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Polar, Functional Diene-Based Materials: Free Radical Polymerization of 2-Cyanomethyl-1,3-Butadiene

by

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF SCHEMES

LIST OF TABLES

GENERAL INTRODUCTION

Introduction

The synthesis and utilization of functionalized polymeric materials have aroused continuing research interests as a result of their unique features.[1,2] First, functionalized polymers provide the possibility of introducing the properties of various functional groups to high molecular weight materials. Furthermore, the chemical dissimilarity between the functional groups and the backbone, such as polar/nonpolar, hydrophilic/hydrophobic, etc, could lead to very unique properties, such as phase separation and association. Using functionalized polymers to form self-assemblies has become a new interesting research topic in recent years.[3]

Due to the new properties introduced by the functional groups into the high molecular weight materials, functional polymers have been developed for wide applications in diverse areas. These areas include chemical, biological and other technological applications.[1,2] Polymeric supports, which have reactive organic groups bound to them, have been used effectively in organic synthesis.[4] Polymer supported catalysts have been utilized widely in industry, taking advantage of easy catalyst recovery and the possibility of using incompatible catalytic systems simultaneously. Functionalized polymers also have many applications in the separations area, for example, in ion exchange chromatography.[5] The application of polymeric materials for medical purposes is also growing quickly with increased research in drug delivery systems, implantation of medical devices and artificial organs.[6] Various applications have also been found in other technological areas, including conductive polymers, chemical sensors, etc.

Functionalized elastomers are one type of functionalized polymer used widely in the polymer industry, especially in the rubber industry. Styrene and 1,3-butadiene are two of the most important commercial monomers. Considerable attention has been given to various styrene-based materials. However, only limited research has focused on functionalized dienes and even less on their copolymers with commercially available monomers, like styrene and acrylonitrile.[7,8] The lack of research is probably due to the relatively difficult synthesis of functionalized dienes.

In 1987, Nakahama's group reported the anionic polymerization of 2-(trimethyloxysilyl)-1,3-butadiene, which has a hydrolyzable alkoxysilyl functionality.[9] They proved the living nature of the anionic polymerization process and determined the polymer microstructures. Their work was extended to a few other trialkylsilyl, trialkoxysilyl and (*N*,*N*'-dialkylamino)silyl butadiene derivatives, also with a focus on anionic polymerization.[10-12] They investigated the conditions under which the anionic polymerizations could be carried out and the influences of several experimental factors, such as solvent, counterion, etc. Microstructures of the resulting polymers were fully characterized by NMR spectroscopy. They found that the substituents on the silicon atom had a major affect on the geometry of the repeating units of the polymers. Under the same conditions, poly(2-diisopropoxymethylsilyl-1,3-butadiene), poly(2-isopropoxydimethylsilyl-1,3-butadiene) and poly(2-trimethylsilyl-1,3-butadiene) consisted mainly of 1,4 (70-80%) and 1,2 (20-30%) linkages, whereas 1,4 was the exclusive microstructure of poly(2-triisopropoxysilyl-1,3-butadiene) and poly(2-trimethoxysilyl-1,3-butadiene). The ratio of 1,4 and 1,2 structures was mainly decided by the electronegativities of the silyl groups, rather than the groups' steric hindrance. The monomers' electronegativity order was also used to explain the reactivity order of this series of monomers.

Other types of silicon-containing butadiene derivatives have also been discussed in the previous literature. Penelle's group reported the free-radical polymerization of 2-(trimethylsiloxy)butadiene (TMSBD) and 2-(*tert*-butyldimethylsiloxy)butadiene (TBMSBD).[13,14] Microstructural analysis of the resulting homopolymers was carried out by 2D NMR techniques. They found that the *cis* structure was favored over the *trans* structure in the polymerization of TBMSBD and the opposite was observed for TMSBD. The authors tried to rationalize these observations by comparing two different influences, the steric hindrance of the siloxy substituents and the interaction between the in-plane terminal allyl hydrogens with the CH_2 groups on the other side in a cisoid conformation. Steric hindrance was the predominant influence in the polymerization of TBMSBD, whereas interactions between the terminal hydrogens were the main factor in the polymerization of TMSBD. Silyl enol ether functionality was incorporated into vinyl polymers by copolymerizing TMSBD or TBMSBD with either styrene or methyl methacrylate. The reactivity of the silyl enol ether in the copolymers was tested by various electrophilic reagents and found to be similar to a low molecular weight analogue.

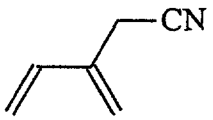
In 1993, Stadler's group reported the anionic polymerization of 5-(*N,N*-diisopropylamino)isoprene, a butadiene derivative with an aliphatic tertiary amino functionality.[15] Though the results of the polymerization were not very satisfactory due to the poor purity of the monomer, their work gave access to an interesting class of diene-based ionomers. The group then extended their research to other 5-(*N,N*-dialkylamino)isoprenes. The alkyl groups included ethyl, *n*-propyl, *n*-butyl, isobutyl, piperidyl, etc.[16,19,20] Through an investigation of the microstructures of the resulting polymers, they found the stereochemistry of the anionic polymerization of aminoisoprenes to be strongly dependent on the bulkiness of the amino groups. Bulky substituents attached to the amino group favor the *cis* structure over the *trans* structure. For example, poly[5-(*N*,*N*-diisopropylamino)isoprene) and poly[5-(*N*,*N*-diisobutylamino)isoprene] had exclusively *cis*-1,4 structure, whereas poly[5-(*N*,*N*-diethylamino)isoprene] and poly[5-(*N*,*N*-di-*n*-propylamino)isoprene] had a mixture of *cis* and *trans*-1,4 structures. Copolymerizations of 5-(*N*,*N*-dialkylamino)isoprenes with styrene and 1,3-butadiene via anionic polymerization have also been reported. It was found that the reactivity of 5-(*N*,*N*-diisopropylamino)isoprene was higher than styrene. In contrast to the isoprene/styrene system, no tapered copolymer was obtained in poly[5-(*N*,*N*-diisopropylamino)isoprene-*co*-styrene] due to the polarity of the aminoisoprene. In the 5-(*N*,*N*-dialkylamino)isoprene/1,3-butadiene system, the reactivity of 5-(*N*,*N*-dialkylamino)isoprene was also higher than 1,3-butadiene and the tendency towards tapered structure increased with increasing bulkiness of the alkyl chains.

For linear polymers, the positions of the functionality could be at the end of the chain (called end-functionalized polymer) or along the backbone of the polymer, either in the main chain itself or at the pendant group of the main chain. In recent years, macromonomers and telechelics have aroused wide research interest, because they can be used to synthesize polymers with unique architectures, such as dendrimers,[20,21] stars, hyperbranched polymers[23,24,25] and block copolymers.

Our group has been interested in diene derivatives with polar functional groups, such as an amine, ester, acid, etc.[26, 27] To introduce the desired functionality into polymers, 1,3-butadiene monomers with specific groups have been synthesized and polymerized.

Compared to another popular route, the introduction of functionality through chemical modification of a non-functionalized polymer, this strategy has many advantages.[1] For example, side reactions accompanying modification are avoided and the distribution of functionality is far better controlled.

In this thesis, the specific functionality incorporated is the cyano group. The monomer, 2-cyanomethyl-1,3-butadiene (CMBD), is shown below. This functional group was chosen because of the interest in investigation of the polar effects of the cyano group on the monomer reactivity, polymer microstructure and final properties. It was anticipated that the cyano group could be converted to different functional groups, making the monomer or the resulting polymer precursors for the synthesis of other functionalized diene polymers. Furthermore, after hydrogenation, the synthesis of polar, functionalized polyolefins with an ethylene cyanoethylene type repeating unit could be obtained. Our interest is not only in synthesizing new, polar diene-based elastomers, but also in modifying existing materials. Specifically, it is anticipated that poly(2-cyanomethyl-1,3-butadiene), poly(CMBD), will be a useful additive to improve the compatibility and mechanical properties of polymer blends. It is also anticipated that the incorporation of the polar monomer as a covalently bound modifier in diene-based materials will aid in crosslinking or in tailoring existing properties. For example, in nitrile rubber (NBR), the higher the acrylonitrile content, the higher the resistance to hydrocarbons, impermeability to gases and thermal resistance, but the lower the



2-cyanomethyl-1,3-butadiene (CMBD)

resilience, the temperature flexibility and solution viscosity.[28,29] In other words, the oil resistance and low temperature flexibility are mutually incompatible. The cyano-substituted monomer could provide an ideal solution to this problem. It could be introduced covalently into NBR or styrene-butadiene rubber (SBR) as a third comonomer, taking advantage of the good solvent and oil resistance properties accompanying the cyano groups without decreasing the flexibility of the copolymer.

Previously, the cyano functionality has been introduced into butadiene at the C-1 or C-2 positions.[2,30] However, the key steps of the synthesis of these two monomers involved a pyrolysis process at temperatures greater than 500 °C. Moreover, 2-cyano-1,3-butadiene displayed a strong tendency to form Diels-Alder dimers. Herein, we report the synthesis of 2-cyanomethyl-1,3-butadiene, in which the cyano functionality was introduced under milder and more controlled conditions.

This thesis presented here focuses on the synthesis of 2-cyanomethyl-1,3-butadiene and the free-radical polymerization of this monomer. In addition to the bulk, solution and emulsion polymerizations, copolymerization with styrene and acrylonitrile will also be discussed. The comonomers were chosen due to the potential applications mentioned above. Furthermore, the thermal properties and microstructures of the homopolymers and the copolymers are examined.

Thesis Organization

This thesis is divided into three chapters. The first chapter discusses the synthesis of the desired monomer and polymers and the characterization methods. The second chapter describes the results of the work presented in the first chapter. The second chapter has three sections. The first section details the synthesis and purification of the desired monomer, CMBD. The second section discusses the results from the homopolymerization of CMBD. Three kinds of free radical polymerizations, bulk, solution and emulsion are described. The thermal properties and the polymer microstructures are discussed. The third section focuses on the copolymerization of CMBD with styrene and acrylonitrile. The spectroscopic, thermal, molecular weight characterization, reactivity ratios determination for both monomer pairs and the polymer microstructure assignment were detailed. The third chapter is the general conclusion that summarizes the results of the entire thesis.

The appendix contains the raw NMR, DSC, GPC and HR-MS data collected in this thesis.

The references include all the cited work in this thesis.

EXPERIMENTAL

Materials

Bromine was purchased from Alfa. All other reagents were purchased from Aldrich. Benzoyl peroxide (BPO) was purified by recrystallization from methylene chloride. Tetrahydrofuran (THF), acetone, dioxane, nitromethane, styrene, *o*-methylstyrene, allyl cyanide and acetonitrile (CH_3CN) were purified by distillation using calcium hydride or potassium. All other chemicals were used as received.

Synthetic Procedures

Monomer Synthesis. 2-Cyanomethyl-1,3-butadiene (III)

The monomer III was made in three steps. Bromine (159.82 g, 1 mol) was added dropwise to isoprene (68.12 g, 1 mol) in a 2 or 3 neck round bottom flask that was cooled using a dry ice/acetone bath.[31] The reaction temperature was monitored internally and was maintained below –20 °C. The yield of this step is > 99%. The product, 1,4-dibromo-2-methyl-2-butene (I), is a yellow liquid. Mass spectrometry (**M-1**): m/e = 228 g/mol. ^{1}H-NMR (300 MHz, $CDCl_3$, **N-1**): δ 5.91 (t, 1H), 3.96 (m, 4H), 1.88 (s, 3H). Compound I was used in the second step without further purification. 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) was added to a stirred solution of compound I using a 2:1 v/v ratio. The solution was heated until the temperature reached 120 °C. Vacuum was applied using an aspirator and 2-bromomethyl-1,3-butadiene (II) was collected (^{1}H-NMR: **N-2**). The product is a light yellow liquid. Mass spectrometry (**M-2**): m/e = 147 g/mol. Compound II was used in the third step without further purification. Compound II (73.5 g, 0.5 mol), sodium cyanide (73.3 g, 1.5 mol), acetonitrile (500 mL) and tetra-*n*-butylammonium chloride (2 g) were added together and stirred at room temperature for 48 hours. The resulting mixture was quenched with water, extracted with ether twice and washed with saturated sodium chloride solution. The overall yield for step 2 and step 3 is 35%. The product, 2-cyanomethyl-1,3-butadiene (III) was verified by ^{1}H-NMR (**N-3**) and GC-MS (**M-3**). Mass spectrometry: m/e = 93 g/mol.

Monomer Purification. 2-Cyanomethyl-1,3-butadiene (III)

The monomer purification was completed in two steps. A 300 mL stainless steel Parr reactor was used for step one. The vessel was precooled before loading by placing it in an acetone/dry ice bath. When the temperature was below –10 °C, it was charged with compound III (30 g), liquid sulfur dioxide (30 mL), methanol (10 mL) and hydroquinone (0.25 g). The vessel was sealed quickly, slowly heated to 85 °C, and maintained at that temperature for 4 hours. After cooling to room temperature, the resulting product, 2-cyanomethyl-1,3-butadienesulfone (IV) was filtered, washed with cold methanol and dried in a vacuum oven. The yield of this step is 35%. The product is a green crystalline solid with a molecular weight of 157 g/mol. The structure was verified by ^{1}H-NMR (**N-4**). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.20 (s, 1H), 3.91 (s, 2H), 3.79 (s, 2H), 3.30 (s, 2H). Compound IV (10 g) was added to a round bottom flask, stirred and heated up to 150 °C. A water aspirator, equipped with a cold trap, was used to collect the clear liquid product, compound III. The yield of this step is 85%. The structure was verified by GC-MS (**M-4**) and high resolution mass spectrometry (HR-MS). The theoretical mass was calculated to be 93.0578492 g/mol; HR-MS showed a measured mass of 93.05785354 g/mol with a deviation of 0.05 ppm. ^{1}H-NMR (300 MHz, $CDCl_3$, **N-5**): δ 6.46 (dd, 1H, J_1 = 12 Hz, J_2 = 8 Hz), 5.47 (s, 1H), 5.33 (s, 1H), 5.24 (d, 1H, *J* = 8 Hz), 5.19 (d, 1H, *J* = 12 Hz), 3.27 (s, 2H). ^{13}C-NMR (300 MHz, $CDCl_3$, **N-6**): δ 119.66, 135.30, 136.37, 115.07, 20.67, 117.27.

Homopolymer Synthesis. Poly(2-cyanomethyl-1,3-butadiene)

Bulk and Solution Polymerization. The monomer, solvent and initiator were added to an ampoule. After three cycles of freeze-pump-thaw, the ampoule was sealed under vacuum and heated to the desired temperature. A stabilizer, 2,6-di-*tert*-butyl-4-methylphenol (BHT), was added at the end of the reaction. The polymer was precipitated in methanol and dried in a vacuum oven. ^{1}H-NMR (300 MHz, CD_3CN): δ 5.52, 5.53 (1H), 3.18, 3.16 (2H), 2.1-2.4 (4H). The theoretical weight percents are 77.38 % C, 7.58 % H and 15.04 % N. Elemental analysis showed 76.58 % C, 7.92 % H and 14.02 % N. After each polymerization, ^{1}H-NMR spectroscopy of the polymerization mixture was performed. The conversion was calculated based on the integration ratio of the remaining monomer to the polymer from the proton NMR spectrum. The most characteristic proton signals used in the calculations were the C-5 methylene proton peaks in the monomer (3.27 ppm) and in the polymer (3.16-3.18 ppm).

Emulsion Polymerization. The monomer (1 g), potassium persulfate ($K_2S_2O_8$, 12 mg), sodium dodecylsulfate (SDS, 40 mg), sodium bicarbonate ($NaHCO_3$, 12 mg) and water (7.2 g) were added to a 50 mL three neck round bottom flask. The flask was supplied with N_2 (via a mineral oil bubbler) through a gas inlet adapter. The solution was degassed for half an hour before it was heated to 50 °C. After the desired reaction time, the vessel was cooled to room temperature. Saturated NaOH solution (2 mL) or acetone (2 mL) was added to destroy the emulsion. The polymer was precipitated in MeOH. The polymer was dissolved in THF containing a stabilizer, 2,6-di-*tert*-butyl-4-methylphenol and reprecipitated in MeOH. The polymer was dried in a vacuum oven and the yield was based on the polymer weight.

Copolymer Synthesis. Poly(2-cyanomethyl-1,3-butadiene-*co*-styrene) and poly(2-cyanomethyl-1,3-butadiene-*co*-acrylonitrile)

The monomers, solvent and initiator were added to an ampoule. After three cycles of freeze-pump-thaw, the ampoule was sealed under vacuum and heated to the desired temperature. A stabilizer, 2,6-di-*tert*-butyl-4-methylphenol, was added at the end of the reaction. The polymer was precipitated in methanol and dried in a vacuum oven. The conversion was calculated based on the amount of unreacted monomers as determined by GC or NMR.

Characterization

Polymer Characterization

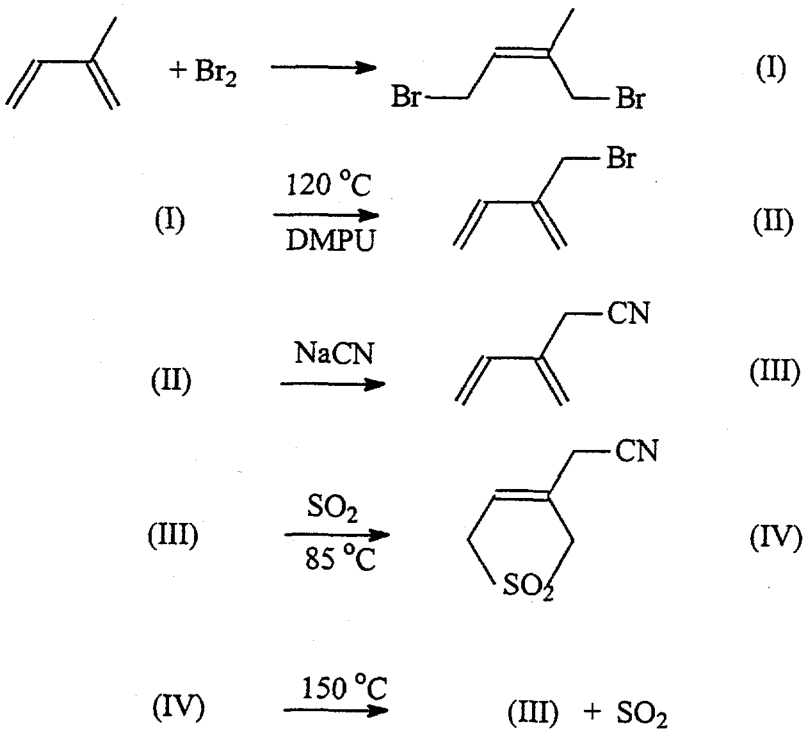
NMR examination was performed with a Varian VXR-300 and VXR-400 in deuterated chloroform or acetonitrile at room temperature. COSY and NOESY experiments were performed to elucidate the polymer microstructures. The molecular weights of the polymers were determined using a Waters gel permeation chromatography using polystyrene standards. The glass transition temperatures (T_g) were determined with a Perkin-Elmer Pyris Differential Scanning Calorimeter at a heating rate of 20 °C with helium purge. Glass transition temperatures were reported based on the second heating.

RESULTS AND DISCUSSION

Monomer Synthesis and Purification

The limited study of the polymerization of substituted 1,3-butadienes is mostly due to the difficulty in synthesizing and purifying the corresponding monomers. Our group first utilized a two-step synthesis to yield an important substituted 1,3-butadiene precursor, 2-bromomethyl-1,3-butadiene (II) starting from isoprene (**Scheme 1**). The first step, 1,4-addition of bromine to isoprene gave 1,4-dibromo-2-methyl-2-butene (I) in nearly quantitative yield.[31] Low reaction temperatures (< -20 °C) were necessary to avoid the production of other isomers. Subsequent dehydrobromination using DMPU gave compound II. Other side products included isomers of compound II and other bromides. Due to the

Scheme 1. Synthesis and Purification of 2-Cyanomethyl-1,3-butadiene



similarities of structures, all attempts to purify compound II using normal physical separation methods, distillation or flash chromatography, from the product mixture failed. Therefore, the mixture from the last step was directly used to proceed to the substitution reaction with sodium cyanide. This led to the desired 2-cyanomethyl-1,3-butadiene (III). Due to the high polymerization reactivity of CMBD, high temperatures were avoided and a phase transfer reagent, tetra-*n*-butylammonium chloride was used to shorten the reaction time. Again, it was almost impossible to purify CMBD using normal physical separation methods. Therefore, a two-step chemical purification using sulfur dioxide was used. The reactions of sulfur dioxide with dienes was first reported by R. L. Frank, *et, al.*[32] The dienes utilized were limited to 1,4-butadiene, isoprene and 2,3-dimethyl-1,3-butadiene. To our knowledge, this report is the first to detail the synthesis of a sulfonediene starting from a diene with a polar substituent. No peak other than 2-cyanomethyl-1,3-butadiene was observed by GC-MS (**G-4**). The proton NMR of compound III is shown in **H-4**.

Homopolymerization

Synthesis of Homopolymer

Three free radical polymerization methods: bulk, solution and emulsion were used to synthesize the homopolymer of 2-cyanomethyl-1,3-butadiene (CMBD). The results of the bulk free radical polymerizations of CMBD are listed in **Table 1** and in **Table 2**. Benzoyl peroxide (BPO) and 2,2'-azobisisobutyronitrile (AIBN) were used as the initiators in the bulk polymerizations. Several observations have been made. First, under the exact same polymerization conditions, AIBN repeatedly gave polymers with higher yields, but with

Table 1. Bulk Free-Radical Polymerization of CMBD at 75 °C

example #	initiator[a]	time (min)	$\langle M_n \rangle$ (x 10^{-3})	PDI	conv. (%)	DA yield (%)[b]	*cis/trans*[c]	GPC #
1	1% BPO	120	39.2	2.11	44	1	40:60	**G-1**
2	1% AIBN	20	20.3	1.50	10	<1	-[d]	**G-2**
3	1% AIBN	40	20.7	1.47	22	1	44:56	**G-3**
4	1% AIBN	60	21.4	1.52	33	1	41:59	**G-4**
5	1% AIBN	80	25.9	1.50	40	2	43:57	**G-5**
6	1% AIBN	100	25.7	1.71	53	2	41:59	**G-6**
7	1% AIBN	120	37.2	1.93	71	2	41:59	**G-7**
8	1% AIBN	140	33.9	3.37	80	3	40:60	**G-8**

[a] mole percentage
[b] Diels-Alder dimer yield
[c] *cis/trans* ratio in 1,4 structure
[d] not available

similar molecular weights as BPO initiated polymers (**Table 1**, Examples 1 and 7). Consequently, AIBN was used in further bulk polymerizations. Secondly, in a kinetic study of the bulk polymerization of CMBD (75 °C, 1% AIBN, **Table 1**, Examples 2-8), it was observed that with increased polymerization time, the conversion increased from 10% to 80% with no obvious autoacceleration seen. The number average molecular weight was nearly constant at approximately 20 x 10^3 g/mol during the first hour and increased at longer times. Within two hours, $\langle M_n \rangle$ reached 37 x 10^3 g/mol. The polymer did crosslink if the polymerization time exceeded 3 hours. The polydispersities of the resulting materials followed the same increasing tendency as the <M_n>. The increasing PDI and <M_n> could be due to the onset of branching, especially in example 8 (**Table 1**) with a PDI of 3.37. This explanation is consistent with the well-known fact that branching increases with conversion and may be a precursor to crosslinking.[22]

Bulk polymerizations were also performed at lower temperatures, 60 °C, using the same amount of initiator, 1 % AIBN. The results are shown in **Table 2** (Examples 1-5). As expected, the lower the polymerization temperature, the lower the propagation rate, as evidenced by significantly lower conversion at equivalent times (**Table 1**, Example 7, and **Table 2**, Example 1). The polydispersities were all near 1.5-1.6 showing no obvious

Table 2. Bulk Free-Radical Polymerization of CMBD at 60 °C and 45 °C

example #	initiator[a]	T (°C)	time (h)	<M_n> ($\times 10^{-3}$)	PDI	conv. (%)	DA yield (%)[b]	*cis/trans*[c]	GPC #
1	1%	60	2	27.6	1.53	12	1	36:64	**G-9**
2	1%	60	3	27.6	1.55	19	1	36:64	**G-10**
3	1%	60	4	27.6	1.64	27	2	36:64	**G-11**
4	1%	60	5	33.7	1.57	34	3	37:63	**G-12**
5	1%	60	6	35.8	1.61	38	4	36:64	**G-13**
6	0.5%	60	5	37.0	1.55	24	3	36:64	**G-14**
7	0.25%	60	5	45.3	1.55	17	3	37:63	**G-15**
8	1%	45	22	62.0	1.86	17	<1	32:68	**G-16**

[a] AIBN, mole percentage
[b] Diels-Alder dimer yield
[c] *cis/trans* ratio in 1,4 structure

change with time. This could be due to a decreased likelihood of branching at the lower 60 °C temperature. Polymerizations using lower AIBN concentrations, 0.5 % and 0.25 %, were also performed (**Table 2**, Examples 6 and 7). As the concentration of initiator decreased, the molecular weight increased and the conversion decreased. Bulk polymerizations were also performed at an even lower temperature, 45 °C (**Table 2**, Example 8). As we expected, the highest molecular weight ($<M_n> = 62 \times 10^3$ g/mol) was obtained at this temperature compared to those experiments at higher temperature with similar conversions (**Table 1**, Example 3, and **Table 2**, Example 2). Obviously, a longer reaction time was needed to reach similar yields due to the lower propagation rate at lower temperatures. In summary, homopolymers of CMBD with $<M_n>$ from 20×10^3 g/mol to 62×10^3 g/mol have been synthesized and the bulk polymerization behavior follows traditional free radical polymerization theory.

In free radical polymerization, polarity has the major effect on the overall rate of addition. In diene type systems, the corresponding radicals are nucleophilic and electron withdrawing substituents facilitate the addition of the nucleophilic radicals. Therefore, the reactivity of CMBD should be larger than isoprene and 5-(*N,N*-dialkylaminoisoprene). Our experiments have confirmed this prediction. Under the same polymerization conditions in **Table 1** (1% AIBN, 75 °C), isoprene afforded less than a 5% yield after 2 hours and 35% after 24 hours. The aminoisoprenes, other polar monomers examined in the Sheares group, have also showed this effect, providing 50 – 60% yield (methyl: 52%, ethyl: 58%, *n*-propyl: 56%, isopropyl: 60%, butyl: 60%) after 24 hours. Isoprene is the least readily polymerized under free radical conditions in bulk presumably due to the high mutual termination of growing radicals.

