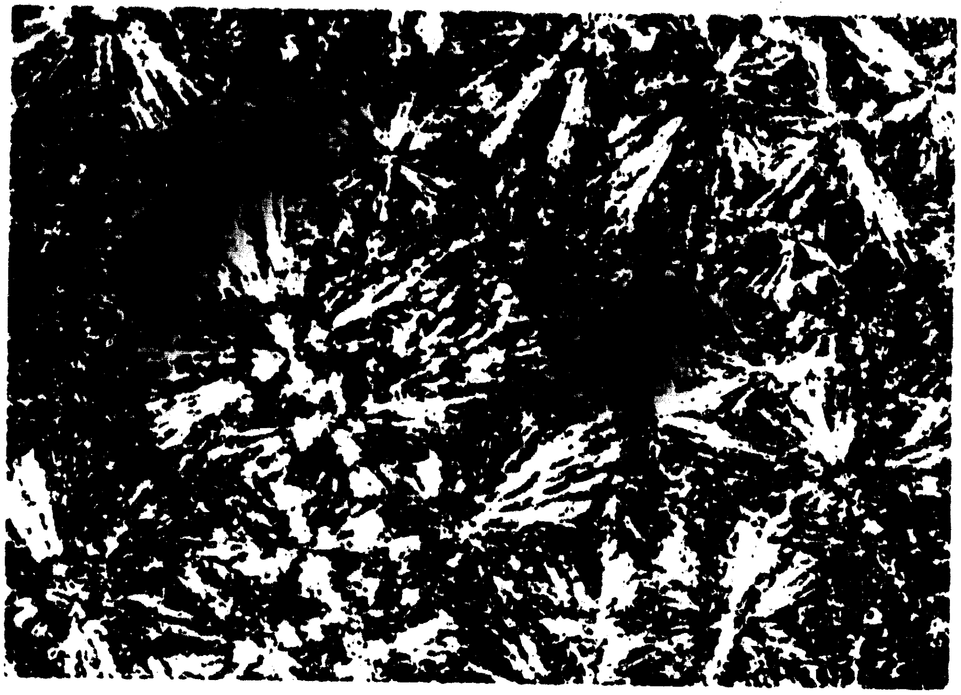


Figure 44. DSC thermogram of polymer 140.

Observed under crossed-polarizers
cooling after isotropic melt

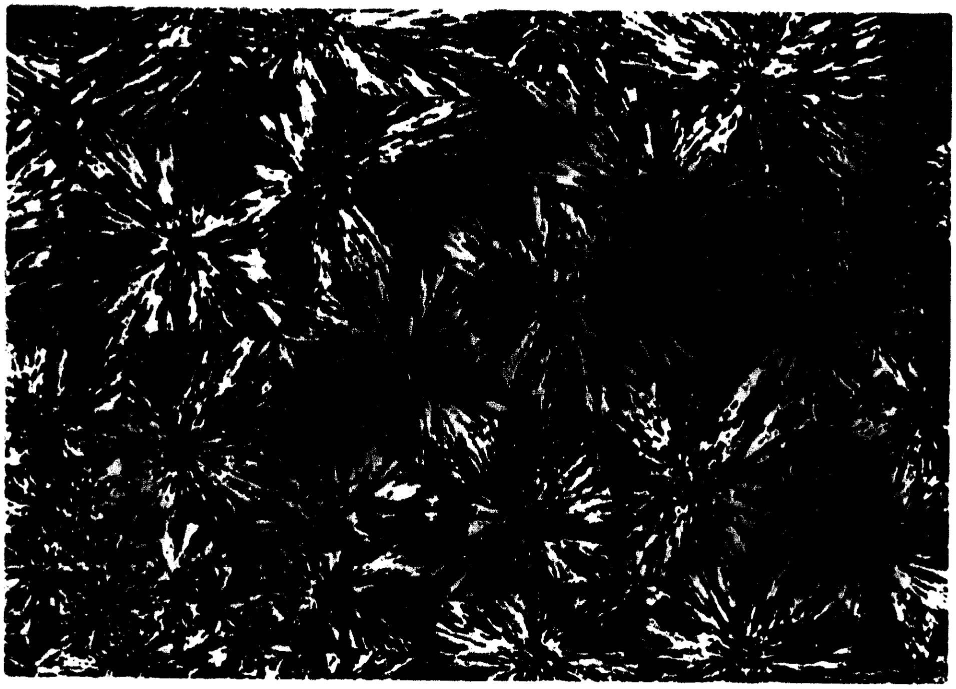
Cooled to 130°C, x125, LC phase



Slow cooling to 120°C
x400, LC phase and crystallization

Figure 45. (a) Polarized microscopic observation of polymer 140

Observed under crossed-polarizers
cooling after isotropic melt



Upon standing at 120°C
x400, crystallization

Figure 45. (b) Polarized microscopic observation of polymer 140

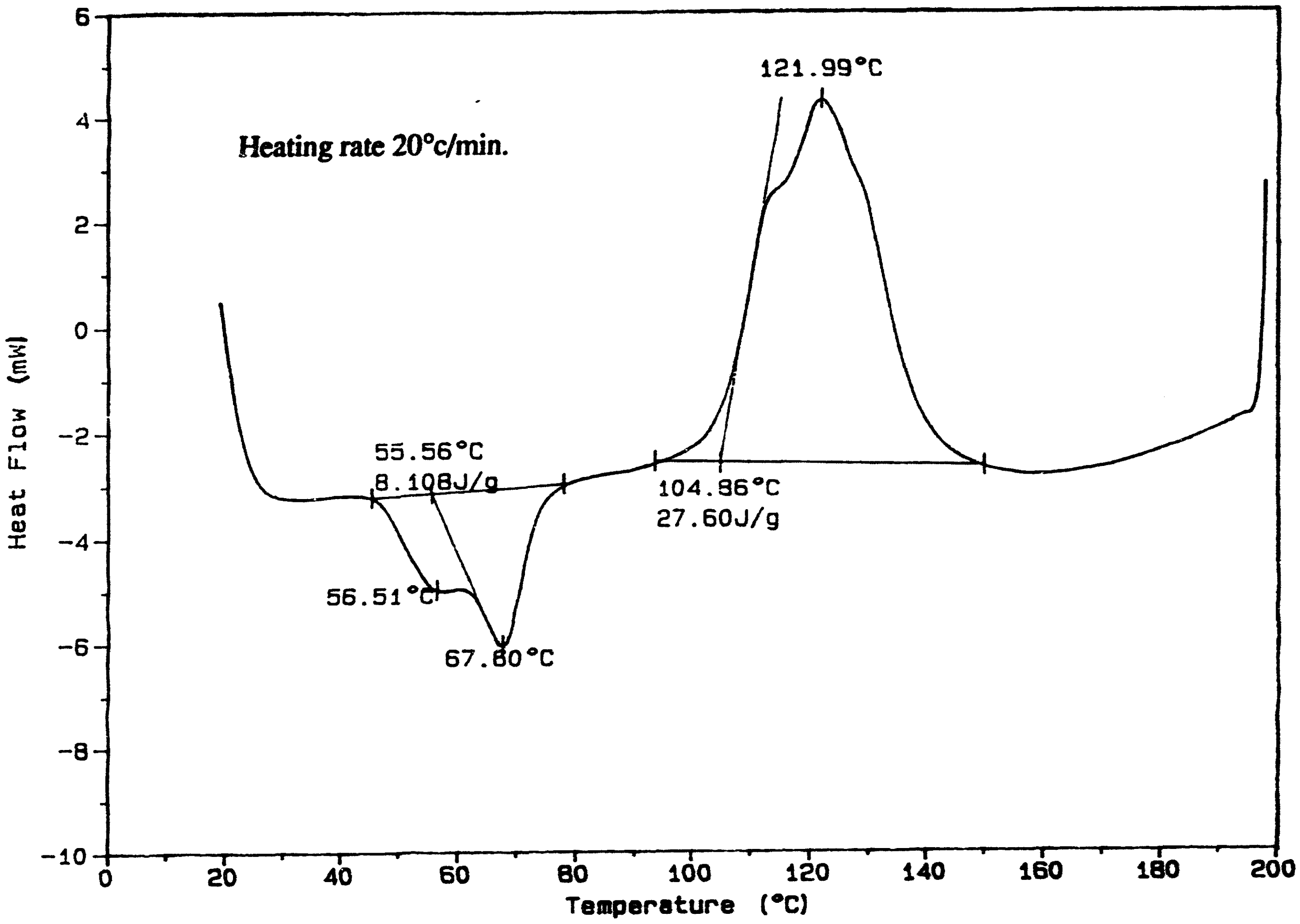


Figure 46. DSC thermogram of polymer 141

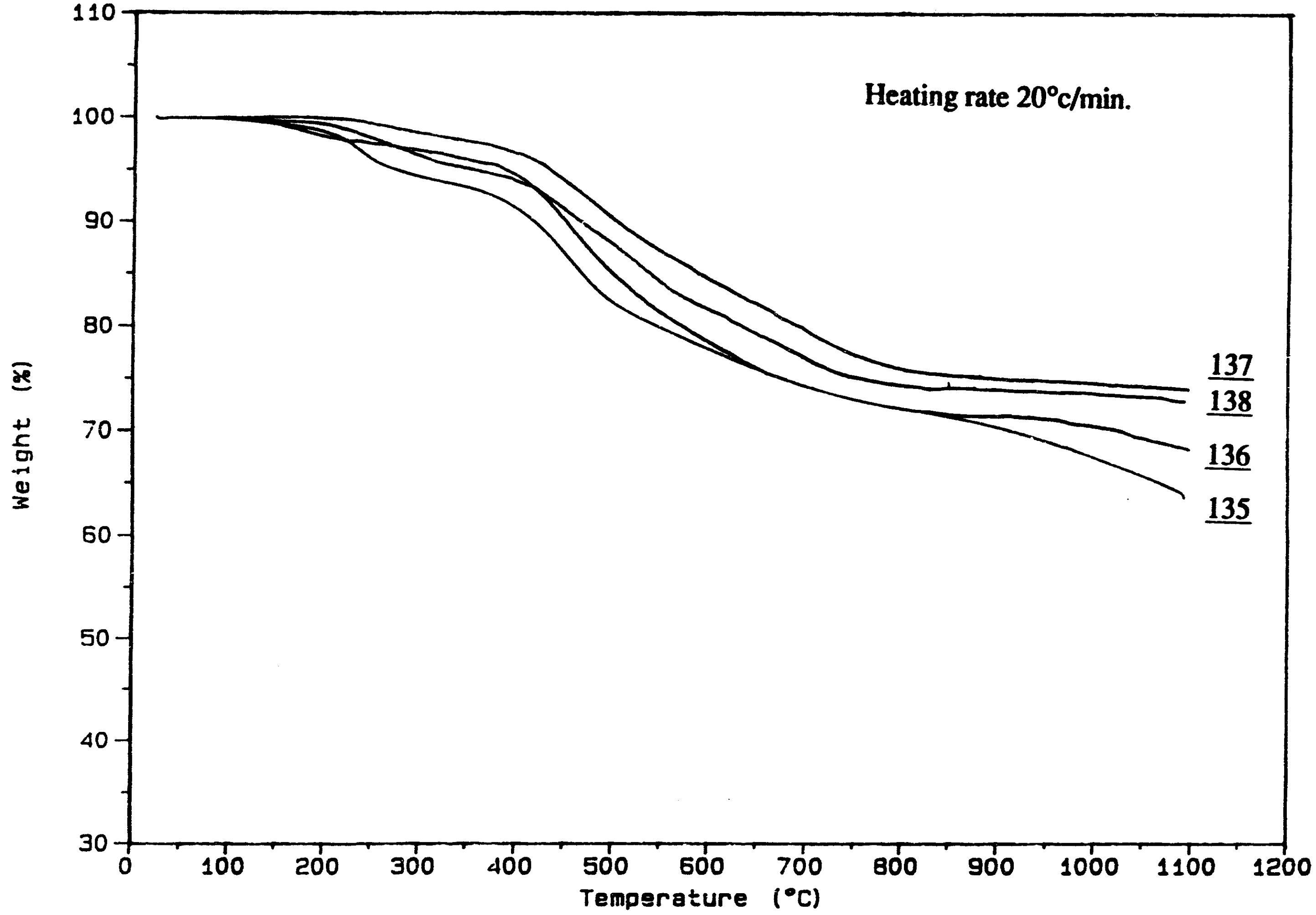


Figure 47. TGA results of polymers <u>135</u>-<u>138</u>

Table 15. Melting points and char yields of **PEArESim**

Polymers	135	136	137	138	139	140	141	142
Tm	Decom	Decom	Decom	90°C	60.4°C	157°C	56.5°C	86°C
Ti				110°C		162°C	68°C	110°C
Char Yield%	64	68	74	73	58	59	59	52

Tm = melting point   Ti = clearing point   Decom = decompositon

UV spectroscopic study of **PEArESim** polymers

The **PEArESim** polymers like **PEPESim** also have strong UV absorption. Figure 48 shows the absorption spectra for polymers 139-142 in THF solution at room temperature. The absorption spectra data is listed in Table 16. There are four strong absorption peaks at 360 nm, 350 nm, 296 nm and 283 nm. Also, there is a tailing peak for these polymers.

Interestingly, polymer 143 with one silicon in the polymer main chain has a slightly different UV absorption spectra. Also the peak of carbon-carbon triple bond in FT-IR exhibit a 7 cm^{-1} shift, which is similar to that of **PEPESi** polymers.

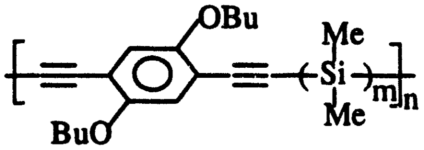
The absorption spectrum (Figure 49) for polymer 140 in the film state shows a red shift presumably due to σ-π conjugation between conjugated ethynyl π bonds and Si-Si σ bonds in the solid state when m was 2. The absorption spectra of polymers 141 and 142 also show a similar absorption feature.

In Figure 50, the emission spectra of the polymer 142 in THF solution at room temperature show three strong emission peaks at λ= 380 nm, 411 nm and 434 nm when excited at 340 nm. There is also a tail extended to 600 nm.

Study of Non-linear optical properties

In a collaboration with Prof. Vardeny of the Department of Physics at the University of Utah, the optical properties of both **PEPESim** and **PEArESim** polymers have been studied. Preliminary results have indicated that the third-order susceptibility $\chi^{(3)}$ of **PEPESi1** polymer 124 ($[\text{-CCPhCCSi(Ph)}_2\text{-}]_n$) at 590 nm is -1.32×10^{-12} esu. For **PEArESim** polymers 140-142, the fifth-order and even seventh-order susceptibility have

Table 16. Absorption spectra data of PEArESim



No	Polymer Structure	IR (cm^{-1})	λ(nm) of peaks and logϵ
<u>139</u>	m= 1	2156	364(3.92), 311(3.54), 290(4.21) 279(4.07), 274(4.06).
<u>140</u>	m= 2	2147	365(4.05), 351(4.05), 296(4.24), 282(4.14).
<u>141</u>	m= 3	2147	360(4.07), 351(4.10), 296(4.27), 283(4.21).
<u>142</u>	m= 4	2147	360(4.11), 351(4.15) 297(4.28).

been observed besides the $\chi^{(3)}$. However, the values of $\chi^{(5)}$ and $\chi^{(7)}$ have not been measured due to experimental difficulties. Further study of these polymers is underway in Vardeny's lab.