The results of solution radical polymerizations of 2-cyanomethyl-1,3-butadiene are shown in **Table 3**. In order to examine the influence of solvent polarity, solubility, chain transfer, etc. on the polymerizations, the solvents chosen were dioxane, THF, acetone, acetonitrile and nitromethane. Using dioxane as the solvent (**Table 3**, Examples 1 and 2), two layers were observed during polymerization, indicating precipitation of the polymers. Therefore, dioxane was not further studied as it is a poor solvent for poly(2-cyanomethyl-1,3-butadiene). Using THF as the solvent and identical polymerization conditions, BPO gave polymers with higher molecular weight than AIBN initiated polymers (**Table 3**, Examples 3-4). This could be a result of BPO having a longer half-life than AIBN at the same temperature. BPO was therefore chosen as the initiator for the remaining solution polymerizations. Various concentrations of initiator and amounts of THF were examined. The results are shown in **Table 3**, Examples 5-14. The polymerization behavior followed traditional free radical polymerization theory. The higher the amount of solvent used, the lower the conversion and the lower the molecular weight of the resulting polymers due to chain transfer to solvent. With a lower concentration of initiator, higher molecular weights were accompanied with lower yields. The highest $<M_n>$ obtained was 87 x 10^3 g/mol, using the lowest amount of initiator (**Table 3**, Example 14). Using varying amounts of THF (**Table 3**, Examples 5-7), the chain transfer constant in THF was calculated to be 1.15 x 10^{-3}, assuming the solvent is the main chain transfer agent. Other polar solvents, acetone, acetonitrile and nitromethane were also used (**Table 3**, Examples 15-17). In each case,

Table 3. Solution Free-Radical Polymerization of CMBD at 75 °C

#	initiator[a]	solvent	ratio[b]	time (h)	<Mn> (x 10^{-3})	PDI	conv. (%)	DA yield[c]	*cis/trans*[d]	GPC#
1	1% BPO	dioxane	3:1	24	18.2	2.59	80	-[e]	-	**G-17**
2	1% BPO	dioxane	5:1	24	14.4	1.99	85	-	-	**G-18**
3	1% BPO	THF	2:1	18	18.3	1.92	60	1	-	**G-19**
4	1% AIBN	THF	2:1	18	9.4	1.78	65	<1	-	**G-20**
5	1% BPO	THF	1:1	12	32.6	2.28	72	3	47:53	**G-21**
6	1% BPO	THF	2:1	12	20.6	1.60	45	1	50:50	**G-22**
7	1% BPO	THF	3:1	12	16.1	1.58	40	1	51:49	**G-23**
8	0.1% BPO	THF	1:1	12	59.0	1.75	34	5	48:52	**G-24**
9	0.1% BPO	THF	1:1	24	66.2	1.89	40	6	46:54	**G-25**
10	0.05% BPO	THF	1:1	24	68.8	1.73	27	10	47:53	**G-26**
11	0.01% BPO	THF	1:1	24	81.2	1.73	17	12	48:52	**G-27**
12	0.1% BPO	THF	0.5:1	24	82.1	2.28	53	12	45:55	**G-28**
13	0.05% BPO	THF	0.5:1	24	78.0	1.94	39	15	45:55	**G-29**
14	0.01% BPO	THF	0.5:1	24	87.3	1.86	29	16	48:52	**G-30**
15	1% BPO	acetone	1:1	12	36.6	4:50	78	-	-	G-31
16	1% BPO	acetonitrile	1:1	12	28.6	2.66	57	-	-	G-32
17	1% BPO	nitromethane	1:1	12	-	very broad	82	-	-	G-33

[a] mole percentage
[b] solvent/monomer volume ratio
[c] Diels-Alder dimer yield
[d] *cis/trans* ratio in 1,4 structure
[e] not available

polymers with polydispersities larger than 2.6 were obtained. This is due to the high degree of chain transfer to these solvents, which have acidic hydrogens.

A very interesting aspect of the polymerization of 1,3-butadienes is the tendency to form Diels-Alder dimers. Although reported in several references, this behavior is not observed in every case.[30,17,18, 33,34] In our research, small amounts of the Diels-Alder dimers of 2-cyanomethyl-1,3-butadiene were observed both in the bulk and solution polymerizations. The dimers were separated and the structure was proven by GC-MS (**M-5**) using the chemical ionization method. The yields of the dimers are listed in **Tables 1-3**. As can be seen, the dimer yield (DA yield %) typically increased with polymerization time, decreasing concentration of initiator and decreasing amount of solvent used. To test this theory, a polymerization was run, optimizing the potential contributing factors (no initiator, bulk, 75 °C). Indeed, this reaction yielded more Diels-Alder dimers than 1,4 and 3,4-addition products combined. It was concluded that the Diels-Alder reaction is a competitive process to the normal addition polymerization reactions and the degree to which it occurs is significantly influenced by the above mentioned factors.

Emulsion polymerization was also used to synthesize poly(2-cyanomethyl-1,3-butadiene). The advantages of the technique are well known, including good thermal control and the use of water instead of an organic solvent. Moreover, increasing the molecular weight while increasing the polymerization rate becomes possible. Various conditions were examined. The recipe used in a few examples and the results obtained are shown in **Table 4**. High molecular weight polymer was obtained in an hour (conv. = 22%, $\langle M_n \rangle = 128 \times 10^3$ g/mol, PDI = 2.46, *cis/trans* in 1,4 structure = 34:66). However, due to the high molecular

Table 4. Emulsion Polymerization of Compound III at 50 °C

example #	time (h)	conv. (%)	$\langle M_n \rangle$ (x 10^{-3})	PDI	GPC #
1	1	22	128	2.46	**G-34**
2	1.5	42	cross-linked		
3	2	56	cross-linked		

Recipe (by weight): monomer 25, water 180, SDS 10, potassium persulfate 0.3, sodium bicarbonate 0.3.

weight and the existence of reactive cyano groups along the backbone, the polymer crosslinked at higher conversions (> 40%). Though it appears not to be practical to synthesize the homopolymer of CMBD using emulsion polymerization techniques, the monomer could be used in small percentages as a potential third comonomer in emulsion copolymerizations. For example, it could be incorporated into commercial NBR or SBR, taking advantage of the high reactivity and the good solvent and oil resistance properties accompanying the cyano groups, without decreasing the flexibility of the copolymer.

Thermal Characterization of Poly (2-cyanomethyl-1,3-butadiene)

The glass transition temperatures of poly(2-cyanomethyl-1,3-butadiene) were measured by DSC. The T_g of example 7 in **Table 1** ($\langle M_n \rangle = 37.2 \times 10^3$ g/mol, *cis* : *trans* = 41 : 59, **T-1**) is –18 °C, which as expected is much higher than the T_g of polyisoprene due to the polar cyano substituent. The T_g of example 4 in **Table 2** ($\langle M_n \rangle = 33.7 \times 10^3$ g/mol, *cis* : *trans* = 37 : 63, **T-8**) is –15 °C, slightly higher than –18 °C due to the higher percentage of *trans* microstructure. The T_g of example 4 in **Table 2** ($\langle M_n \rangle = 87.3 \times 10^3$ g/mol, *cis* : *trans*

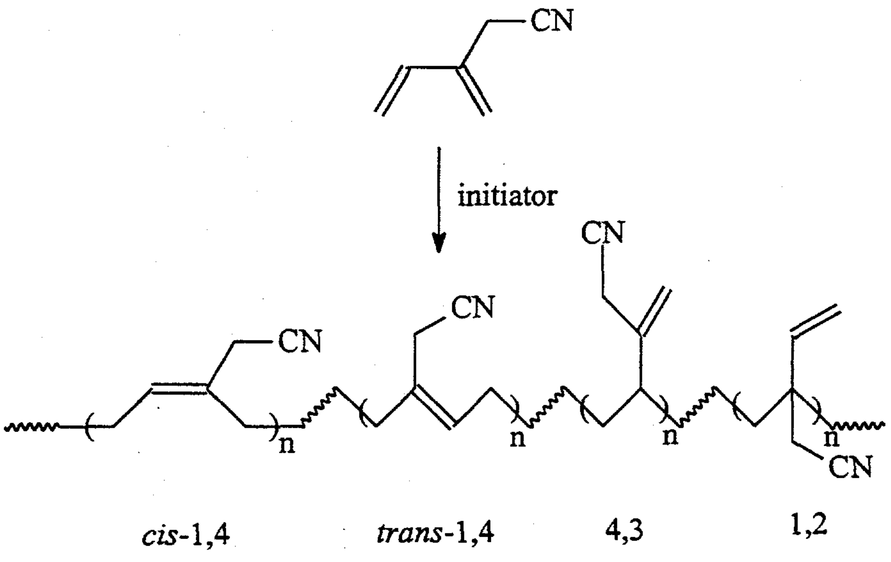
= 48 : 52) is –15 °C, also higher than –18 °C though it has a higher *trans* microstructure. The reason is due to its much higher molecular weight than example 7 in **Table 1**.

Polymer Microstructure.

Due to the close relationship between microstructure and polymer properties, the elucidation of the polymer microstructure is not only interesting, but also crucial in establishing structure/property relationships. There are four possible microstructures of CMBD, as shown in **Scheme 2**: *cis*-1,4, *trans*-1,4, 4,3 and 1,2.

The ^{1}H-NMR spectrum of poly(2-cyanomethyl-1,3-butadiene) in CD_3CN is shown in **Figure 1**. As can be seen, there are two signals at δ 5.52 and 5.43 ppm, which correspond to the vinylic protons in the 1,4 structures. A small amount of 4,3 structure (~ 5%) was observed, as determined by the characteristic vinylic proton peak at approximately δ 5.0

Scheme 2. Polymerization of 2-Cyanomethyl-1,3-butadiene



ppm, upfield from the 1,4 hydrogens. No obvious 1,2 structure was seen. The peaks attributed to the C-5 methylene protons next to the cyano group appeared as one peak at δ 3.12 ppm in $CDCl_3$ and were split into two peaks at δ 3.18 ppm and 3.16 ppm in CD_3CN. The signals at δ 2.1- 2.4 ppm were attributed to the methylene protons along the polymer backbone. The integration ratio of peak areas at δ 5.5, δ 3.2 and δ 2.2 was close to 1:2:4, respectively, which verified the polymer microstructure was almost all 1,4 structure.

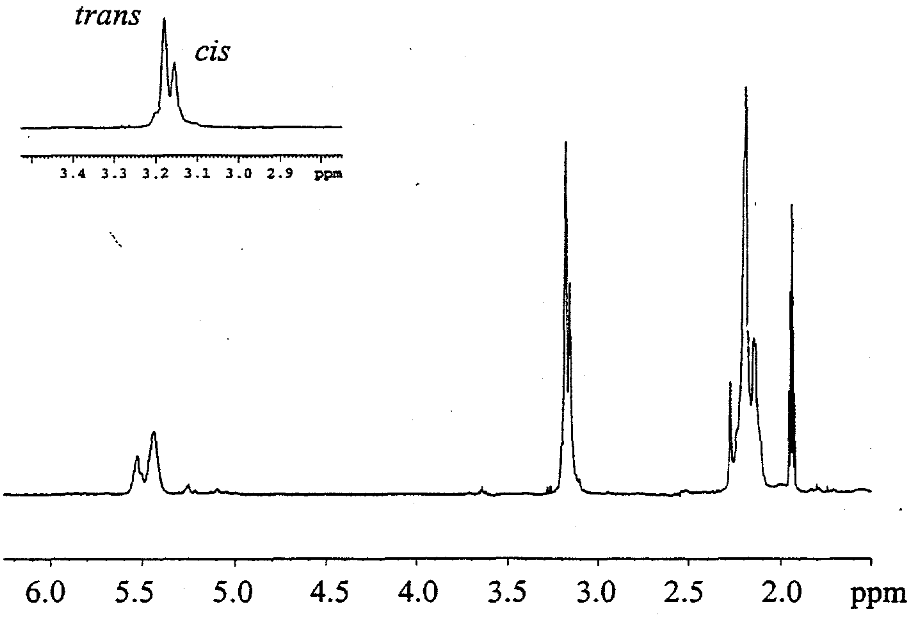


Figure 1. ^{1}H-NMR spectrum of poly(CMBD).

To elucidate the designation of *cis* and *trans* microstructure in the proton NMR spectrum, COSY and NOESY experiments were performed. Similar experiments were utilized previously to distinguish the microstructures of other substituted dienes.[16] **Figure 2** (N-7) shows the COSY spectrum of poly(2-cyanomethyl-1,3-butadiene) using CD_3CN as the solvent. The crosspeaks at (2.2, 5.4) and (2.2, 5.5) correspond to the coupling between vinylic protons and methylene protons along the polymer backbone. Only in the *cis*-1,4 microstructure is long distance coupling seen between the vinylic proton and the C-5 methylene protons. In the *trans* structure, this coupling does not exist and is not seen. Therefore, the existence of a crosspeak at (3.16, 5.5) and the absence of a crosspeak at (3.18, 5.4) was strong evidence for the designation of the *cis* and *trans* vinylin protons in the ^{1}H-NMR spectrum. Using $CDCl_3$ as the solvent, the same behavior was observed. Similar evidence was also obtained in the NOESY experiment. Since the short distance contacts between the vinylic protons and C-5 protons are only expected in the *cis* structure, it was easy to distinguish *cis* from *trans* in the spectra. **Figure 3 (N-8)** shows the resulting NOESY spectrum using $CDCl_3$ as the solvent, whose pattern was very similar to that of COSY.

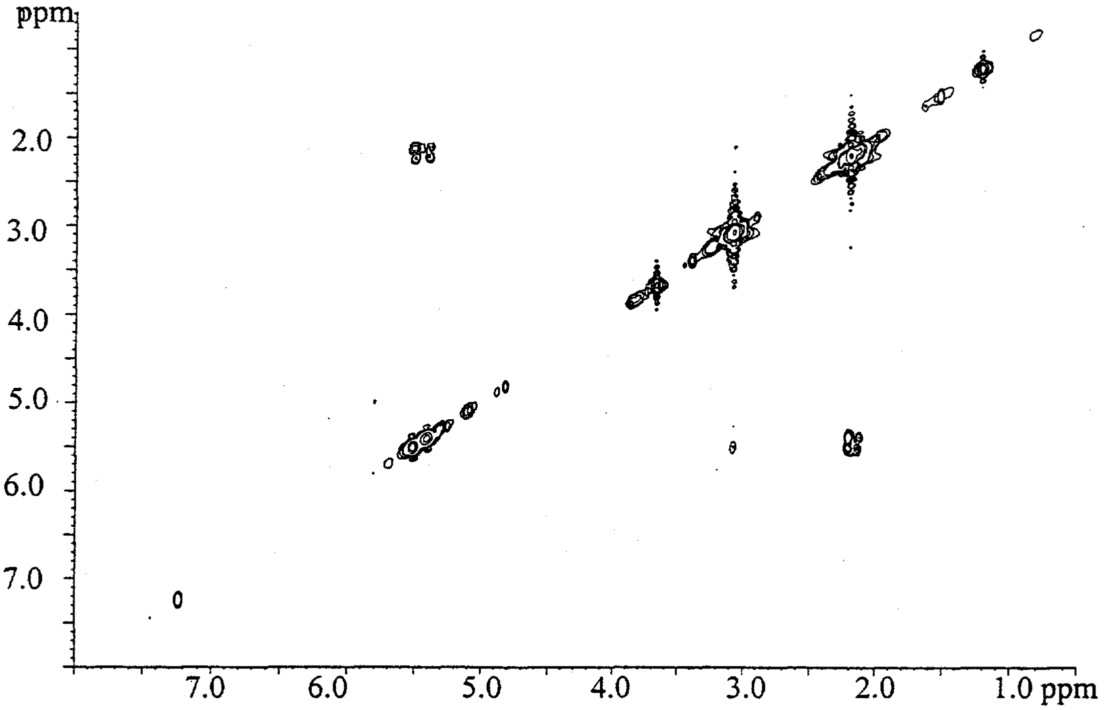


Figure 2. ^{1}H 2D-COSY spectrum of poly(CMBD).

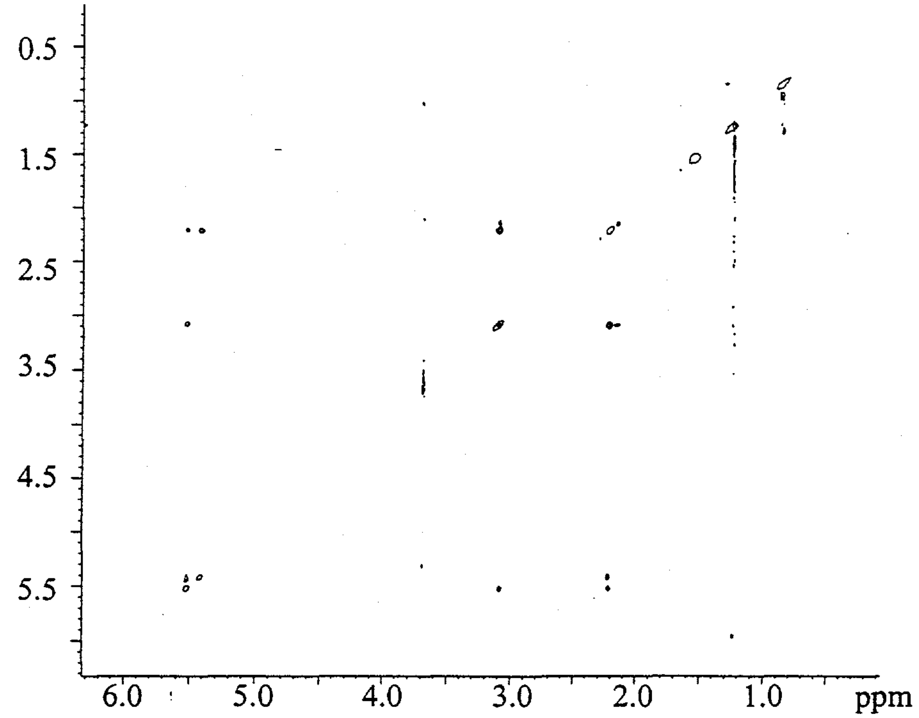


Figure 3. ^{1}H 2D-NOESY spectrum of poly(CMBD).

Crosspeaks at (2.2, 5.5) and (2.2, 5.4) were both observed. This was easily explained as the short distance contacts between vinylic protons and methylene protons along the polymer backbone. A crosspeak at (3.16, 5.5) was observed, but there was no sign of a crosspeak at (3.18, 5.4). This nicely supported our previous designation of vinylic protons in the ^{1}H-NMR spectrum. Due to the short distance between the C-5 methylene peaks in the proton spectrum and the small chemical shifts in the two-dimensional NMR spectra, there is no direct evidence for distinguishing the C-5 protons in different microstructures from the experimental results described previously. However, logical assignments can be made by correlating the methylene hydrogens and the vinylic hydrogens. For example, an increase in the peak area at δ 3.16 ppm with the increase of the *cis/trans* ratio was always observed. Therefore, it is reasonable to attribute the peak at δ 3.16 ppm as the C-5 protons in the *cis* microstructure and the peak at δ 3.18 ppm as *trans* microstructure. The integration ratios are also consistent with our conclusion.

Based on the previous designation of polymer microstructure, the ratios of *cis* and *trans* microstructures in the obtained polymers were determined based on the integration ratio of peaks at δ 3.16 ppm and δ 3.18 ppm. The results of various polymers obtained under different polymerization conditions were compared. The most obvious factor that was found to influence the microstructure was the polymerization temperature. In bulk or solution polymerizations, at the same temperature, polymers with almost the same microstructure ratios were obtained (**Tables 1-3**). It is well-known that temperature affects the microstructure distributions of diene polymers in free radical polymerization. For polyisoprene or polychloroprene, the higher the temperature, the higher the percentage of *cis* structure.[35] Similar tendencies were observed in poly(2-cyanomethyl-1,3-butadiene). The *cis*/*trans* ratio increased from approximately 32% to 36% to 45%, as the polymerization temperature was increased from 45 °C to 60 °C to 75 °C. It seemed that no obvious relationship existed between microstructure and the type of the initiator, the concentration of the initiator or the reaction time. At the same 75 °C temperature, the *cis*/*trans* ratios in bulk polymerization were consistently slightly lower than those in solution polymerization. This may be some indication that the microstructure could also be dependent on the polymerization method as well.

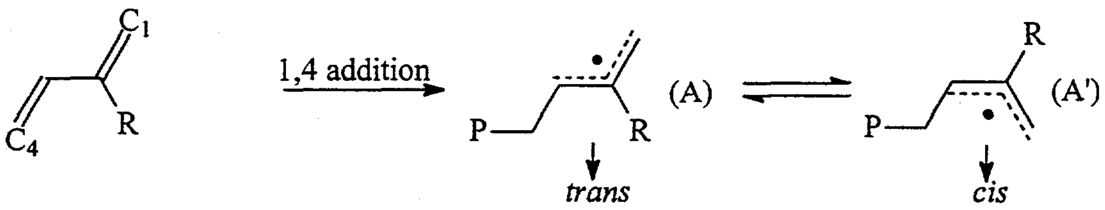
As can be seen in **Table 5**, at the same temperature 75 °C, the *trans*-1,4 structure is favored over the *cis*-1,4 structure in poly(CMBD) and polyisoprene and the contrary is observed for poly(*N*,*N*-dialkylaminoisoprene). Those observations can be rationalized by arguments similar to those used by Penelle's group to explain the mictrostructures of poly(TMSBD) and poly(TBMSBD).[13] **Scheme 3** shows the main polymerization addition route for butadiene derivatives, 1,4 addition. Two radicals A and A' are formed and in equilibrium. The radical A will result in the *trans* structure and A' will result in the *cis* structure. In the equilibrium A is usually favored over A' to avoid the interaction between

Table 5. Microstructure of Various Butadiene Derivatives

Polymer	T (^{o}C)	% *cis* ratio in 1,4-structure
Poly(CMBD)	45	32
	60	36
	75	42 - 48
Polyisoprene	75	18
Poly(*N*, *N*'-dimethylaminoisoprene)	75	74
Poly(*N*, *N*'-diisopropylaminoisoprene)	75	95
Poly(TMSBD)[a, 13]	60	39
	90	43
Poly(TBSMBD)[b, 13]	60	56
	90	66

[a]: 2-(trimethylsiloxy)butadiene [b]: 2-(*tert*-butyldimethylsiloxy)butadiene.

Scheme 3. The 1,4-Addition of Butadiene Derivatives



the terminal allyl hydrogen atom in the rigid system and the CH_2 group on the other side. Once the side group's size became bulky, the equilibrium will shift to the right side due to the steric hindrance. This can explain the *cis* structure series in **Table 5**, poly(*N,N*-dialkylaminoisoprene) > poly(CMBD) > polyisoprene. If the side group is very bulky, *cis* structure will predominate. For example, poly(*N,N*-diisopropylaminoisoprene) has 95% *cis* structure.

Copolymerization

Synthesis of Copolymers

Copolymers of CMBD with styrene and acrylonitrile were synthesized via solution free-radical polymerization in THF using BPO as the initiator (**Scheme 4**). The conversions and the copolymer compositions were monitored by NMR or GC.

The results of poly(2-cyanomethyl-1,3-butadiene-*co*-styrene) (CMBD-Styrene) are listed in **Table 6**. As can be seen, when the CMBD feed composition increased from 15% to 85%, the copolymer composition increased from 28% to 94% within 12 hours. The number-average molecular weight of the copolymers s1 - s5 increased from 17.7 x 10^3 g/mol to 29.6 x 10^3 g/mol, which was close to the number-average molecular weight of poly(CMBD) synthesized under the same polymerization conditions. In each run, the CMBD composition in the copolymer was always higher than the CMBD feed composition. This suggested a higher reactivity of CMBD compared to styrene. This behavior was consistent with our measured reactivity ratios for the monomer pair, which will be illustrated later in this thesis. When the CMBD unit percentage in the copolymer increased from 28% to 94%,

Scheme 4. Copolymerization of CMBD with Styrene and Acrylonitrile

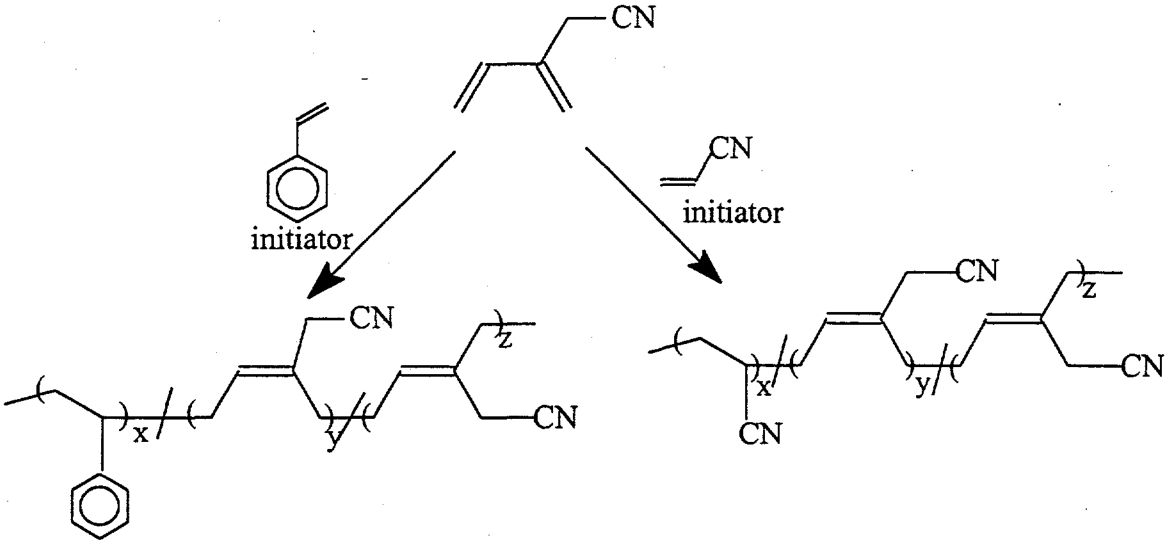


Table 6. Copolymerization of CMBD with Styrene (I)

Example #	Feed composition (c)[a]	Conv. % (c)[b]	Conv. % (s)[c]	Composition (c)[d]	$<M_n>$[e] ($x10^{-3}$)	PDI[e]	T_g (°C)[f]	GPC #	DSC #
s1	0.15	80	37	0.28	17.7	1.58	60.6	**G-35**	**D-2**
s2	0.25	70	22	0.51	18.7	1.77	45.7	**G-36**	**D-3**
s3	0.53	64	17	0.77	21.6	1.97	13.6	**G-37**	**D-4**
s4	0.75	62	16	0.92	25.8	2.08	2.7	**G-38**	**D-5**
s5	0.85	64	23	0.94	29.6	2.10	-2.9	**G-39**	**D-6**

Polymerization condition: solution free-radical polymerization, 75 °C, 1% BPO as the initiator, 1:1 THF as the solvent, 12 hours.

[a]: percentage of CMBD in the feed
[b]: percentage conversion of CMBD
[c]: percentage conversion of styrene
[d]: content of CMBD in the copolymer
[e]: data obtained by GPC
[f]: data obtained by DSC

the copolymer appearance changed from a white solid to a tacky solid. All the copolymers were soluble in chloroform, but not completely soluble in the more polar solvent acetonitrile. This differs from the solubility of homopoly(CMBD), which was soluble in acetonitrile and not completely soluble in chloroform. This is easily understood because the less polar styrene unit contained in the copolymer decreased the solubility parameter of the copolymer compared to the homopolymer.

Table 7 shows the kinetic results of one copolymerization starting with a 50:50 feed

Table 7. Copolymerization of CMBD with Styrene (II)

Example #	Initiator	Time (h)	Conv. % (c)[a]	Conv. % (s)[b]	Conv. % (t)[c]	Copolymer composition (c)[d]	$<M_n>$[e] ($x10^{-3}$)	PDI[e]	GPC #
s6	1%	4	32	5	18	0.97	20.7	1.74	**G-40**
s7	1%	8	54	20	37	0.73	19.9	1.91	**G-41**
s8	1%	12	77	26	52	0.75	21.7	2.33	**G-42**
s9	1%	16	84	29	56	0.74	21.9	2.52	**G-43**
s10	1%	20	91	37	64	0.71	20.6	2.90	**G-44**
s11	1%	24	94	45	70	0.68	20.2	3.37	**G-45**
s12	0.1%	24	55	18	37	0.76	64.3	1.71	**G-46**

Polymerization condition: solution free-radical polymerization, 75 °C, BPO as the initiator, 1:1 THF as the solvent, CMBD:styrene feed ratio = 50:50.

[a]: percentage conversion of CMBD

[b]: percentage conversion of styrene

[c]: total conversion

[d]: content of CMBD in the copolymer

[e]: data obtained by GPC

ratio over a 24 hour period. As the polymerization proceeded, the conversions of CMBD and styrene increased. The CMBD composition in the copolymer dropped from 97% to 73% from 4 hours to 8 hours and then decreased slowly to 68% when the reaction was stopped at 24 hours. The number-average molecular weight of the copolymers s6 - s11 held constant near 20 x 10^3 g/mol as expected. The corresponding polydispersities of copolymers s6 – s11 increased from 1.74 to 3.37 with the polymerization time, suggesting an increase in polymer branching. Polymerization with a lower initiator concentration, 0.1% BPO, was also carried out (s12). Compared to copolymer s11, a relatively high molecular weight ($<M_n> = 64.3 \times 10^3$ g/mol) was obtained with a lower yield.