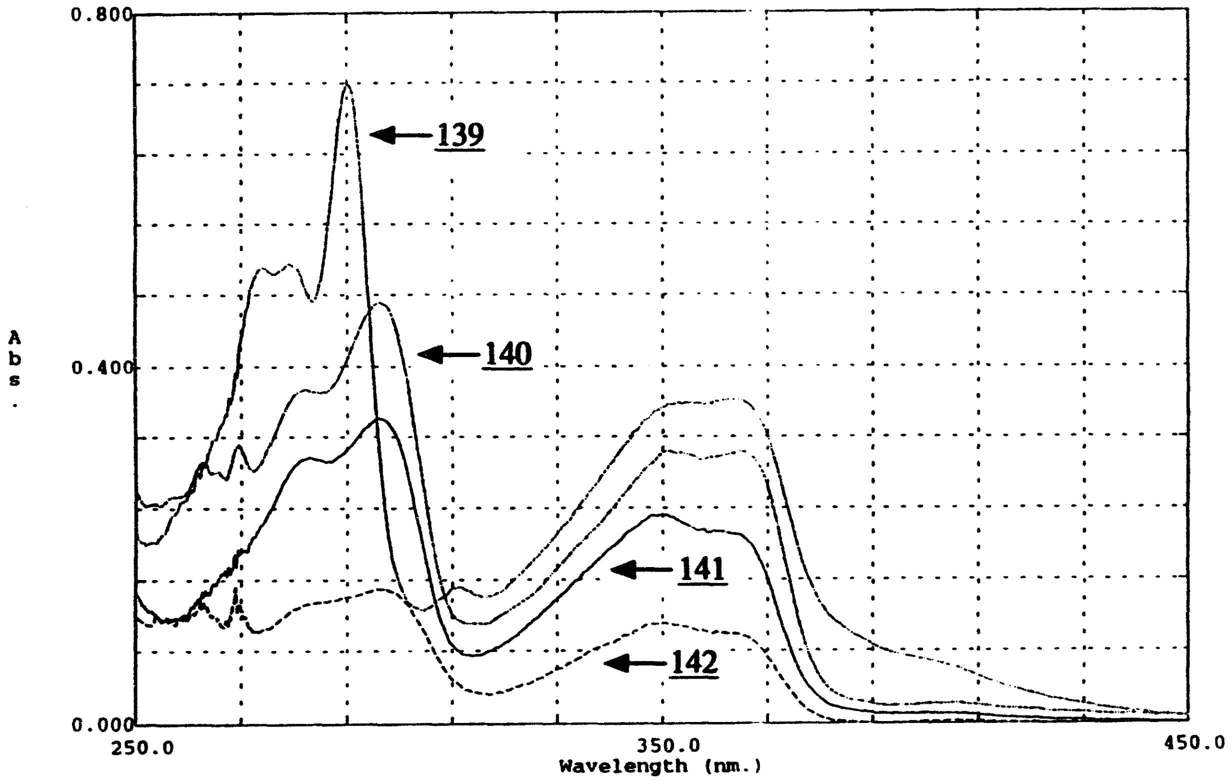


Figure 48. The UV absorption spectra of polymers 139-142 in THF solution

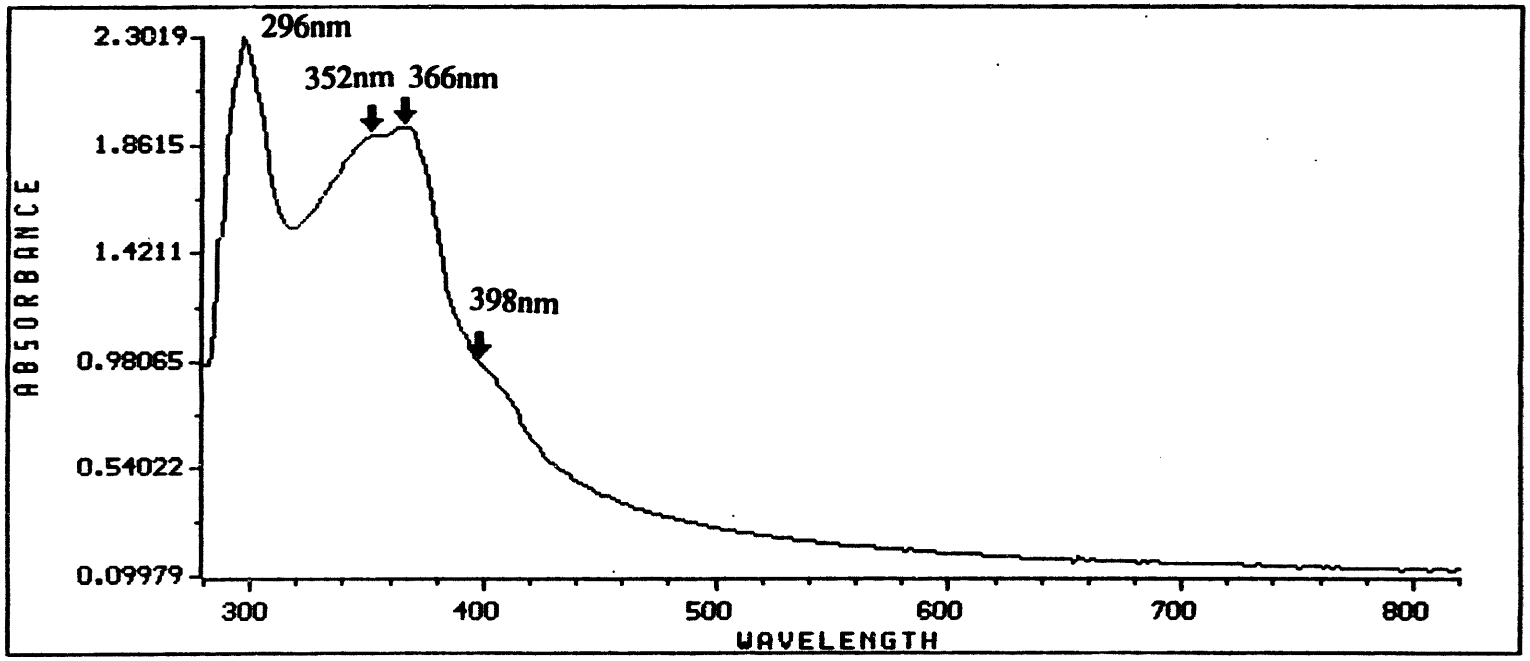


Figure 49. The UV absorption spectrum of polymer 140 in the film state

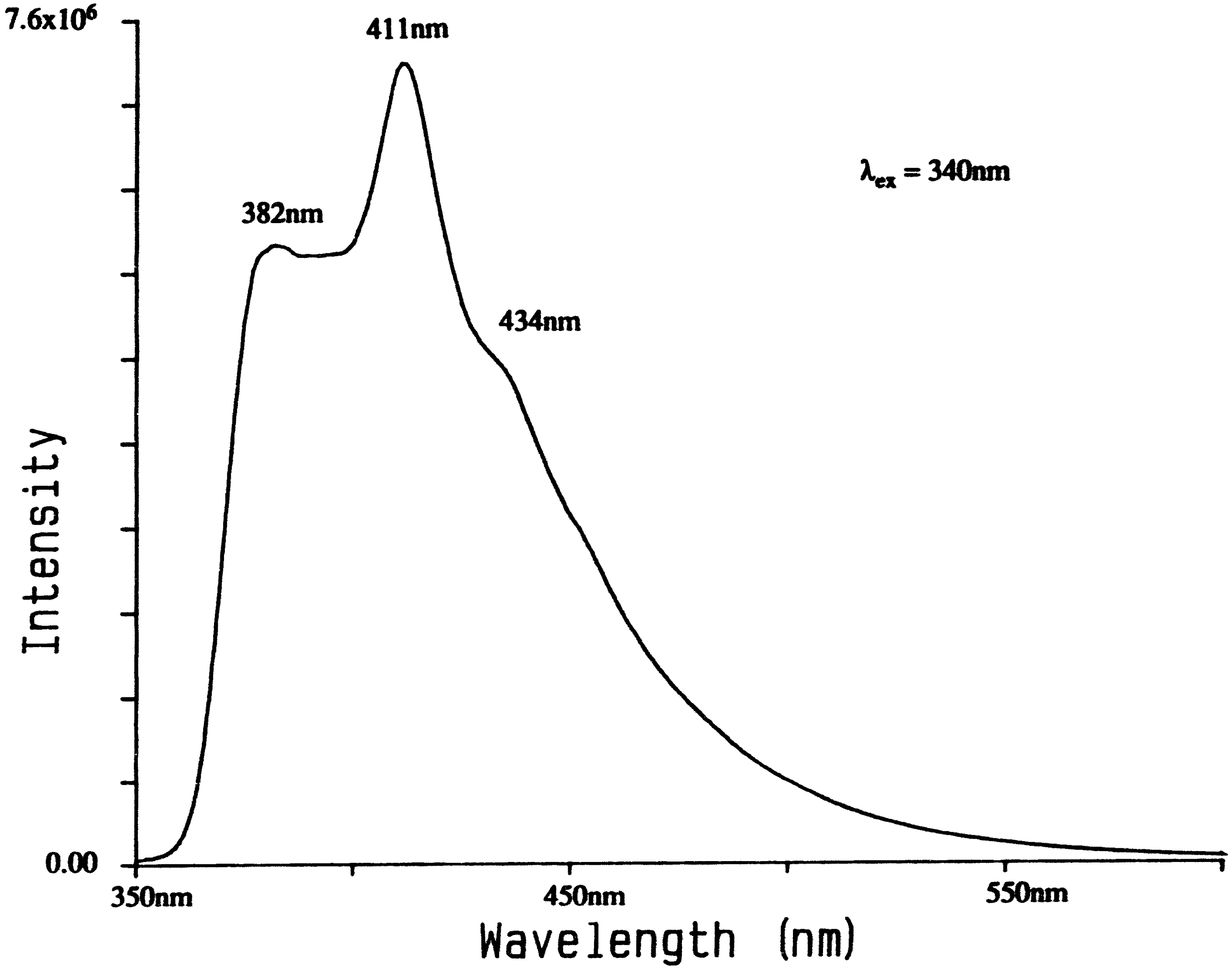


Figure 50. The emission spectrum of polymer 142 in THF solution

CONCLUSIONS

In this section, a series of novel **PEArESim** polymers were conveniently synthesized via a palladium-catalyzed polymerization. Since these polymers dissolved in a variety of organic solvents, they were characterized by multi-nuclear-NMR, FTIR and GPC. The weight average molecular weights of these polymers ranged from $5.0\text{x}10^3$ to $40\text{x}10^3$.

As expected, these **PEArESim** have low melting points and their thermotropic LC properties were studied by using differential scanning calorimeter and polarized microscopy. Polymers 135-137 with the methoxy as the side chains decompose before melting and polymer 138 has a liquid crystalline phase. Polymers 140-142 with the butoxy as the side chains have a liquid crystalline phase while polymer 139 does not exhibit a liquid crystalline phase. Decomposition or crosslinking does not occur to polymers 139-142 upon heating. Presumably this is due to the fact that longer side chains increase the distance among the polymer chains and prevent these polymers from thermo-decomposition or crosslinking.

These **PEArESim** polymers also emit strong luminescence at about $\lambda = 430$ nm, they are potential candidates for 'blue' LED materials and the research is under way. Preliminary study of these **PEArESim** polymers indicated that these polymers exhibit third-order, fifth-order, and seventh-order optical non-linearity.

SECTION FOUR:

THE SYNTHESIS OF POLY(SILYLENE-ETHYNYLENE)S VIA A NOVEL PALLADIUM-CATALYZED POLYMERIZATION

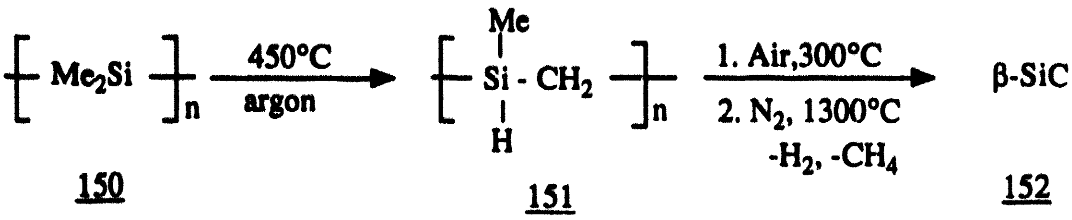
INTRODUCTION

Silicon carbide (SiC) is of interest as a high performance material because of its high hardness, excellent oxidation resistance and high melting point. Many methods have been used to synthesize silicon carbide. Among these[75] are the carbothermal reduction of silica or compounds containing silica and pyrolysis of synthetic polymers (precursor route). The carbothermal reduction of silica as shown in Scheme 42 is a method generally used for the manufacture of commercial SiC products. Its use of inexpensive silica and coke and its ability to produce fine-grained powders of relatively high purity by heating to 1500-1900°C have led to its use in industry. The precursor route to silicon-carbide has been the subject of intensive study over the past 20 years[76]. In principle, the precursor route to silicon-carbide is similar to that of PPV polymers. The precursor polymers are synthesized first and then they are converted to silicon carbide thermally. This principle was first demonstrated by Yajima[77] in a two-step thermal conversion of polydimethylsilane to SiC fiber as shown in Scheme 43. Yajima's process has been commercialized to produce SiC fiber and cloth under the Nicalon trade name. Several groups[78] also reported the studies of polycarbosilane precursors to silicon carbide. Most linear polycarbonsilanes[65] tend to depolymerize upon heating and afford little or no ceramic yield. In order to increase ceramic yield, functionalities which afford thermal crosslinking are needed in the polymer.

$$\mathrm{SiO_2} + 3\mathrm{C} \xrightarrow{1500\text{-}1900^{\circ}\mathrm{C}} \underset{\underline{149}}{\mathrm{SiC}} + 2\mathrm{CO}$$

Scheme 42. Carbothermal reduction of silica[75]

Study of the precursor route to silicon carbide has been one of the projects in

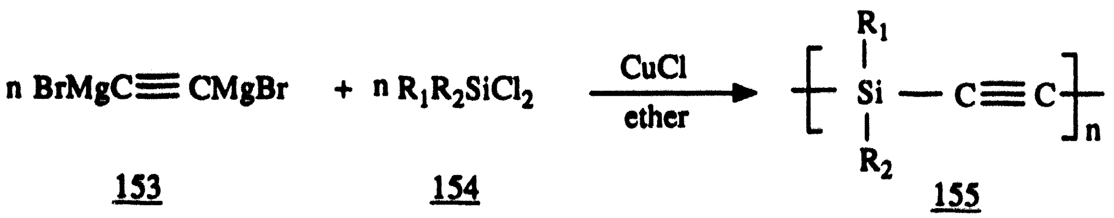


Scheme 43. Yajima's process[77]

Barton's group since 1984. Silylene acetylene polymers (poly(silylene-ethynylene)s) which contain a crosslinking group have been studied as excellent candidates to SiC. Korshak[79] first reported the synthesis of silylene acetylene polymers by the condensation polymerization between a dichlorosilane 154 and a diGrignard 153 as shown in Scheme 44. Since the stoichiometric ratio between the diGrignard 153 and the dichlorosilane 154 is crucial in making high molecular weight polymers, this route suffers since it is very difficult to control the concentration of diGrignard acetylides in the metallization of acetylene.

Later, Seyferth[80] reported the similar condensation polymerization between magnesium acetylide 156 and dichlorosilanes 157 as shown in Scheme 45. This method afforded only low molecular weight polymers or oligomers 158 since the stoichiometric problem still remained.

In order to improve the above synthetic method, it is necessary to control the concentration of dianion in solution. In 1990, Barton[66,81] discovered that dilithioacetylide 159 could be quantitatively generated via the reaction of trichloroethylene 149 with three equivalents of n-BuLi. As shown in Scheme 46, this dilithioacetylide 159 was quenched by a variety of dichlorosilanes to give polymers 160-163 with molecular weights ranging from 20,000 to 70,000 in high yields. These silylene acetylene polymers are air stable and have a long shelf life. They are meltable and soluble in a variety of organic solvents.

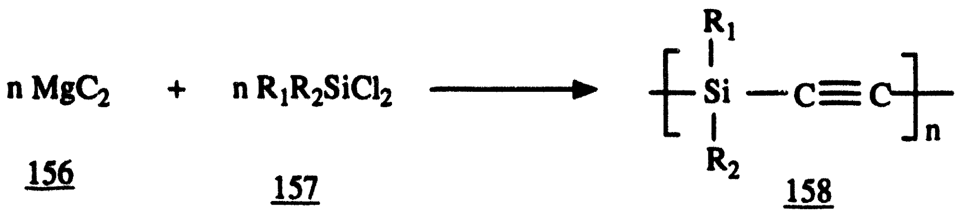


$$n\ \mathrm{BrMgC{\equiv}CMgBr} + n\ \mathrm{R_1R_2SiCl_2} \xrightarrow[\text{ether}]{\text{CuCl}} \left[\mathrm{Si(R_1)(R_2)-C{\equiv}C}\right]_n$$

153 154 155

R_1	R_2	Mw	Solubility
CH_3	CH_3	- -	insoluble
CH_3	Ph	2700	soluble in C_6H_6
Ph	Ph	1400	soluble in C_6H_6

Scheme 44. Synthesis of silylene acetylene polymers by using a diGrignard acetylide[79]

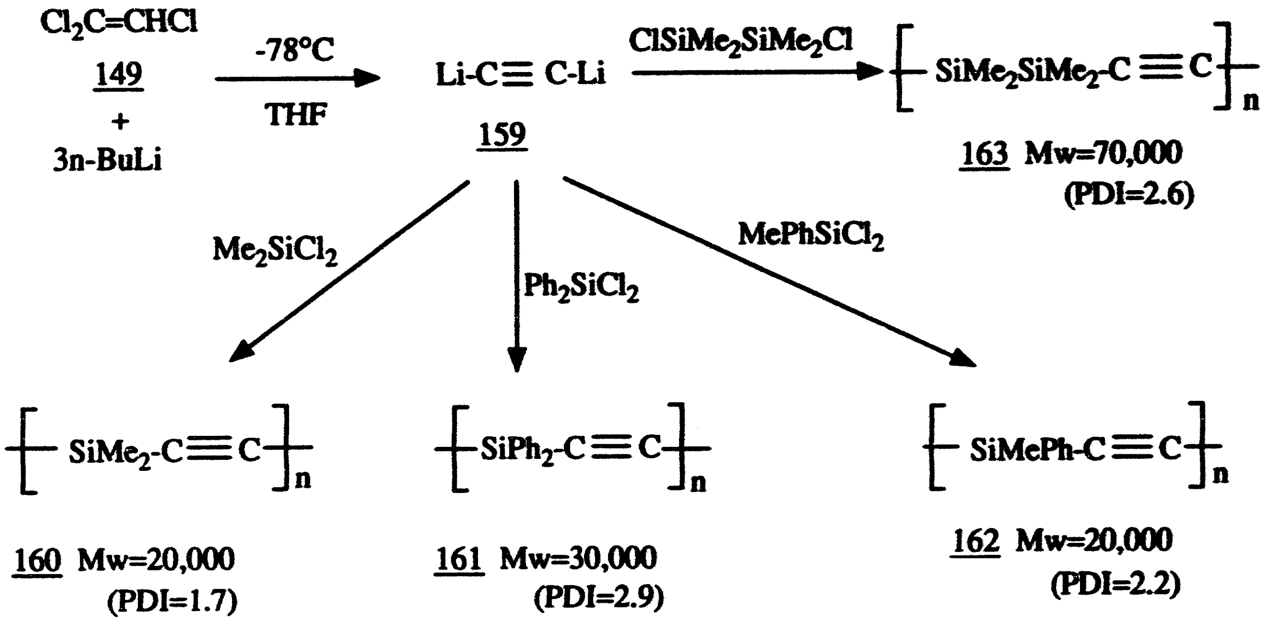


$$n\ \mathrm{MgC_2} + n\ \mathrm{R_1R_2SiCl_2} \longrightarrow \left[\mathrm{Si(R_1)(R_2)-C{\equiv}C}\right]_n$$

156 157 158

R_1	R_2	Mw
CH_3	CH_3	insoluble
CH_3	H	900
CH_3	$CH_2{=}CH_2$	1100

Scheme 45. Synthesis of silylene acetylene polymers by using magnesium acetylide[80]



Scheme 46. Synthesis of silylene acetylene polymers by using dilithioacetylide[81]

They are easily processed to films or fibers from melt or solution, and thermally converted to SiC containing ceramics in high yield at high temperature. They are excellent preceramic polymer candidates as binders for the powder processing of ceramics.

However, this method to synthesize silylene acetylene polymers is rather expensive due to the consumption of three equivalents of n-BuLi. The polymers with functionalities which are incompatible with dianions cannot be synthesized by this method. Also, there is a difficulty in making silylene-acetylene alternating copolymers 164 by using this method. Thus, it is necessary to seek other routes to synthesize these polymers.

$$\left[\!-\mathrm{SiR_1R_2{-}C{\equiv}C{-}SiR_3R_4{-}C{\equiv}C}-\!\right]_n$$

164

RESULTS AND DISCUSSION

In the previous section, palladium-catalyzed polymerization in which coupling of diethynylsilanes and 1,4-diiodobenzene afforded silylene-diethynylbenzene polymers in excellent yields has been established. Whether the Pd-catalyzed polymerization can be extended to make silylene acetylene polymers will depend on the model reaction.

Taniguchi[82] et al in 1981 have reported an interesting reaction shown in Scheme 47. Trimethyl silylation of acetylene compounds 156 was achieved by using a combination of chlorotrimethylsilane and 1,8-diaza-bicyclo [5.4.0] undec-7-ene (**DBU**) in good yield. Silver chloride was used as a catalyst. A variety of trimethylsilyl-acetylene compounds 166 were synthesized. This method was used to prepare silylacetylene polymers 168 as shown in Scheme 48. However, this method did not have any big advantage over other methods due to the difficulty of removing silver chloride during the purification.

$$\mathrm{RC{\equiv}CH} \xrightarrow[\mathrm{DBU,\ AgCl(cat)}]{\mathrm{Me_3SiCl\ \ ,\ CH_2Cl_2}} \mathrm{RC{\equiv}CSiMe_3}$$

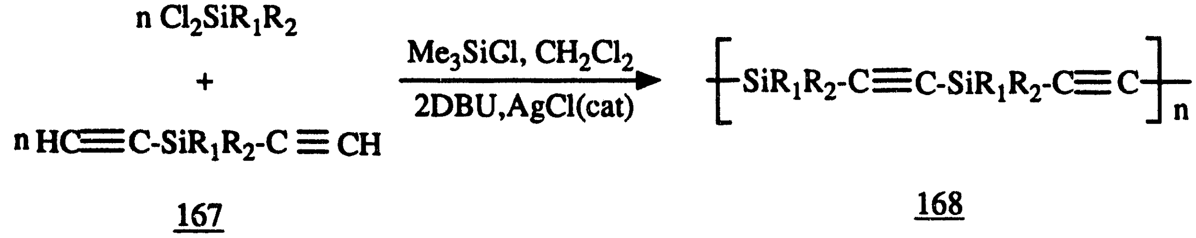
R = alkyl, phenyl.