A similar series of poly(2-cyanomethyl-1,3-butadiene-*co*-acrylonitrile)s (CMBD-acryonitrile) a1 - a11 were synthesized in THF and their results are shown in **Table 8** and in **Table 9**. When the CMBD feed composition was lower than or equal to 35% (a1 and a2), the conversion of CMBD reached 100% within 12 hours. Since the homopolymer of acrylonitrile or copolymer with a high percentage of acrylonitrile is not soluble in THF, precipitation of polymer a1 and a2 from the solvent was observed and the polymerization reaction mixture became heterogeneous. Therefore, no data was reported for Examples a1 and a2. For copolymers a3 - a5, similar polymerization behavior was observed compared to s1 - s5. The CMBD composition was always higher than the feed composition, indicating a higher reactivity than that of acrylonitrile. Within 12 hours, the CMBD unit percentage in the copolymers increased from 65% to 84% when the CMBD feed composition increased from 50% to 80%. It was also noticed that the differences between the feed and actual compositions in the copolymers in CMBD/acrylonitrile system were not as large as in

Table 8. Copolymerization of CMBD with Acrylonitrile (I)

#	Feed[a] composition (c)	Conv. % (c)[b]	Conv. % (a)[c]	Copolymer composition (c)[d]	$<M_n>$[e] ($x10^{-3}$)	PDI[e]	T_g (°C)[f]	GPC #	DSC #
a1	0.25	-[g]	-	-	-	-	-		
a2	0.35	-	-	-	-	-	-		
a3	0.50	87	47	0.65	16.4	1.54	9.2	**G-47**	**D-7**
a4	0.65	83	52	0.75	24.3	1.76	5.0	**G-48**	**D-7**
a5	0.80	76	57	0.84	29.5	2.48	-0.2	**G-49**	**D-7**

Polymerization condition: solution free-radical polymerization, 75 °C, 1% BPO as the initiator, 1:1 THF as the solvent, 12 hours.

[a]: percentage of CMBD in the feed

[b]: percentage conversion of CMBD

[c]: percentage conversion of acrylonitrile

[d]: content of CMBD in the copolymer

[e]: data obtained by GPC

[f]: data obtained by DSC

[g]: not available

the CMBD/styrene system. For example, the difference in polymer s3 in **Table 6** was 23% while the difference in polymer a3 in **Table 7** was 15%. The kinetics of the copolymerization of CMBD with acrylonitrile were similar to that with styrene (**Table 9**). The conversions of CMBD and acrylonitrile increased with time and the CMBD composition in the corresponding copolymers decreased from 80% to 65% within 12 hours. The number-average molecular weights of the copolymers a6 - a9 were all near 16 x 10^3 g/mol. However, the increasing polydispersities were not observed as in the CMBD/styrene system. The PDI of copolymer a6 - a9 remained constant near 1.5. The copolymerization matrix became

Table 9. Copolymerization of CMBD with Acrylonitrile (II)

Example #	Initi-ator	Time (h)	Conv. % (c)[a]	Conv. % (a)[b]	Conv. % (t)[c]	Copolymer composition (c)[d]	$\langle M_n \rangle$[e] ($x10^3$)	PDI[e]	GPC #
a6	1%	3	34	8	21	0.80	16.8	1.50	**G-50**
a7	1%	6	64	27	45	0.71	16.3	1.50	**G-51**
a8	1%	9	87	49	67	0.65	13.5	1.64	**G-52**
a9	1%	12	87	47	67	0.65	16.4	1.54	**G-47**
a10	1%	15	-[f]	-	-	-	-	-	
a11	0.1%	12	38	25	0.60	0.60	23.6	1.43	**G-53**

Polymerization condition: solution free-radical polymerization, 75 °C, BPO as the initiator, 1:1 THF as the solvent.

[a]: percentage conversion of CMBD

[b]: percentage conversion of acrylonitrile

[c]: total conversion

[d]: content of CMBD in the copolymer

[e]: data obtained by GPC

[f]: not available

heterogeneous within 12-15 hours. The polymer precipitated from a10 was not completely soluble in THF, but was soluble in more polar solvents, such as acetone. Therefore, it was reasonable to conclude that the reason for precipitation during polymerization was not due to crosslinking, but was due to the poor solubility of CMBD-acrylonitrile containing a high percentage of acrylonitrile. All the CMBD-acrylonitrile copolymers were tacky solids due to the amount of CMBD the copolymers contained. The solubility of CMBD-acrylonitrile was close to the homopolymer of CMBD. They were all soluble in acetone, acetonitrile and THF and not completely soluble in chloroform. Therefore, the CD_3CN was used as the solvent in all NMR spectra of CMBD-acrylonitrile shown later. Polymerization with a lower initiator concentration, 0.1% BPO, was also carried out (a11). Compared to copolymer a9, a higher molecular weight ($<M_n> = 23.6 \times 10^3$ g/mol) was obtained with a lower yield.

Reactivity Ratios

Since a copolymer's composition and monomer sequence distribution are mainly dependent on the concentration of the monomers and the reactivity of the monomers relative to the propagating chain ends, it is crucial to investigate the reactivity ratios of monomer pairs in a copolymerization system. Two methods have been used to determine reactivity ratios in the previous literature on copolymerization.[35,36] One is based on the data of copolymer composition/conversion and the other is obtained from the information about monomer sequence distribution, typically gained from the copolymer NMR. The second method has some limitations, such as instrumental discrimination, ambiguous assignment of NMR signals to monomer sequences, etc. Thus, it has been used in few cases to calculate reactivity ratios directly. In this paper, the first method was utilized. Instead of the most traditional way, which usually needs the determination of copolymer composition at conversions close to zero (at least lower than 5%), a slightly different approach was taken, which involved the use of the Mayo-Lewis equation. The Mayo-Lewis equation, an integration equation derived from the copolymer composition differential equation, is compatible in cases with relatively higher conversions (higher than 10%). In the CMBD/styrene system, several copolymerizations with various feed ratios were performed. The polymerizations were stopped at conversions lower than 30% and were monitored by GC. The internal standards chosen, *o*-methylstyrene and allyl cyanide, were proven to have good correlations with styrene and CMBD, respectively. The values of data points plotted in **Figure 4** were obtained using the Mayo-Lewis equation. The intersection circle shows that r_1 (CMBD) is 3.0 ± 0.1 and r_2 (styrene) is 0.23 ± 0.03. In the CMBD/acrylonitrile system, similar polymerizations were carried out. Due to the inability to detect the acrylonitrile using

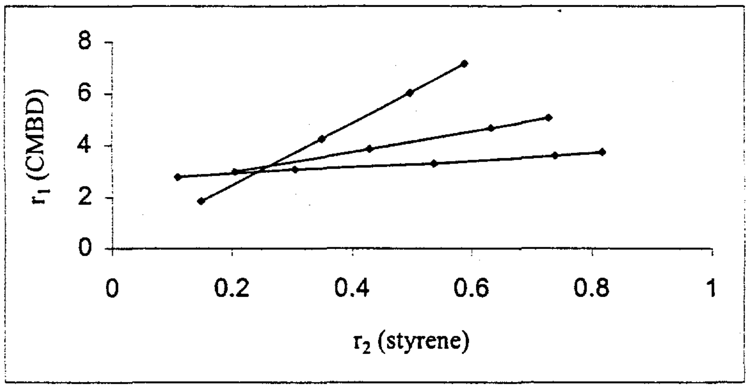


Figure 4. Reactivity ratios of CMBD and styrene.

the GC, NMR techniques were used instead to quantify the conversions. The calculations are based on the NMR integration ratio of the unreacted monomers and the internal standard. A similar r_1/r_2 plot was drawn and is shown in **Figure 5**. Because of the higher instrumental error of the NMR technique than the GC, the lines in the r_1/r_2 graph did not intersect in a circle as small as the CMBD/styrene system. The r_1 (CMBD) is 1.5 ± 0.3 and r_2 (acrylonitrile) is 0.4 ± 0.2. Therefore, the Q-e scheme was also tried to determine the reactivity ratios of CMBD and acrylonitrile. The Q-e values for styrene and acrylonitrile were obtained from literature and those for CMBD were derived from the measured reactivity ratio with styrene mentioned earlier ($Q = 2.67$, $e = -0.191$).[36] The calculation results show that r_1 (CMBD) is 4.2 and r_2 (acrylonitrile) is 0.03. This data is less reliable

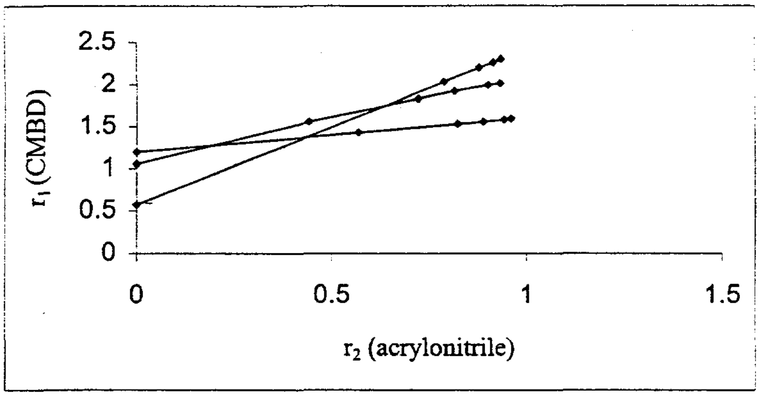


Figure 5. Reactivity ratios of CMBD and acrylonitrile.

compared to that from the r_1/r_2 plot due to the limited accuracy of Q-e parameters and the reliability of the Price-Alfrey equation assumption.

Table 10 shows various monomer reactivities with polymeric styrene and acrylonitrile radicals.[13, 36,37] As can be seen from the first column, CMBD had the highest monomer reactivity with the styrene radical. Because of the polar electron withdrawing cyano group, CMBD is more reactive than isoprene. The value is higher than butadiene due to the polarity in addition to the e-withdrawing group. CMBD was much more reactive than 2-(dimethylsiloxy)butadiene (2-TMSBD) and 2-(*tert*-butyldimethylsiloxy)butadiene (2-TBSMBD), because of the e-withdrawing nature of the cyano group compared with the e-donating siloxy groups and the steric hindrance of the silicon containing side groups. With the acrylonitrile radical, the trend is vague, probably due to the strong alternating tendency between acrylonitrile and butadiene or isoprene. The values of r_1r_2 for various monomer pairs are shown in **Table 11**.[13, 36,37] The greater the difference of the two monomer polarities, the lower the r_1r_2 value and the stronger the tendency to form alternating copolymers instead of random copolymers. The polarity of CMBD is between styrene and acrylonitrile

Table 10. Radical Reactivity (1/r) of Monomers with Various Polymer Radicals

	Polymer Radical	
Monomer	Styrene	Acrylonitrile
1,3-butadiene	1.72	21.7
isoprene	1.95	33.3
2-TMSBD	1.56	-[a]
2-TBMSBD	1.01	-
CMBD	4.35	2.5

[a]: not available.

and the polarity of butadiene and isoprene is close to styrene. The value of CMBD is the lowest in the first column because CMBD is the most polar monomer and the polarity difference with styrene is the highest. Similarly, the value of CMBD is the highest in the second column because its polarity difference with acrylonitrile is the smallest.

Table 11. The Values of r_1r_2 in Free-radical Copolymerizations

	Styrene	Acrylonitrile
1,3-butadiene	0.81	0.017
isoprene	0.99	0.014
2-TMSBD	0.77	-[a]
2-TBMSBD	0.70	-
CMBD	0.69	0.60

[a]: not available.

The determined reactivity ratios for the two copolymerizations are consistent with the polymerization behavior observed and they can be used to explain copolymer composition, monomer sequence distribution, etc. For example, the reactivity ratio of CMBD is higher than the other monomer in both copolymerization systems, which indicates a higher reactivity for CMBD compared to styrene or acrylonitrile. Since $r_1 > 1$, $r_2 < 1$ and $r_1r_2 < 1$ in both systems, the two copolymerization systems can be represented by two curved lines which do not intersect with the diagonal in a F/f graph (See **Figure 6**, F = instantaneous copolymer composition and f = monomer feed composition). Both of the systems belong to a nonideal nonazeotropic copolymerization. According to the plot, the copolymer will always be richer in CMBD than in styrene or acrylonitrile, which is consistent with what was observed. Under the exact same polymerization conditions including the monomer feed ratio, the difference between the copolymer composition and the initial monomer feed

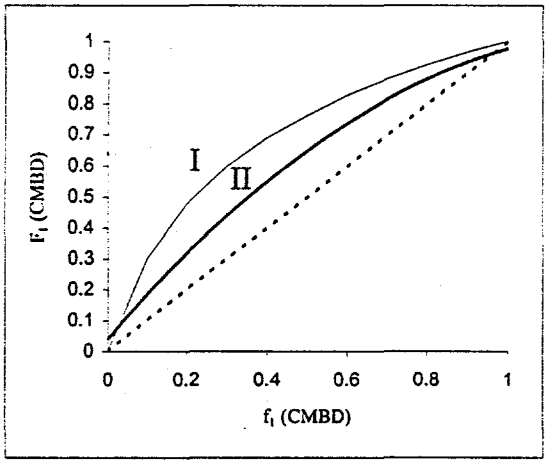


Figure 6. Dependence of the instantaneous copolymer composition F_1 on the initial comonomer feed composition f_1. Curve I: CMBD/styrene. Curve II: CMBD/acrylonitrile.

composition was always higher in the CMBD/styrene system than in the CMBD/acrylonitrile one. This was supported by the fact that curve I is further away from the diagonal than curve II in the F/f plot (See **Figure 6**), representing the ideal azeotropic copolymerization where the copolymer composition will be equal to the monomer feed ratio.

Thermal properties.

The glass transition temperatures (T_g) of the copolymers s1 - s5 are shown in **Figure 7** and those of a3 – a5 are shown in **Figure 8**. All the copolymers showed only one glass transition temperature, characteristic of a random copolymer. From **Figure 7**, it can be seen that the higher the CMBD content in the copolymer, the lower the glass transition temperature. The T_g decreased from 60.6 °C to –2.9 °C when the percentage of

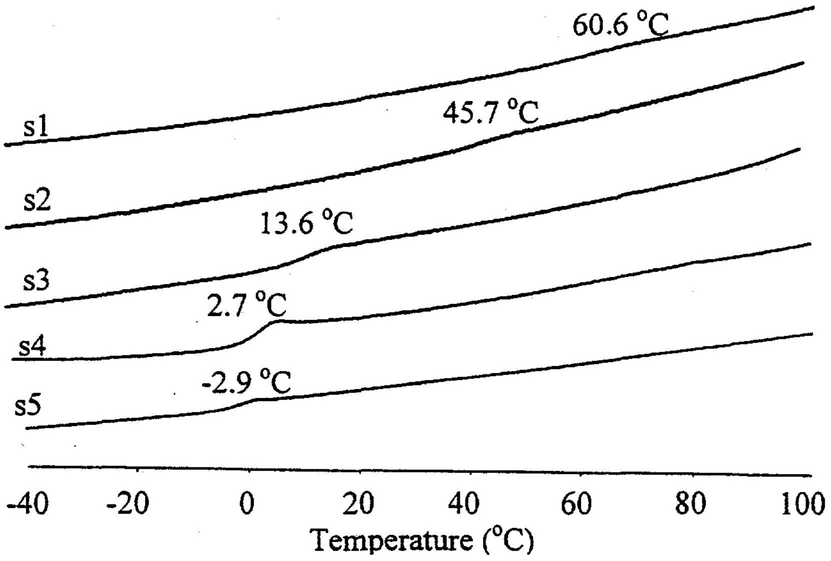


Figure 7. DSC data for the copolymers s1 – s5.

CMBD increased from 25% to 94%. A similar tendency is observed in **Figure 8**. When the CMBD composition in the copolymer increased from 65% to 84%, the T_g dropped from 9.2 °C to –0.2 °C. **Figure 9** illustrates the dependence of the glass transition temperature of the copolymers s1 – s5 on the weight percentage of CMBD in the copolymers. The theoretical line was obtained from the Gordon-Taylor equation, which usually fits the non-crystalline, random copolymer and was previously used successfully in the styrene-butadiene system. It can be seen that the data points for CMBD-Styrene fit the equation very well. Although not shown, the copolymers a3- a5 also fit the Gordon-Taylor equation.

NMR characterization of the copolymers.

The ^{1}H-NMR spectra of the copolymers s1 – s5 are shown in **Figure 10**. By comparing the ^{1}H-NMR spectra of the homopolymers, poly(CMBD) (See **Figure 1**) and

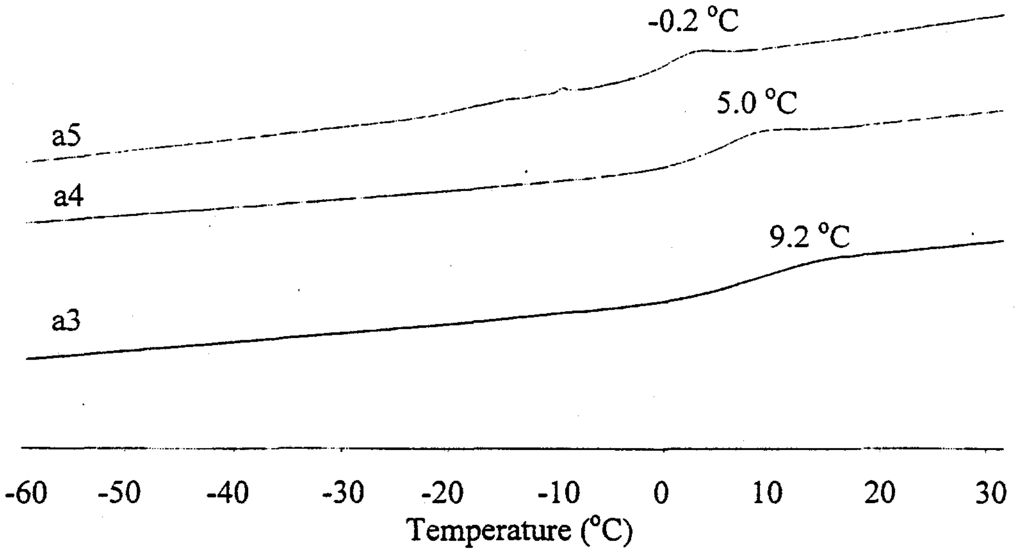


Figure 8. DSC data for the copolymers a3 – a5.

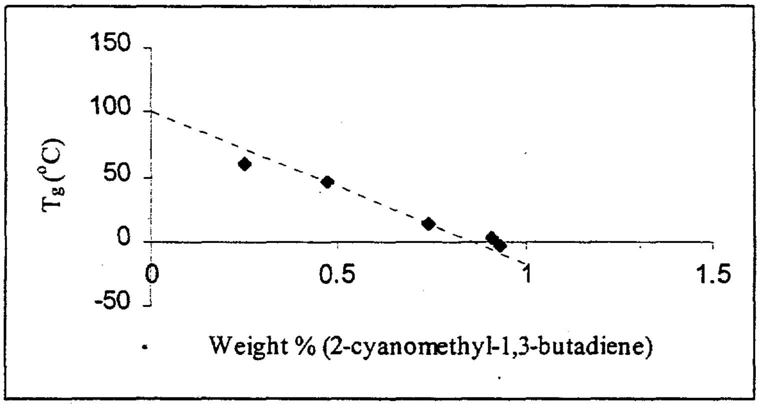


Figure 9. Copolymers s1 – s5: glass transition temperature T_g as a function of the weight of CMBD in the copolymer.

polystyrene, the signals of the copolymer spectra are easily assigned. The peaks attributed to the methylene protons next to the cyano group appear at δ 3.12 ppm with the upfield shoulders at δ 2.8 – 3.0 ppm possibly due to the presence of the hetero sequence. The signals at δ 1.0 – 2.5 ppm are attributed to methylene and methine protons along the backbone. The signals around δ 5.5 ppm correspond to the vinylic protons in the 1,4 structure of the CMBD unit in the copolymer. A small amount of 4,3 structure (< 5%) is observed, as determined by the characteristic vinylic proton peak at approximately δ 5.0 ppm, upfield from the 1,4 hydrogens. No obvious 1,2 structure is seen. The two signals at approximately δ 5.5 ppm are assigned to the *cis* and *trans*-1,4 structure as indicated in the homopolymer spectrum (See **Figure 1**). This pattern was only observed in the copolymer s3 – s5, but not in s1 and s2. This could be due to the equivalence of the *cis* and *trans* vinylic protons in the copolymer

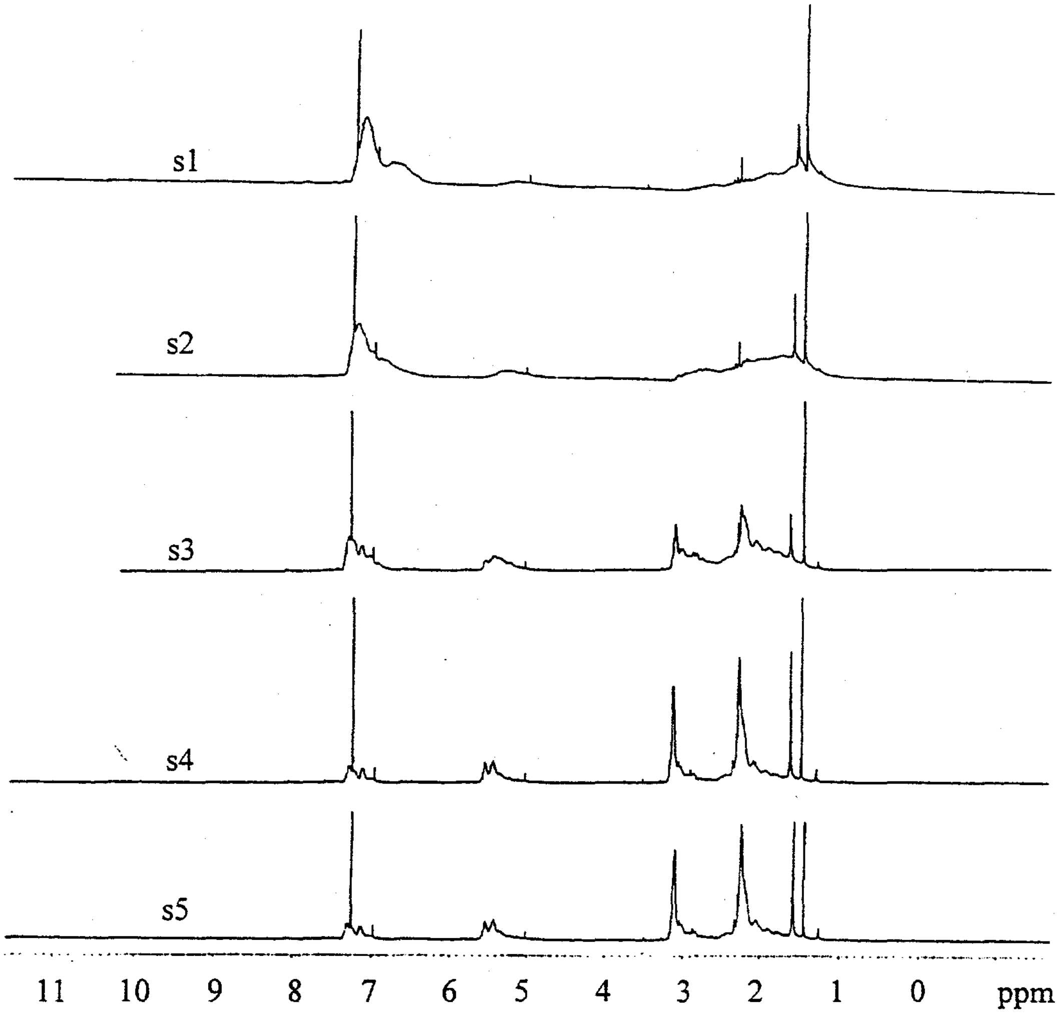


Figure 10. ^{1}H-NMR spectra of the copolymers s1 – s5. $CDCl_3$ as the solvent.

with a short CMBD sequence length. Therefore, it is reasonable to conclude that the CMBD sequence length increased from the copolymer s1 to s5, which is consistent with the increasing CMBD content from s1 – s5. The aromatic protons in the styrene unit appear from δ 6.9 – 7.4 ppm and the chemical shifts of the *ortho*-protons are further downfield than the chemical shifts of the *meta*- and *para*-protons. The integration ratio of the aromatic protons and the vinylic signals can be used to determine the copolymer composition. The results were consistent with what was calculated previously.

The ^{1}H-NMR spectra of the copolymers a3 – a5 are shown in **Figure 11**. As can be seen, the vinylic proton signals are further split compared to the NMR spectra of the poly(CMBD) (See **Figure 1**). Two new signals at δ 5.72 ppm and δ 5.60 ppm appear and the integration of the two new peaks increases with the acrylonitrile composition in the copolymer. It is reasonable to assign the two new peaks to the hetero sequence of CMBD. Therefore, the CMBD sequence length increases with its composition in the copolymer, from

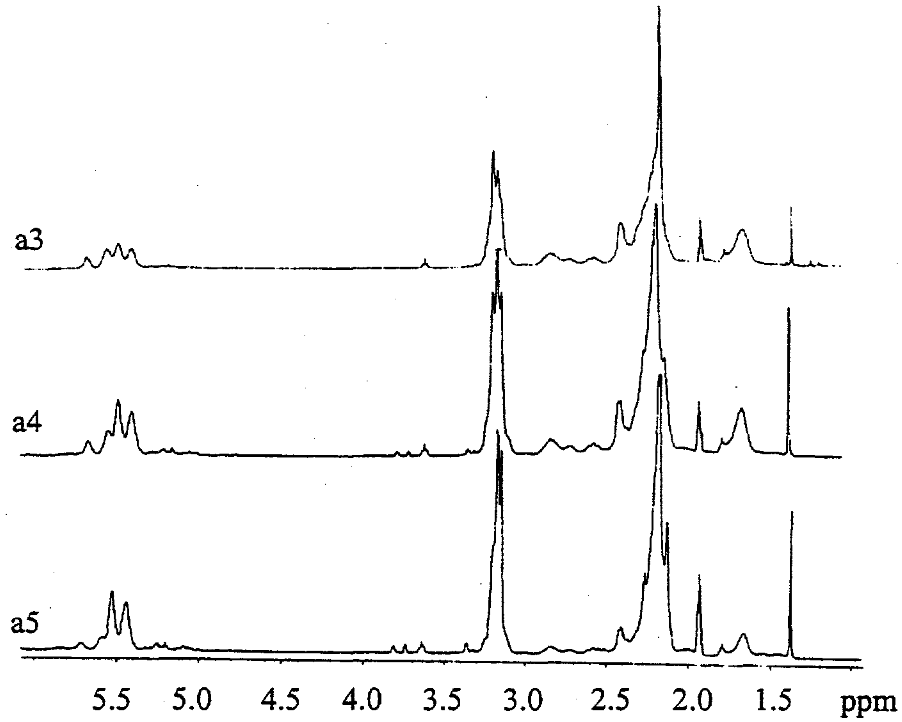


Figure 11. ^{1}H-NMR spectra of the copolymers a3 – a5. CD_3CN as the solvent.

a3 – a5. This is consistent with the splitting of the methylene proton signals around δ 3.2 ppm. In addition to the two signals, δ 3.16 ppm and δ 3.18 ppm, which appear in the spectra of the homopolymer, two new signals appear at δ 3.21 ppm and δ 3.25 ppm and follow the same decreasing trend as the sequence length of CMBD increases from the copolymer a3 – a5. Similar to the homopolymer and CMBD-Styrene, only a small amount of 4,3 structure is observed near δ 5.0 ppm and no obvious 1,2-structure is seen. The signals from δ 2.4 ppm to δ 2.9 ppm are attributed to the methine proton next to the cyano group in the acrylonitrile unit. The signals from δ 1.3 – 2.4 ppm correspond to the different methylene protons along the copolymer backbone.