165

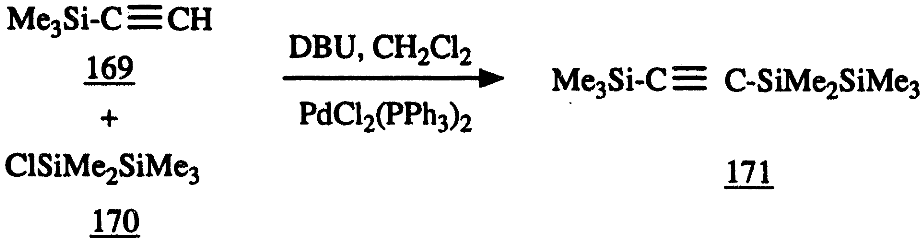
166

Scheme 47. The model coupling reaction[82]

Palladium catalysts were successfully used in the condensation polymerization to synthesize **PPE** and **PEPESi** polymers. However, whether the Pd-catalyzed polymerization can be applied or extended to make silylene-acetylene polymers will depend on the following Pd-catalyzed coupling (Scheme 49) between an acetylene compound 169 and a chlorosilane compound 170. This model reaction was performed

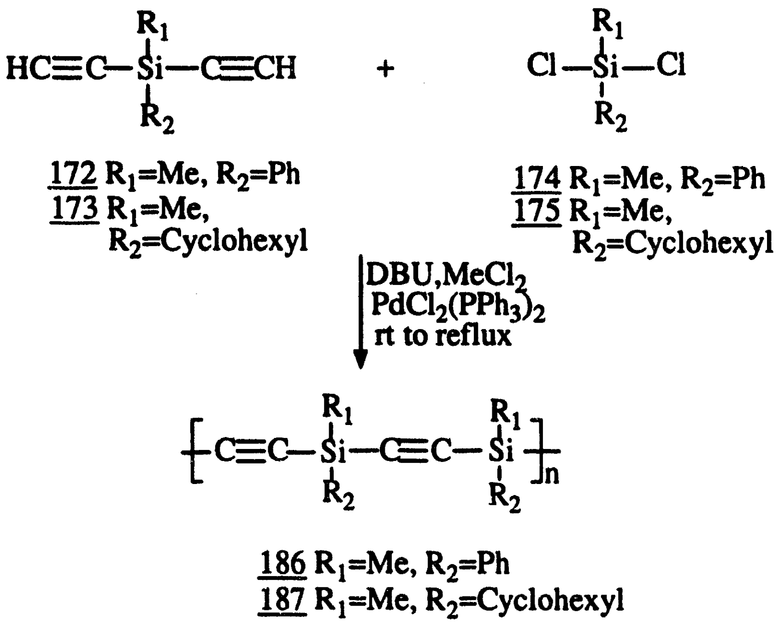


Scheme 48. AgCl catalyzed polymerization



Scheme 49. Pd-catalyzed coupling reaction

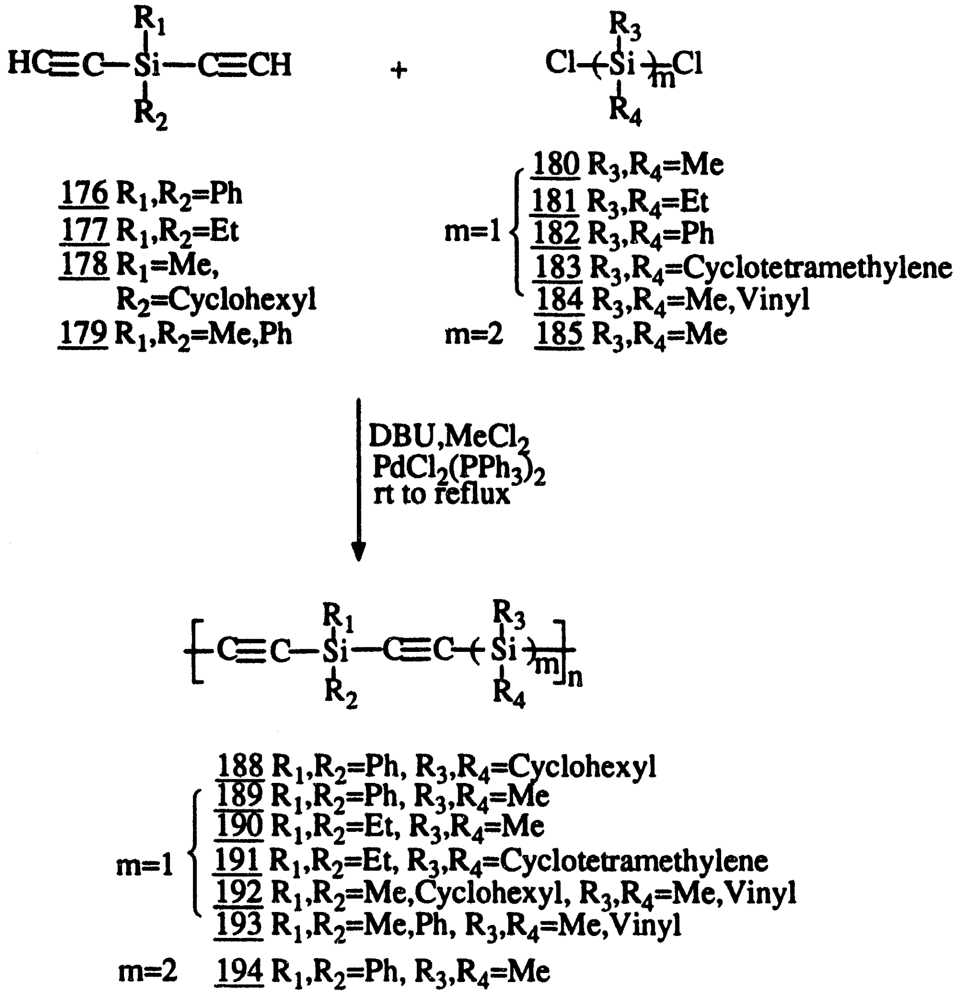
under an argon atmosphere and after 12 hours reflux, compound 171 formed with 60% GC yield. Therefore, this Pd-catalyzed coupling could be applied to synthesize silylene acetylene polymers. The polymerization is shown in Scheme 50. In a typical polymerization, diethynylsilane 172 was dissolved in methylenechloride and a catalytic amount of $PdCl_2(PPh_3)_2$ and two equivalents of Diazo-bicyclic-undec(DBU) were added to it. After argon was bubbled through the solution for a few minutes, one equivalent of dichlorosilane 174 was added to the solution. After the polycondensation ran at room temperature for 24 hours, the solution was refluxed for 12 hours under an argon atmosphere and then quenched with excess methanol. After purification, polymer 186 was dried under vacuum. Both 186 and 187 were characterized by multi nuclear NMR, FTIR and GPC since they were soluble in a variety of organic solvents.



Scheme 50. The synthesis of poly(silylene-ethynylene) homopolymers via a novel Pd-catalyzed polymerization

Based on this Pd-catalyzed polymerization, several alternating copolymers as shown in Scheme 51 were synthesized by using different monomers under the same polymerization condition. These alternating copolymers were characterized by the same methods used for polymer 186. Some of the results are summarized in Table 17.

The weight average molecular weights of these polymers ranged from $56\text{x}10^3$ to $5.3\text{x}10^3$ and the polydispersities were between 1.3 and 3.9. The yields ranged from 64% to 83%. Not only homo-polymers, but also alternative copolymers, which have not been made before, have been synthesized by this palladium catalyzed polymerization. Furthermore, copolymers with vinyl group attached to silicon have been made with good char yield.



176 R_1,R_2=Ph
177 R_1,R_2=Et
178 R_1=Me, R_2=Cyclohexyl
179 R_1,R_2=Me,Ph

m=1: 180 R_3,R_4=Me; 181 R_3,R_4=Et; 182 R_3,R_4=Ph; 183 R_3,R_4=Cyclotetramethylene; 184 R_3,R_4=Me,Vinyl
m=2: 185 R_3,R_4=Me

DBU,$MeCl_2$
$PdCl_2(PPh_3)_2$
rt to reflux

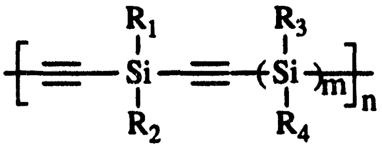
188 R_1,R_2=Ph, R_3,R_4=Cyclohexyl
m=1: 189 R_1,R_2=Ph, R_3,R_4=Me; 190 R_1,R_2=Et, R_3,R_4=Me; 191 R_1,R_2=Et, R_3,R_4=Cyclotetramethylene; 192 R_1,R_2=Me,Cyclohexyl, R_3,R_4=Me,Vinyl; 193 R_1,R_2=Me,Ph, R_3,R_4=Me,Vinyl
m=2: 194 R_1,R_2=Ph, R_3,R_4=Me

Scheme 51. The synthesis of poly(silyene-ethynylene) alternating copolymers via a novel Pd-catalyzed polymerization

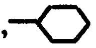
The characterization of poly(silylene-ethynylene) polymers and copolymers

Since poly(silylene-ethynylene) polymers and copolymers are soluble in a variety of organic solvents, they can be well characterized by FTIR, NMR and GPC. ^{1}H-NMR spectrum (Figure 51) for polymer 190 shows a singlet at 0.303 ppm and a triplet at 1.01 ppm for two methyl groups respectively, and a quartet between 0.62 and 0.75 ppm for the

Table 17. Poly(silylene-ethynylene) polymers and copolymers



$$\left[\equiv \overset{R_1}{\underset{R_2}{\mathrm{Si}}} \equiv \left(\overset{R_3}{\underset{R_4}{\mathrm{Si}}} \right)_m \right]_n$$

No	Polymer Structure		Yield%	$Mwx10^{-3}$	Mw/Mn	Char Yield%
<u>186</u>	m=1	R_1,R_3=Me R_2,R_4=Ph	67%	12.5	1.3	74%
<u>187</u>	m=1	R_1,R_3=Me R_2,R_4= 	80%	14	3.9	51%
<u>188</u>	m=1	R_1,R_2=Me,  R_3,R_4=Ph	72%	9.4	1.7	63%
<u>189</u>	m=1	R_1,R_2=Ph R_3,R_4=Me	83%	56	2.7	78%
<u>190</u>	m=1	R_1,R_2=Et R_3,R_4=Me	82%	35	1.3	79%
<u>191</u>	m=1	R_1,R_2=Et R_3,R_4= 	64%	30	2.7	68%
<u>192</u>	m=1	R_1,R_2=Me,  R_3,R_4=Me,Vinyl	53%	5.3	1.9	59%
<u>193</u>	m=1	R_1,R_2=Me,Ph R_3,R_4=Me,Vinyl	79%	16	3.0	83%
<u>194</u>	m=2	R_1,R_2=Ph R_3,R_4=Me	78%	41	1.8	77%

Polystyrenes were used as the standards.

methylene group. ^{13}C-NMR spectrum (Figure 52) for polymer 193 shows two peaks at 132.06 ppm and 136.06 ppm for the vinyl carbons respectively, two peaks at 110.6 ppm and 110.32 ppm for the ethynyl carbons and two peaks at -0.28 ppm and -1.25 ppm for the methyl carbons respectively. Four peaks at 134.14 ppm, 132.67 ppm, 130.21 ppm and 128.05 ppm represent the phenyl carbons. Figure 53 shows a ^{29}Si-NMR spectrum of polymer 193. Since polymer 193 has two silicones in its structural unit, only two peaks at -47.6 ppm and -45.6 ppm appeared. The rest of the NMR data are given in the experimental part.

The thermal stability of poly(silylene-ethynylene) polymers and copolymers

The thermal stability of poly(silylene-ethynylene) polymers and copolymers were studied by thermogravic analysiser. Figure 54 shows a typical TGA result. This polymer 193 started to lose weight at 470°C. Other TGA results are given in Table 17. The char yields depend on the pendant groups on silylene and range from 51% to 83%. However, the chars contain excess carbon and are not stable upon heating in air. Further study of this method to synthesize new silylene acetylene polymers with high char yield and high SiC content is underway.

Thermotropic liquid crystalline properties.

Thermotropic liquid crystalline properties of **PEArESim** polymers have been discussed in the previous section. Interestingly, silylene-acetylene polymers have also been found[83] to exhibit thermotropic liquid crystalline (LC) properties. One example is poly(tetramethyldisilylacetylene) which show liquid crystalline phase between 80°C and