GENERAL CONCLUSION

This thesis is a fundamental study of the free radical polymerization of a butadiene derivative with a strong polar cyano group, 2-cyanomethyl-1,3-butadiene (CMBD). It has been demonstrated that the monomer can be produced in a three-step synthesis under reasonable conditions. The monomer can reach more than 99% purity after a two-step chemical purification, making subsequent polymerizations feasible.

Homopolymers have been successfully made through bulk, solution and emulsion free radical polymerization techniques. Kinetics and the influence of various experimental factors have been examined. It has been found that in bulk polymerization, the reactivity of CMBD is larger than isoprene and 5-(*N*,*N*-dialkylaminoisoprene) (alkyl: methyl, ethyl, *n*-propyl, isopropyl, butyl). The reason is due to the strong electron withdrawing group, which facilitates the addition of the nucleophilic growing radicals. Diels-Alder dimers are found during the polymerization and their structures are verified by NMR and GC-MS. It has been determined that the Diels-Alder reaction is a competitive process to the normal addition polymerization and the yield of dimers typically increases with polymerization time, decreasing concentration of initiator and decreasing amount of solvent used.

The final polymers, with glass transition temperatures around –18 °C, are potential candidates after crosslinking for functionalized elastomers. The T_g is much higher than that of polyisoprene due to the polar cyano group.

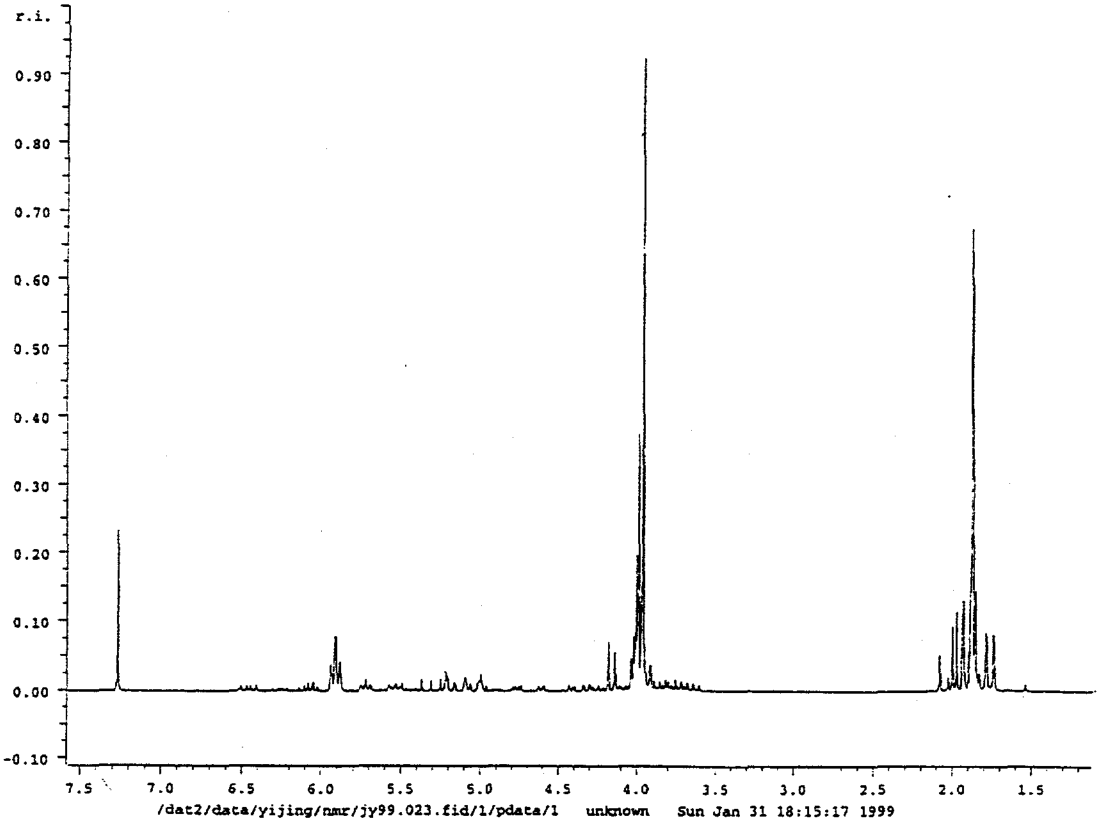
The microstructures of poly(CMBD) have been fully characterized by NMR. The *cis* and *trans*-1,4 structural designation is confirmed by COSY and NOESY spectra. The most obvious factor that is found to influence the microstructure is the polymerization temperature. The higher the temperature, the higher the percentage of *cis* structure. The *cis*/*trans* ratio increases from approximately 32% to 36% to 45%, as the polymerization temperature is increased from 45 °C to 60 °C to 75 °C. This tendency is consistent with polyisoprene and polychloroprene. It seems that no obvious relationship exists between the microstructure and the type of the initiator, the concentration of the initiator or the reaction time. The microstructure may also be dependent on the polymerization method.

Poly(2-cyanomethyl-1,3-butadiene-*co*-styrene) and poly(2-cyanomethyl-1,3-butadiene-*co*-acrylonitrile) have been successfully synthesized via free-radical solution polymerization and the copolymerization behavior investigated.

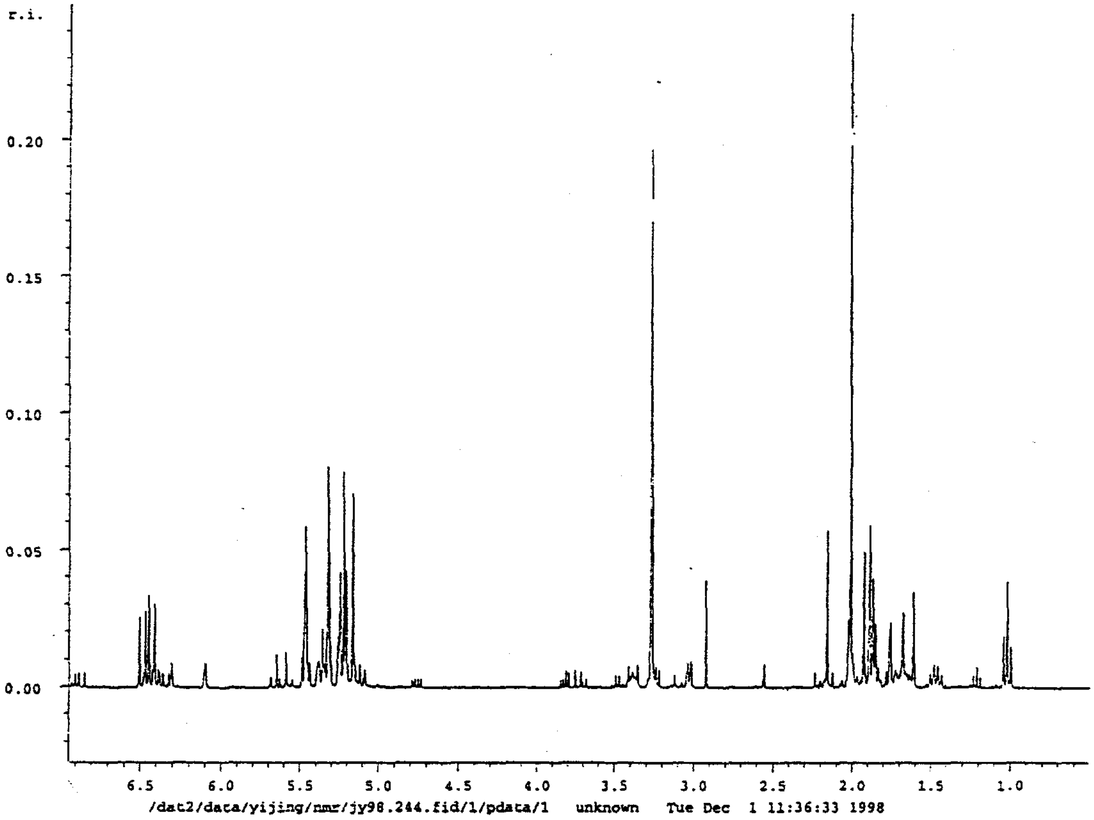
The reactivity ratios of CMBD with styrene and acrylonitrile have been determined by the Mayo-Lewis equation. The cyano-substituted monomer, CMBD, has a higher reactivity than styrene and acrylonitrile. Compared to butadiene, isoprene, 2-TMSBD and 2-TBMSBD, CMBD had the highest monomer reactivity with the styrene or acrylonitrile radical due to the strong electron-withdrawing group. The resulting copolymers' glass transition temperatures are dependent on the copolymer composition and fit the Gordon-Taylor equation. The copolymer composition is mainly controlled by the monomer feed ratio. All of the copolymers obtained are random, non-crystalline polymers, which showed only one T_g by DSC.

Although the results focus on the two-monomer copolymerizations, they imply that CMBD can be used potentially as a third comonomer in existing materials, such as SBR or NBR. Advantage can be taken of CMBD's high reactivity, as well as the good solvent and oil resistance properties accompanying the introduction of cyano groups, without decreasing the flexibility of the copolymers.

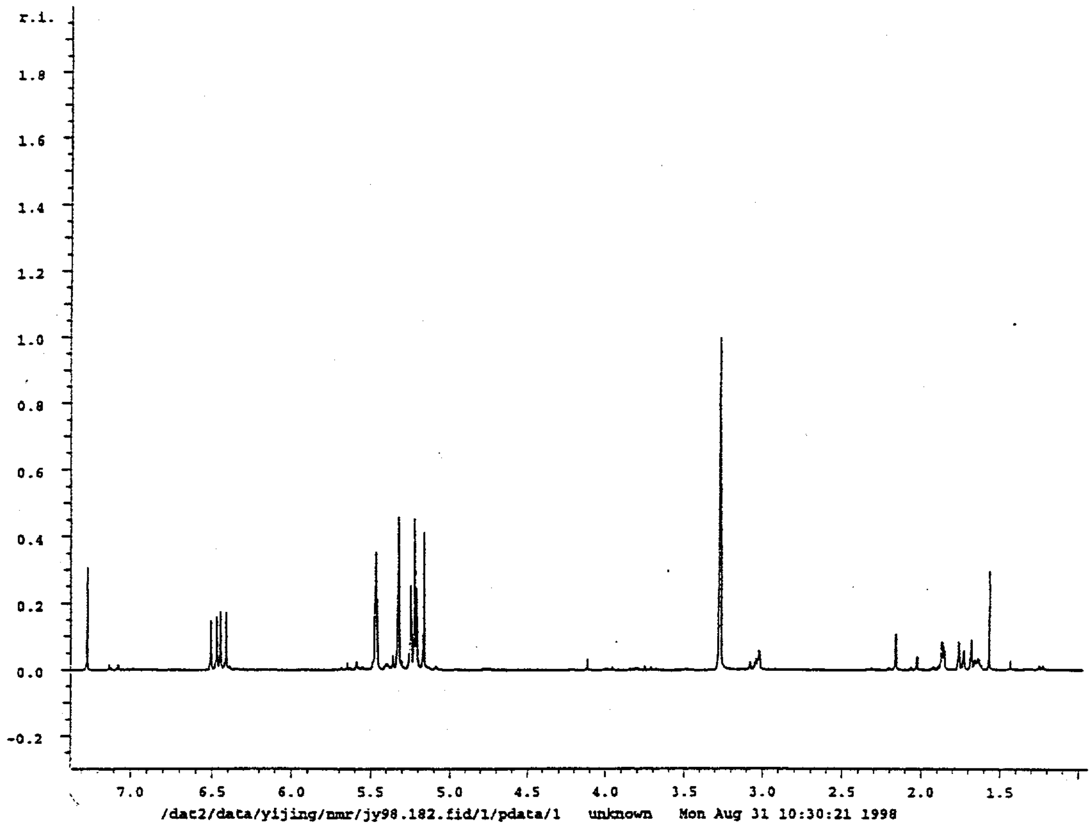
APPENDIX. RAW DATA



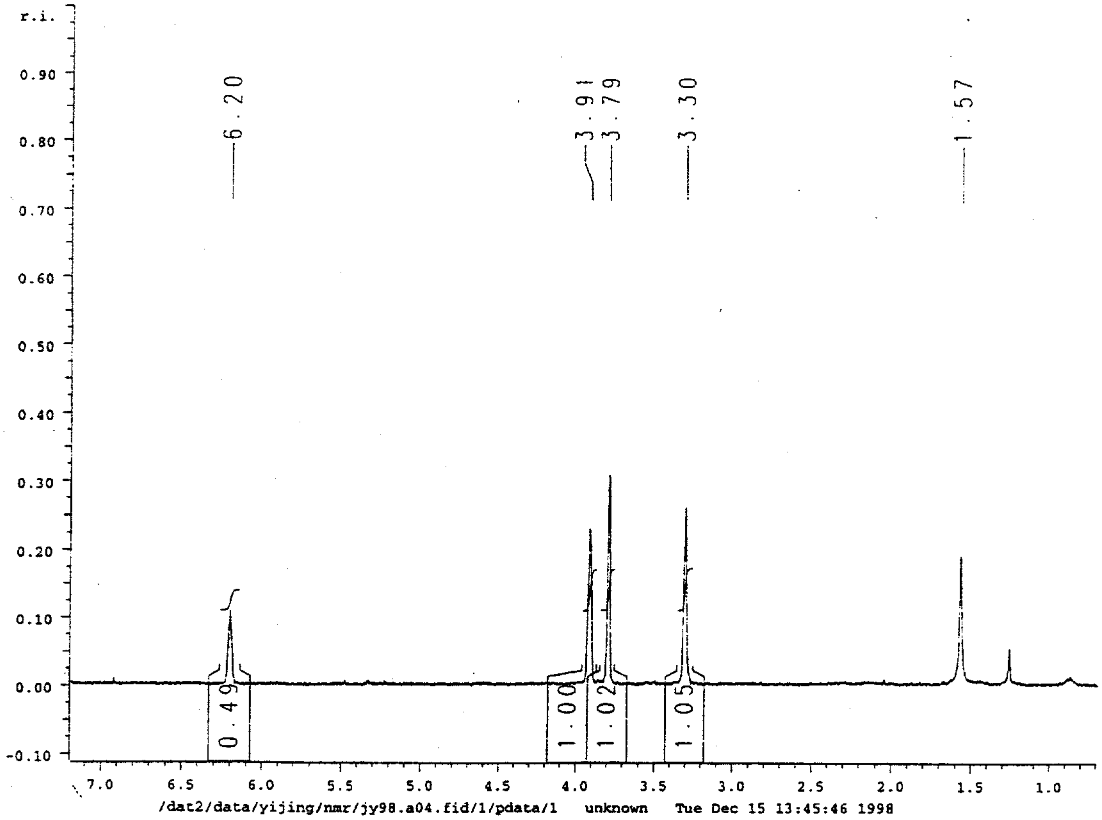
N-1. ^{1}H-NMR spectra of 1,4-dibromo-2-methyl-1,3-butadiene



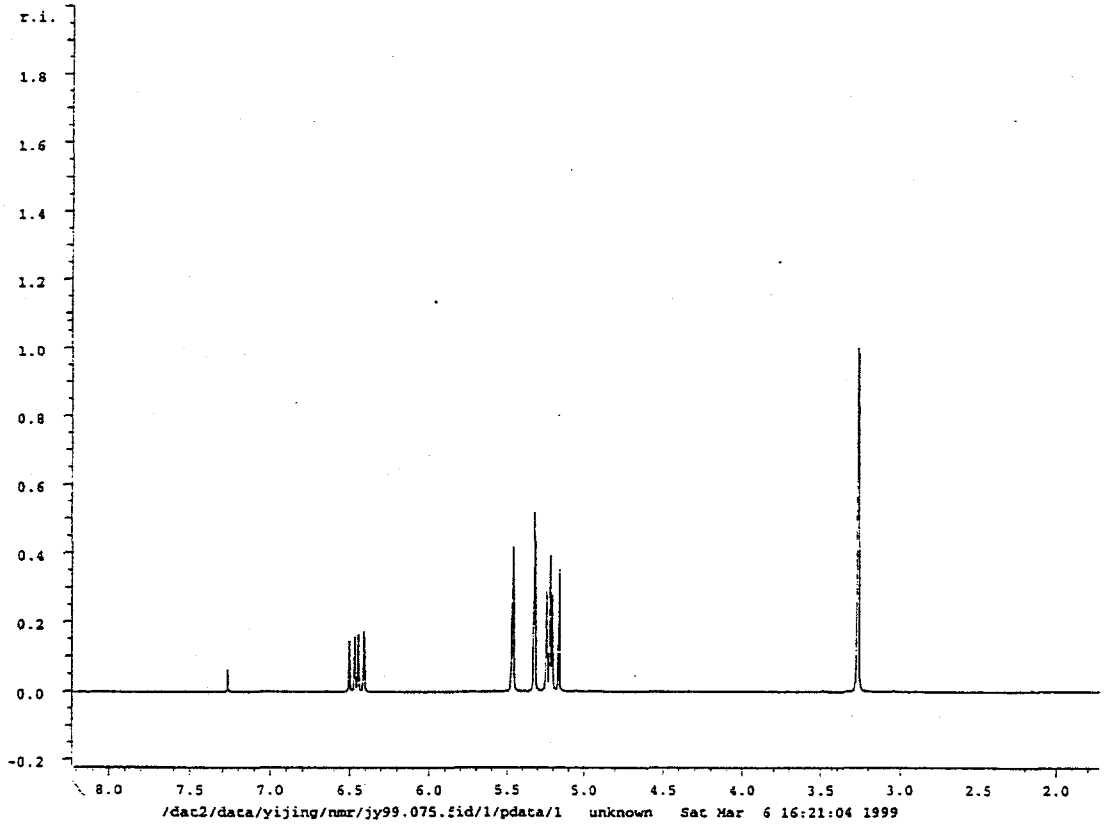
N-2. ^{1}H-NMR spectra of 2-bromomethyl-1,3-butadiene



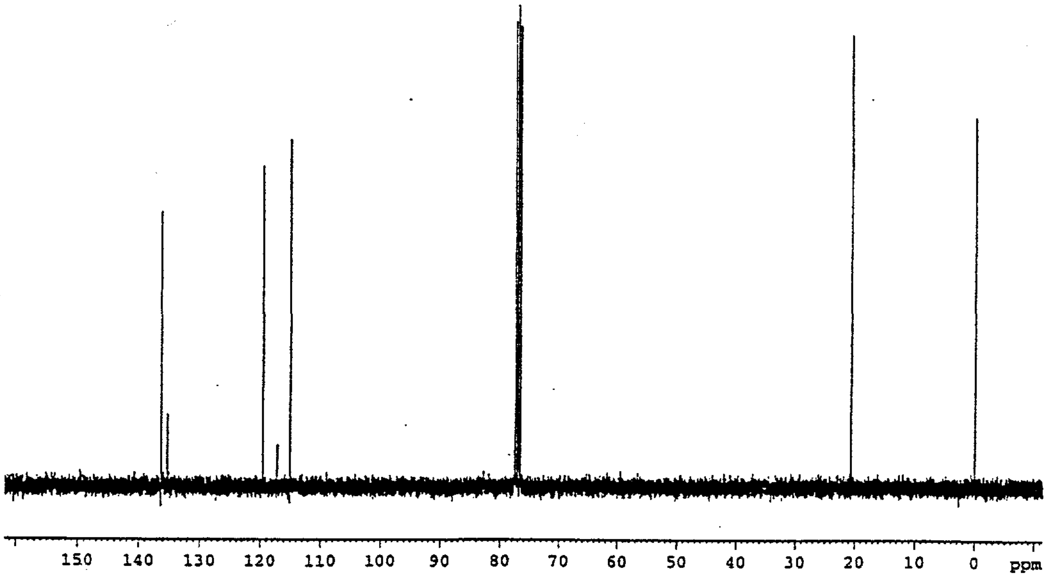
N-3. ^{1}H-NMR spectra of crude 2-cyanomethyl-1,3-butadiene



N-4. ^{1}H-NMR spectra of 2-cyanomethyl-1,3-butadiene sulfone



N-5. ^{1}H-NMR spectra of 2-cyanomethyl-1,3-butadiene



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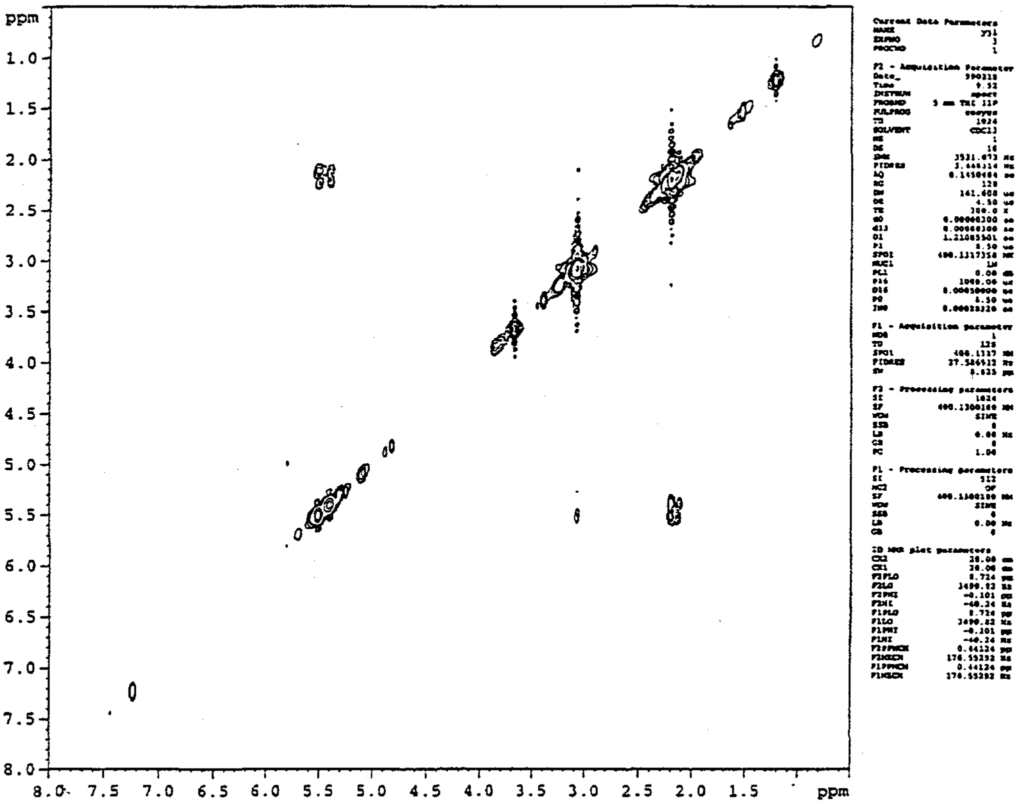
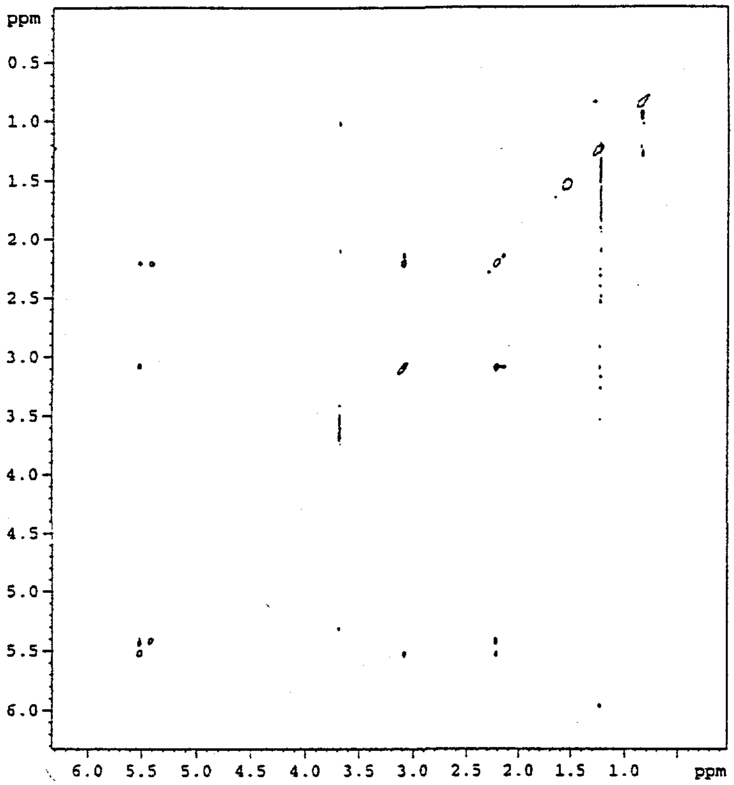


N-7. COSY spectra of poly(2-cyanomethyl-1,3-butadiene)



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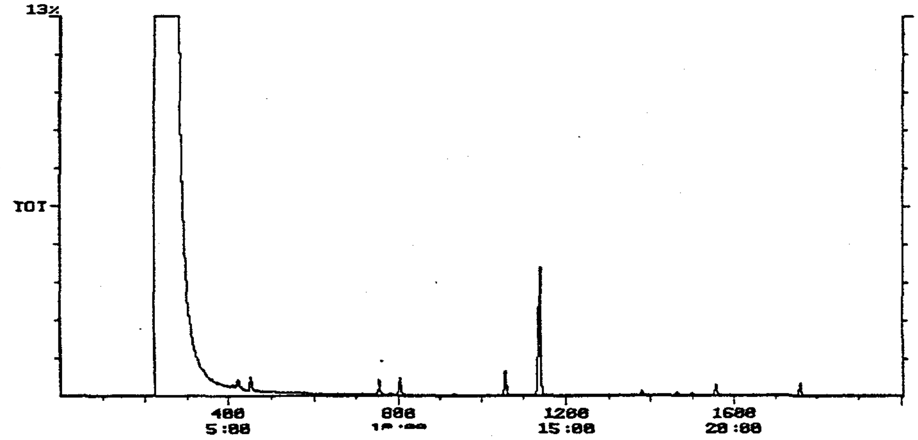

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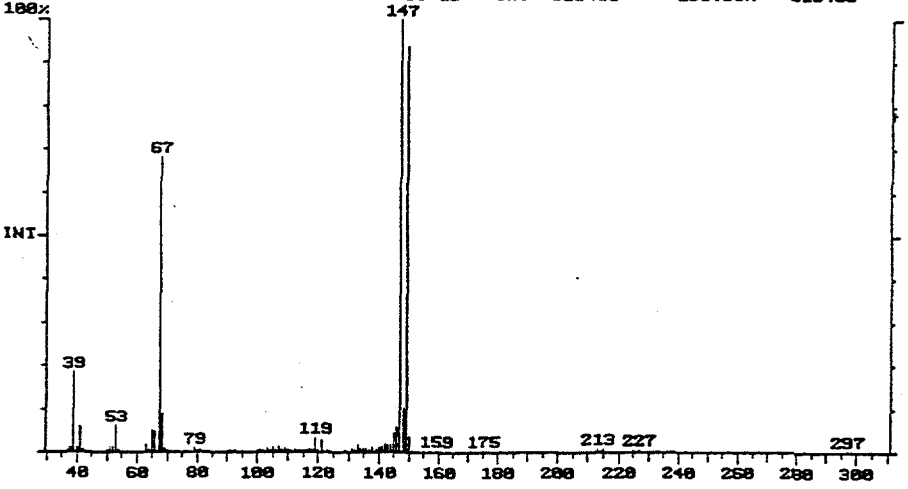