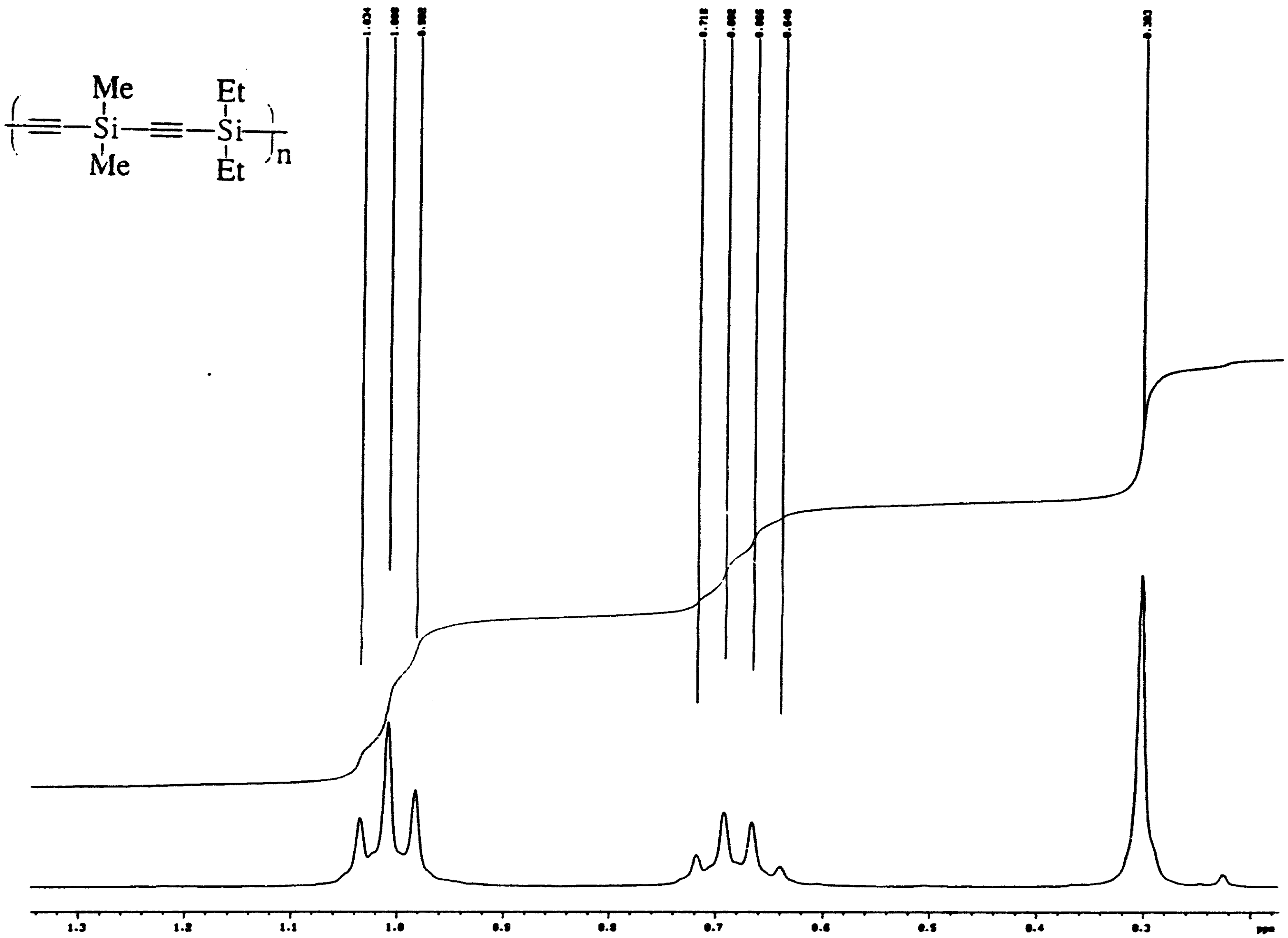


Figure 51. ¹H-NMR spectrum of polymer <u>190</u>

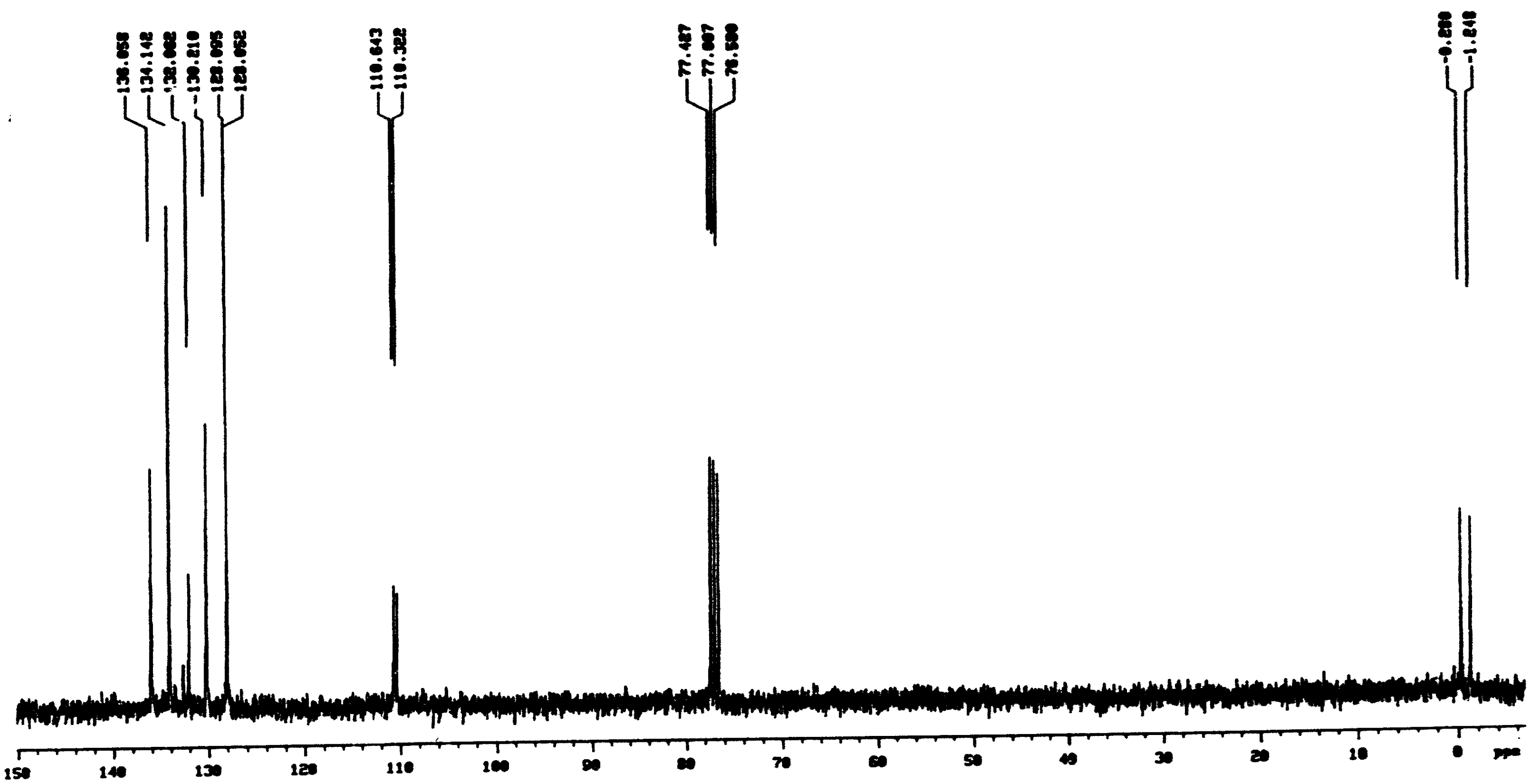


Figure 52. ^{13}C-NMR spectrum of polymer 193

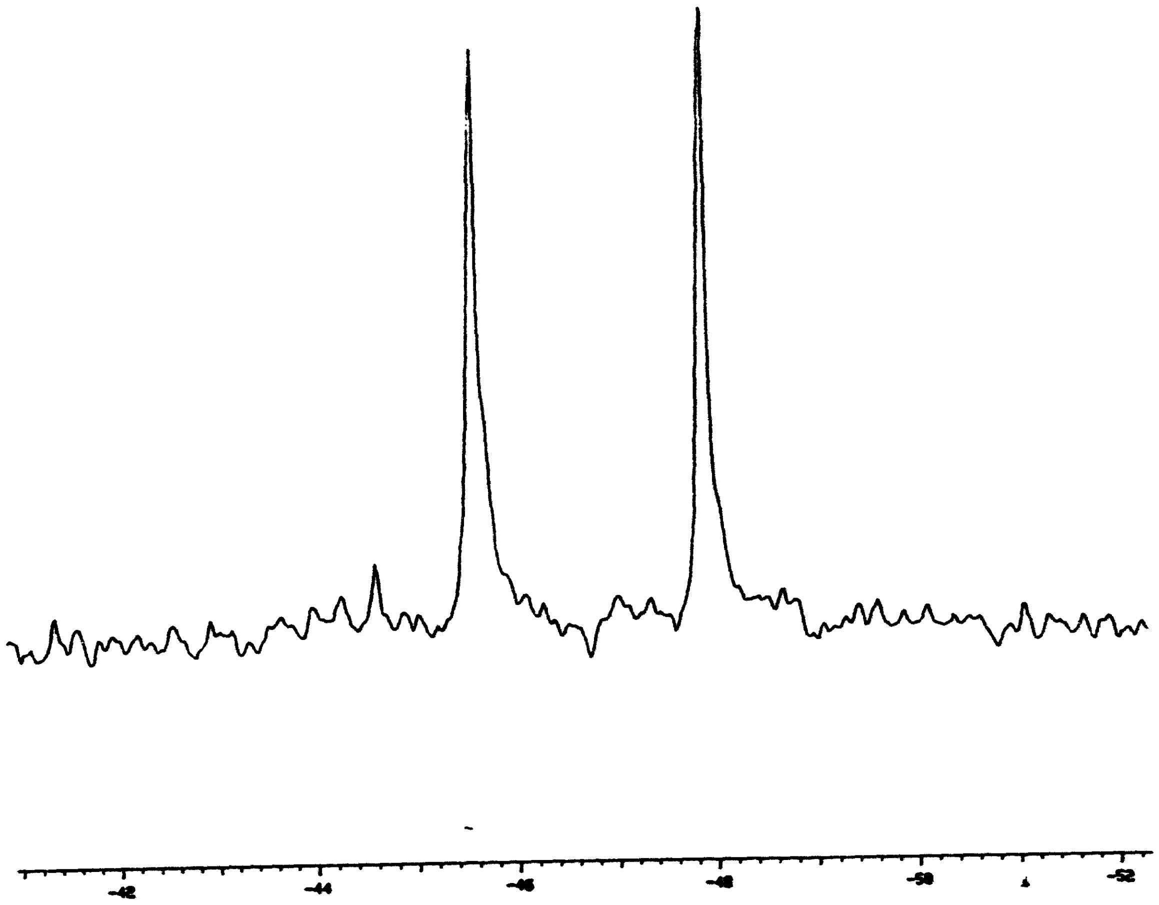


Figure 53. ^{29}Si-NMR spectrum of polymer <u>193</u>

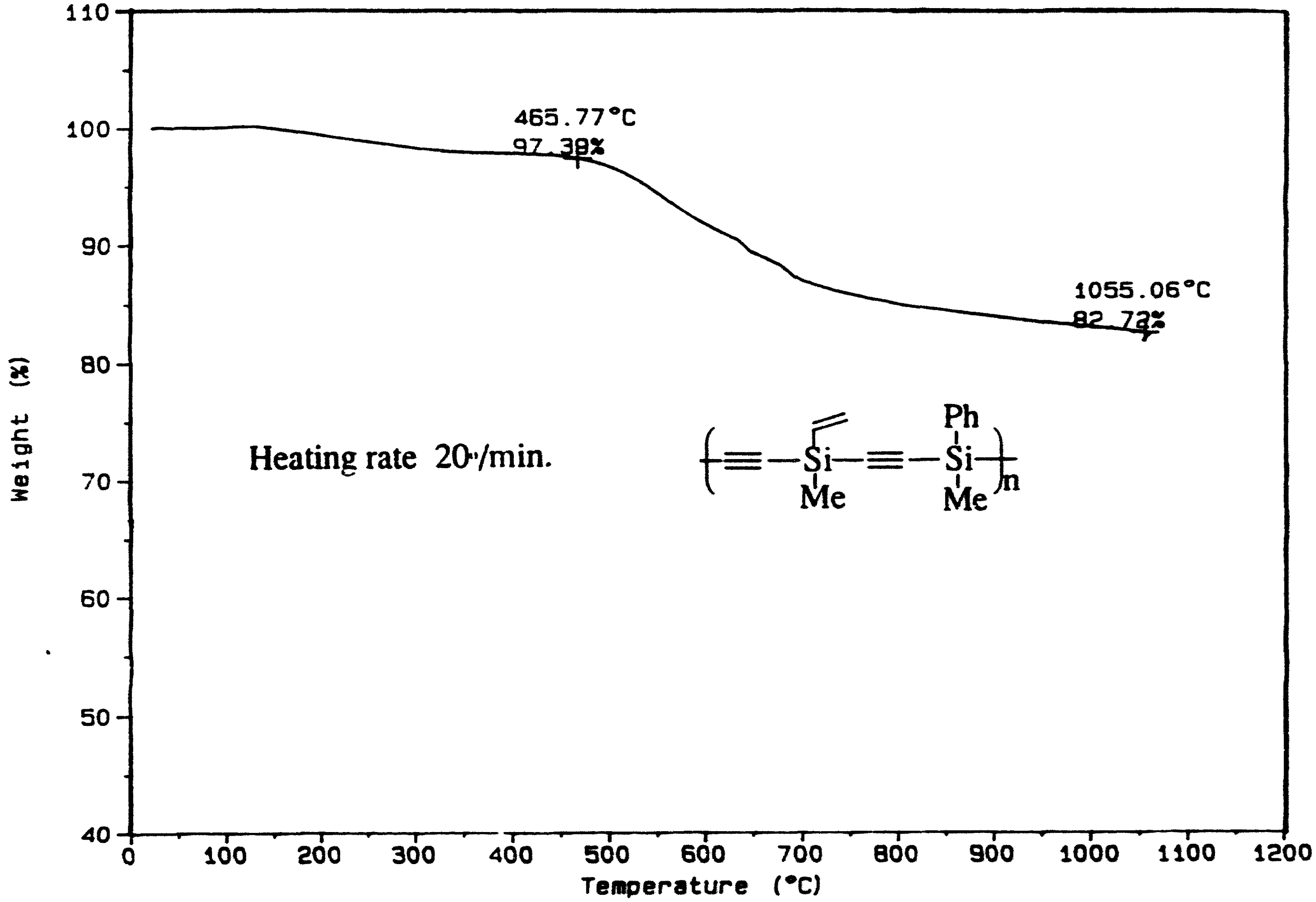


Figure 54. TGA result of polymer 193.

160°C as indicated by two endothermal peaks at both temperatures in DSC experiment. Polarized microscopy observations also agreed with DSC result.

Among the silylene-acetylene polymers and alternating copolymers, only polymer 190 exhibited interesting properties. Figure 55 shows the thermogram of polymer 190. Two endothermal peaks at 69°C and 81°C appear. This result indicates that polymer 190 started to melt at 69°C and the crystalline phase of 190 converted into a liquid crystalline phase. Continuous heating resulted in the second phase transition of 190 at 81°C from a liquid crystalline phase to an isotropic liquid phase. At both transitions, heat was required and thus, two endothermal peaks appeared in this DSC experiment.

Also observation of this polymer under a polarized microscopy as shown in Figure 56a and 56b (color pictures) agreed with the DSC result. Schlerin texture in the picture supports that a liquid crystalline phase existed between 69°C and 81°C.

Other polymers did not show the LC properties. The substituents on silicon, the silicon number in the polymer main chain, and the molecular weights of polymers all affected the polymer properties. It is very difficult to predict which silylene-acetylene polymer will exhibit thermotropic liquid crystalline properties since there has not been a systematic study on these properties.

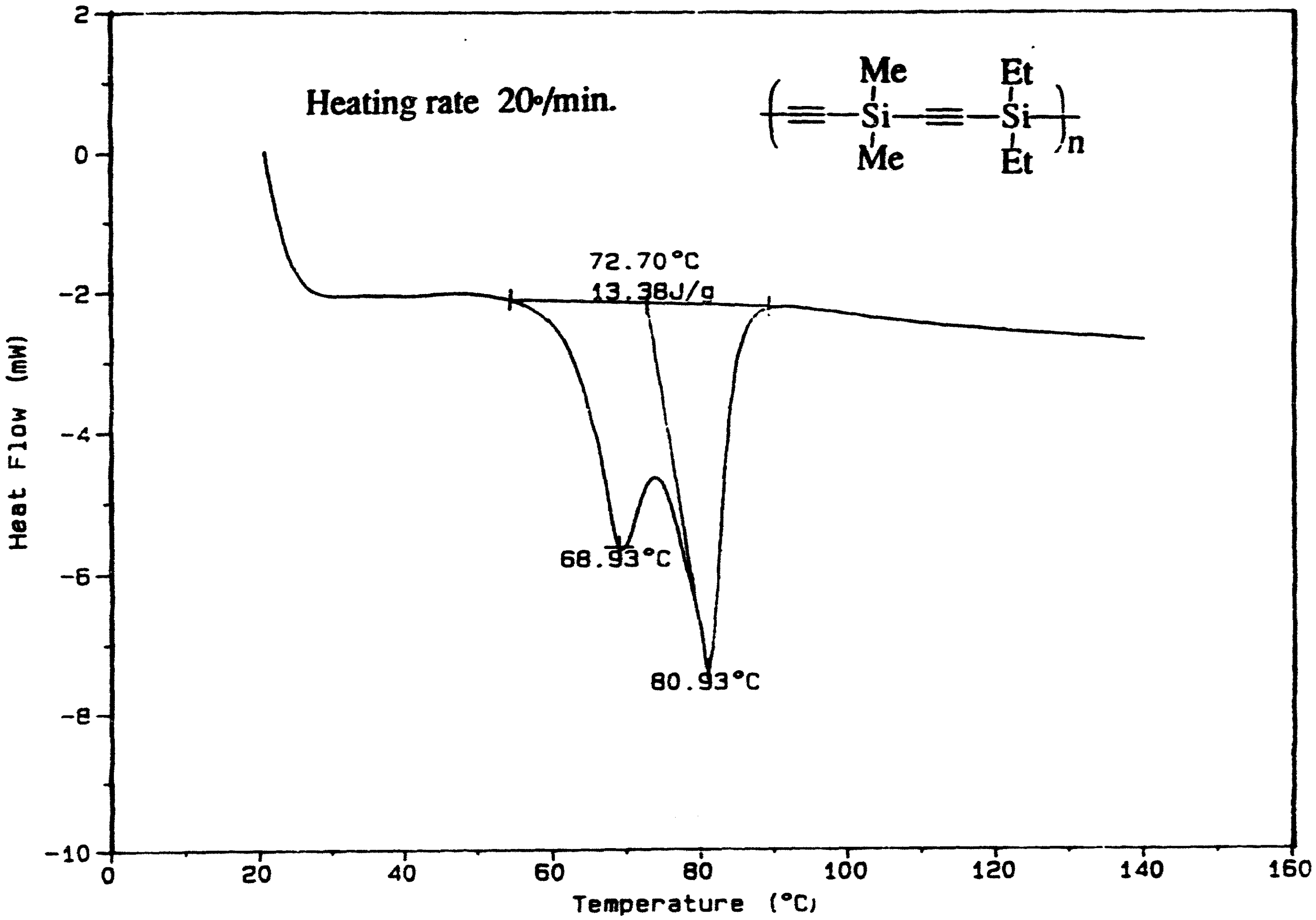


Figure 55. DSC thermogram of polymer 190

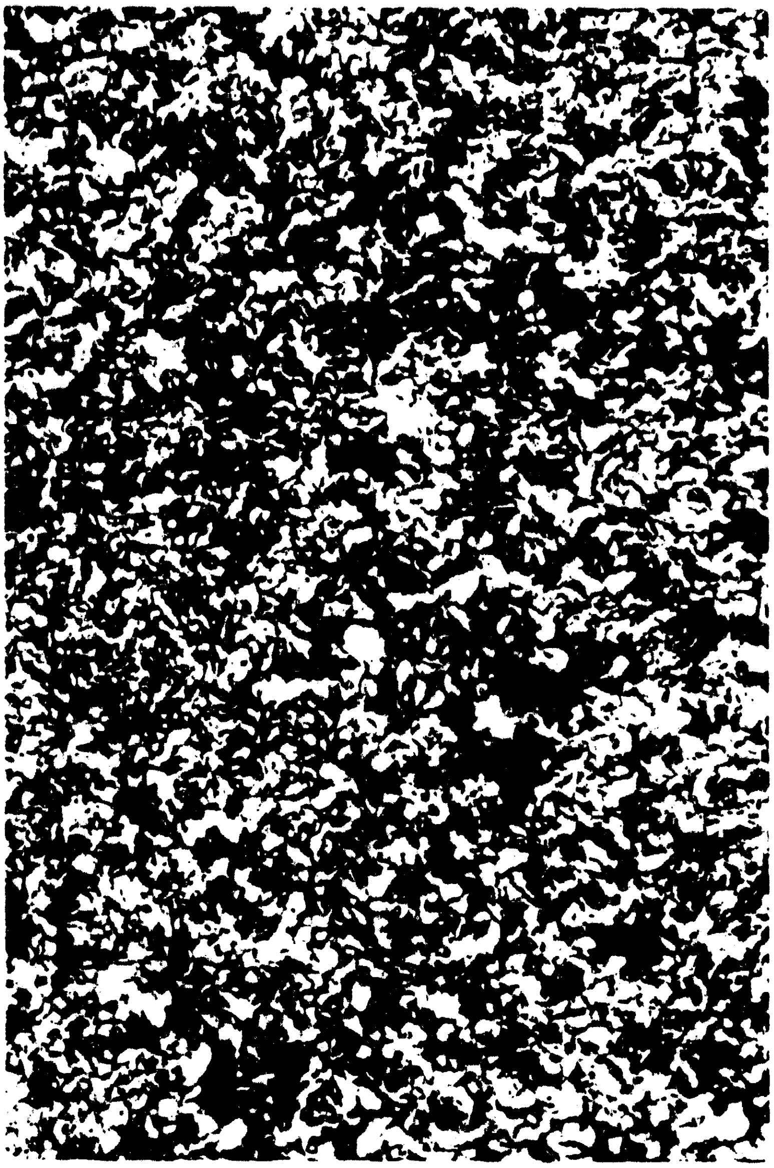
Observed under crossed-polarizers
cooling after isotropic melt

Cooled to 25°C
x400, Crystallization

Figure 56. (a) Polarized microscopic observation of polymer <u>190</u>

Observed under crossed-polarizers

cooling after isotropic melt



Cooled to 68°C

x400, LC phase

Figure 56. (b) Polarized microscopic observation of polymer 190

CONCLUSIONS

In this section, the synthesis of a series of silylene-ethynylene polymers and alternating copolymers, which are precursors to silicon-carbide, are discussed. These precursor polymers were conveniently synthesized via a novel palladium-catalyzed polymerization with good yield. Unlike the other method developed in our group, this palladium-catalyzed route can be used to synthesize both polymers and alternating copolymers. Also, the copolymer with the vinyl functionality, not previously synthesized, was made through this novel route. It was found that one of these polymers exhibited thermotropic liquid crystalline properties.

EXPERIMENTAL

1,4-dialkoxybenzenes were synthesized with good yields according to the literature[42]. 1,4-dimethoxy-2,5-diiodobenzene 55 was prepared according to the literature[38]. Trimethylsilylacetylene, hydroquinonone bis(2-hydroxyethyl)ether CuI, $PdCl_2(PPh_3)_2$, and $Pd(PPh_3)_4$ were used as received from Aldrich without further purification. Triethylamine was received from Eastman Kodak and dried over potassium hydroxide. Acetic acid, isopropanol, methanol, and sodium bisulfite were used as received from Fisher without further purification. Toluene, benzene, THF, and MTHF were distilled over calcium hydride. Benzyltrimethylammonium dichloroiodate ($BTMAICl_2$) was synthesized according to the literature[39] with 90% yield. Diethynylsilanes were synthesized according to the literature[65].

^1H and ^{13}C-NMR spectra were recorded on a Nicolet Model NT-300 MHz or a Varian VXR-300 MHz spectrometer. ^{29}Si-NMR spectra were only recorded on a Varian VXR-300 MHz spectrometer. Solid state NMR spectra were obtained on a Bruker MSL 300 spectrometer. Infrared spectra were recorded on an IBM IR-90 series FTIR spectrometer. The exact mass measurements were performed on a Kratos MS 50 mass spectrometer with 10,000 resolution. Routine mass spectra were obtained on a Hewlett Packard 5970 GCMS operating at 70 ev. Thermogravimetric analyses (TGA) were performed on a Du Pont 951 TGA under helium. Differential scanning calorimetry (DSC) analyses were also performed on a Du Pont 910 differential scanning calorimeter. Powder X-ray diffraction experiments were performed on a Scintag machine. The UV absorption spectra were recorded on a Shimadzu UV instrument. The emission spectra were obtained with a Spex Fluoromax. Elemental analyses were performed at Desert Analytics lab in Tucson, Arizona.

Molecular weights of the polymers were determined by gel permeation chromatography (GPC) with 6 Microstyragel columns in a series of 500Å, 1x10^3Å, 1X10^4Å, 1X10^5Å, 1X10^6Å, and 1X10^7Å. Both toluene and THF were used as eluents at a flow rate of 1.0 ml/min. The system was calibrated by polystyrene standards. The detection system used was a Waters Associates differential refractometer. The polymer viscosities were measured on a Viscotak Differential Viscometer model 110.

The preparation of 1,4-dibutoxy-2,5-diiodobenzene (50)

To a solution of 1,4-dibutoxybenzene (10.20 g, 45.9 mmol) in acetic acid (600 ml) were added zinc chloride (10.00 g, 73.4 mmol) and $BTMAICl_2$ (52.1 g, 150 mmol). It was stirred for 24 hours at 50-60°C. The reaction was quenched by adding 200 ml water and then a saturated sodium bisulfite aqueous solution (300 ml) was added to consume the unreacted $BTMAICl_2$. The precipitated solid was collected by filtration and washed by water. Recrystallization of this solid from a mixture of methanol and water (15:1) gave white needle crystals (16.0 g, 74%). MP= 86-88°C. FTIR (cm^{-1}, 2955(s), 2939(s), 2864(s), 1487(s), 1468(s), 1452(s), 1369(w), 1377(w), 1352(s), 1271(w), 1261(m), 1209(vs), 1161 (w), 1123(w), 1055(s), 1032(m), 1005(m), 905(w), 851(s), 791(s), 743(m).). ^{1}H-NMR (299.949 MHz, CD_2Cl_2) δ(ppm) 7.18-7.25(2H, s), 3.90-4.10(4H, t), 1.75-1.90(4H, m), 1.46-1.66(4H, m), 0.92-1.10(6H, t). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 152.82, 122.73, 86.27, 70.02, 31.22, 19.29, 13.81. Exact mass m/e 473.95588 (calc. for $C_{14}H_{20}O_2I_2$ 473.95528).

Anal. ($C_{14}H_{20}O_2I_2$) Calc. C-35.47%, H-4.25%, I-53.53%.

Found C-35.76%, H-4.04%, I-53.89%.

The preparation of 1,4-dipentoxy-2,5-diiodobenzene (51)

The procedure was similar that for 50. To a solution of 1,4-dipentoxybenzene (5.75 g, 24.5 mmol) in acetic acid (170 ml) were added zinc chloride (6.98 g, 51.3 mmol) and BTMAICl$_2$ (18.01 g, 51.7 mmol). It was stirred for 12 hours at 50-60°C. The isolation procedure was similar to that for 50. Recrystallization from a mixture of methanol and water (15:1) gave white crystals (6.3 g, 55%). MP= 73-75°C. FTIR (cm^{-1}, 2953(s), 2937(s),2866(s), 1489(s), 1468(s), 1448(s), 1393(m), 1377(w), 1350(vs), 1265(m), 1244(w), 1211(vs), 1126(w), 1053(s), 1018(s), 1011(s), 893(w), 849(m), 797(m), 737(w).). ^{1}H-NMR (299.949 MHz, CDCl$_3$) δ(ppm) 7.10-7.19(2H, s), 3.83-4.00(4H, t), 1.70-1.90(4H, m), 1.30-1.60(8H, m), 0.83-1.00(6H, t). ^{13}C-NMR (75.429 MHz, CDCl$_3$) δ(ppm) 152.84, 122.78, 86.30, 70.34, 28.83, 28.19, 22.36, 14.03. Exact mass m/e 501.98656 (calc. for $C_{16}H_{24}O_2I_2$ 501.98658).

Anal. ($C_{16}H_{24}O_2I_2$) Calc. C-38.27%, H-4.82%, I-50.54%.

Found C-38.62%, H-4.87%, I-50.14%.

The preparation of 1,4-dihexoxy-2,5-diiodobenzene (52)

The procedure was similar to that for 50. To a solution of 1,4-dihexoxybenzene (10.60 g, 38.1 mmol) in acetic acid (300 ml) were added zinc chloride(12.10 g, 89.0 mmol) and BTMAICl$_2$(31.00 g, 89.1 mmol). The mixture was stirred for 12 hours at 50-60°C. The isolation procedure was similar to that for 50. Recrystallization from methanol twice gave white crystals (11.55 g, 57%). MP= 58-59°C. FTIR (cm^{-1}, 2950(m), 2934(m), 2854(m), 1487(s), 1466(s), 1448(s), 1393(w), 1348(s), 1265(w), 1231(w), 1211(vs), 1055(s), 1016(m), 955(w), 851(m), 797(m),733(w).). ^{1}H-NMR (299.949 MHz, CDCl$_3$) δ(ppm) 7.15-7.19(2H, s), 3.85-4.00(4H, t), 1.72-1.86(4H, m), 1.28-1.58(12H, m), 0.86-0.96(6H, t). ^{13}C-NMR (75.429 MHz, CDCl$_3$) δ(ppm) 152.85, 122.78, 86.30, 70.36, 31.47, 29.11, 25.71, 22.59, 14.04. Exact mass m/e 530.1708 (calc. for $C_{18}H_{28}O_2I_2$ 530.1788).

Anal. ($C_{18}H_{28}O_2I_2$) Calc. C-40.77%, H-5.32%, I-47.87%.

Found C-41.11%, H-5.34%, I-48.29%.

The preparation of 1,4-dioctoxy-2,5-diiodobenzene (53)

The procedure was similar to that for 50. To a solution of 1,4-dioctoxybenzene (2.10 g, 6.29 mmol) in acetic acid (200 ml) were added zinc chloride (2.52 g, 18.5 mmol) and $BTMAICl_2$(9.02 g, 25.9 mmol). The mixture was stirred for 24 hours at 50-60°C. The reaction was quenched by 100 ml water. Then a saturated sodium bisulfite aqueous solution (100 ml) was added to the solution. The precipitated white solid was collected by filtration and washed with water. The white solid was finally recrystallized from methanol and dried in vacuum to afford white crystals (2.54 g, 69%). MP= 56-57°C. FTIR (cm^{-1}, 2948(m), 2932(s), 2920(vs), 2849(vs), 1485(vs), 1466(s), 1460(s), 1448(m), 1389(m), 1352(s), 1263(m), 1234(w), 1217(vs), 1144(w),1069(m), 1051(m), 1018(w), 962(m), 847(m), 835(w), 787(w).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 7.10-7.16(2H, s), 3.82-3.94(4H, t), 1.65-1.82(4H, m), 1.15-1.55(20H, m), 0.80-0.95(6H, t). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 152.84, 122.77, 86.30, 70.36, 31.80, 29.24, 29.22, 29.14, 26.03, 22.66, 14.12. Exact mass m/e 586.08012 (calc. for $C_{22}H_{36}O_2I_2$ 586.08048).

Anal. ($C_{22}H_{36}O_2I_2$) Calc. C-45.07%, H-6.19%, I-43.29%.

Found C-45.36%, H-5.91%, I-42.88%.

The preparation of 1,4-didecoxy-2,5-diiodobenzene (54)

The procedure was similar to that for 50. To a solution of 1,4-didecoxybenzene (12.10 g, 30.8 mmol) in acetic acid (320 ml) were added zinc chloride (10.0 g, 74.1 mmol) and BTMAICl$_2$ (24.7 g, 71.0 mmol). The mixture was stirred for 48 hours at 50-60°C. The isolation procedure was similar to that for 50. The precipitated white solid was collected and washed with methanol. Finally the solid was recrystallized in isopropanol and dried in vacuum to afford white crystals (9.0 g, 45%). MP= 59-61°C. FT-IR (cm^{-1}, 2950(m), 2934(m), 2918(vs), 2849(s), 1485(s), 1464(vs), 1448(s), 1391(m), 1352(vs), 1263(m), 1211(vs), 1053(m), 1015(m), 991(w), 845(m), 797(m), 721(m).). ^{1}H-NMR (299.949 MHz, CDCl$_3$) δ(ppm) 7.12-7.20(2H, s), 3.80-4.00(4H, t), 1.70-1.90(4H, m), 1.10-1.60(28H, m), 0.80-0.95(6H, t).). ^{13}C-NMR (75.429 MHz, CDCl$_3$) δ(ppm) 152.83, 122.76, 86.29, 70.34, 31.90, 29.55(2), 29.32, 29.28, 29.14, 26.03, 22.69, 14.12.). Exact mass m/e 642.14350 (calc. for $C_{26}H_{44}O_2I_2$ 642.14309).

Anal. ($C_{26}H_{44}O_2I_2$) Calc. C-48.61%, H-6.90%, I-39.51%.
Found C-48.51%, H-7.12%, I-39.90%.

The preparation of 2,5-diiodo-hydroquinonone bis(2-acetoxylethyl)ether (58)

To 250 ml acetic acid were added hydroquinonone bis(2-hydroxyethyl) ether (11.01 g, 0.056 mol), ZnCl$_2$ (8.01 g, 0.059 mol) and BTMAICl$_2$ (40.04 g, 0.12 mol). After it was stirred at room temperature for 3 hours and at 40°C for 10 hours, ZnCl$_2$ (7.5 g, 0.055 mol) and BTMAICl$_2$ (6.0 g, 0.017 mol) were added to the solution. After further stirring another 10 hours at 40°C, BTMAICl$_2$ (6.0 g, 0.017 mol) was added again. Finally after it was stirred for another 10 hours, the reaction was quenched by adding 250 ml saturated sodium bisulfite aqueous solution. The precipitated solid was collected by the filtration and washed with water. Recrystallization of this solid in excess methanol afforded white crystals (12.2 g, 49%). MP= 156-158°C. FTIR (cm^{-1}, 3098(w), 2963(m), 2887(w), 1738(s), 1487(s), 1462(s), 1443(s), 1404(s), 1367(s), 1296(m), 1256(s), 1238(s), 1215(s), 1074(s), 1053(s), 951(s), 912(m), 856(s), 831(s), 766(m).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 7.15-7.23 (singlet, 2H), 4.35-4.50 (triplet, 4H), 4.10-4.20 (triplet, 4H), 2.05-2.15 (singlet, 6H). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 170.92, 152.96, 123.73, 86.54, 68.48, 62.44 and 20.93. Exact mass m/e 533.90421 (calc. for $C_{14}H_{16}O_6I_2$ 533.90364).

The preparation of 2,5-diiodo-hydroquinonone bis(2-hydroxyethyl)ether (59)

To 25 ml ethanol (95%) were added 2,5-diiodo-hydroquinonone bis(2-acetoxyethyl)ether (0.504 g, 0.94 mmol) and saturated NaOH aqueous solution (3 ml). The solution was refluxed for 5 hours. Then it was cooled in ice bath. The white solid was collected by the filtration and recrystallization of this white solid in ethanol (95%) afforded white needle crystals (0.355 g, 84%). MP= 162-163°C. FTIR (cm^{-1}, 3196 (broad, s), 2963(s), 1688 (m), 1487(s), 1445(s), 1400(s), 1375(s), 1346(s), 1286(m), 1263(s), 1217(s), 1076(s), 930(s), 897(s), 854(s), 768(s), 731(s).). ^{1}H-NMR (299.949 MHz, DMSO) δ(ppm) 7.34-7.40 (2H, s), 3.93-4.02 (4H, t), 3.63-3.73 (4H, t), 3.30-3.38 (H for hydroxy, d). ^{13}C-NMR (75.429 MHz, DMSO) δ(ppm) 152.67, 123.08, 87.07, 71.87, 59.60, 59.54. Exact mass m/e 449.88317 (calc. for $C_{10}H_{12}O_4I_2$ 449.88251).

The preparation of 2,5-diiodo-hydroquinonone bis(2-trimethylsiloxyethyl)ether (60)

To a mixture of 30 ml benzene and 5 ml triethylamine was added 2,5-diiodo-hydroquinonone bis(2-hydroxyethyl)ether (1.280 g, 2.84 mmol). After the solution was degassed, trimethylchlorosilane (3 ml) was added into the solution by using a syringe. The solution was stirred at room temperature for 24 hours. After the precipitated amine salt was removed by the filtration, the solution was condensed to a white solid. Purification of the white solid through a silica gel column afforded a white solid (1.41 g, 83%). Mp= 73-74.5°C. FT-IR (cm^{-1}, 3099(w), 2955(s), 2928(m), 2872(m), 2794(w), 1483(s), 1445(s), 1409(m), 1379(m), 1348(s), 1254(s), 1217(s), 1130(s), 1099(s), 1063(s), 1045(s), 966(s), 920(s), 852(s).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 7.10 (s, 2H), 3.85-3.90 (m, 4H), 3.75-3.82 (m, 4H), 0.01 (s, 18H). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 153.11, 123.57, 86.28, 71.77, 61.26, -0.349. Exact mass m/e 593.96329 (calc. for $C_{16}H_{28}O_4Si_2$ 593.96315).

The preparation of 1,4-dibutoxy-2,5-bis[(trimethylsilyl)ethynyl]benzene (61)

To a degassed solution of 1,4-dibutoxy-2,5-diiodobenzene (3.50 g, 7.38 mmol) in a mixture of 50 ml benzene and 50 ml triethylamine were added trimethylsilylacetylene (1.68 g, 17.1 mmol) and a mixture of 33 mg CuI and 90 mg $PdCl_2(PPh_3)_2$. It was stirred for 4 hours at room temperature under an argon atmosphere. The amine salt was removed by filtration and the solvent was evaporated to give a brown solid. Recrystallization of this brown solid from a mixture of methanol and water gave yellow crystals (2.36 g, 77%). MP= 106-107°C. FTIR (cm^{-1}, 2959(m), 2939(m), 2987(m), 2156(w), 1501(s), 1464(m), 1408(m), 1387(vs), 1265(w), 1240(s), 1224(vs), 1205(s), 1040(vs), 1013(vs), 887(w), 866(m), 843(vs), 760(s), 744(w), 698(w).). ^{1}H-NMR (299.949 MHz, CD_2Cl_2) δ(ppm) 6.85-6.95(2H, s), 3.92-4.02(4H, t), 1.70-1.85(4H, m), 1.46-1.65(4H, m), 0.95-1.07(6H, t), 0.20-0.40(18H, s)). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 154.02, 117.18, 113.96, 101.02, 100.05, 69.18, 31.34, 19.21, 13.85, -0.10. Exact mass m/e 414.24071 (calc. for $C_{24}H_{38}O_2Si_2$ 414.24104).

The preparation of 1,4-dipentoxy-2,5-bis[(trimethylsilyl)ethynyl]benzene (62)

To a degassed solution of 1,4-dipentoxy-2,5-diiodobenzene (2.98 g, 5.93 mmol) in a mixture of 50 ml benzene and 50 ml triethylamine were added trimethylsilylacetylene(1.30 g, 13.2 mmol) and a mixture of 90 mg $PdCl_2(PPh_3)_2$ and 23 mg CuI. It was stirred at room temperature under an argon atmosphere for 3 hours and another 6 hours after trimethylsilylacetylene (0.35 g) was added. The amine salt was filtered out and the solvent was evaporated to give a brown or yellow solid. Recrystallization of this solid from methanol gave yellow crystals (2.25 g, 86%). MP= 83-85°C. FT-IR (cm^{-1}, 2959(m), 2939(m), 2897(m), 2156(w), 1501(s), 1470(m), 1408(m), 1385(vs), 1277(w), 1248(s), 1225(vs), 1205(s), 1061(w), 1024(vs), 906(w), 878(w), 854(m), 839(vs), 758(s), 733(w), 696(w), 667(w).). ^1H-NMR (299.949 MHz, C_6D_6) δ(ppm) 6.95-7.05(2H, s), 3.35-3.50(4H, t), 1.47-1.60(4H, m), 1.15-1.42(8H, m), 0.83-0.95(6H, t), 0.24-0.34(18H, s). ^{13}C-NMR (75.429 MHz, C_6D_6) δ(ppm) 154.53, 117.42, 114.59, 102.46, 100.01, 68.89, 29.18, 28.44, 22.73, 14.27, 0.082. Exact mass m/e 442.27203 (calc. for $C_{26}H_{42}O_2Si_2$ 442.27234).

The preparation of 1,4-dihexoxy-2,5-bis[(trimethylsilyl)ethynyl]benzene (63)

To a degassed solution of 1,4-dihexoxy-2,5-diiodobenzene (3.60 g, 6.79 mmol) in a mixture of 40 ml benzene and 40 ml triethylamine were added trimethylsilylacetylene (1.57 g, 16.0 mmol) and a mixture of 21 mg CuI and 67 mg $PdCl_2(PPh_3)_2$. It was stirred for 4 hours and another 3 hours after 0.240 g (2.44 mmol) trimethylsilylacetylene more was added at room temperature under an argon atmosphere. The purification procedure was similar to that for 61. Recrystallization from methanol gave yellow crystals (2.05 g, 64%). MP= 88-89°C. FTIR (cm^{-1}, 2957(m), 2939(s), 2897(m), 2156(w), 1499(s), 1466(m), 1408(m), 1385(s), 1275(w), 1248(s), 1225(vs), 1204(s), 1126(w), 1059(w), 1032(vs), 999(w), 897(w), 864(m), 841(vs), 758(m), 731(m), 698(w), 667(w).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 6.85-6.92(2H, s), 3.90-4.00(4H, t), 1.72-1.86(4H, m), 1.28-1.42(8H, m), 0.84-0.96(6H, t), 0.00-0.50(18H, s). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 153.99, 117.18, 113.92, 101.06, 100.07, 69.43, 31.61, 29.29, 25.69, 22.64, 14.08, -0.05. Exact mass m/e 470.30452 (calc. for $C_{28}H_{46}O_2Si_2$ 470.30364).

The preparation of 1,4-dioctoxy-2,5-bis[(trimethylsilyl)ethynyl]benzene (64)

To a degassed solution of 1,4-dioctoxy-2,5-diiodobenzene (3.478 g, 5.93 mmol) in a mixture of 40 ml benzene and 40 ml triethylamine were added trimethylsilylacetylene (1.31 g, 133 mmol) and a mixture of 38 mg CuI and 92 mg $PdCl_2(PPh_3)_2$. It was stirred for 4 hours at room temperature under an argon atmosphere. After the precipitated amine salt was removed by filtration, the solvent was evaporated to give a yellow or brown solid. Recrystallization of this solid from a mixture of methanol and isopropanol gave yellow crystals (2.40 g, 77%). MP= 64-65°C. FTIR (cm^{-1}, 2948(m), 2926(s), 2856(m), 2154(m), 1497(m), 1468(m), 1406(m), 1385(m), 1273(w), 1248(m), 1223(m), 1202(m), 1032(w), 879(m), 841(vs), 758(m), 725(w), 698(w), 627(w).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 6.85-6.92(2H, s), 3.88-4.00(4H, t), 1.72-1.86(4H, m), 1.42-1.57(4H, m), 1.22-1.41(16H, m), 0.84-0.94(6H, t), 0.16-0.30(18H, s). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 154.00, 117.17, 113.93, 101.06, 100.07, 69.44, 31.86, 29.41, 29.36, 29.31, 26.04, 22.68, 14.10, -0.04. Exact mass m/e 526.36621 (calc. for $C_{32}H_{54}O_2Si_2$ 526.36624).

The preparation of 1,4-didecoxy-2,5-bis[(trimethylsilyl)ethynyl]benzene (65)

To a degassed solution of 1,4-didecoxy-2,5-diiodobenzene (3.00 g, 5.15 mmol) in a mixture of 50 ml benzene and 50 ml triethylamine were added trimethylsilylacetylene (1.35 g, 13.7 mmol) and a mixture of 21 mg CuI and 85 mg $PdCl_2(PPh_3)_2$. It was stirred for 12 hours at room temperature under an argon atmosphere. After the salt was filtered, the solvent was evaporated to afford a yellow solid. Recrystallization of this solid from a mixture of methanol and isopropanol gave yellow crystals (2.45 g, 90%). MP= 73-74°C. FTIR (cm^{-1}, 2939(m), 2918(vs), 2898(m), 2158(w), 1499(s), 1472(m), 1408(m), 1387(vs), 1273(w), 1250(s), 1223(vs), 1202(s), 1049(m), 1032(m), 1020(m), 895(w), 866(m), 841(vs), 760(s), 723(w), 700(w).). ^{1}H-NMR (299.949 MHz, C_6D_6) δ(ppm) 6.85-6.95(2H, s), 3.88-4.01(4H, t), 1.72-1.86(4H, m), 1.42-1.55(4H, m), 1.18-1.41(24H, m), 0.83-0.95(6H, t), 0.24-0.28(18H, s). ^{13}C-NMR (75.429 MHz, C_6D_6) δ(ppm) 154.54, 117.49, 114.62, 102.49, 100.04, 68.91, 32.31, 30.92, 30.02, 29.79(2), 29.59, 26.33, 23.10, 14.36, 0.12. Exact mass m/e 582.42934 (calc. for $C_{36}H_{62}O_2Si_2$ 582.42884).

The preparation of 2,5-bis[(trimethylsilyl)ethynyl] hydroquinonone bis(2-hydroxyethyl)ether (95)

To a mixture of 100 ml THF and 50 ml triethylamine was added 2,5-diiodo-hydroquinonone-bis(2-hydroxyethyl)ether (2.80 g, 6.2 mmol). After the solution was degassed, a mixture of 42 mg $PdCl_2(PPh_3)_2$ and 10 mg CuI, and trimethylacetylene (3.54 g, 36.1 mmol) were added. It was stirred at 40-50°C for 6 hours under an argon atmosphere. The salt was removed by the filtration and the solvent was evaporated to give a solid. Recrystallization of this solid in hexane afforded yellow crystals (1.34 g, 60%). MP= 156-157°C. FTIR (cm^{-1}, 3288(broad, m), 2959(m), 2897(w), 2152(s), 1502(s), 1481(m), 1398(s), 1275(m), 1250(s), 1226(s), 1205(m), 1080(w), 1042(s), 893(s), 867(s), 840(s), 760(s).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 6.95 (s, 2H), 4.00-4.20 (t, 4H), 3.80-3.95 (t, 4H), 0.244 (s, 18H). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 153.88, 118.72, 115.05, 101.19, 100.33, 71.77, 61.20, -0.16. Exact mass m/e 390.16927 (cala. for $C_{20}H_{30}O_4Si_2$ 390.16827).

The preparation of 1,4-dibutoxy-2,5-diethynylbenzene (66)

To a degassed solution of 1,4-dibutoxy-2,5-bis[(trimethylsilyl)ethynyl]benzene (1.05 g, 2.54 mmol) in methanol (120 ml) was added 0.5 ml saturated NaOH aqueous solution. It was stirred for 2 hours at 40-50°C under an argon atmosphere. Then the solvent was evaporated to afford a brown solid. Recrystallization of this solid from methanol gave yellow crystals (0.605 g, 88%). MP= 104-106°C. FTIR(cm^{-1}, 3271(vs), 2963(w), 2943(m), 2860(m), 1499(s), 1466(s), 1404(s), 1387(s), 1273(s), 1223(vs), 1200(m), 1126(w), 1063(m), 1040(w), 1026(m), 1013(w), 978(m), 893(w), 864(m), 818(w), 679(w), 660(w), 644(w).). ^{1}H-NMR (299.949 MHz, CDCl$_3$) δ(ppm) 6.94-6.97(2H, s), 3.94-4.04 (4H, t), 3.31-3.34 (4H, s), 1.72-1.85 (4H, m), 1.42-1.59 (4H, m), 0.92-1.02 (6H, t)). ^{13}C-NMR (75.429 MHz, CDCl$_3$) δ(ppm) 153.93, 117.67, 113.19, 82.39, 79.73, 69.30, 31.17, 19.13, 13.82. Exact mass m/e 270.16139 (calc. for $C_{18}H_{22}O_2$ 270.16198).

The preparation of 1,4-dipentoxy-2,5-diethynylbenzene (67)

To a degassed solution of 1,4-dipentoxy-2,5-bis[(trimethylsilyl)ethynyl]benzene (2.10 g, 4.74 mmol) in methanol (100 ml) was added 0.05 ml saturated NaOH aqueous solution. It was stirred for 1 hour at 50°C under an argon atmosphere. The solution was cooled to 0°C and a yellow solid precipitated. Recrystallization of this solid from methanol give yellow crystals (1.20 g, 85%). MP= 106-107.5°C. FTIR (cm^{-1}, 3263(vs), 2947(m), 2866(m), 1501(vs), 1466(m), 1387(vs), 1317(w), 1275(m), 1248(w), 1219(vs), 1200(s), 1120(w), 1063(w), 1018(s), 897(w), 876(w), 858(m), 694(m), 660(m).). ^{1}H-NMR (299.949 MHz, CDCl$_3$) δ(ppm) 6.90-7.00(2H, s), 3.90-4.05(4H, t), 3.32-3.36(2H, s), 1.74-1.88(4H, m), 1.30-1.52(8H, m), 0.87-0.98(6H, t). ^{13}C-NMR (75.429 MHz, CDCl$_3$) δ(ppm) 153.95, 117.70, 113.20, 82.42, 79.77, 69.63, 28.81, 28.07, 22.41, 14.04. Exact mass m/e 298.19283 (calc. for $C_{20}H_{26}O_2$ 298.19328).

The preparation of 1,4-dihexoxy-2,5-diethynylbenzene (68)

To a degassed solution of 1,4-dihexoxy-2,5-bis[(trimethylsilyl)ethynyl]benzene (1.50 g, 3.19 mmol) in methanol (140 ml) was added 0.3 ml saturated NaOH aqueous solution. It was stirred for 4 hours at 30-50°C under an argon atmosphere. Then the solution was cooled to 0°C and a yellow solid precipitated out. Recrystallization of this solid from methanol gave yellowish crystals (0.85 g, 82%). MP= 71-72°C. FTIR (cm^{-1}, 3281(s), 2966(m), 2939(m), 2919(m), 2853(m), 1499(s), 1470(s), 1408(m), 1385(vs), 1273(m), 1217(vs), 1198(s), 1126(w), 1059(m), 1020(s), 991(m), 862(m), 735(w), 673(s).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 6.90-7.00(2H, s), 3.90-4.05(4H, t), 3.30-3.36(2H, s), 1.72-1.86(4H, m), 1.43-1.56(4H, m), 1.27-1.42(8H, m), 0.86-0.98(6H, t). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 153.93, 117.69, 113.20, 82.39, 79.74, 69.63, 31.48, 29.05, 25.54, 22.55, 13.98. Exact mass m/e 326.22499 (calc. for $C_{22}H_{30}O_2$ 326.22458).

The preparation of 1,4-dioctoxy-2,5-diethynylbenzene (69)

To a degassed solution of 1,4-dioctoxy-2,5-bis[(trimethylsilyl)ethynyl]benzene (1.272 g, 2.41 mmol) in a mixture of methanol(75 ml) and isopropanol(25 ml) was added (0.5 ml) saturated NaOH aqueous solution. It was stirred for 3 hours at 50°C under an argon atmosphere. Then the solution was cooled to 0°C and a yellowish solid precipitated. Recrystallization of this solid from a mixture of methanol, isopropanol and water gave yellow crystals (0.74 g, 80%). MP= 64-65°C. FTIR (cm^{-1}, 3285(vs), 2939(m), 2924(s), 2853(s), 2876(w), 1501(s), 1470(m), 1462(m), 1385(vs), 1273(m), 1219(vs), 1200(m), 1065(w), 1040(s), 999(m), 860(m), 727(w), 673(m), 646(m).).