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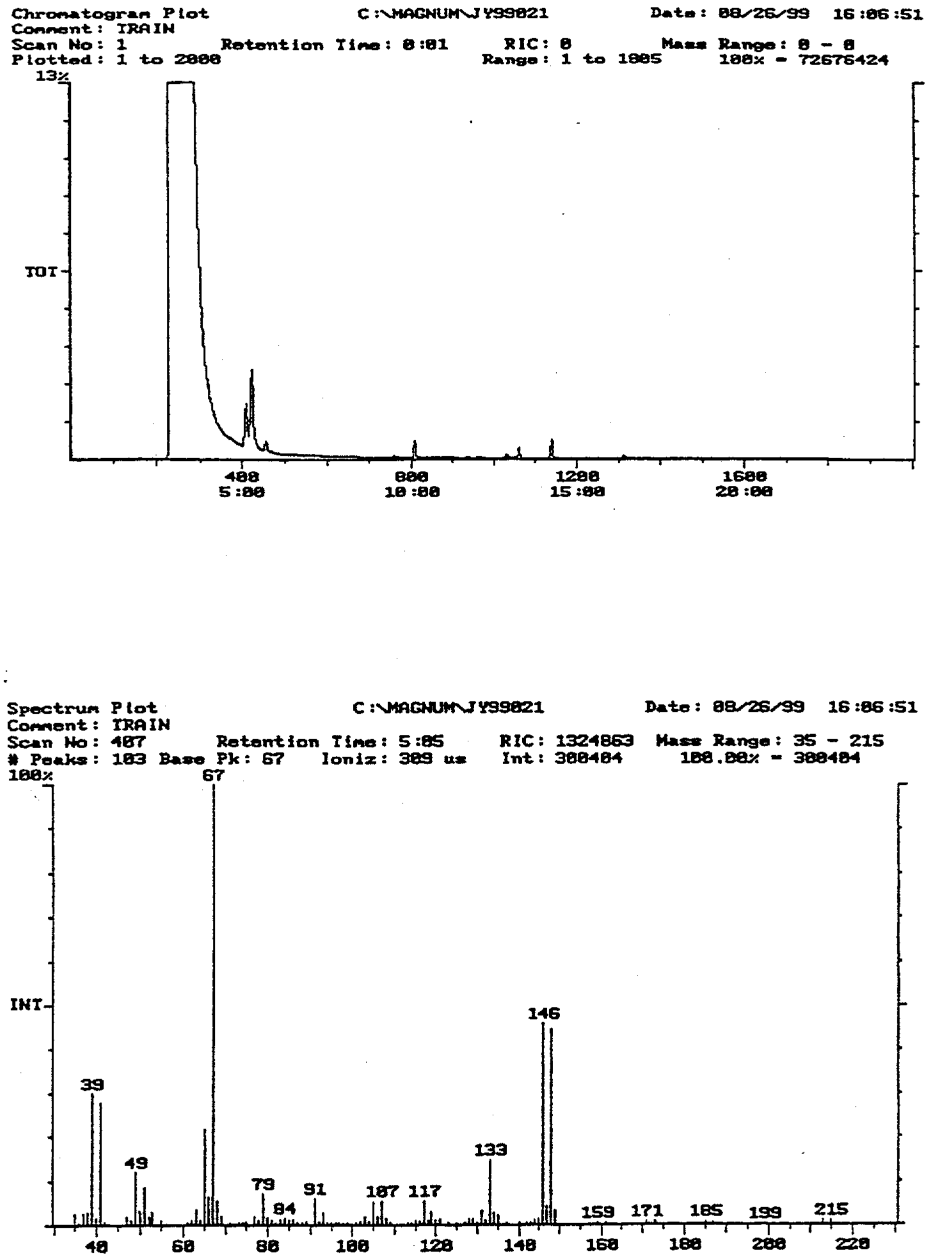
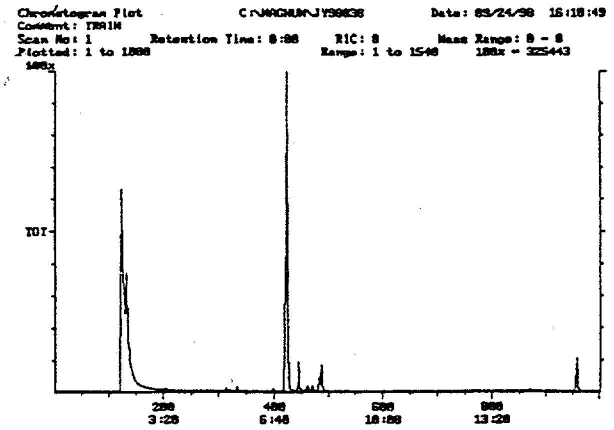
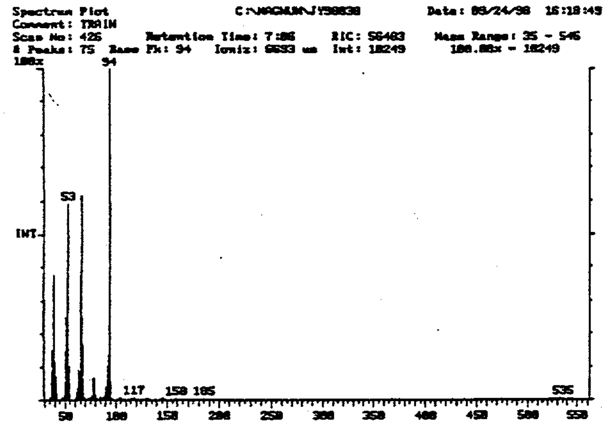
M-1. GC-MS spectra of 1,4-dibromo-2-methyl-1,3-butadiene.

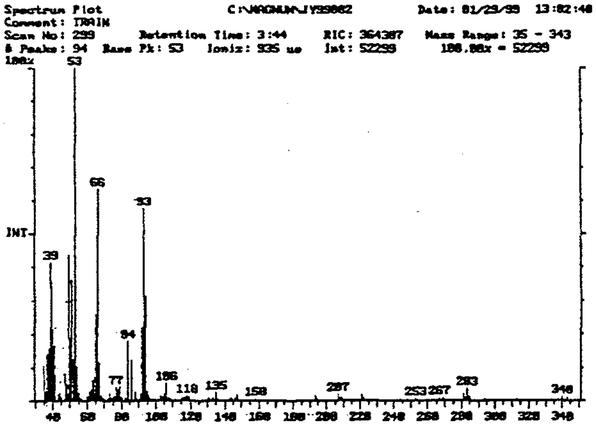


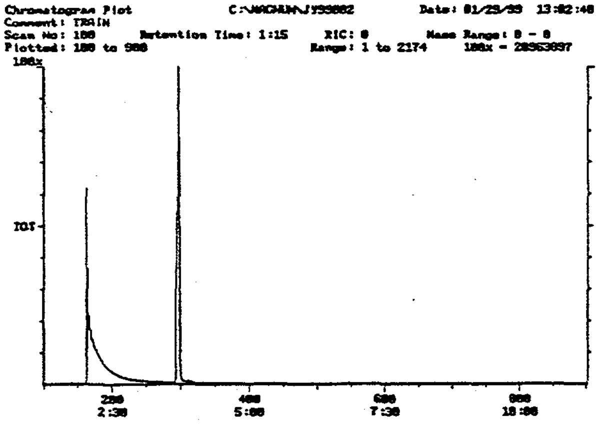
M-2. GC-MS spectra of 2-bromomethyl-1,3-butadiene.



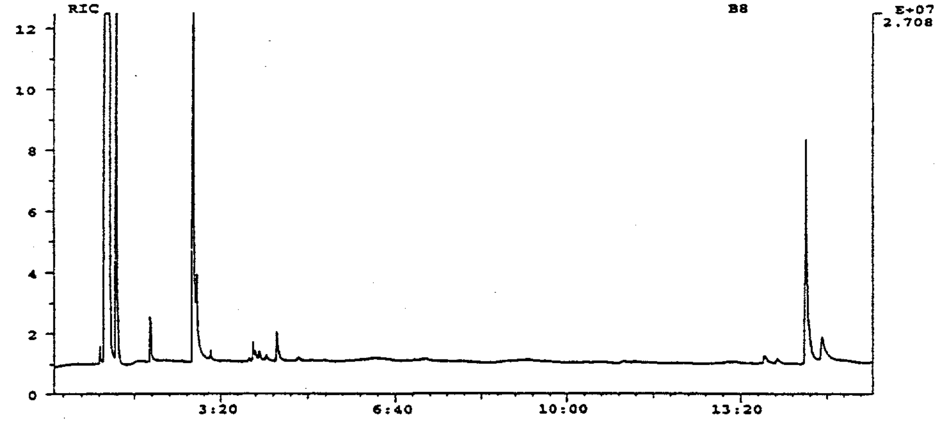


M-3. GC-MS spectra of crude 2-cyanomethyl-1,3-butadiene.





M-4. GC-MS spectra of 2-cyanomethyl-1,3-butadiene.



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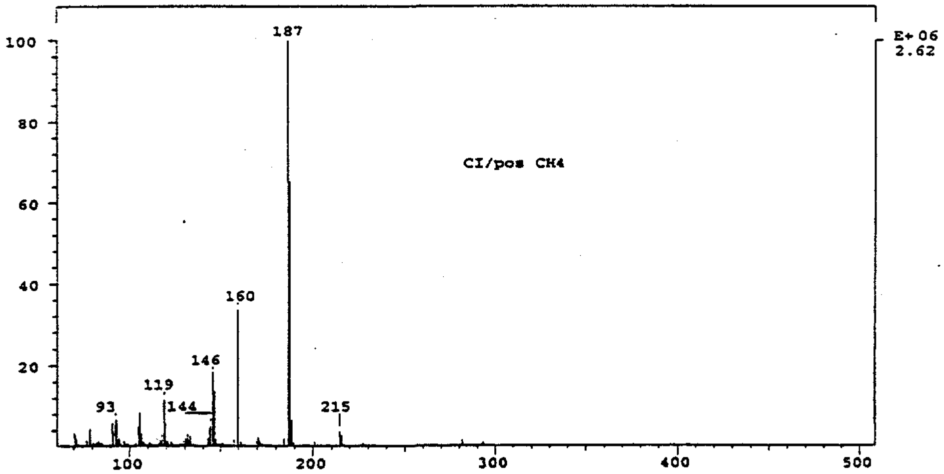

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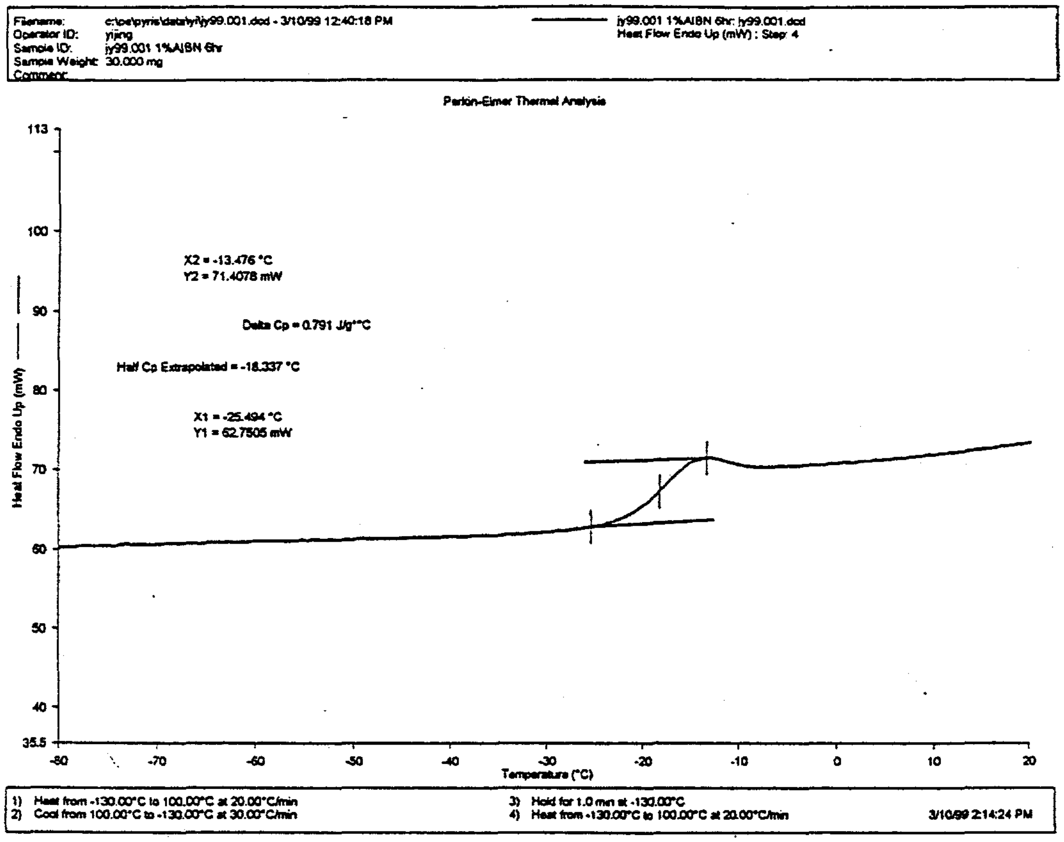
M-5. GC-MS spectra of 2-cyanomethyl-1,3-butadiene and its dimers.



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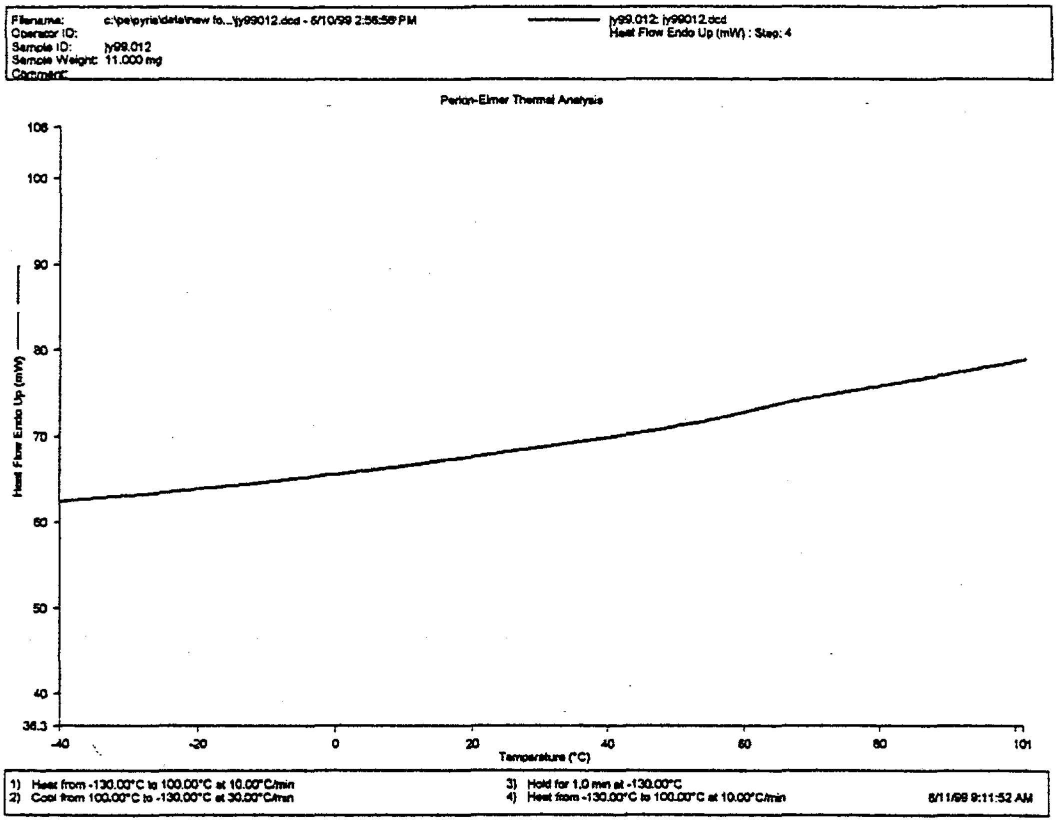

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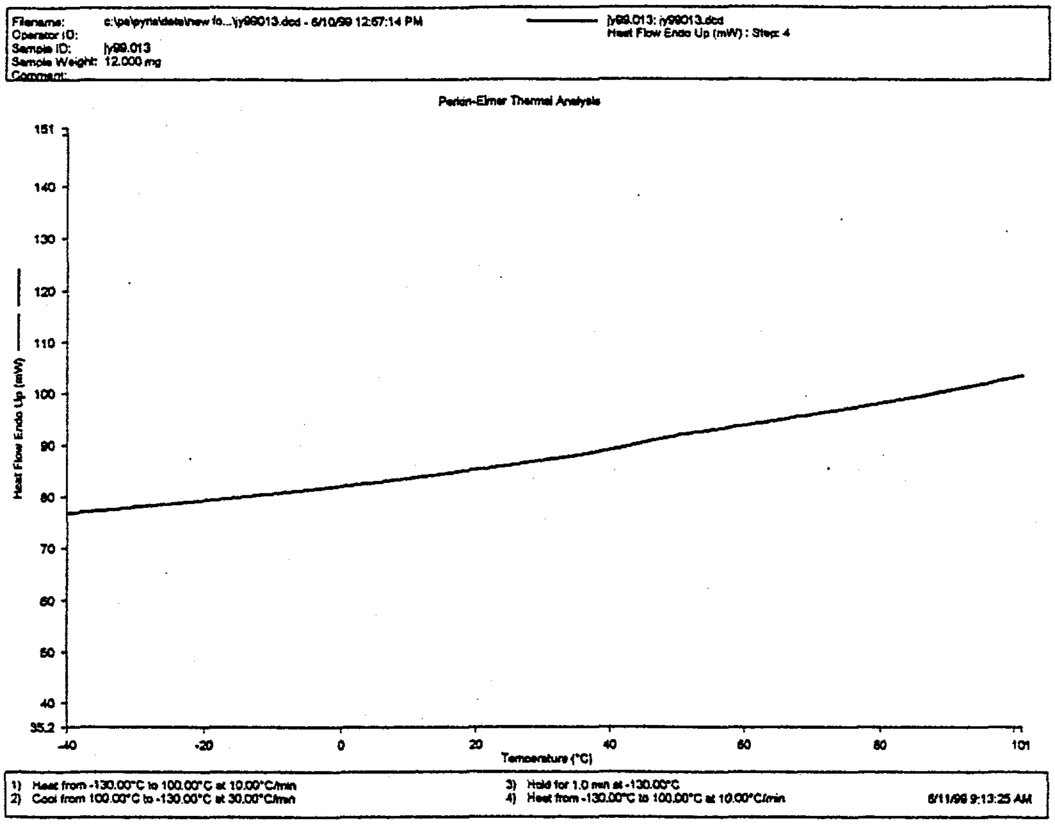

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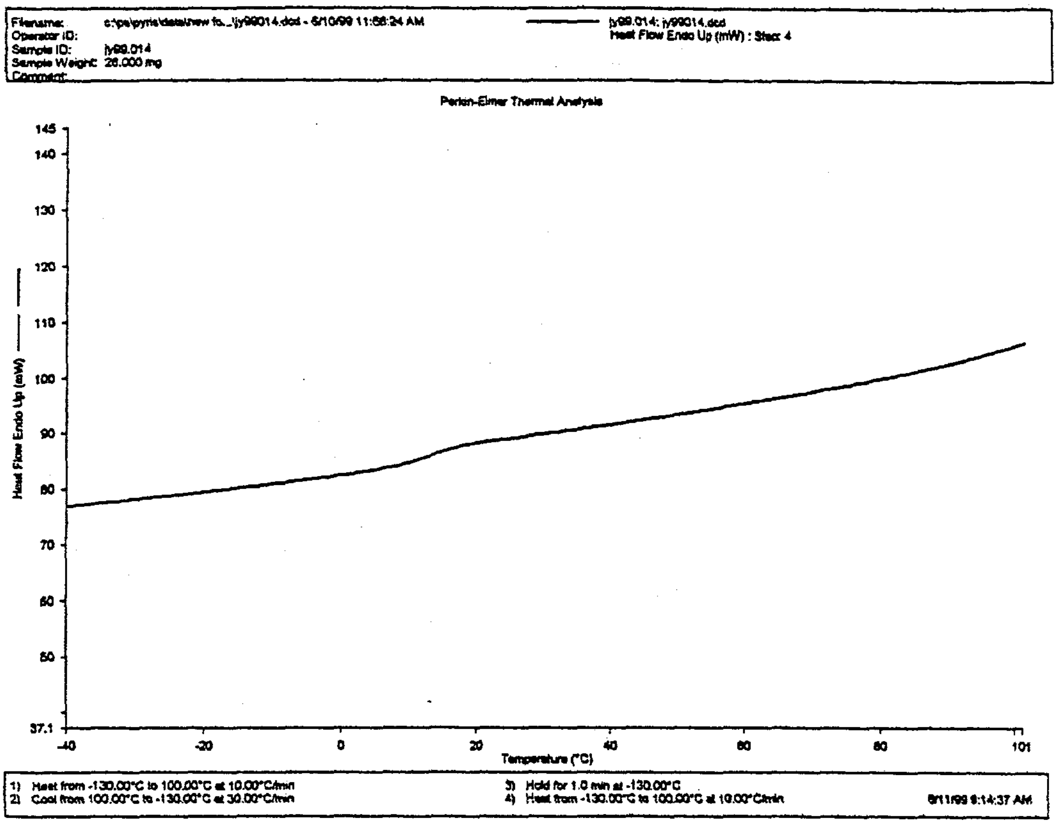

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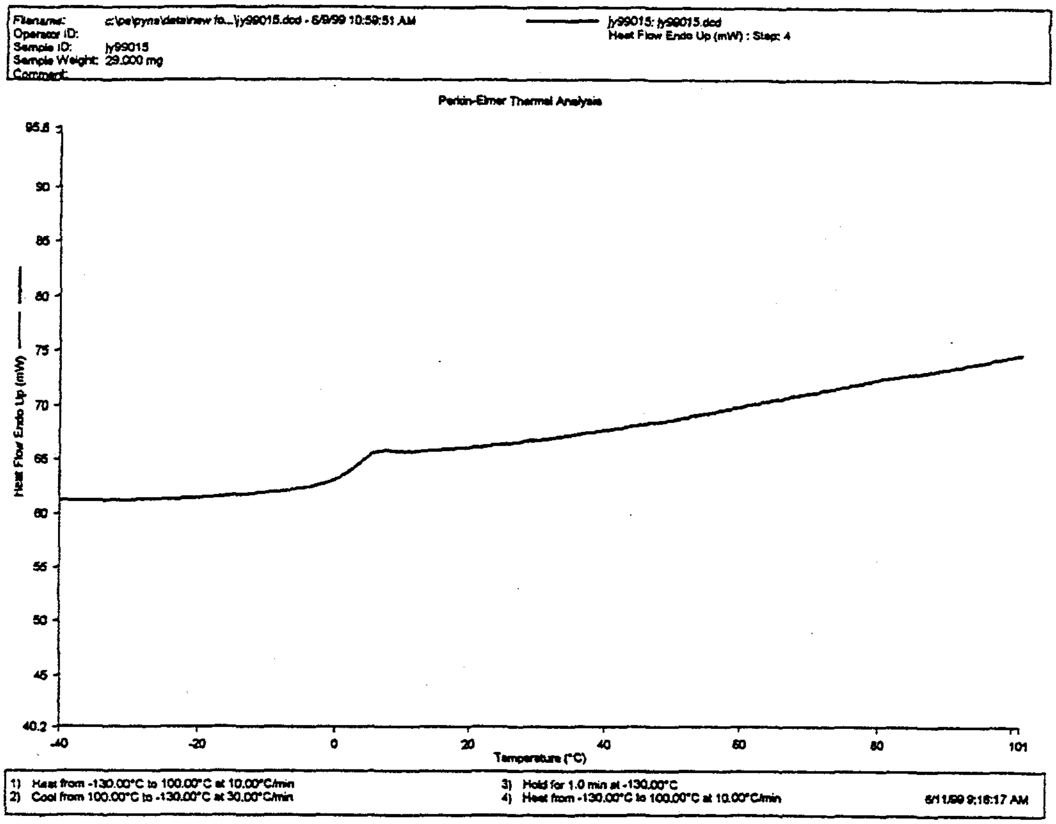

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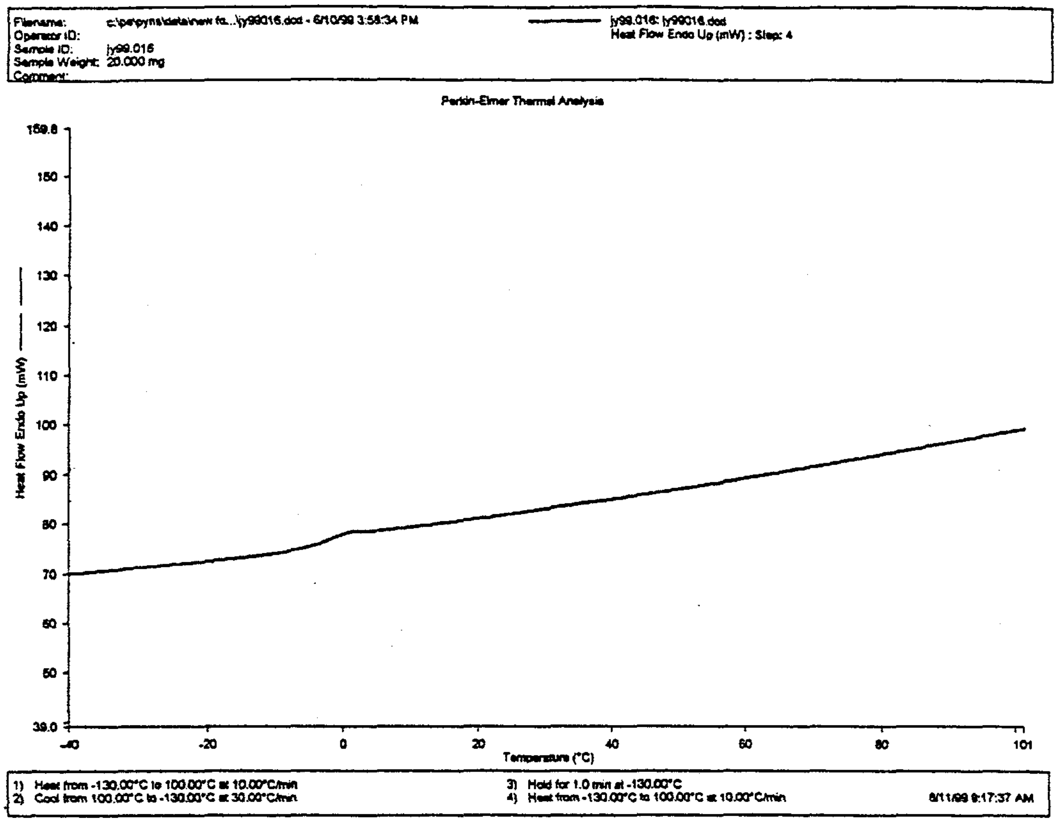