^{1}H-NMR (299.949 MHz, CDCl$_3$) δ(ppm) 6.90-6.95(2H, s), 3.90-3.99(4H, t), 3.30-3.32(2H, s), 1.70-1.84(4H, m), 1.20-1.52(16H, m), 0.80-0.92(6H, t). ^{13}C-NMR (75.429 MHz, CDCl$_3$) δ(ppm) 153.94, 117.70, 113.21, 82.38, 79.76, 69.64, 31.78, 29.27, 29.20, 29.10, 25.88, 22.64, 14.10. Exact mass m/e 382.28721 (calc. for $C_{26}H_{38}O_2$ 382.28718).

The preparation of 1,4-didecoxy-2,5-diethynylbenzene (70)

To a degassed solution of 1,4-didecoxy-2,5-bis[(trimethylsilyl)ethynyl]benzene (2.11 g, 3.62 mmol) in a mixture of 60 ml isopropanol and 25 ml THF was added 0.3 ml saturated NaOH aqueous solution. It was stirred for 7 hours at 40°C under an argon atmosphere. The solvent was then evaporated to afford a yellow solid. Recrystallization of this solid from isopropanol gave yellow crystals (1.48 g, 93%). MP= 72-73.5°C. FTIR (cm^{-1}, 3286(vs), 2959(w), 2943(m), 2924(vs), 2874(m), 2851(vs), 1501(s), 1464(s), 1385(vs), 1271(m), 1244(w), 1219(vs), 1200(m), 1047(m), 1030(m), 1016(m), 991(w), 868(m), 847(m), 725(w), 671(m), 646(m).). ^{1}H-NMR (299.949 MHz, CDCl$_3$) δ(ppm) 6.91-6.98(2H, s), 3.90-4.00(4H, t), 3.30-3.35(2H, s), 1.70-1.88(4H, m), 1.38-1.52(4H, m), 1.18-1.38(24H, m), 0.82-0.92(6H, t). ^{13}C-NMR (75.429 MHz, CDCl$_3$) δ(ppm) 153.94, 117.69, 113.21, 82.37, 79.76, 69.63, 31.90, 29.55, 29.52, 29.31(2), 29.10, 25.87, 22.66, 14.10). Exact mass m/e 438.34898 (calc. for $C_{30}H_{46}O_2$ 438.34978).

The preparation of 2,5-diethynyl hydroquinonone bis(2-hydroxyethyl)ether (95a)

To a methanol solvent (45 ml) was added 2,5-bis[(trimethylsilyl)ethynyl] hydroquinonone bis(2-hydroxyethyl)ether (0.94 g, 2.4 mmol). After the solution was degassed, a saturated NaOH aqueous solution (0.1 ml) was added into the solution. It was stirred at room temperature for 30 minutes under an argon atmosphere. Then, water (20 ml) was added to the solution. The yellow product was collected by the filtration. Recrystallyzation of this yellow product in a mixture of methanol and water afforded yellow crystals (0.41 g, 70%). MP= 132-134°C. FTIR (cm^{-1}, 3585(s), 3287(vs), 2963(m), 2934(m), 2880(m), 2108(w), 1637(m), 1501(s), 1458(m), 1400(s), 1366(m), 1271(m), 1223(vs), 1198(s), 1088(s), 1074(s), 1049(s), 939(s), 895(s), 862(s), 694(m).). ^{1}H-NMR (299.949 MHz, CD_3OD) δ(ppm) 6.94-7.00(2H, s), 4.70-4.85(H from hydroxy, s), 3.90-4.00 4H, t), 3.73-3.83(4H, t), 3.60-3.67(2H, s). ^{13}C-NMR (75.429 MHz, DMSO) δ(ppm) 153.64, 117.91, 112.95, 86.31 (ethynyl carbon), 80.05 (ethynyl carbon), 71.07, 59.76. Exact mass m/e 246.08985 (calc. for $C_{14}H_{14}O_4$ 246.08921).

The preparation of poly(1,4-(2,5-dibutoxy)phenyleneethynylene) (71)

To a 250 ml round flask equipped with magnetic stirring bar, septa and balloon were added 1,4-dibutoxy-2,5-diiodobenzene (0.554 g, 1.17 mmol), 1,4-dibutoxy-2,5-diethynylbenzene (0.320 g, 1,17 mmol) and a mixture of 60 ml toluene and 50 ml triethylamine. After the solution was degassed, a mixture of 14 mg CuI and 46 mg $PdCl_2(PPh_3)_2$ was added. It was stirred under an argon atmosphere for 3 hours at room temperature and 5 hours at 50-60°C. Then, a little 1,4-dibuutoxy-2,5-diethynylbenzene (10 mg) was added to the solution and the solution was stirred at 70-80°C for 12 hours. The precipitated amine salt was filtered immediately. The solution was poured into 200 ml methanol. The collected yellow polymer was dissolved in toluene slowly and carefully. Finally the solution was poured into methanol (200 mL) containing 0.1 ml of 2N HCl. A yellow polymer (0.53 g, 92%) was collected after filtration and dried in vaccum. ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 6.91-7.15(2H, m), 3.90-4.20(4H, m), 1.71-1.98(4H, m), 1.45-1.70(4H, m), 0.91-1.10(6H, t). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 153.45, 117.19, 114.26, 91.60, 69.34, 31.38, 19.26, 13.95. FTIR (cm^{-1}, 2955(s), 2952(s), 2870(s), 1512(m), 1466(m), 1425(m), 1379(m), 1275(s), 1209(s), 862(w).). Mn= 7.9×10^3. Mw= 24×10^3. Mw/Mn= 3.1

Anal. ($C_{16}H_{20}O_2$) Calc. C-78.76%, H-8.25%.

Found C-76.05%, H-7.86%, I-2.73%.

The preparation of poly(1,4-(2,5-dipentoxy)phenyleneethynylene) (72)

To a 250 ml round flask equipped with magnetic stirring bar, septa and balloon were added 1,4-dipentoxy-2,5-diethynylbenzene (0.516 g, 1.76 mmol), 1,4-dipentoxy-2,5-diiodobenzene (0.872 g, 1.75 mmol) and a mixture of 45 ml toluene and 40 ml triethylamine. After the solution was degassed, a mixture of 12 mg CuI and 55 mg $PdCl_2(PPh_3)_2$ was added into the solution. It was stirred for 16 hours under an argon atmosphere at 30°C. Then the precipitated salt was sucked off and the solution was poured into 400 ml of methanol. The collected yellow polymer was dissolved in 75 ml of toluene. The solution was poured into 400 ml of methanol containing 1 ml 2N HCl. The precipitated solid was collected and dried to give a yellow polymer (0.885 g, 94%). ^{1}H-NMR (299.949 MHz, C_6D_6) δ(ppm) 7.25-7.33(2H, s), 3.65-3.85(4H, t), 1.64-1.78(4H, m), 1.18-1.48(8H, m), 0.81-0.94(6H, t). ^{13}C-NMR (75.429 MHz, C_6D_6) δ(ppm) 154.30, 117.81, 115.20, 92.63 (ethynyl carbon), 69.52, 29.36, 28.51, 22.80, 14.29. FTIR (cm^{-1}, 2955(s), 2952(s), 2870(s), 1512(s), 1468(m), 1427(s), 1389(m), 1277(s), 1213(s), 854(w).). Mw= 30×10^3. Mn= 6.7×10^3. Mw/Mn= 4.5.

Anal. ($C_{18}H_{24}O_2$) Calc. C-79.37%, H-8.88%.

Found C-75.86%, H-8.25%, I-3.02%.

The preparation of poly(1,4-(2,5-dihexoxy)phenyleneethynylene) (73)

To a 250 ml round flask equipped magnetic stirring bar, septa and balloon were added 1,4-dihexoxy-2,5-diiodobenzene (0.666 g, 1.26 mmol), 1,4-dihexoxy-2,5-diethynylbenzene (0.410 g, 1.26 mmol) and a mixture of 54 ml toluene and 50 ml triethylamine. After the solution was degassed, a mixture of 68 mg $PdCl_2(PPh_3)_2$ and 17 mg CuI was added into the solution. It was stirred under an argon atmosphere for 12 hours at room temperature and 4 hours at 50-60°C. After it was cooled to room temperature, the precipitated amine salt was filtered. The solution was evaporated to 50 ml and poured to 300 ml of methanol. The collected yellow polymer was dissolved in 100 ml of toluene. The solution was poured into 400 ml of methanol containing 1 ml of 2N HCl. A yellow polymer (0.721g, 95%) was collected after dried. ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 6.95-7.05(2H, s), 3.92-4.10(4H, t), 1.70-1.95(4H, m), 1.20-1.65(12H, m), 0.80-1.00(6H, t). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 153.51, 117.27, 114.31, 91.60(ethynyl carbon), 69.70, 31.65, 29.32, 25.71, 22.66, 14.05. FTIR (cm^{-1}, 2930(s), 2860(s), 1514(s), 1468(m), 1429(s), 1389(m), 1275(s), 1213(s), 858(m).). Mw= 24×10^3. Mn= 10×10^3. Mw/Mn= 2.4.

Anal. ($C_{20}H_{28}O_2$) Calc. C-79.96%, H-9.39%.

Found C-77.05%, H-8.90%, I-2.60%.

The preparation of poly(1,4-(2,5-dioctoxy)phenyleneethynylene) (74)

The procedure was similar to that described above. To a degassed solution of 1,4-dioctoxy-2,5-diethynylbenzene (0.541 g, 1.41 mmol) and 1,4-dioctoxy-2,5-diiodobenzene (0.830 g, 1.42 mmol) in a mixture of 60 ml toluene and 60 ml triethylamine was added a mixture of 87 mg $PdCl_2(PPh_3)_2$ and 23 mg CuI. It was stirred under an argon atmosphere for 14 hours at room temperature and another 10 hours at 50°C. After the precipitated amine salt was filtered, the solution was poured into 400 ml of methanol containing 1 ml of 2N HCl solution. The collected polymer was dissolved in toluene and the solution was poured into 400 ml of methanol. After dried, a yellow polymer (0.96g, 94%) was collected. ^{1}H-NMR (299.949 MHz, C_6D_6) δ(ppm) 7.22-7.38(2H, s), 3.72-3.90(4H, t), 1.65-1.85(4H, m), 1.25-1.55(20H, m), 0.85-1.00(6H, t). ^{13}C-NMR (75.429 MHz, C_6D_6) δ(ppm) 154.32, 117.85, 115.21, 92.57(ethynyl carbon), 69.57, 32.28, 29.83, 29.78, 29.70, 26.42, 23.12, 14.38. FTIR (cm^{-1}, 2926(s), 2854(s), 1512(m), 1468(m), 1427(m), 1387(m), 1275(m), 1213(s), 858(w).). Mw= 45.7x10^3. Mn= 12.4x10^3. Mw/Mn= 3.7.

Anal. ($C_{24}H_{36}O_2$) Calc. C-80.85%, H-10.18%.

Found C-78.95%, H-9.81%, I-1.52%.

<u>The preparation of poly(1,4-(2,5-didecoxy)phenyleneethynylene) (75)</u>

To a 250 ml round flask equipped with magnetic stirring bar, septa and balloon were added 1,4-didecoxy,2,5-diethynylbenzene (0.600 g, 1.37 mmol), 1,4-didecoxy,2,5-diiodobenzene (0.798 g, 1.37 mmol) and a mixture of 70 ml toluene and 50 ml triethylamine. After the solution was degassed, a mixture of 72 mg $PdCl_2(PPh_3)_2$ and 19 mg CuI was added to the solution. It was stirred for 10 hours at room temperature and for another 14 hours at 40-50°C under an argon atmosphere. Following the polymerization, the amine salt gradually precipitated out and a strong green fluorescence was observed. Then the salt was filtered out and the solution was poured into excess (400 ml) methanol. The yellow polymer was collected and dissolved in 120 ml of toluene. Finally, it was precipitated in methanol (400 ml) containing 0.5 ml of 1N HCl, which was used to neutralize the trace of triethylamine. After dried in vacuum, a yellow polymer (0.971g, 93%) was collected. ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 6.95-7.05(2H, s), 3.90-4.10(4H, t), 1.70-1.95(4H, m), 1.05-1.65(28H, m), 0.75-1.00(6H, t)). ^{13}C-NMR (75.429 MHz, C_6D_6) δ(ppm) 154.31, 117.85, 115.20, 92.64(ethynyl carbon), 69.58, 32.40, 30.17, 30.13, 29.93, 29.88(2), 29.79, 26.47, 23.17, 14,42.). FTIR (cm^{-1}, 2924(s), 2854(s), 1514(m), 1468(m), 1429(m), 1389(w), 1277(m), 1215(m), 856(w).). Mw= 68x10^3. Mn= 22x10^3. Mw/Mn= 3.1.

Anal. ($C_{28}H_{44}O_2$) Calc. C-81.50%, H-10.75%.
Found C-80.45%, H-10.56%.

The preparation of copolymer **(PPE-1-10)** (75a)

To a degassed solution of 1,4-dimethoxy-2,5-diiodobenzene (0.585 g, 1.50 mmol) and 1,4-didecoxy-2,5-diethynylbenzene (0.659 g, 1.50 mmol) in a mixture of 40 ml toluene and 30 ml triethylamine was added a mixture of 54 mg $PdCl_2(PPh_3)_2$ and 14 mg CuI. It was stirred at room temperature for 5 hours and another 24 hours at 50°C-60°C under an argon atmosphere. After the amine salt and crosslinked polymer was filtered, the solution was poured into excess methanol (200 ml). The yellow polymer was collected and dissolved in a mixture of THF and toluene in a 1:1 ratio. The solution was poured into excess methanol again. The yellow solid was collected by the filtration. Drying of this solid in vacuum afforded a yellow polymer (0.345 g, 40%). FT-IR(cm^{-1}, 2949(m), 2924(vs), 2854(s), 2206(w), 1599(w), 1512(m), 1466(m), 1418(m), 1391(m), 1277(m), 1217(s), 1042(m), 862(w), 800(w), 723(w).). ^{13}C-NMR (75.429 MHz, C_6D_6) δ(ppm) 14.403, 23.143, 26.349, 29.682, 29.825, 30.053, 30.088, 32.346, 55.847 (MeO carbon), 69.245(CH_2O carbon), 92.794, 92.773, 114.954, 116.315. Mw= 34x10^3. Mn= 12x10^3. Mw/Mn= 2.7.

The preparation of **PPE-4** (88) by using **DBU** as the base

To a degassed solution of 1,4-dibutoxy-2,5-diiodobenzene (0.518 g, 1.09 mmol) and 1,4-butoxy-2,5-diethynylbenzene (0.299 g, 1.11 mmol) in a mixture of 50 ml toluene and 2.8 g DBU was added a mixture of 54 mg $PdCl_2(PPh_3)_2$ and 10 mg CuI. It was stirred at room temperature for 30 minutes under an argon atmosphere. A lot of salt precipitated during the polymerization. Toluene (50 ml) was added to the solution to dissolve precipitated polymer. It was stirred at room temperature for another 7 hours. The salt was removed by filtration and the solution was poured into excess methanol. The collected yellow polymer was redissolved in THF and poured into excess methanol again. The precipitated solid was collected again by the filtration. Drying of this solid afforded a yellow polymer (0.512 g, 97%). Mw= 13×10^3. Mn=5.1×10^3. Mw/Mn=2.5. The characterization is the same as before.

The preparation of block copolymer of **PPE-4** with amine as the tether (92)

To a degassed solution of 1,4-dibutoxy-2,5-diiodobenzene (0.508 g, 1.07 mmol) and 1,4-dibutoxy-2,5-diethynylbenzene (0.255 g, 0.943 mmol) in a mixture of 65 ml toluene and 0.470 g DBU was added a mixture of 33 mg $PdCl_2(PPh_3)_2$ and 7 mg CuI. After the solution was stirred at room temperature for 3 hours under an argon atmosphere, toluene (35 ml) was added to dissolve the precipitated polymer. Then bis(4-ethynylphenyl)hexylamine (39 mg, 0.13 mmol) was added to the solution by a syringe and it was stirred at 50-60°C for 16 hours. The same amine (11 mg, 0.036 mmol) was added to the solution by a syringe again and the solution was stirred for another 3 hours. The salt was removed by filtration and the solution was poured into excess methanol. The precipitated polymer was collected and dissolved in toluene. The solution was poured into excess methanol again. The polymer was collected and dried in vacuum.

Finally, a yellow polymer (0.493 g) was obtained. FT-IR (cm^{-1}, 2956(s), 2953(s), 1514(m), 1468(m), 1276(s).). ^{1}H-NMR (299.949 MHz, C_6D_6) δ(ppm) 7.55-7.65(H on phenylene, m), 7.2-7.3(H on arylene, s), 3.65-3.80(H on -OCH_2-, m), 3.48-3.64(H on -CH_2N-, m), 1.55-1.75(H on methylene of butoxy), 1.30-1.54, 1.0-1.25(H on hexyl), 0.75-0.95(H on methyl of butoxy, m). Mw= 21x10^3. Mn= 8.6x10^3. Mw/Mn= 2.4. Anal. Found C-75.86%, H-7.70%, N-0.56%, I-3.32%.

The preparation of block copolymer of **PPE-8** with silicon as the tether (148)

To a degassed solution of 1,4-dioctoxy-2,5-diiodobenzene (0.607 g, 1.03 mmol) and 1,4-dioctoxy-2,5-diethynylbenzene (0.201 g, 5.26 mmol) in a mixture of 50 ml toluene and 50 ml triethylamine was added a mixture of 55 mg $PdCl_2(PPh_3)_2$ and 13 mg CuI. After the solution was stirred at room temperature for 12 hours under an argon atmosphere, diethynyl diphenylsilane (0.118 g, 5.08 mmol) was added to the solution. Then, it was stirred at room temperature for 24 hours. The salt was removed by filtration and the solution was poured into excess methanol. The collected polymer was dissolved in toluene and the solution was poured into excess methanol. After dried in vacuum, a yellow polymer (0.579 g) was collected. Mn= 13.6x10^3. Mw=21.9x10^3. Mw/Mn= 1.6. FT-IR (cm^{-1}, 2951(s), 2925(vs), 2855(s), 2152(m), 1502(m), 1468(m), 1426(m), 1388(m), 1275 (m), 1213 (s), 1117(w), 1028 (m).). ^{1}H-NMR (299.949 MHz, C_6D_6) δ(ppm) 8.2 -8.4(m), 7.2-7.4(m), 6.8-7.12(m), 3.7-3.9(m, OCH_2), 1.55-1.85(m, CH_2), 1.2-1.55(m, CH_2), 0.85-1.00(m, CH_3).

The polymer modification reaction to remove the iodine

To a 25 ml round flask equipped with magnetic stirring bar, septa and ballon were added a mixture of 15 ml toluene and 15ml triethylamine and 200 mg **PPE-4** with

5.38% iodine in it. After the solution was degassed, a mixture of 10mg $PdCl_2(PPh_3)_2$ and 2 mg CuI and 0.070 g phenylacetylene were added. It was stirred at room temperature for 7 hours. After the salt was removed by the filtration, the solution was poured into excess methanol. The collected and dried polymer was redissolved in toluene again. The elemental analysis indicated that only a little of iodine (0.5%) was left in the polymer.

The polymer modification reaction to introduce trimethylsilylethynyl group

To a 50 ml round flask equipped with magnetic stirring bar, septa and balloon were added a mixture of 25 ml toluene and 20 ml triethylamine and 0.215 g **PPE-5** with 3.02% iodine in it. After the solution was degassed, a mixture of 15 mg $PdCl_2(PPh_3)_2$ and 7 mg CuI was added. Then, trimethyl silylacetylene (0.200 g) was added to the solution by a syringe. It was stirred at room temperature for 24 hours under an argon atmosphere. The salt was removed by vacuum filtration. The solution was poured into excess methanol. The collected polymer was dissolved in toluene and the solution was poured into excess methanol again. The precipitated polymer (0.170 g) was collected and dried. FT-IR (cm^{-1}, 3242, 2955, 2934, 2870, 2203, 2152, 1512, 1468, 1427, 1391, 1277, 1215, 1124, 1074, 1051, 1028, 924, 856, 731.). ^1H-NMR (299.949 MHz, CD_2Cl_2) δ(ppm) 6.98-7.10(s, 2H), 3.95-4.15(4H, t), 1.76-1.96(4H, m), 1.34-1.64(8H, m), 0.88-1.00(6H, t), 0.24-0.28(s). ^{13}C-NMR (75.429 MHz, CD_2Cl_2) δ(ppm) 153.82, 117.35, 114.45, 91.92, 69.99, 29.38, 28.54, 22.85, 14.24, -0.051. Found: I-0.45%.

The preparation of alcohol soluble PPE polymer (96)

To a mixture of 10 ml methanol and 10 ml triethylamine were added 2,5-diiodo-hydroquinonone bis(2-hydroxyethyl)ether (0.106 g, 0.24 mmol) and 2,5-diethynyl-hydroquinonone bis(2-hydroxyethyl)ether (0.058 g, 0.24 mmol). After argon was bubbled through the solution for 3 minutes, a mixture of $PdCl_2(PPh_3)_2$ (11 mg) and CuI (5 mg) was added. It was stirred at room temperature for 10 hours under an argon atmosphere and both amine salt and polymer precipitated from the solution. Then, both salt and polymer were collected by filtration and the salt was washed out with water. After dried in vaccum at room temperature, polymer 96 (0.096 g, 93%) was insoluble in any solvents.

The preparation of PEPESi1 polymer (126)

To a mixture of 10 ml benzene and 6 ml triethylamine was added 1,4-diiodobenzene (2.318 g, 7.02 mmol). After the solution was degassed, diethynyldimethylsilane (0.765 g, 7.03 mmol) and a mixture of 67 mg $PdCl_2(PPh_3)_2$ and 17 mg CuI were added to the solution. After 2 hours, a lot of solid precipitated, which contained both the salt and polymer. The solid collected by filtration was washed by water and dilute HCl aqueous solution alternatively. After purification, a yellow polymer (1.25 g, 97%) was collected. FTIR (cm^{-1}, 2963(m), 2160(vs), 1601(vw), 1497(s), 1404(m), 1252(s), 1234(m), 1220(m), 1177(vw), 1103(w), 1016(w), 839(vs), 785(s), 671(m).). ^{1}H-NMR (299.949 HMz, $CDCl_3$) δ(ppm) 7.40(4H, s), 0.433(6H, s). ^{13}C-NMR (75.429 MHz, solid state, CP and MAS) δ(ppm) 132.03, 123.31, 105.09(ethynyl carbon), 93.61(ethynyl carbon), 1.05. ^{29}Si-NMR (59.591 MHz, solid state, MAS) δ(ppm) -39.66. Mn= $1.6x10^3$. Mw= $4.7x10^3$. Mw/Mn= 2.9

Anal. ($C_{12}H_{10}Si$) Calc. C-79.06%, H-5.53%.

Found C-77.76%, H-5.59%.

The preparation of PEPESi1 polymer (127)

To a mixture of 5 ml benzene and 7 ml triethylamine were added 1,4-diiodobenzene (1.858 g, 5.63 mmol) and diethynylphenylmethylsilane (0.9581 g, 5.63 mmol). After the solution was degassed, a mixture of 45 mg $PdCl_2(PPh_3)_2$ and 12 mg CuI was added. Then it was stirred at room temperature for 10 minutes under an argon atmosphere. The salt was removed by filtration. The solution was pourred to excess methanol. The collected polymer was dissolved in THF and repricipitated in excess methanol again. Finally the polymer was collected by filtration again. After dried, a yellow polymer (1.05 g, 76%) was collected. FTIR (cm^{-1}, 3069(vw), 3022(vw), 2963(w), 2160(s), 1496(m), 1429(m), 1404(w), 1254(w), 1236(w), 1115(m), 1016(w), 822(vs), 725(m), 696(m).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 7.86-7.78(2H, m), 7.39-7.53(7H, m), 0.80-0.65(3H, s). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 134.12 (2C), 132.09 (1C), 132.04 (4C), 130.26 (1C), 128.14 (2C), 123.07 (2C), 106.70 (2C), 91.28 (2C), -0.12 (1C). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -43.44 (1Si). Mn= $6.3x10^3$. Mw= $10x10^3$. Mw/Mn= 1.6.

Anal. ($C_{17}H_{12}Si$) Cala. C-83.54%, H-4.95%.

Found C-83.35%, H-5.07%.

The preparation of PEPESi1 polymer (128)

To a mixture of 20 ml benzene and 7 ml triethylamine were added 1,4-diiodobenzene (1.632 g, 4.95 mmol) and diethynyldiphenylsilane (1.149 g, 4.95 mmol). After the solution was degassed, a mixture of 41 mg $PdCl_2(PPh_3)_2$ and 12 mg CuI was added to the solution. It was stirred at room temperature for 10 minutes under an argon atmosphere. After purification, which was similar to that for (127), a yellow polymer (1.35 g, 89%) was collected. FTIR (cm^{-1}, 3069(vw), 3022(vw), 2160(vs), 1497(s), 1429(s), 1404(vw),1265(vw), 1236(w), 1117(s), 837(s), 816(vs), 741(m),). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 7.70-7.82(4H, m), 7.41-7.51(4H, s), 7.29-7.40(6H, m). ^{13}C-NMR (300 MHz, $CDCl_3$) δ(ppm) 134.90(4C), 132.38(2C), 132.18(4C), 130.44(2C), 128.18(4C), 123.11(2C), 108.01(2C), 90.03(2C). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -47.99(1Si). Mn= 7.0×10^3. Mw= 16×10^3. Mw/Mn= 2.3.

Anal. ($C_{22}H_{14}Si$) Calc. C-86.23%, H-4.60%.

Found C-83.51%, H-4.88%.

The preparation of PEPESi1 polymer (129)

To a mixture of 15 ml benzene and 6 ml triethylamine were added 1,4-diiodobenzene (1.372 g, 4.16 mmol) and diethynyldi-sec-butylsilane (0.801 g, 4.16 mmol). After the solution was degassed, a mixture of 41 mg $PdCl_2(PPh_3)_2$ and 12 mg CuI was added. It was stirred at room temperature for 24 hours. After purification, which was similar to that for (127), a yellow polymer (0.95g, 86%) was collected. FTIR (cm^{-1}, 2959(s), 2928(s), 2158(s), 2068(vw), 1506(m), 1495(s), 1236(m), 1219(m), 1096(m), 1016(w), 837(vs), 810(vs).). ^{1}H-NMR spectra has been given on page 93. ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 131.86(4C), 123.06(2C), 106.51(2C), 91.41(2C), 24.78(2C), 19.68(2C), 13.78(2C), 13.24(2C). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -25.62(1Si). Mn= 48,000. Mw= 82,000. Mw/Mn= 1.7

Anal. ($C_{18}H_{22}Si$) Calc. C-81.13%, H-8.32%.

Found C-79.02%, H-7.98%, I-1.02%.

The preparation of PEPESim polymer (130)

To a mixture of 10 ml benzene and 5.4 ml triethylamine was added 1,4-diiodobenzene (1.067 g, 3.236 mmol). After the solution was degassed, 1,1,2,2-tetramethyl-1,2-diethynyldisilane (0.5379 g, 3.235 mmol) and a mixture of 32 mg $PdCl_2(PPh_3)_2$ and 37 mg CuI were added. It was stirred at room temperature for 1 hour under an argon atmosphere. Since this polymer also has low solubility in the reaction media, it precipitated gradually. The purification was the same as that for 126. After purification, a yellow polymer (0.70 g, 90%) was collected. FTIR (cm^{-1}, 2957(s), 2895(m), 2152(vs), 2062(vw), 1495(vs), 1404(s), 1246(vs), 1221(s), 1101(w), 1089(w), 1019(w), 843(vs), 798(vs), 771(vs).). ^{13}C-NMR (75.429 MHz, solid state, CP and MAS) δ(ppm) 131.42, 123.06, 95.30, -4.19. ^{29}Si-NMR (59.591 MHz, solid state, CP and MAS) δ(ppm) -37.326(2Si). Mn= 5.9×10^3. Mw= 27×10^3. Mw/Mn=4.6.

Anal. ($C_{14}H_{16}Si_2$) Calc. C-69.93%, H-6.71%.

Found C-63.39%, H-6.25%.

The preparation of PEPESim polymer (131)

To a mixture of 19 ml benzene and 19 ml triethylamine were added 1,4-diiodobenzene (1.391 g, 4.216 mmol). After the solution was degassed, 1,1,2,2,3,3-hexmethyl-1,3-diethynyl-1,2,3-trisilane (0.956 g (99%), 4.215 mmol) and a mixture of 66 mg $PdCl_2(PPh_3)_2$ and 14 mg CuI were added to the solution. It was stirred at room temperature for 48 hours under an argon atmosphere. After purification, which was similar to that for 127, a yellow polymer (1.01 g, 80%) was collected. FTIR (cm^{-1}, 2955(m), 2893(w), 2152(s), 1495(m), 1404(w), 1246(m), 1221(w), 1101(vw), 1018(vw), 837(vs), 785(vs), 768(s).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 7.32-7.34(s, 4H), 0.32-0.35(s, 12H), 0.25-0.27(s, 6H). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm)

131.63(4C), 123.25(2C), 107.25(2C), 95.42(2C), -2.12(4C), -6.95(2C). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -33.922(2Si), -46.13(1Si). Mn= 9,500. Mw= 20,000. Mw/Mn= 2.1

The preparation of PEPESim polymer (132)

To a mixture of 15 ml benzene and 15 ml triethylamine were added 1,4-diiodobenzne(0.334 g, 1.012 mmol) and 1,1,2,2,3,3,4,4-octamethyl-1,4-diethynyl-1,2,3,4-tetrasilane (0.298 g, 1.012 mmol). After the solution was degassed, a mixture of 46 mg $PdCl_2(PPh_3)_2$ and 8 mg CuI was added to the solution. It was stirred at room temperature for 120 hours. After purification, which was similar to that for 127, a yellow polymer (0.314 g, 87%) was collected. FTIR (cm^{-1}, 2951(m), 2893(w), 2152(m), 1495(m), 1404(w), 1246(m), 1221(w), 1101(vw), 1018(vw), 835(vs), 773(vs), 731(m).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 7.299(s, 4H), 0.271(s, 12H), 0.227(s, 12H). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 131.59(4C), 123.24(2C), 107.17(2C), 95.76(2C), -1.98(2C), -5.92 (2C). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -27.412(2Si), -37.361(2Si). Mn= 18,000. Mw= 22,000. Mw/Mn= 1.2.

The preparation of PEArESim polymer (135)

To a mixture of 7 ml benzene and 7 ml triethylamine was added 1,4-diiodo-2,5-dimethoxybenzene (0.931 g, 2.39 mmol). After the solution was degassed, diethynyldimethylsilane (0.258 g, 2.38 mmol) and a mixture of 54 mg $PdCl_2(PPh_3)_2$ and 11 mg CuI were added. It was stirred at room temperature for 55 hours under an argon atmosphere. Benzene (20 ml) was added to dissolve the precipitated polymer. After the salt was removed by the filtration, the solution was poured into excess methanol. After collected by filtration and dried in vacuum, a yellow yellow (5.09 g, 88%) was obtained. FTIR (cm^{-1}, 2959(vw), 2849(vw), 2151(s), 2037(vw), 1499(vs), 1466(m), 1391(s), 1281(w), 1250(w), 1224(vs), 1205(s), 1038(vs), 876(vs), 816(s).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 6.91(s, 2H), 3.79(s, 6H), 0.48(s, 6H). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 0.49(2C), 56.43(2C), 96.86(2C), 101.66(2C), 113.39(2C), 116.31(2C), 154.33(2C). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -38.99(1Si). Mn= 4,200. Mw= 5,000. Mw/Mn= 1.2.

The preparation of PEArESim polymer (136)

To a mixture of 7 ml benzene and 7 ml triethylamine was added 1,4-diiodo-2,5-dimethoxybenzene (0.561 g, 1.44 mmol). After the solution was degassed, 1,1,2,2-tetramethyl-1,2-diethynylsilane (0.240 g, 1.44 mmol) and a mixture of 58 mg $PdCl_2(PPh_3)_2$ and 13 mg CuI were added. After it was stirred at room temperature for 5 hours under an argon atmosphere, benzene (10 ml) was added to the solution. It was stirred at room temperature for 11 hours more. The salt was filtered and the solution was poured into excess methanol (120 ml). The precipitated polymer was collected and redissolved in THF. Then the THF solution was poured into excess methanol (100 ml) again. The precipitated solid was collected by filtration and then dried to afford a yellow polymer (0.216 g, 50%). FT-IR (cm^{-1}, 2957(w), 2851(w), 2147(m), 1497(vs), 1464(s), 1391(s), 1279(m), 1246(m), 1223(vs), 1205(s), 1042(vs), 872(vs), 837(m), 793(vs), 737(m).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 6.84(s, 2H), 3.73(s, 6H), 0.38(s, 12H). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) -2.94(4C), 56.34(2C), 98.63(2C), 103.54(2C), 113.64(2C), 116.08(2C), 154.30(2C). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -36.65(2Si). Mn= 4,100. Mw= 9,100. Mw/Mn = 2.2.

The preparation of PEArESim polymer (137)

To a mixture of 20 ml benzene and 18 ml triethylamine was added 1,4-diiodo-2,5-dimethoxybenzene (1.238 g, 3.17 mmol). After the solution was degassed, 1,1,2,2,3,3-hexamethyl-1,3-diethynyl-1,2,3-trisilane (0.724 g (99%), 3.19 mmol) and a mixture of 65 mg $PdCl_2(PPh_3)_2$ and CuI 15 mg were added. It was stirred at room temperature for 96 hours under an argon atmosphere. The purification procedure was the same as that for 127. After purification, a yellow-brown polymer (1.07 g, 60%) was collected. FTIR (cm^{-1}, 2959(s), 2901(m), 2851(w), 2147(s), 1499(vs), 1466(s), 1391(vs), 1279(s), 1246(vs), 1221(vs), 1042(vs), 870(vs), 835(vs), 735(vs).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 6.84(s, 2H), 3.73(s, 6H), 0.328(12H, s), 0.264(6H, s). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) -6.98(2C), -2.09(4C), 56.14(2C), 99.51(2C), 103.51(2C), 113.57(2C), 115.86(2C), 154.12(2C). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -33.81(2Si), -45.93(1Si). Mn= 9,400. Mw = 19,700. Mw/Mn = 2.1.

The preparation of PEArESim polymer (138)

To a mixture of 7 ml benzene and 7 ml triethylamine was added 1,4-diiodo-2,5-dimethoxybenzene (0.389 g, 0.998 mmol). After the solution was degassed, 1,1,2,2,3,3,4,4-octamethyl-1,4-diethynyl-1,2,3,4-tetrasilane (0.294 g (96%), 0.998 mmol) and a mixture of 47 mg $PdCl_2(PPh_3)_2$ and 10 mg CuI were added. It was stirred at room temperature for 96 hours under an argon atmosphere. The purification was the same as that for 127. After purification, a yellow polymer (0.220 g, 53%) was collected. FT-IR (cm^{-1}, 2953(m), 2851(v), 2143(m), 1499(s), 1464(m), 1391(s), 1279(m), 1246(m), 1223(m), 1205(m), 1042(s), 870(vs), 835(s), 802(s), 731(s).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) 6.82(2H, s), 3.78(6H, s), 0.29(12H, s), 0.250(12H, s). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) -5.95(4C), -1.882(4C), 56.17(2C), 99.71(2C), 103.50(2C), 113.57(2C), 115.86(2C), 154.15(2C). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -43.42(2Si), -33.42(2Si). Mn= 6.58x10^3. Mw= 12.5x10^3. Mw/Mn= 1.90.

The preparation of PEArESim polymer (139)

To a mixture of 10 ml benzene and 10 ml triethylamine was added 1,4-diiodo-2,5-dibutoxybenzene (1.544 g, 3.26 mmol). After it was degassed, dimethyldiethynylsilane (0.325 g, 3.26 mmol) and a mixture of 62 mg $PdCl_2(PPh_3)_2$ and 15 mg CuI were added. It was stirred at room temperature for 24 hours under an argon atmosphere. The purification procedure was the same as that for 127. After purification, a brown polymer (0.756 g, 71%) was collected. FTIR (cm^{-1}, 2959(vs), 2876(s), 2156(vs), 1499(vs), 1468(s), 1408(s), 1277(m), 1250(m), 1204(vs), 1067(m), 1026(m), 976(w), 891(m), 835(vs), 818(vs).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 6.79-7.03(2H, s), 3.78-4.14(4H, t), 1.64-1.92(4H, m), 1.37-1.63(4H, m), 0.76-1.13(6H, t), 0.25-0.67 (6H, s). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 0.362(2C), 13.84(2C), 19.20(2C), 31.28(2C), 69.23(2C), 96.51(2C), 101.82(2C), 113.97(2C), 117.32(2C), 154.17(2C). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -39.33(1Si). Mn= 5.78x10^3. Mw= 10.7x10^3. Mw/Mn= 1.85

Anal. ($C_{20}H_{26}SiO_2$) Calc. C-73.57%, H-8.03%.

Found C-70.30%, H-7.45%. I-0.92%

The preparation of PEArESim polymer (140)

To a mixture of 14 ml benzene and 14 ml triethylamine was added 1,4-diiodo-2,5-dibutoxybenzene (3.168 g, 6.72 mmol). After the solution was degassed, 1,1,2,2-tetramethyl-1,2-diethynyl-disilane (1.14 g (98%), 6.72 mmol) and a mixture of 55 mg $PdCl_2(PPh_3)_2$ and 12 mg CuI were added to the solution. It was stirred at room temperature for 24 hours under an atmosphere. The purification procedure was the same as that for 127. After purification, a yellow polymer (2.27 g, 88%) was collected. FTIR (cm^{-1}, 2959(vs), 2872(s), 2147(s), 1497(vs), 1468(s), 1406(s), 1275(m), 1246(m), 1204(s), 1067(m), 1028(m), 906(m), 889(m), 791(vs), 771(s), 733(w).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 0.35(12H, s), 0.91(6H, t), 1.40-1.50(4H, m), 1.66-1.76(4H, m), 3.82-3.92(4H, t), 6.83(2H, s). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) -2.94(4C), 13.86(2C), 19.25(2C), 31.33(2C), 69.08(2C), 98.03(2C), 103.68(2C), 113.99(2C), 117.15(2C), 153.87(2C). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -37.03(2Si). Mn= $17.0x10^3$. Mw= $36.0x10^3$. Mw/Mn = 2.1

Anal. ($C_{22}H_{32}Si_2O_2$) Calc. C-68.69%, H-8.39%.

Found C-67.22%, H-8.16%, I-0.45%.

The preparation of PEArESim polymer (141)

To a mixture of 10 ml toluene and 10 ml triethylamine was added 1,4-diiodo-2,5-dibutoxybenzene (1.003 g, 2.12 mmol). After the solution was degassed, 1,1,2,2,3,3-hexamethyl-1,3-diethynyl-1,2,3-trisilane (0.482 g (98%), 2.12 mmol) and a mixture of 43 mg $PdCl_2(PPh_3)_2$ and 10 mg CuI were added. It was stirred at room temperature for 66 hours under an argon atmosphere. The purificaiton was the same as that for 127. After purification, a brown polymer (0.657 g, 70%) was collected. FTIR (cm^{-1} 2959(vs), 2874(s), 2147(s), 2069(w), 1497(vs), 1468(s), 1406(s), 1275(m), 1246(s), 1202(s), 1067(m), 1028(m), 905(m), 889(m), 837(s), 810(s), 783(vs), 773(w).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 6.82(2H, s), 3.82-3.94(4H, t), 1.65-1.80(4H, m), 1.35-1.55(4H, m), 0.85-1.00(6H, t), 0.310(12H, s), 0.255(6H, s). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) -6.93(2C), -2.00(4C), 13.87(2C), 19.25(2C), 31.34(2C), 69.06(2C), 99.00(2C), 103.65(2C), 114.05(2C), 117.18(2C), 153.77(2C). ^{29}Si-NMR (59.591 MHz,

$CDCl_3$) δ(ppm) -33.94(2Si), -46.33(1Si). Mn= 5.8x10^3. Mw= 18.0x10^3. Mw/Mn = 3.1 Anal. ($C_{24}H_{38}Si_3O_2$) Calc. C-65.10%. H-8.65.

Found C-62.59%, H-8.09%, I-1.76%.

The preparation of PEPESim polymer (142)

To a mixture of 15 ml benzene and 15 ml triethylamine was added 1,4-diiodo-2,5-dibutoxybenzene (0.1278 g, 2.70 mmol). After it was degassed, 1,1,2,2,3,3,4,4-octamethyl-1,4-diethynyl-1,2,3,4-tetrasilane (0.802 g (95%), 2.70 mmol) and a mixture of 47 mg $PdCl_2(PPh_3)_2$ and 10 mg CuI were added. It was stirred at room temperature for 72 hours under an argon atmosphere. The purification procedure was the same as that for 127. After purification, a yellow polymer (0.95 g, 70%) was collected. FT-IR (cm^{-1}, 2959(vs), 2874(s), 2147(s), 1497(vs), 1468(s), 1406(s), 1275(m), 1246(s), 1202(s), 1067(m), 1028(m), 905(m), 889(m), 803(s), 777(vs), 731(w).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 6.81(2H, s), 3.87(4H, t), 1.70(4H, m), 1.47(4H, m), 0.904(6H, t), 0.275(12H, s), 0.230(12H, s). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) -5.89(4C), -1.85(4C), 13.87(4C), 19.25(2C), 31.34(2C), 69.02(2C), 99.20(2C), 103.66(2C), 114.03(2C), 117.10(2C), 153.76 (2C). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -33.43(2Si), -43.57(2Si). Mn= 20.3x10^3. Mw= 40.5x10^3. Mw/Mn= 2.00. Anal. ($C_{26}H_{44}Si_4O_2$) Calc. C-62.38%, H-8.86%.