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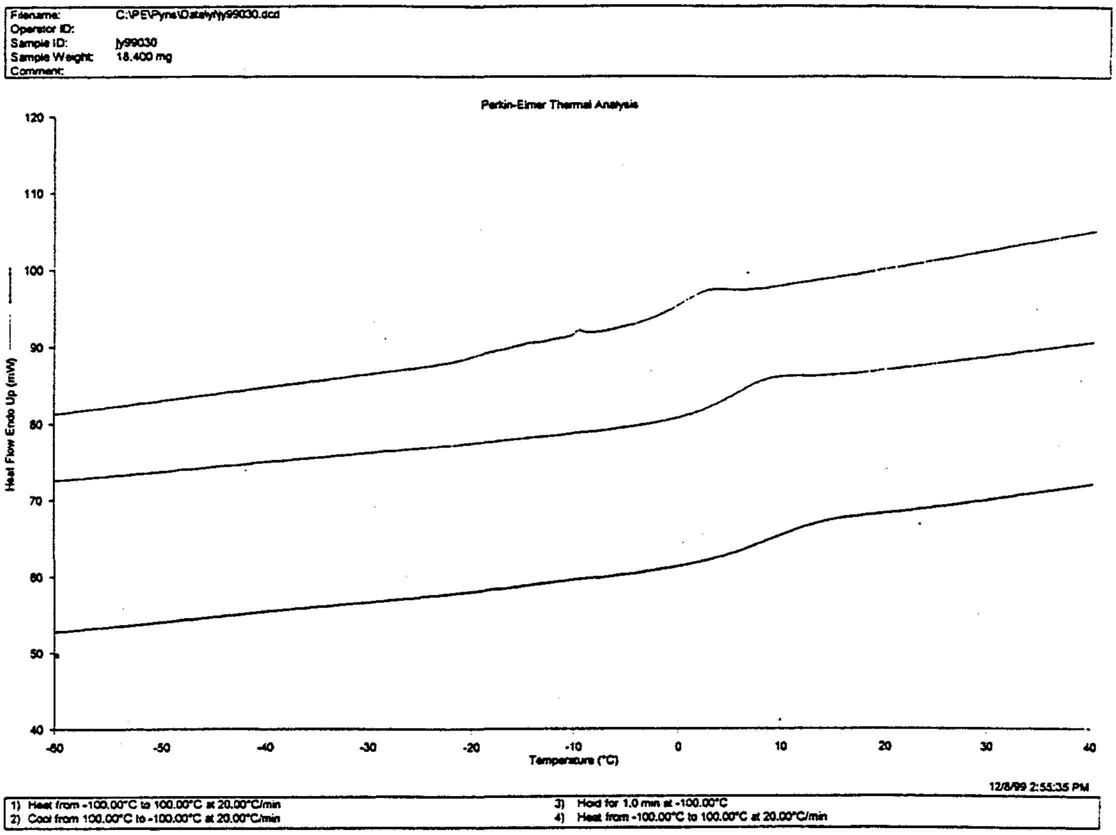

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Perkin-Elmer Thermal Analysis

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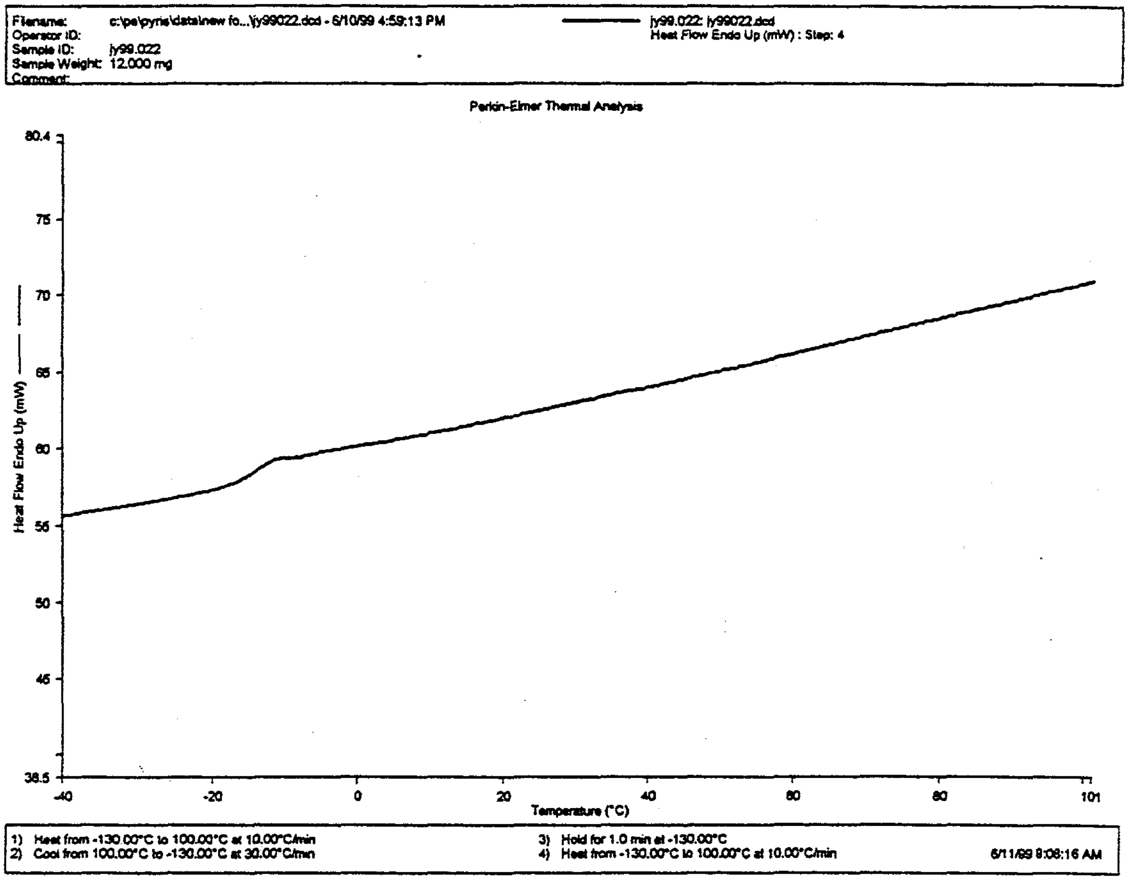
4) Heat from -100.00°C to 100.00°C at 20.00°C/min

D-7



Filename: c:\pe\pyris\data\new fo...\jy99022.dcd - 6/10/99 4:59:13 PM
Operator ID:
Sample ID: jy99.022
Sample Weight: 12.000 mg
Comment:

jy99.022: jy99022.dcd
Heat Flow Endo Up (mW) : Step: 4

Perkin-Elmer Thermal Analysis

1) Heat from -130.00°C to 100.00°C at 10.00°C/min
2) Cool from 100.00°C to -130.00°C at 30.00°C/min
3) Hold for 1.0 min at -130.00°C
4) Heat from -130.00°C to 100.00°C at 10.00°C/min

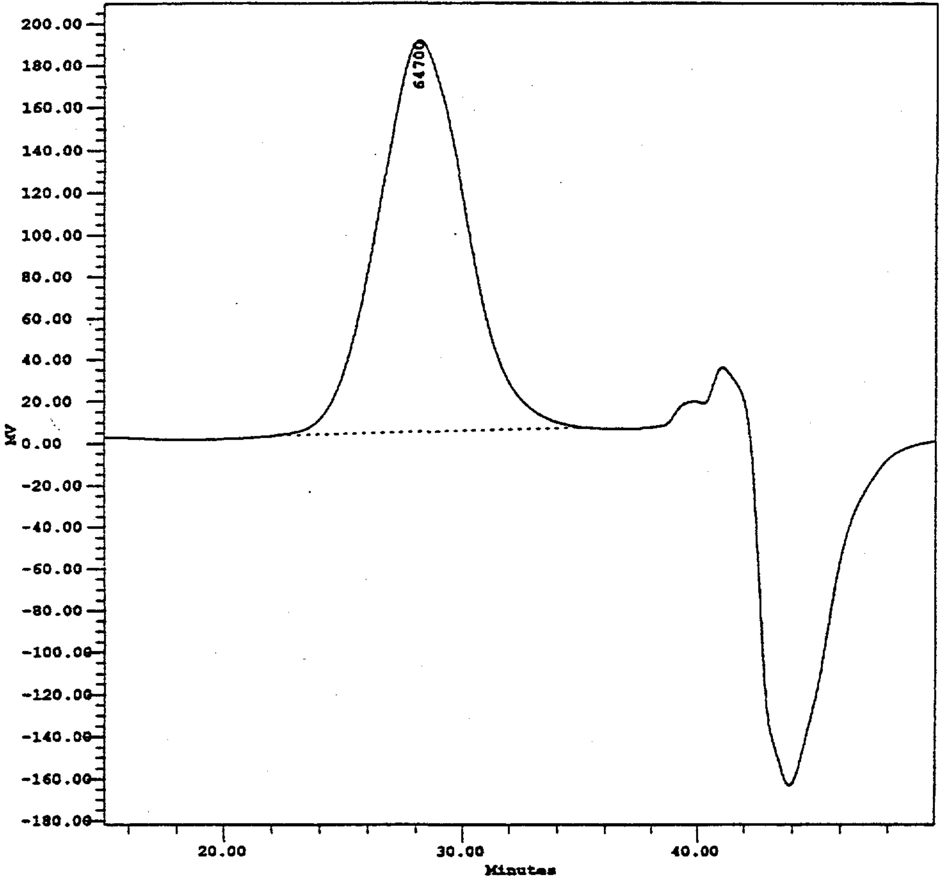
6/11/99 8:08:16 AM

Millennium Sample Information

Project Name: Paul99
Sample Name: jy99044
Vial: 14
Injection: 1
Channel: 410
Date Acquired: 04/16/99 01:06:53 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/16/99 02:01:27 PM
Dilution: 1.00000

MP: 64700 Mw: 82478 Mn: 39175 Polydispersity: 2.105365
Retention Time: 28.117

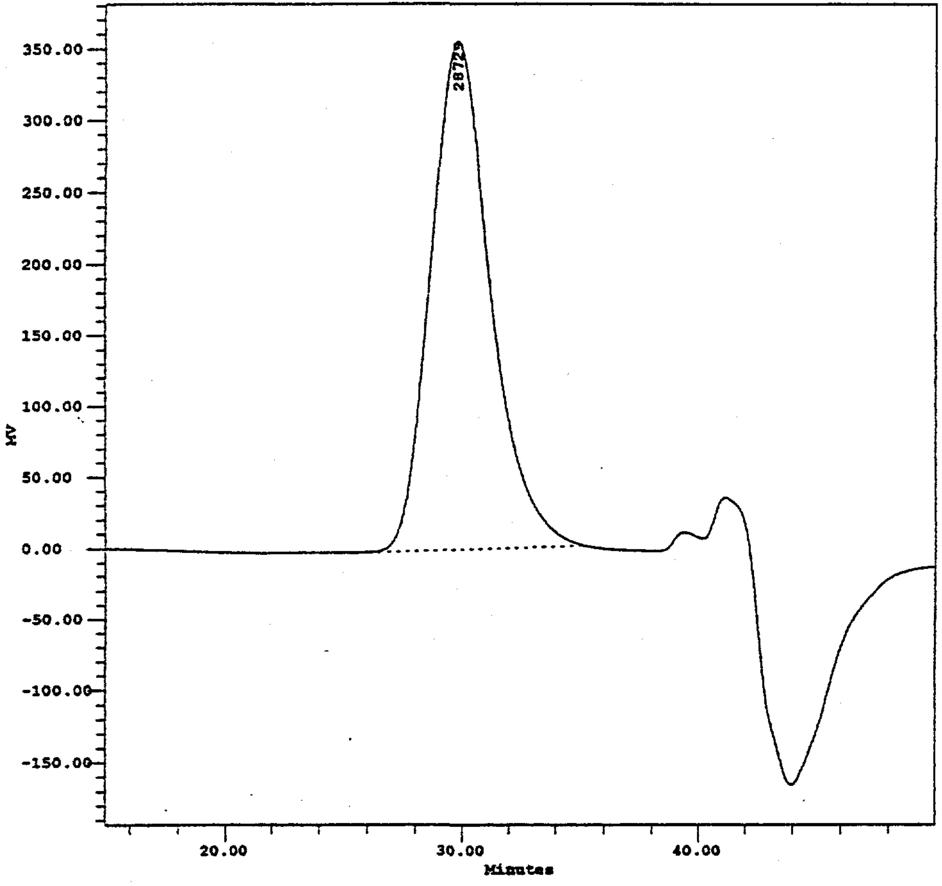


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99045
Vial: 1
Injection: 2
Channel: 410
Date Acquired: 04/20/99 09:24:08 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/21/99 08:09:35 AM
Dilution: 1.00000

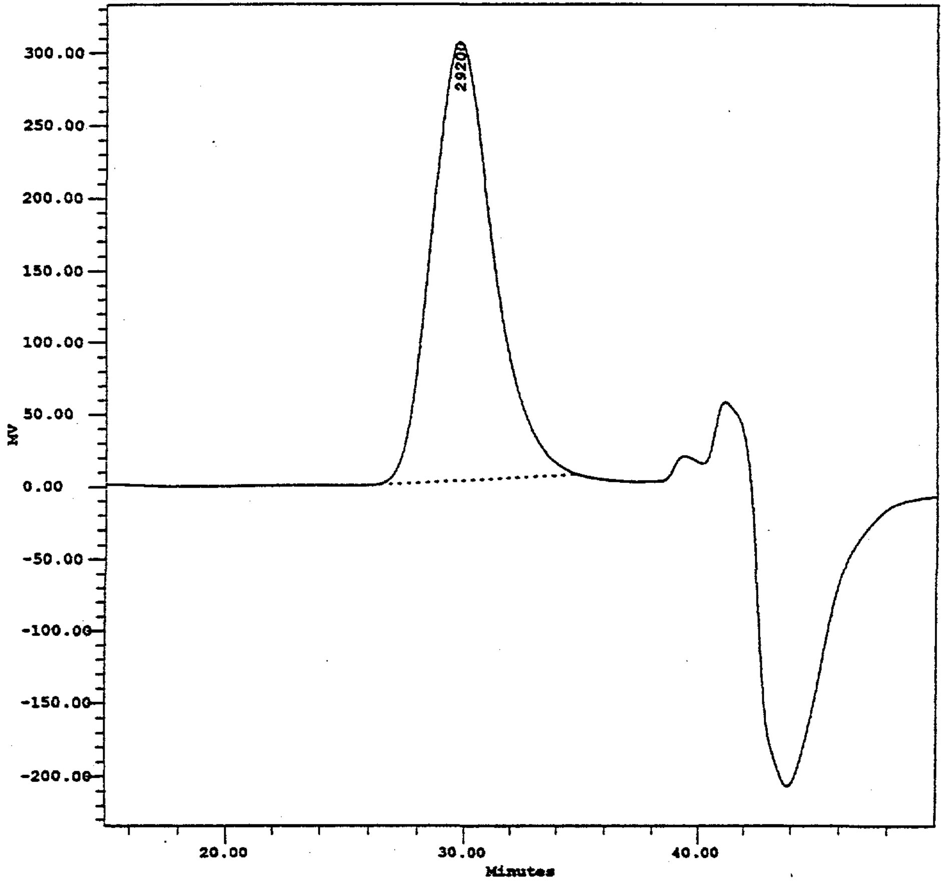
MP: 28729 Mw: 29569 Mn: 20262 Polydispersity: 1.459348
Retention Time: 29.783



Millennium Sample Information

Project Name:	Paul99		
Sample Name:	jy99046		
Vial:	2	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	04/20/99 10:18:02 PM	Date Processed:	04/21/99 08:10:15 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	Dawson		

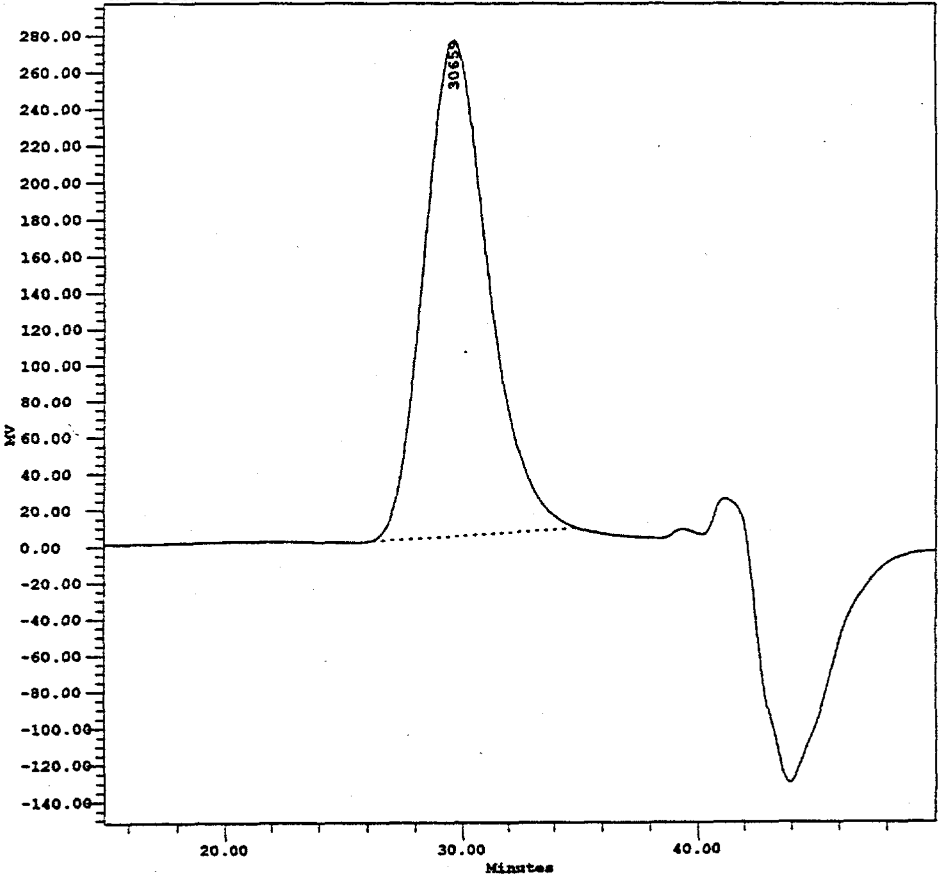
MP: 29200 Mw: 30538 Mn: 20732 Polydispersity: 1.473005
Retention Time: 29.750



Millennium Sample Information

Project Name:	Paul99		
Sample Name:	jy99047		
Vial:	3	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	04/20/99 11:11:47 PM	Date Processed:	04/21/99 08:11:35 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	Dawson		

MP: 30659 Mw: 32611 Mn: 21411 Polydispersity: 1.523080
Retention Time: 29.650

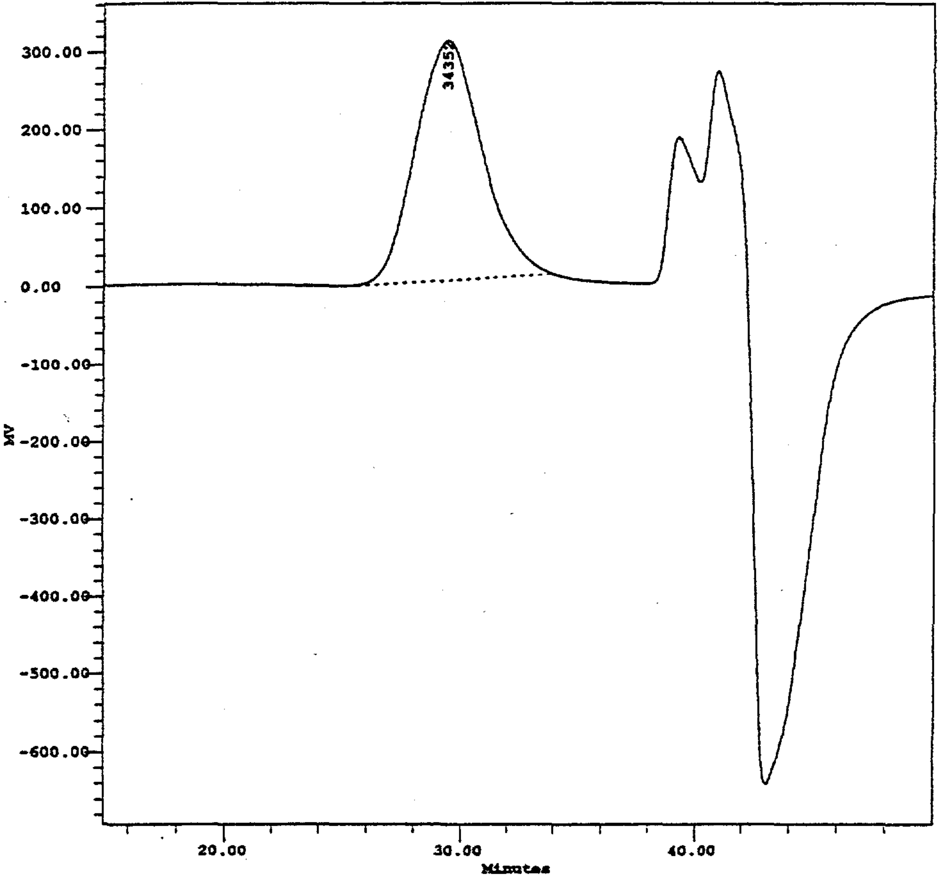


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99048
Vial: 4
Injection: 1
Channel: 410
Date Acquired: 04/21/99 12:05:33 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/21/99 08:12:20 AM
Dilution: 1.00000

MP: 34352 Mw: 38938 Mn: 25940 Polydispersity: 1.501086
Retention Time: 29.417

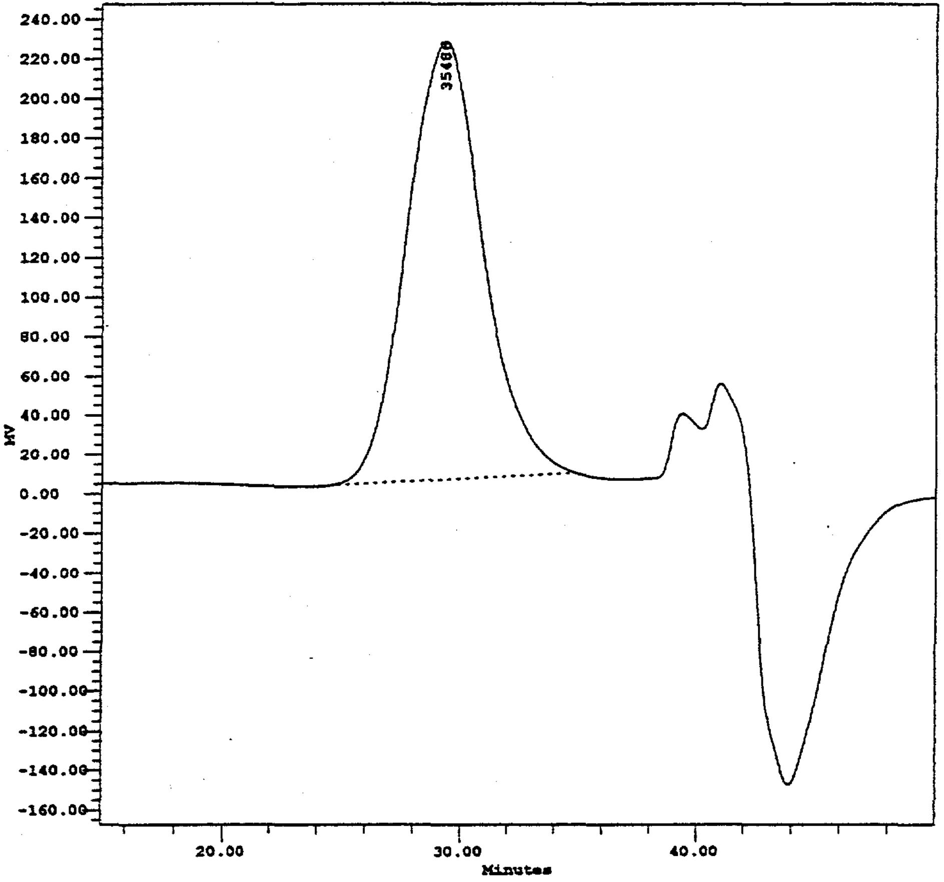


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99049
Vial: 5
Injection: 1
Channel: 410
Date Acquired: 04/21/99 12:59:18 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/21/99 08:12:51 AM
Dilution: 1.00000

MP: 35486 Mw: 44119 Mn: 25730 Polydispersity: 1.714707
Retention Time: 29.350

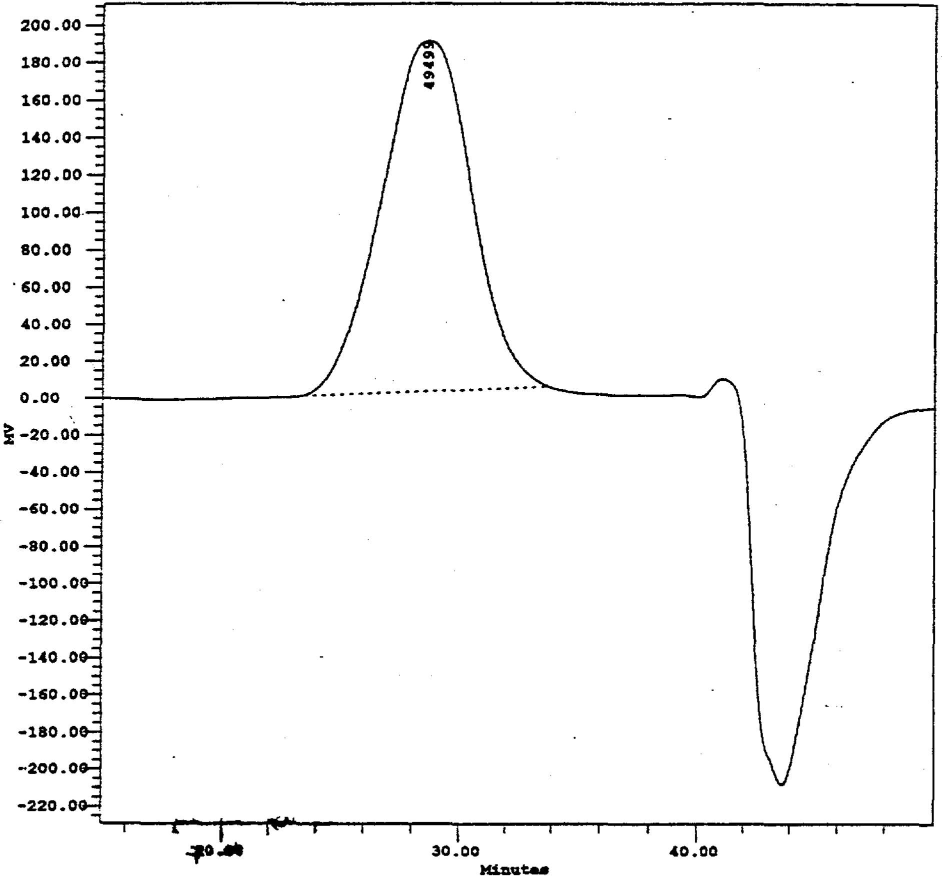


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99050
Vial: 4
Injection: 1
Channel: 410
Date Acquired: 04/22/99 10:59:36 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/23/99 02:36:36 PM
Dilution: 1.00000

MP: 49499 Mw: 71587 Mn: 37182 Polydispersity: 1.925312
Retention Time: 28.667

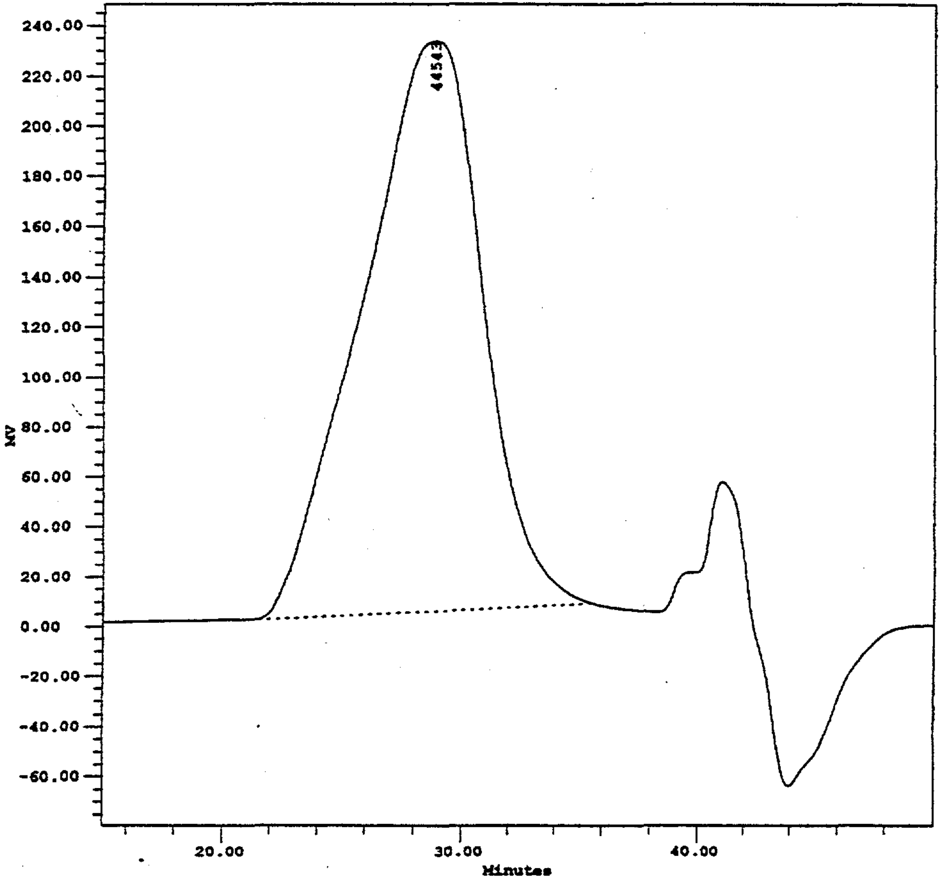


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99051
Vial: 5
Injection: 1
Channel: 410
Date Acquired: 04/22/99 11:53:22 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/23/99 02:37:10 PM
Dilution: 1.00000

MP: 44543 Mw: 114446 Mn: 33910 Polydispersity: 3.374955
Retention Time: 28.883

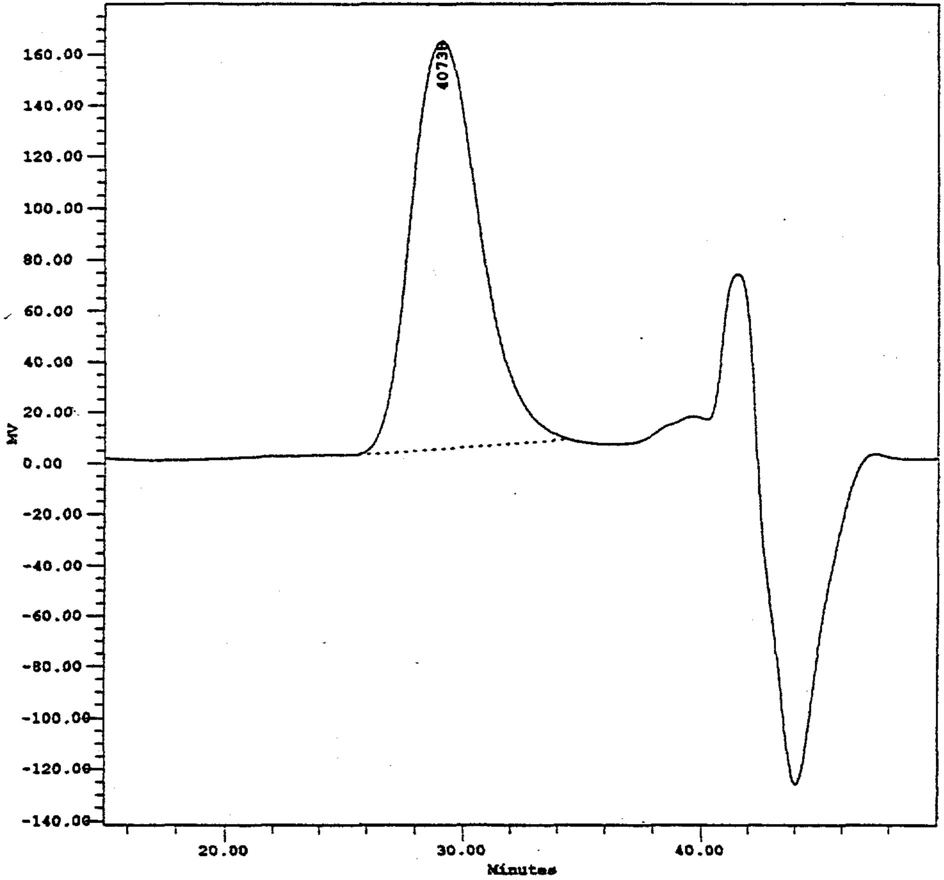


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99034
Vial: 4
Injection: 1
Channel: 410
Date Acquired: 04/16/99 04:09:23 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/16/99 02:08:02 PM
Dilution: 1.00000

MP: 40738 Mw: 42316 Mn: 27645 Polydispersity: 1.530725
Retention Time: 29.067

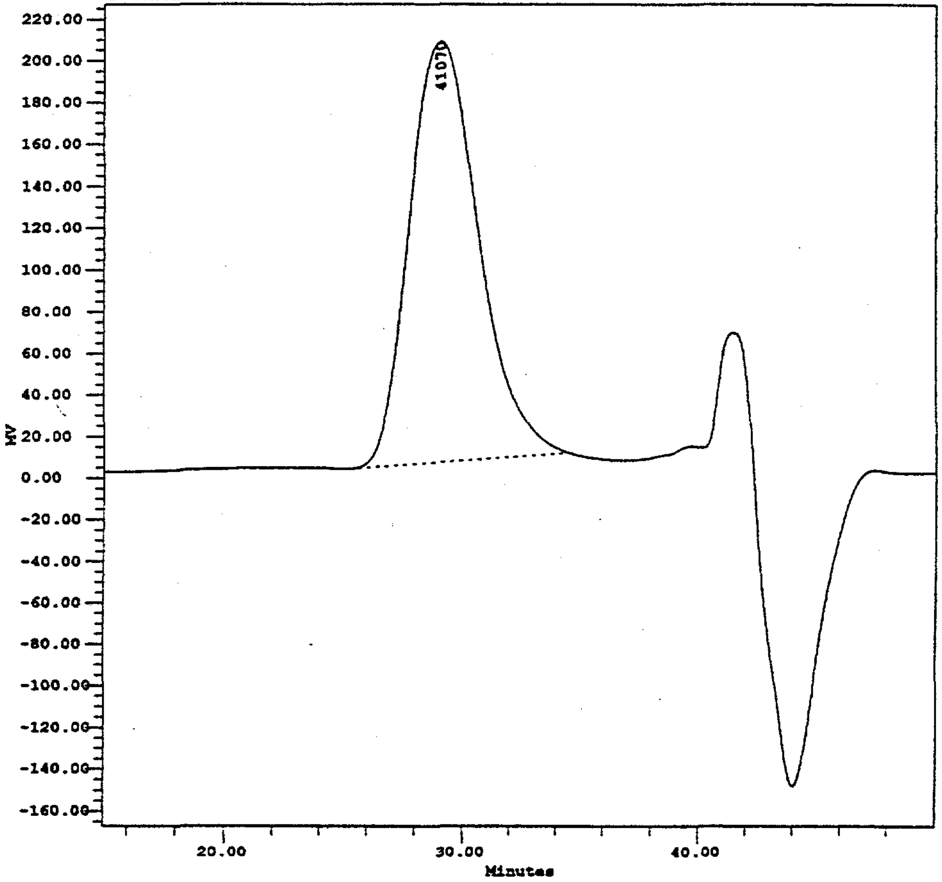


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99035
Vial: 5
Injection: 1
Channel: 410
Date Acquired: 04/16/99 05:03:09 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/16/99 02:07:36 PM
Dilution: 1.00000

MP: 41070 Mw: 42836 Mn: 27618 Polydispersity: 1.550998
Retention Time: 29.050

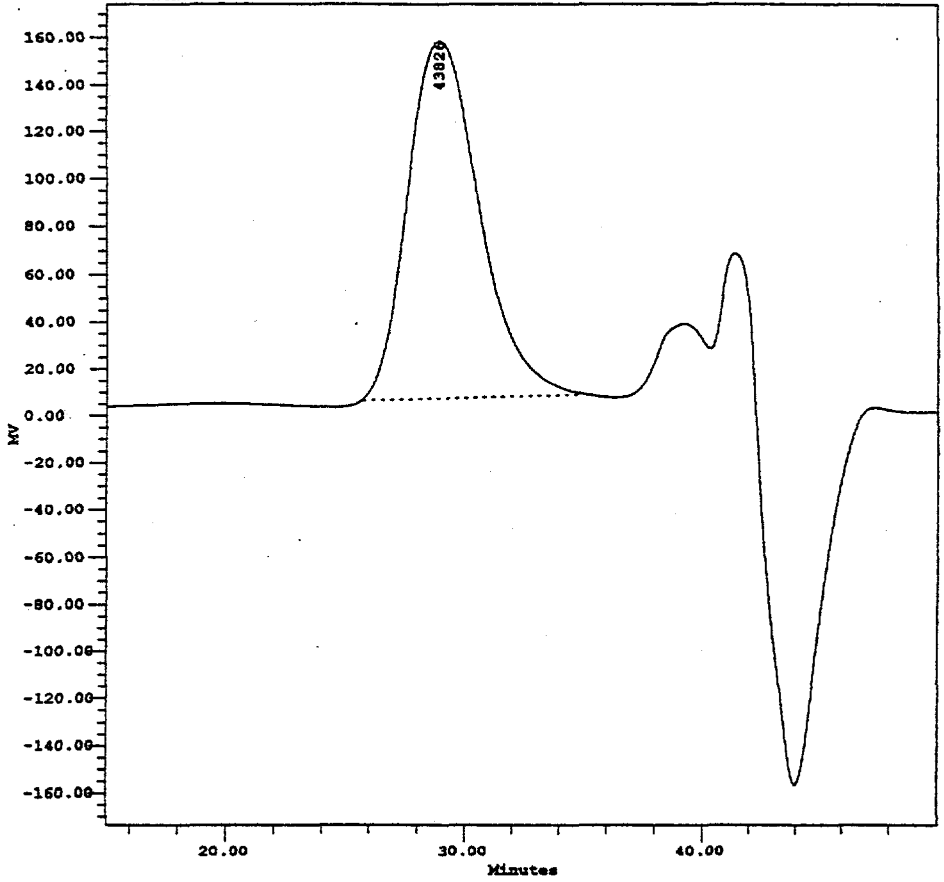


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99036
Vial: 6
Injection: 1
Channel: 410
Date Acquired: 04/16/99 05:56:54 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/16/99 02:07:02 PM
Dilution: 1.00000

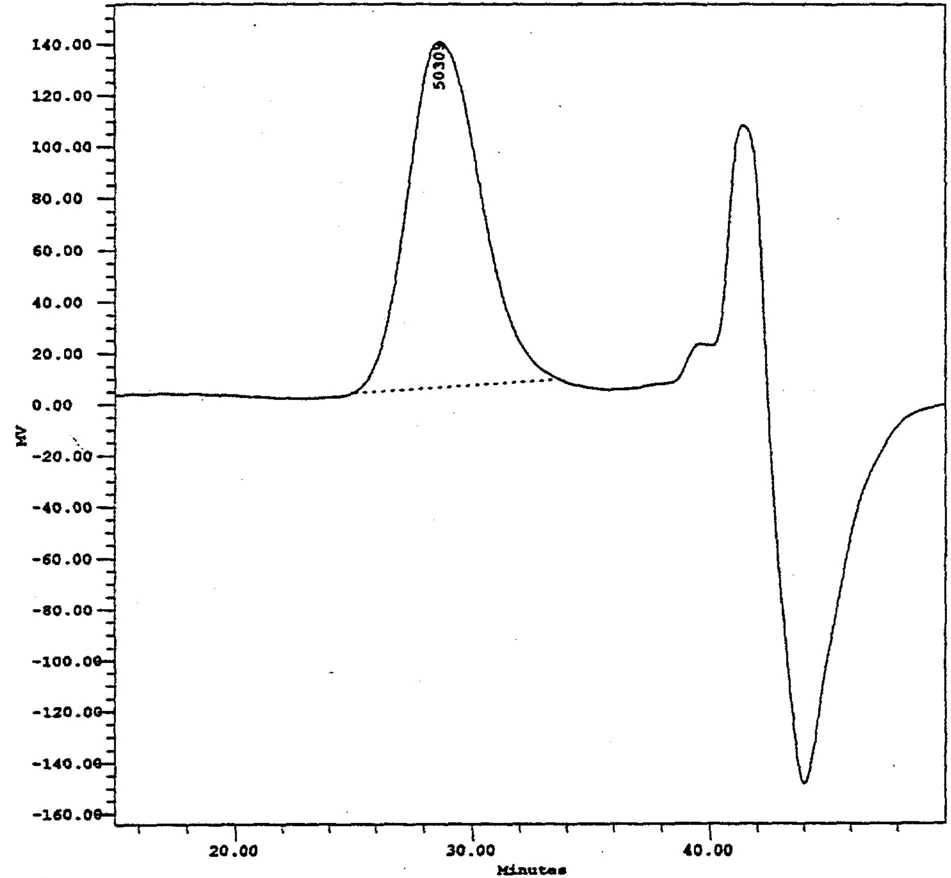
MP: 43826 Mw: 45173 Mn: 27595 Polydispersity: 1.636997
Retention Time: 28.917



Millennium Sample Information

Project Name:	Paul99		
Sample Name:	jy99037		
Vial:	7	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	04/16/99 06:50:39 AM	Date Processed:	04/16/99 02:06:21 PM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	Dawson		

MP: 50309 Mw: 52849 Mn: 33697 Polydispersity: 1.568365
Retention Time: 28.633

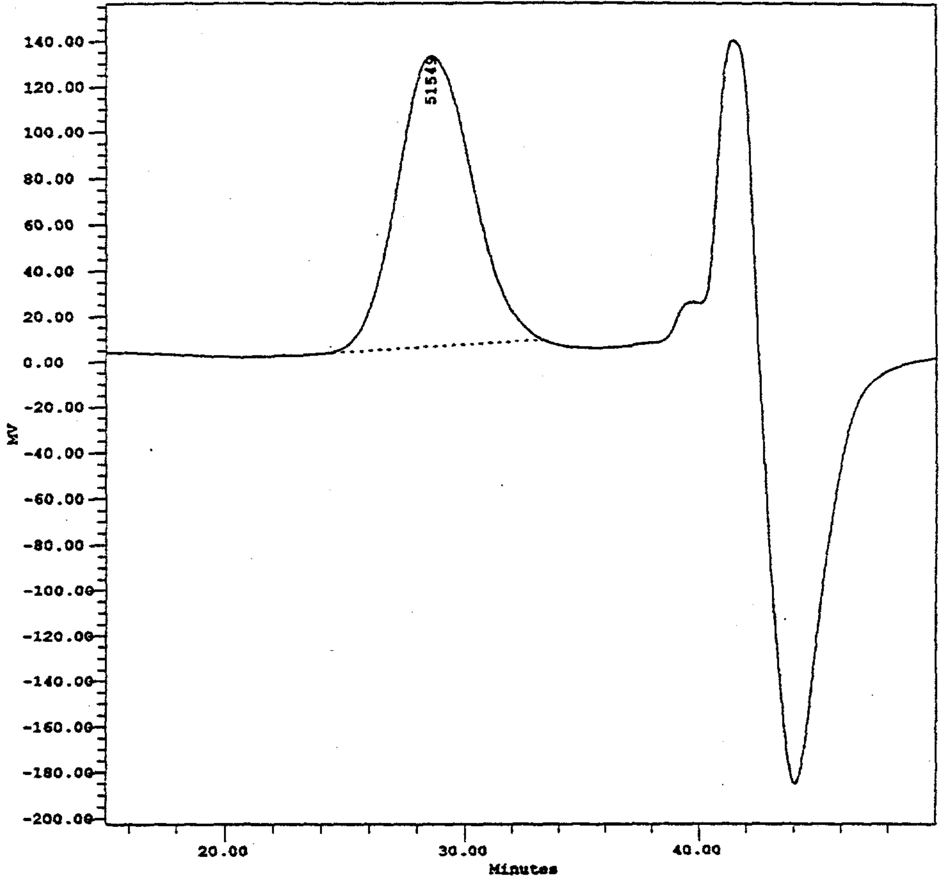


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99038
Vial: 8
Injection: 1
Channel: 410
Date Acquired: 04/16/99 07:44:24 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/16/99 02:05:31 PM
Dilution: 1.00000

MP: 51549 Mw: 57507 Mn: 35797 Polydispersity: 1.606490
Retention Time: 28.583

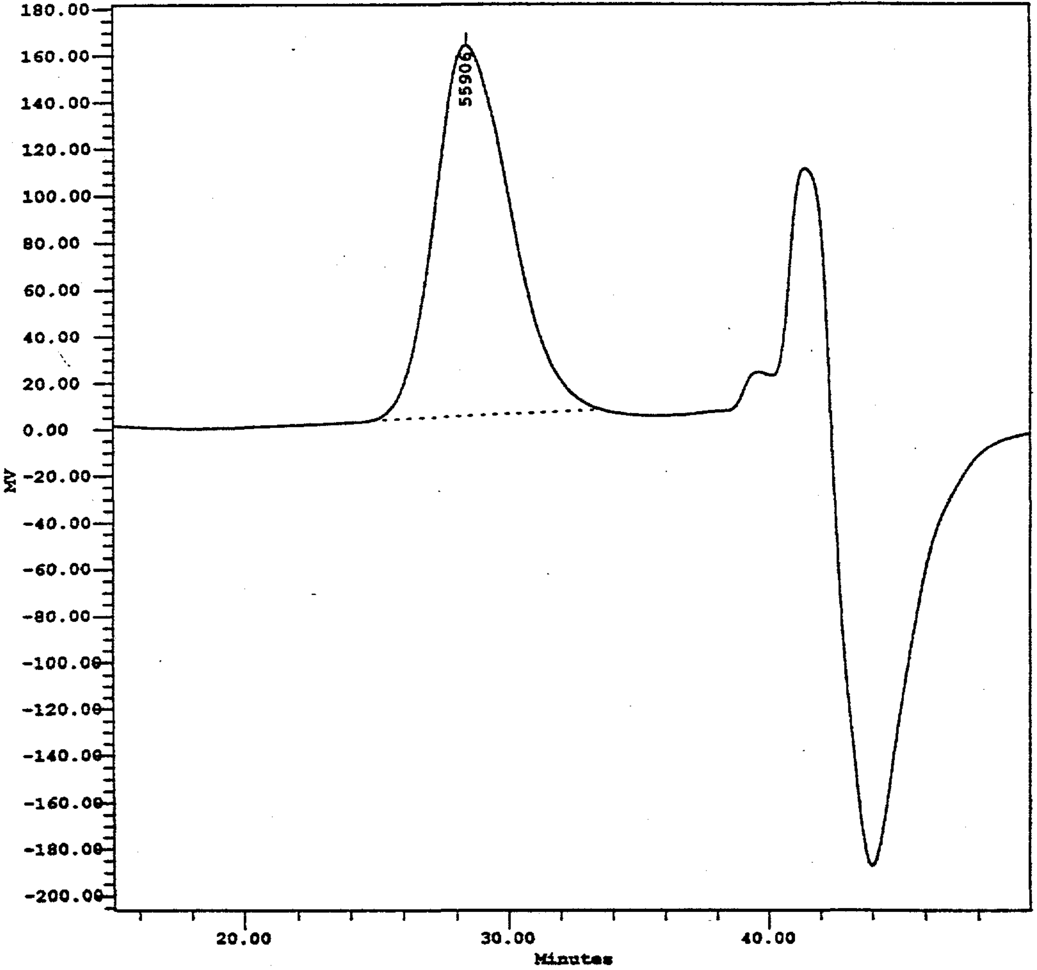


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99039
Vial: 9
Injection: 1
Channel: 410
Date Acquired: 04/16/99 08:38:08 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/16/99 02:04:43 PM
Dilution: 1.00000

MP: 55906 Mw: 57350 Mn: 36979 Polydispersity: 1.550875
Retention Time: 28.417

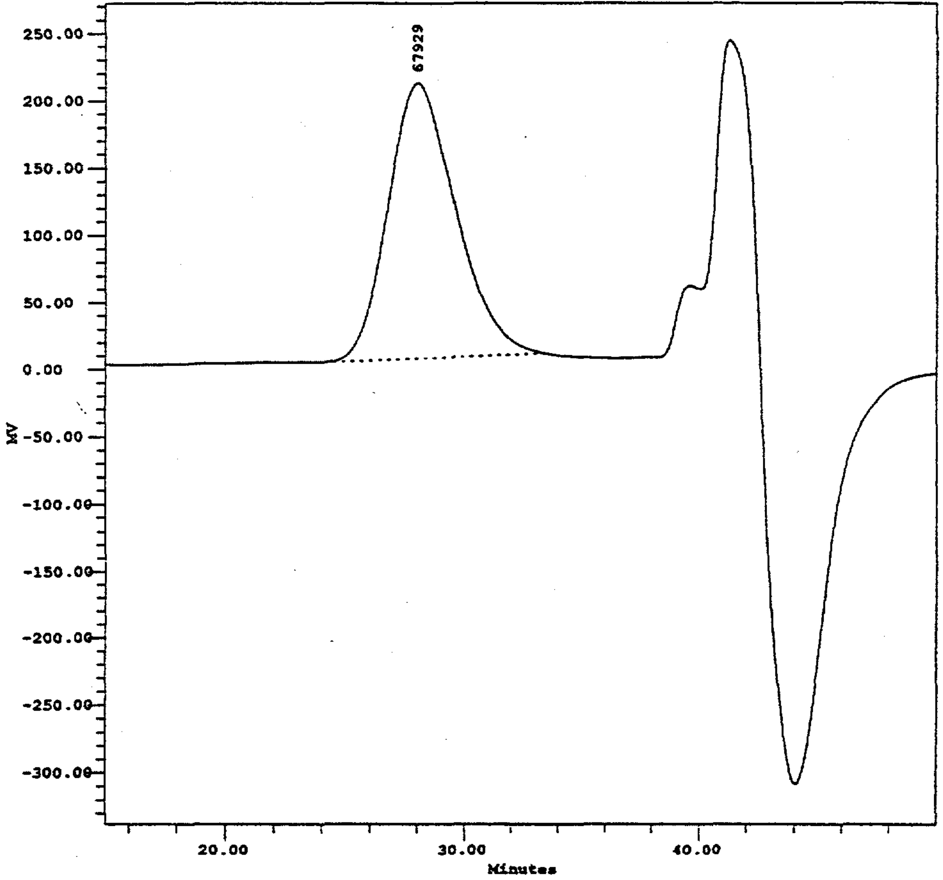


Millennium Sample Information

roject Name: Paul99
ample Name: jy99040
Vial: 10
Injection: 1
Channel: 410
Date Acquired: 04/16/99 09:31:54 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/16/99 02:04:10 PM
Dilution: 1.00000

MP: 67929 Mw: 70459 Mn: 45316 Polydispersity: 1.554826
Retention Time: 28.017

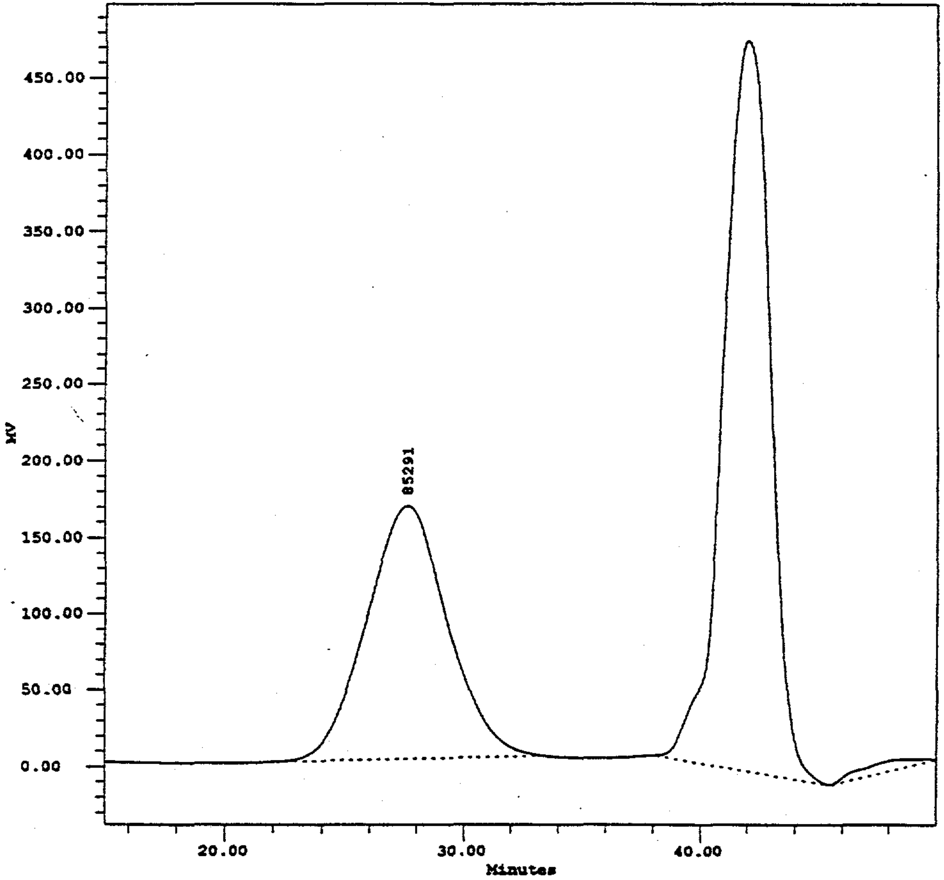


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99003
Vial: 2
Injection: 1
Channel: 410
Date Acquired: 02/11/99 05:01:19 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Durham

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 02/11/99 05:51:38 PM
Dilution: 1.00000

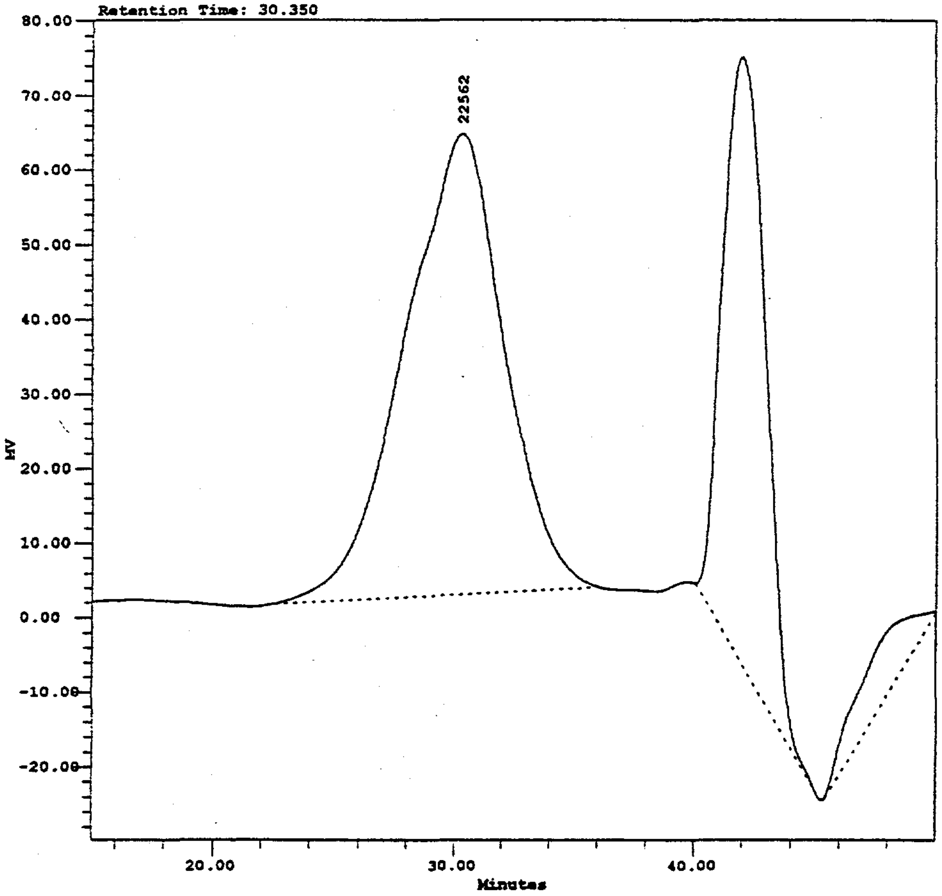
MP: 85291 Mw: 115012 Mn: 61888 Polydispersity: 1.858397
Retention Time: 27.633