Found C-58.73%, H-8.53%, I-0.55%.

The preparation of PEPESi polymer (145)

To a mixture of 20.0 ml benzene and 20.0 ml triethylamine was added 1,4-diiodobenzene (1.032 g, 3.097 mmol). After the solution was degassed, 1,3-diethynyl-1,1,3,3-tetramethyl-1,3-disilylpropane (0.567 g (99%), 3.111 mmol) and a mixture of 64 mg $PdCl_2(PPh_3)_2$ and 14 mg CuI were added to the solution. It was stirred at room temperature for 60 hours under argon atmosphere. The purification procedure was the same as that for 127. After dried in vacuum, a grey polymer (0.550 g, 69%) was collected. FT-IR (cm^{-1}, 2959(m), 2901(w), 2160(m), 2068(w), 1495(m), 1406(w), 1352(w), 1250(m), 1221(w), 1101(w), 1053(m), 1018(w), 837(s), 690(w), 658(w).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 0.14-0.17(2H, s), 0.31-0.37(12H, s), 7.32-7.35(4H, s). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 1.011(4C), 3.305(1C), 96.861(2C), 104.96(2C), 123.160(2C), 131.622(4C). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -17.994(2Si). Mn= 41,000. Mw= 92,000. Mw/Mn = 2.32

The preparation of PEArESi polymer (146)

To a mixture of 13.0 ml benzene and 13.0 ml triethylamine was added 1,4-dibutoxy-2,5-diiodobenzene (0.563 g, 1.187 mmol). After the solution was degassed, 1,3-diethynyl-1,1,3,3-tetramethyl-1,3-disilylpropane (0.216 g (99%), 1.186 mmol) and a mixture of 56 mg $PdCl_2(PPh_3)_2$ and 15 mg CuI were added to the solution. It was stirred at room temperature for 120 hours under an argon atmosphere. The purification procedure was the same as that for 127. After dried in vacuum, a pink polymer (0.310 g, 65%) was collected. FT-IR (cm^{-1}, 2959(s), 2935(s), 2154(s), 1497(s), 1468(m), 1406(m), 1275(m), 1250(s), 1202(s), 1053(s), 1028(m), 905(m), 891(m), 816(s), 758(m).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 0.17-0.20 (2H, s), 0.32-0.37(12H, s), 0.90-1.05 (6H, t), 1.45-1.60(4H, m), 1.67-1.83(4H, m), 3.86-3.94(4H, t), 6.84-6.88(2H, s). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 1.019(4C), 3.455(1C), 13.904(2C), 19.240(2C), 31.335(2c), 69.116(2C), 100.637(2C), 101.441(2C), 113.985(2C), 117.162(2C), 153.897(2C). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -18.068. Mn= 19,000. Mw= 36,400. Mw/Mn= 1.94.

The preparation of PEArEGe polymer (147)

To a mixture of 15 ml toluene and 15 ml diethylamine were added 1,4-diiodo-2,5-dibutoxybenzene (0.414 g, 0.873 mmol) and diphenyldiethynylgermane (0.242 g, 0.874 mmol). After the solution was degassed, a mixture of 26 mg $PdCl_2(PPh_3)_2$ and 7 mg CuI was added to the solution. It was stirred at room temperature for 30 hours under an argon atmosphere. Since the amine salt was soluble in reaction media, the reaction was quenched by pouring the solution into excess methanol without the filtration. The precipitated polymer was collected by the filtration and washed with methanol to get rid of amine salt. After dried in vacuum, a yellow polymer (0.390 g, 93%) was collected. Mw= $15.2x10^3$. Mn= $8.1x10^3$. Mw/Mn = 1.9. FTIR (cm^{-1}, 3069(w), 3050(w), 2958(s), 2933(s), 2871(s), 2157(s), 2071(w), 1498(vs), 1468(s), 1433(s), 1408(s), 1388(s), 1275(m), 1222(vs), 1202(s), 1026(m), 1095(m), 737(vs), 696(vs).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 7.80-7.88(4H, m), 7.40-7.46(6H, m), 6.95-7.04(2H, s), 3.80-4.05(4H, t), 1.60-1.85(4H, m), 1.35-1.60(4H, m), 0.83-0.96(6H, t). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 154.21(2C), 133.90(4C), 133.84(2C), 129.80(2C), 128.38(4C), 117.20(2C), 113.80(2C), 103.19(2C), 92.69(2C), 69.14(2C), 31.37(2C), 19.19(2C), 13.87(2C).

The preparation of poly(methylphenylsilylene-ethynylene)(186)

To a solution of diethynylphenylmethylsilane (3.974 g, 23.3 mmol), DBU (7.32 g, 48.1 mmol) and methylenechloride (12 ml) was added $PdCl_2(PPh_3)_2$ (82 mg). After argon was bubbled through the solution for 3 minutes, methylphenyldichlorosilane (4.547 g, 23.8 mmol) was added into this solution by a syringe. Finally methylphenyl diethynylsilane (0.120 g, 0.7 mmol) was added into this solution. It was stirred at room temperature for 36 hours. Then the solvent was removed in 5 hours by slow distillation. Methylenechloride (10 ml) was added into this viscous solution and it was refluxed for 3 hours. After the CH_2Cl_2 was removed again by distillation, excess methanol was added to this viscous residue to quench the reaction. The collected solid was washed with water and dissolved in THF. The solution was poured into excess methanol and the precipitated polymer was collected by filtration. After dried, a brown polymer (4.60 g, 67%) was obtained. FTIR (cm^{-1}, 3071(w), 2966(w), 1589(w), 1487(vw), 1429(m), 1254(m), 1190(w), 1115(m), 999(vw), 797(vs), 739(m), 696(m).). ^{1}H-NMR (299.429 MHz, $CDCl_3$) δ(ppm) 7.9-7.7(2H, m), 7.3-7.5(3H,), 0.1-0.5(3H, s). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 134.17, 132.62, 130.23, 128.06, 110.92, -0.31. ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -45.32. Mn= $9.84x10^3$. Mw= $1.25x10^4$. DP= 1.3.

The preparation of poly(cyclohexylmethylsilylene-ethynylene) (187)

To a solution of methylenechloride (3 ml), cyclohexylmethyldiethynylsilane (1.797 g (94%), 9.58 mmol) and DBU (2.922 g, 19.2 mmol) was added $PdCl_2(PPh_3)_2$ (55 mg). After argon was bubbled through the solution for 3 minutes, methylcyclohexyl dichlorosilane (1.893 g, 9.60 mmol) was added into the solution by syringe. The solution turned viscous gradually. After it was stirred at room temperature for 48 hours, the solvent was removed in 5 hours by slow distillation. Then excess methanol was added to this viscous solution to quench the reaction. The polymer collected was washed with methanol, 0.2 N HCl and water respectively. After the washed polymer was dissolved in THF, the THF solution was poured into excess methanol. The precipitated solid was collected by filtration and dried in vacuum to afford a brownish polymer (2.03 g, 80%). FTIR (cm^{-1}, 2922(vs), 2849(s), 2071(vw), 1447(m), 1408(w), 1252(m), 1186(v), 1171(v), 1099(m), 995(m), 889(s), 849(s), 825(s), 797(vs).). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 110.40, 27.67, 26.78, 25.41, -3.60, -3.63, -3.66. ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -36.58, -36.77. Mw= $14x10^3$. Mn= $3.6x10^3$. DP= 3.9.

The preparation of copolymer of poly(diphenylsilylene-ethynylene-cyclohexylmethylsilylene-ethynylene) (188).

To a solution containing diethynyldiphenylsilane(0.866 g, 3.73 mmol), methylenechloride(3 ml) and DBU (0.920 g, 8.1 mmol) was added $PdCl_2(PPh_3)_2$ (34 mg). After argon was bubbled through the solution for 3 minutes, methylcyclohexyl dichlorosilane (0.742 g, 3.76 mmol) was added to the solution by a syringe. The solution was refluxed for 36 hours. After the solution was cooled to room temperature, excess methanol was added to the solution to quench the polymerization. The precipitated solid was collected by filtration and washed with methanol, 0.2 N HCl aqueous solution and water alternatively and dissolved in THF. The THF solution was poured into excess solution of water and methanol in a 1:1 volume ratio. The precipitated solid was collected by filtration again and dried in vacuum to afford a brittle yellow-orange polymer (0.95 g, 72%). FTIR(cm^{-1}, 3069(w), 2920(s), 2847(m), 2039(vw), 1447(w), 1429(m), 1254(w), 1188(vw), 1117(s), 1070(m), 997(w), 912(vw), 889(m), 849(m), 797(vs).). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 134.79, 132.10, 130.30-130.23, 128.10-127.99, 113.16, 108.43, 27.57, 26.78-26.62, 26.19, 25.26, -2.47, -3.86. ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -35.47, -50.60, -50.65. Mw= $9.4x10^3$. Mn= $5.6x10^3$. DP= 1.7.

The preparation of copolymer of poly(diphenylsilylene-ethynylene-dimethylsilylene-ethynylene) (189)

To a solution containing diethyldiethynylsilane (0.629 g, 2.71 mmol), methylenechloride(2 ml) and DBU (0.830 g, 5.45 mmol) was added $PdCl_2(PPh_3)_2$ (14 mg). After Argon was bubbled through the solution for 3 minutes, dimethyldichlorosilane (0.350 g, 2.71 mmol) was added to the solution by a syringe. After the solution was stirred at room temperature for 15 hours, it refluxed for another hour. The residual was dissolved in THF and the THF solution was poured into excess methanol. The collected solid was dried in vacuum to afford a yellow polymer (0.70 g, 83%). FTIR (cm^{-1}, 3069(w), 2961(s), 2039(vw), 1429(m), 1377(w), 1254(m), 1117(s), 1049(m), 997(vw), 824(vs), 773(vs), 741(s).). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 135.03, 132.03, 130.55-130.52, 128.33-128.28, 114.51, 107.86, 2.12. ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -40.16, -50.60. Mw= 56×10^3. Mn= 21×10^3. Mw/Mn= 2.7

The preparation of copolymer of poly(diethylsilylene-ethynylene-dimethylsilylene-ethynylene) (190)

To a solution containing diethyldiethynylsilane (2.097 g (91%), 14.0 mmol), methylenechloride(6 ml) and DBU (4.55 g, mmol) was added $PdCl_2(PPh_3)_2$ (57 mg). After argon was bubbled through the solution for 2 minutes, dimethyldichlorosilane (1.88 g, 14.4 mmol) was added to the solution by a syringe. After the solution was stirred at room temperature for 24 hours, it refluxed for 24 hours. (After 12 hours reflux, diethyldiethynylsilane (67 mg, 0.45 mmol) was added to react with the end group of chlorosilane) The solvent was distilled out in 2 hours. After the viscous solution was cooled to room temperature, excess methanol was added to the solution. The collected residue was washed with methanol, 0.2 N HCl aqueous solution and water alternatively. The residual was dissolved in THF and the THF solution was poured to excess methanol. The collected solid was dried in vacuum to afford a yellow polymer (2.30 g, 82%). FTIR (cm^{-1}, 2963(vs), 2937(s), 2835(w), 2071(w), 2039(w), 1460(m), 1412(m), 1381(w), 1254(s), 1234(m), 1090(m), 1009(m), 825(vs), 775(vs), 729(vs).). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 0.92-1.10(6H, t), 0.61-0.76(4H, t), 0.26-0.34(6H, t). ^{13}C-NMR (75.429 MHz, C_6D_6) δ(ppm) 111.95, 109.11, 7.07, 6.12, 0.04. ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -32.55, -41.49. Mw= 35×10^3. Mn= 27×10^3. Mw/Mn= 1.3

The preparation of copolymer of poly(diethylsilylene-ethynylene-cyclotetramethylene silylene-ethynylene) (191)

To a solution containing diethyldiethynylsilane (2.656 g (91%), 17.7 mmol), methylenechloride (6.2 ml) and $PdCl_2(PPh_3)_2$ (53 mg) were added DBU (5.45 g, 35.8 mmol). After argon was bubbled through the solution for 3 minutes, 1,1-dichlorosila cyclopentane (2.72 g, 17.5 mmol) was added to the solution by a syringe. After the solution was stirred at room temperature for 24 hours, it refluxed for 4 hours. Then the solvent was distilled out in 5 hours. After the viscous solution was cooled to room temperature, excess methanol was added to it. The collected residue was washed by methanol, 0.2 N HCl aqueous and water alternatively and then was dissolved in THF. The THF solution was poured into excess methanol and the precipitated solid was collected again and dried in vacuum to afford a yellowish polymer (2.45 g, 64%). FTIR(cm^{-1}, 2959, 2935, 2071, 2039, 1460, 1404, 1379, 1315, 1232, 1076, 1028, 1018, 806, 775, 729.). ^1H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 1.5-1.8(4H, m), 0.92-1.2(6H, t), 0.78-0.92(4H, m), 0.50-0.78(4H, q). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 110.63, 110.49, 27.77, 14.05, 7.07, 6.07. ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -32.55 , -41.49 ppm. Mw= $30x10^3$. Mn= $11x10^3$. Mw/Mn= 2.7.

The preparation of copolymer of poly(methylvinylsilylene-ethynylene-cyclohexylmethylsilylene-ethynylene) (192)

To a solution containing methylcyclohexyldiethynylsilane (1.908 g (94%), 10.2 mmol), methylenechloride (7 ml) and $PdCl_2(PPh_3)_2$ (72 mg) was added DBU (3.80 g, 25 mmol) by a syringe. After argon was bubbled through the solution for 3 minutes, vinylmethyldichlorosilane (1.641 g, 11.6 mmol) was added to the solution by a syringe. Then methylcyclohexyldiethynylsilane (0.280 g, 1.5 mmol) was added to the solution to meet the requirement of molar ratio. After the solution refluxed for 36 hours, the solvent was distilled out in 3 hours. After the viscous solution was cooled to room temperature, excess methanol was added to the solution. The residue was washed with methanol, 0.2 N HCl aqueous solution and water alternatively and dissolved in THF. The THF solution was poured into excess methanol and the precipitated solid was collected and dried in vacuum to afford a pink polymer (1.50 g, 53%). FT-IR(cm^{-1}, 3275(vw), 3057(w), 2924(vs), 2851(s), 2039(w), 1595(), 1448(m), 1404(), 1254(s), 1099(m), 999(), 964(w), 849(m), 797(vs), 735(m).). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm) 135.63, 132.60, 94.91 (end), 84.89 (), 27.64, 26.70, 25.21, -1.01 , -1.05 (), -3.733. ^{29}Si-NMR (60 MHz, $CDCl_3$) δ(ppm) -36.21, -36.35, -48.46. Mw= 5.3x10^3. Mn= 2.9x10^3. Mw/Mn= 1.9

The preparation of copolymer of poly(methylvinylsilylene-ethynylene-methylphenylsilyl-ethynylene) (193)

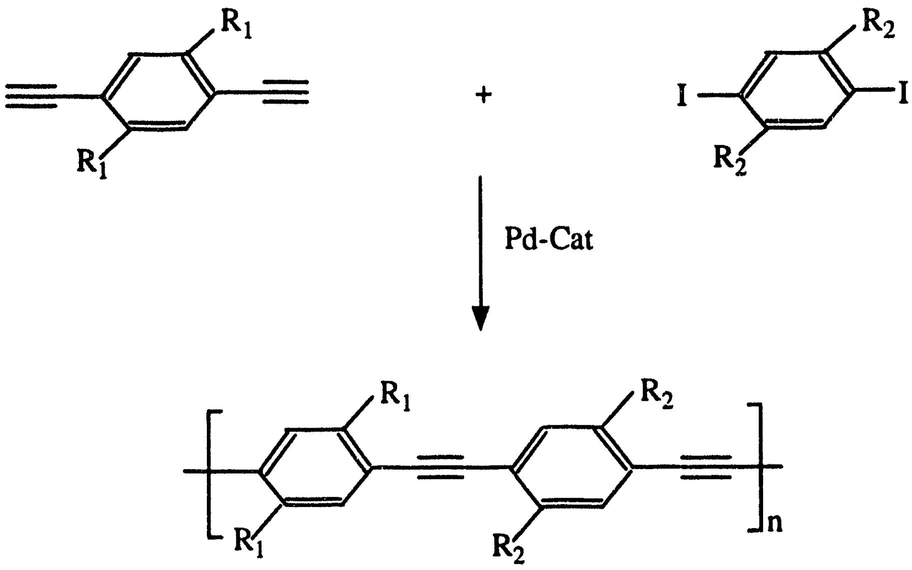
To a solution containing methylphenyldiethynylsilane (3.652 g, 21.4 mmol), methylenechloride (12 ml) and DBU (6.70 g, 44 mmol) was added $PdCl_2(PPh_3)_2$ (72 mg). After argon was bubbled through the solution for 3 minutes, methylvinyldichlorosilane (2.95 g, 20.9 mmol) was added to the solution by a syringe. Red color appeared in the solution, which implied that a complex formed in the solution. After the solution was refluxed for 20 hours, the solvent was removed in 3 hours by slow distillation. Excess methanol was added to the viscous gel to quench the polymerization. The residue was washed with methanol, 0.2 N HCl aqueous solution and water alternatively and then was dissolved in THF. The THF solution was poured into excess methanol. The precipitated solid was collected by filtration and dried in vacuum to afford a pink polymer (3.80 g, 79%). FTIR (cm^{-1}, 3273, 3071, 3055, 2905, 2041, 1593, 1487, 1431, 1404, 1256, 1190, 1115, 1005, 966, 798, 739, 696.). ^{1}H-NMR (299.949 MHz, $CDCl_3$) δ(ppm) 7.6-7.8(2H, m), 7.26-7.48(3H,), 5.92-6.20(3H,), 0.50-0.60(3H, s), 0.35-0.45(3H,). ^{13}C-NMR (75.429 MHz, C_6D_6) δ(ppm) 136.06 (vinyl carbon), 134.14, 132.67, 132.06 (vinyl carbon), 130.21, 128.05, 110.64 (ethynyl carbon), 110.32 (ethynyl carbon), -0.28 (methyl carbon), -1.25 (methyl carbon). ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -45.57, -47.87. Mw=16x10^3. Mn=5.3x10^3. Mw/Mn= 3.0

<u>The preparation of copolymer of poly(diphenylsilyl-ethynylene-1,1,2,2-tetramethyl-disilylene-ethynylene) (194)</u>

To a solution containing diphenyldiethynylsilane (1.284 g, 5.53 mmol), methylenechloride (4 ml) and DBU (1.370 g, 11.6 mmol) was added $PdCl_2(PPh_3)_2$ (30 mg). After Argon was bubbled through the solution for 3 minutes, 1,1,2,2-tetramethyl-1,2-dichlorodisilane (1.041 g, 5.57 mmol) was added to the solution by a syringe. After the solution was stirred at room temperature for 48 hours, the solvent was removed in 3 hours by slow distillation. The solution was cooled to room temperature and excess methanol was added to it. The residue was washed with methanol, 0.2 N HCl aqueous solution and water and dissolved in THF. The solution was poured into excess methanol and the precipitated solid was collected and dried in vacuum to afford a yellow polymer (1.5 g, 78%). FTIR(cm^{-1}, 3071(w), 3051(v), 2905(m), 2897(w), 2039(w), 1589(w), 1485(w), 1429(s), 1404(w), 1252(s), 1117(s), 1069(m), 999(w), 841(vs), 775(vs), 741(s).). ^{13}C-NMR (75.429 MHz, $CDCl_3$) δ(ppm): 134.75, 134.69, 132.57, 130.21, 130.12, 128.02, 127.95, 116.69, 109.44, -3.91. ^{29}Si-NMR (59.591 MHz, $CDCl_3$) δ(ppm) -36.70, -51.41. Mw= 41x10^3. Mn= 15x10^3. Mw/Mn= 1.8.

FUTURE WORK

Several different types of polymers have been synthesized via pallidium-catalyzed polymerzations. However, there are still a lot of work remained. The following novel poly(2,5-dialkyl-1,4-phenyleneethynylene)s as well as other substituted **PPE** polymers as shown in Scheme 52 could be conveniently prepared by the same Pd-catalyzed polymerization established before. The polymer properties can be controlled by using desirable monomers.



Scheme 52. Synthesis of **PPE** polymers

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