Millennium Sample Information

Project Name:	Paul99		
Sample Name:	jy99008		
Vial:	3	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	02/19/99 01:53:35 AM	Date Processed:	02/19/99 10:37:39 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	Durham		

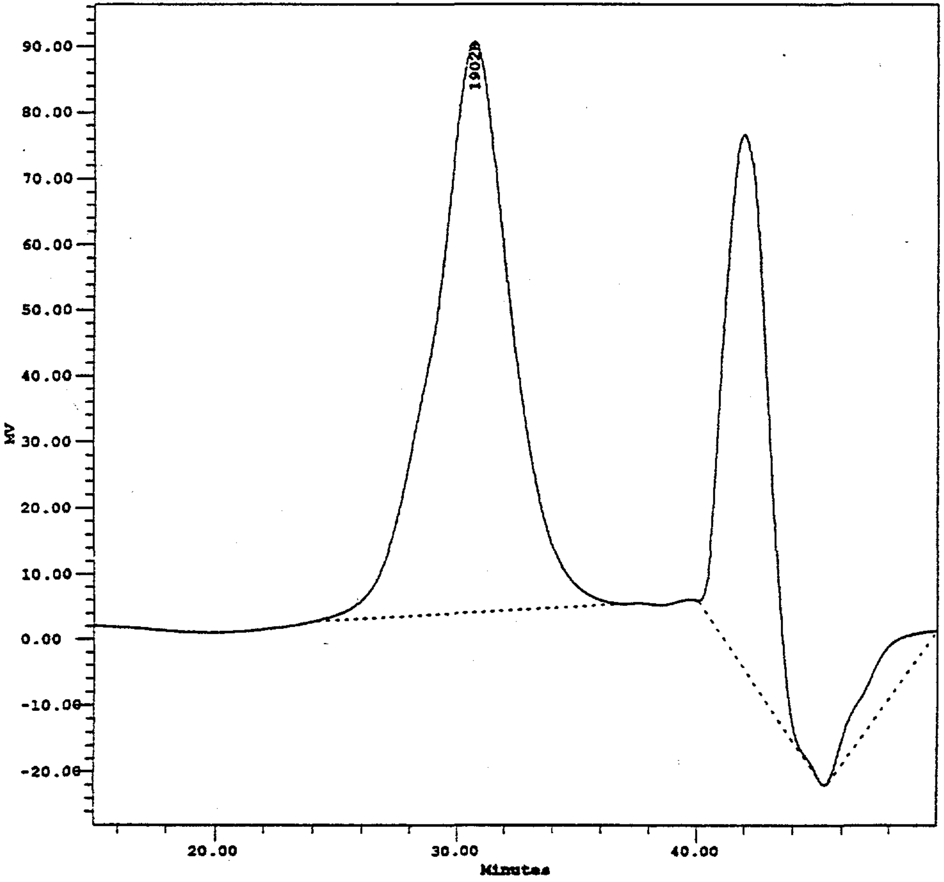
MP: 22562 Mw: 47134 Mn: 18204 Polydispersity: 2.589165
Retention Time: 30.350



Millennium Sample Information

Project Name:	Paul99		
Sample Name:	jy99009		
Vial:	4	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	02/19/99 02:47:21 AM	Date Processed:	02/19/99 10:38:04 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	Durham		

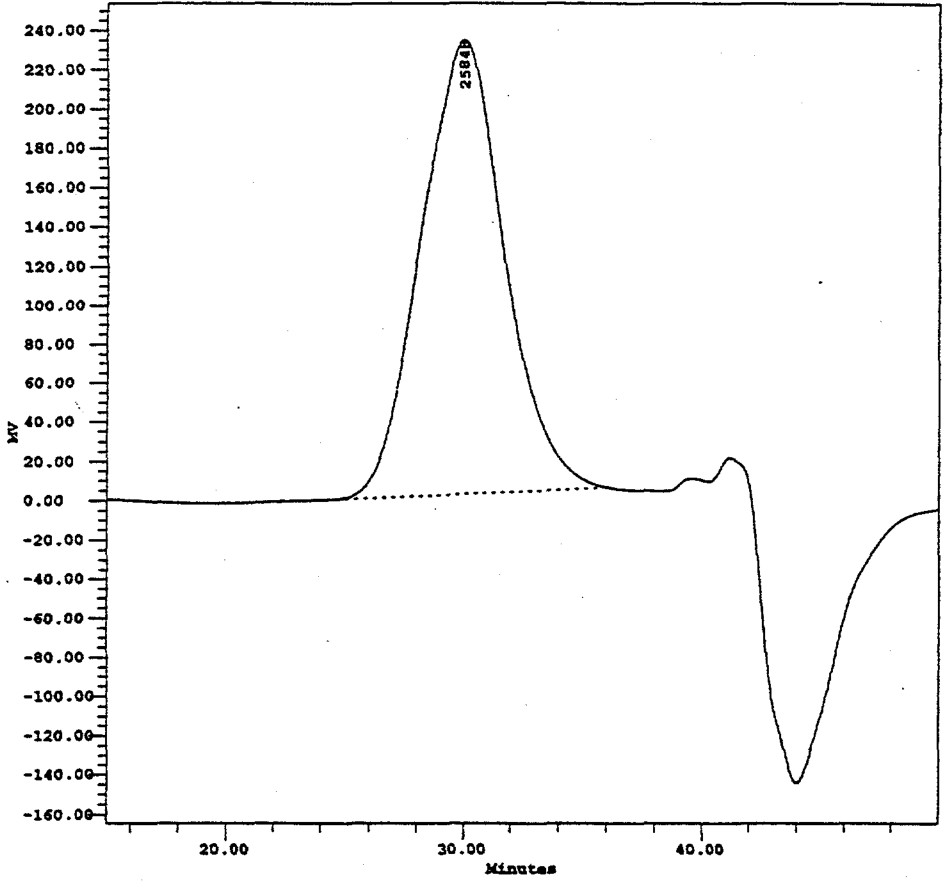
MP: 19028 Mw: 28753 Mn: 14443 Polydispersity: 1.990724
Retention Time: 30.700



Millennium Sample Information

Project Name:	Paul99		
Sample Name:	jy99055		
Vial:	4	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	04/25/99 08:50:26 PM	Date Processed:	04/30/99 09:22:42 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	Dawson		

MP: 25848 Mw: 35292 Mn: 18349 Polydispersity: 1.923415
Retention Time: 30.000

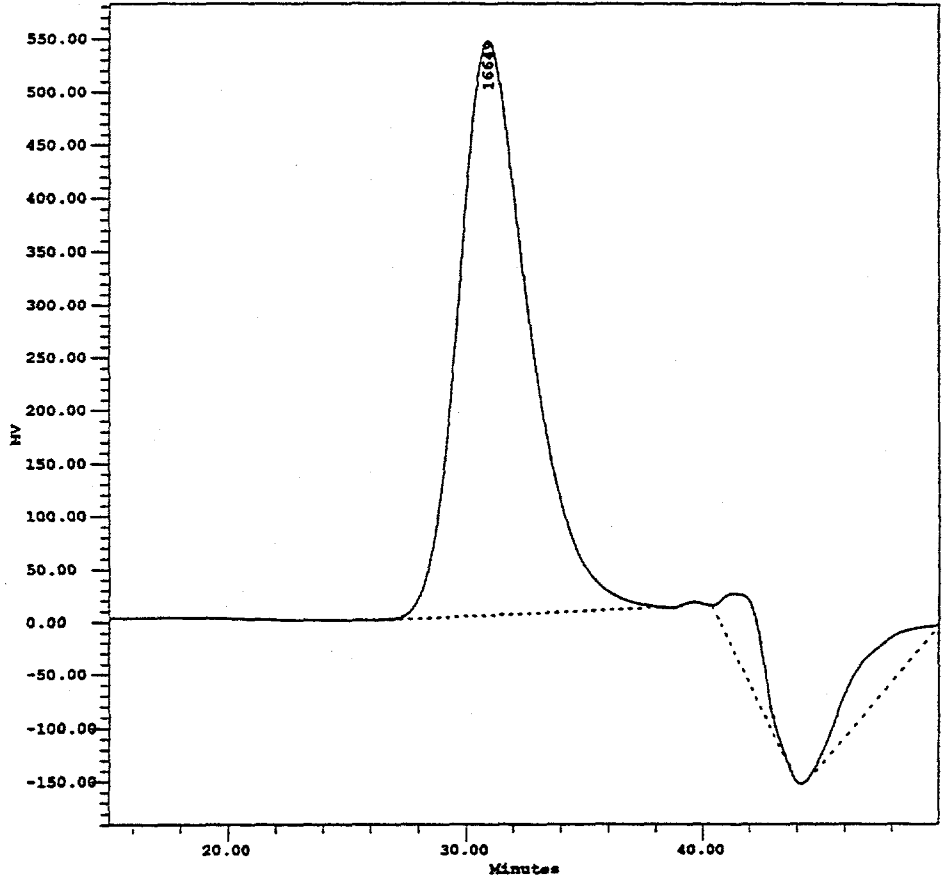


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99053
Vial: 2
Injection: 1
Channel: 410
Date Acquired: 04/25/99 07:02:56 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/25/99 07:53:14 PM
Dilution: 1.00000

MP: 16649 Mw: 16744 Mn: 9423 Polydispersity: 1.776947
Retention Time: 30.900

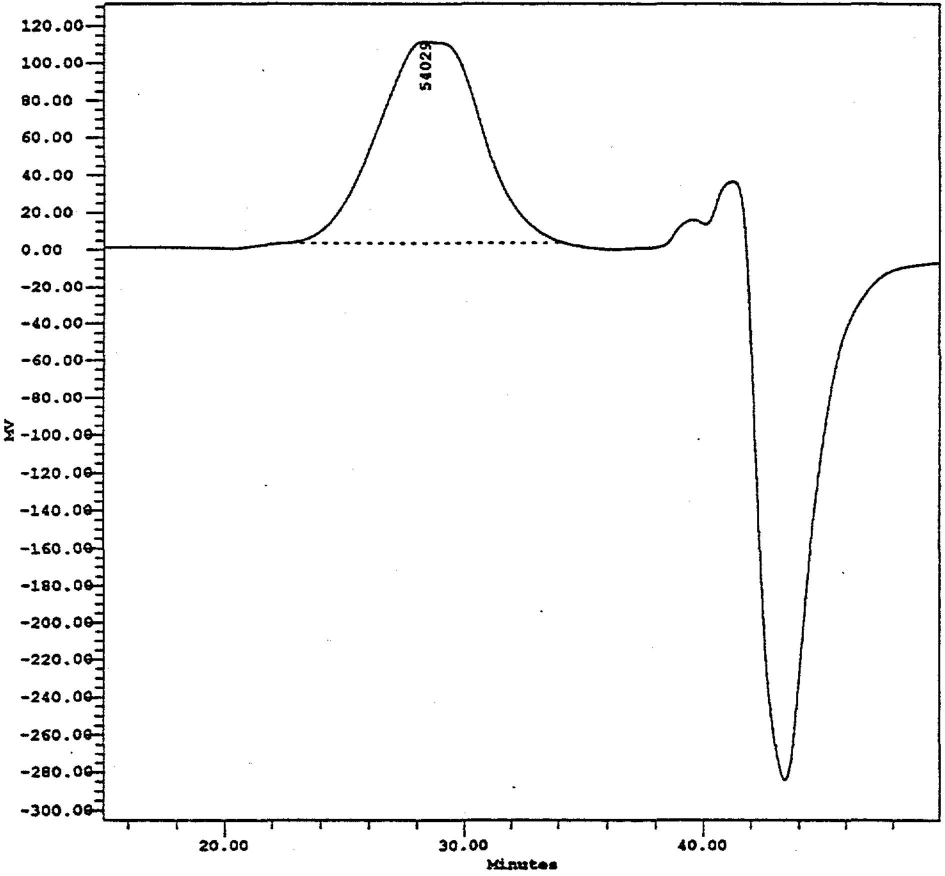


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99076
Vial: 2
Injection: 1
Channel: 410
Date Acquired: 05/25/99 03:31:32 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Trout

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 05/26/99 07:42:42 AM
Dilution: 1.00000

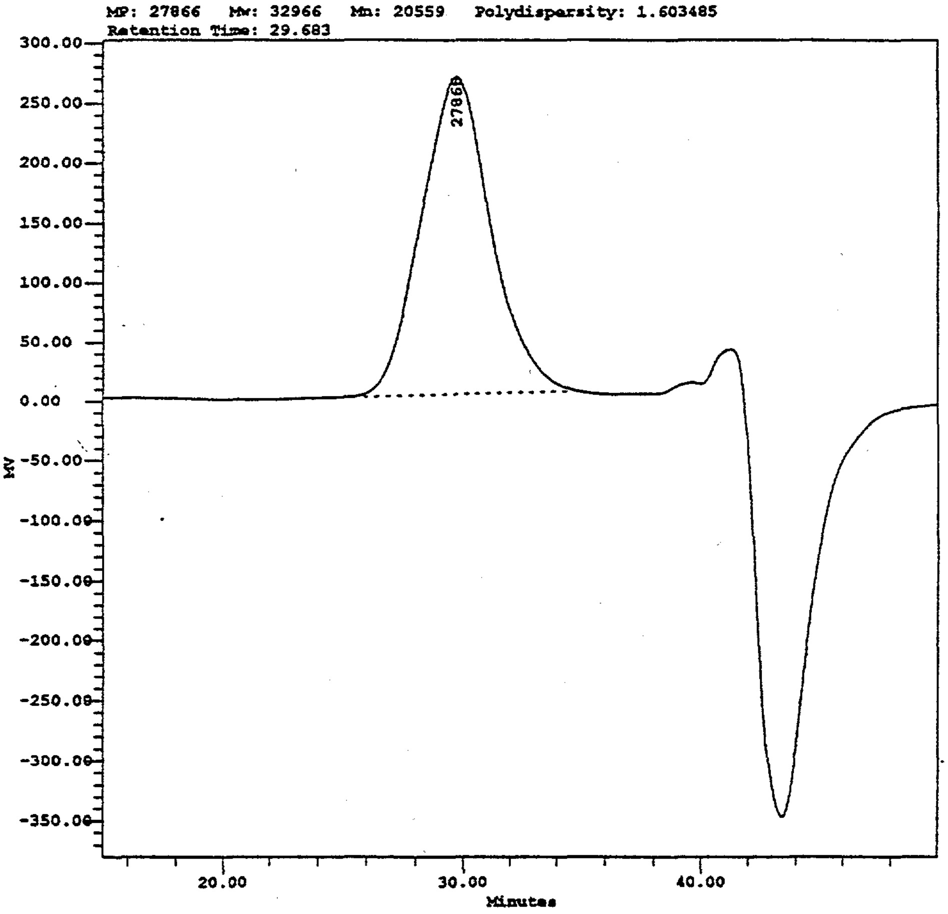
MP: 54029 Mw: 74215 Mn: 32552 Polydispersity: 2.279846
Retention Time: 28.333



Millennium Sample Information

Project Name: Paul99
Sample Name: jy99077
Vial: 3
Injection: 1
Channel: 410
Date Acquired: 05/25/99 04:25:18 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Trout

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 05/26/99 07:43:17 AM
Dilution: 1.00000

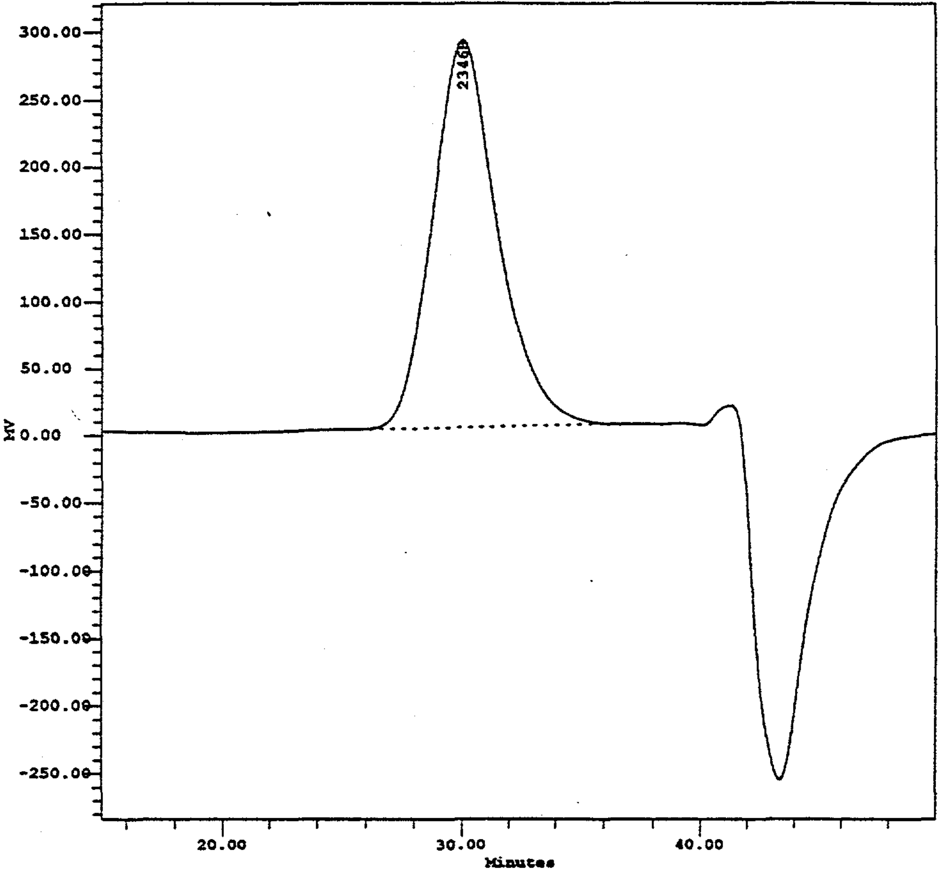

MP: 27866 Mw: 32966 Mn: 20559 Polydispersity: 1.603485
Retention Time: 29.683

Millennium Sample Information

Project Name: Paul99
Sample Name: jy99078
Vial: 4
Injection: 1
Channel: 410
Date Acquired: 05/25/99 05:19:04 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Trout

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 05/26/99 07:43:39 AM
Dilution: 1.00000

MP: 23468 Mw: 25481 Mn: 16120 Polydispersity: 1.580643
Retention Time: 30.033

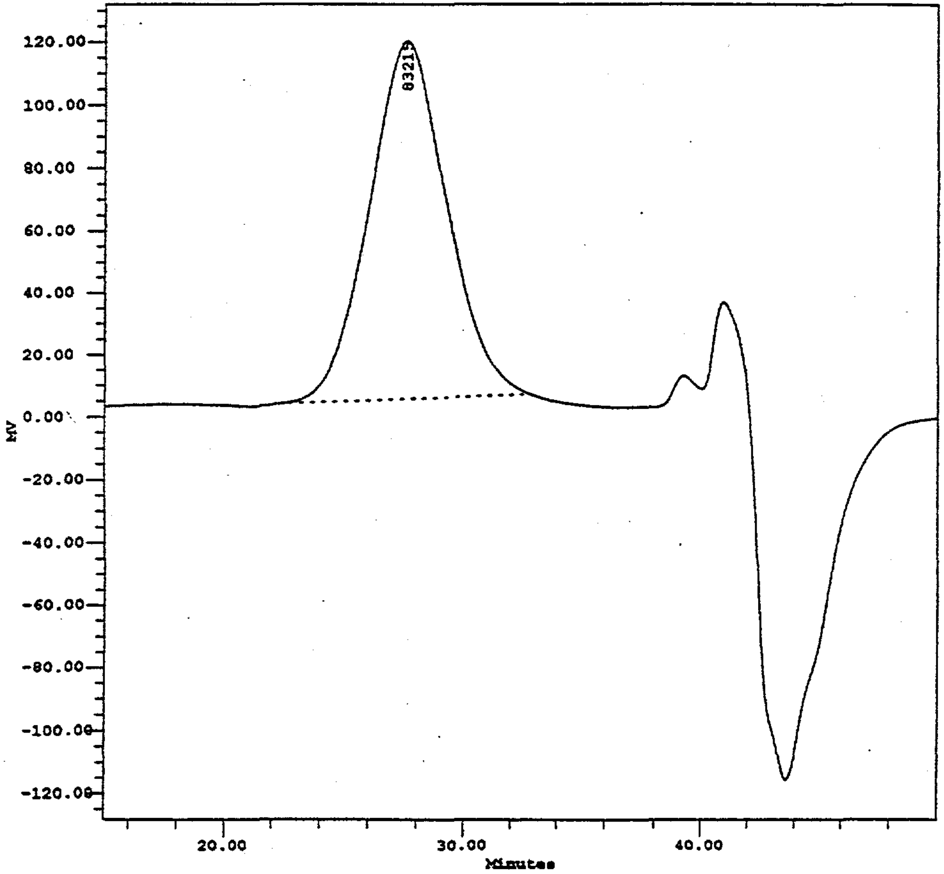


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99070
Vial: 5
Injection: 1
Channel: 410
Date Acquired: 05/17/99 02:06:52 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 05/17/99 06:16:57 AM
Dilution: 1.00000

MP: 83215 Mw: 103351 Mn: 59037 Polydispersity: 1.750622
Retention Time: 27.600

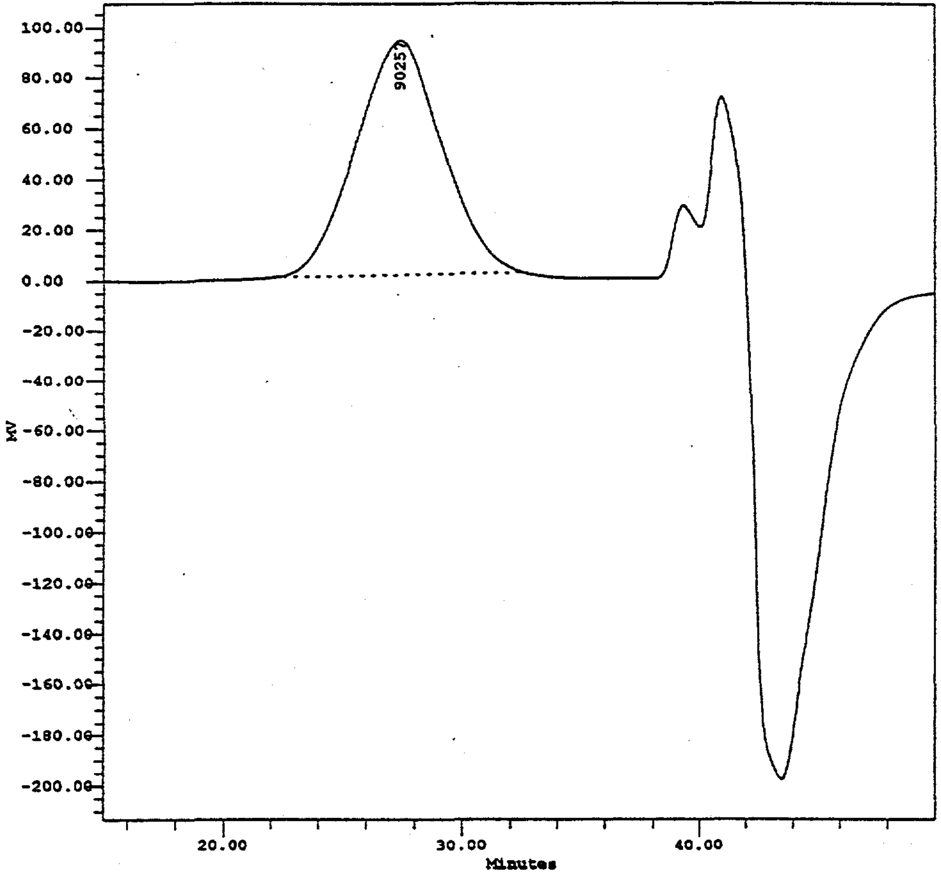


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99061
Vial: 1
Injection: 2
Channel: 410
Date Acquired: 05/09/99 11:02:10 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Dawson

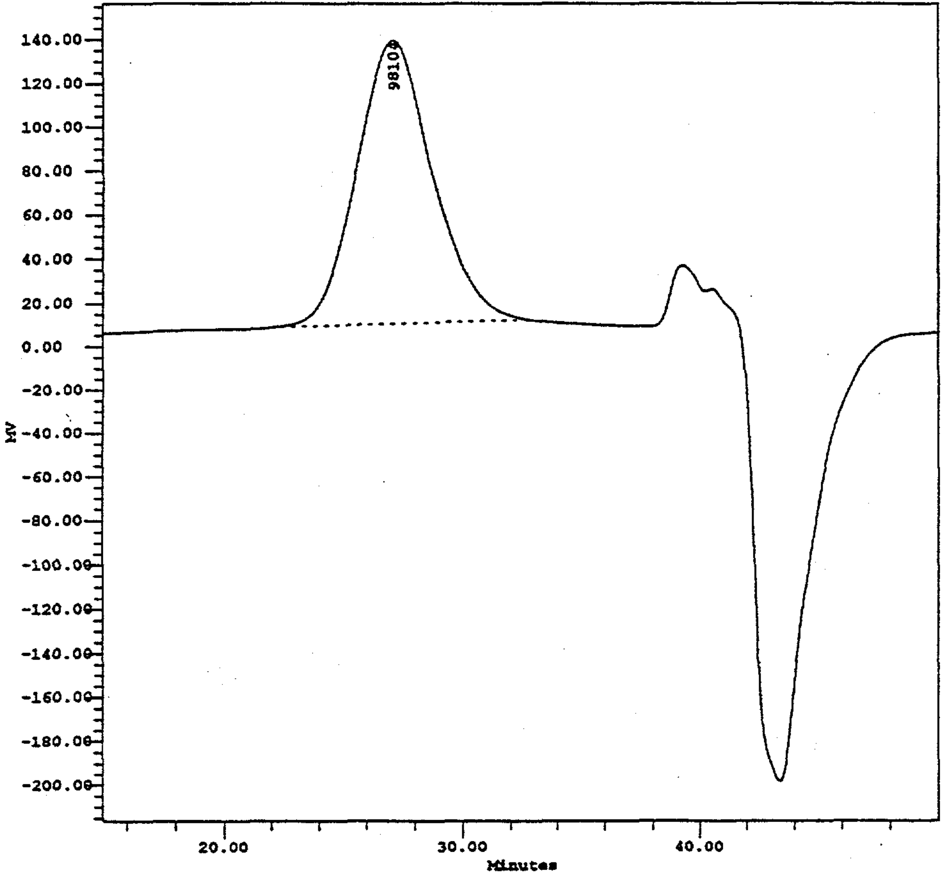
Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 05/10/99 07:12:50 AM
Dilution: 1.00000

MP: 90257 Mw: 124923 Mn: 66178 Polydispersity: 1.887678
Retention Time: 27.433



```
                    Millennium Sample Information

Project Name:        Paul99
Sample Name:         jy99080
Vial:                6                        Sample Type:      Broad Unknown
Injection:           1                        Volume:           300.00
Channel:             410                      Run Time:         50.0 min
Date Acquired:       05/25/99 07:06:34 PM     Date Processed:   05/26/99 07:44:39 AM
SampleWeight:        1.00000                  Dilution:         1.00000
Acq Meth Set:        meth_set1
Processing Method:   Trout
```

MP: 98104   Mw: 118734   Mn: 68802   Polydispersity: 1.725749
Retention Time: 27.117

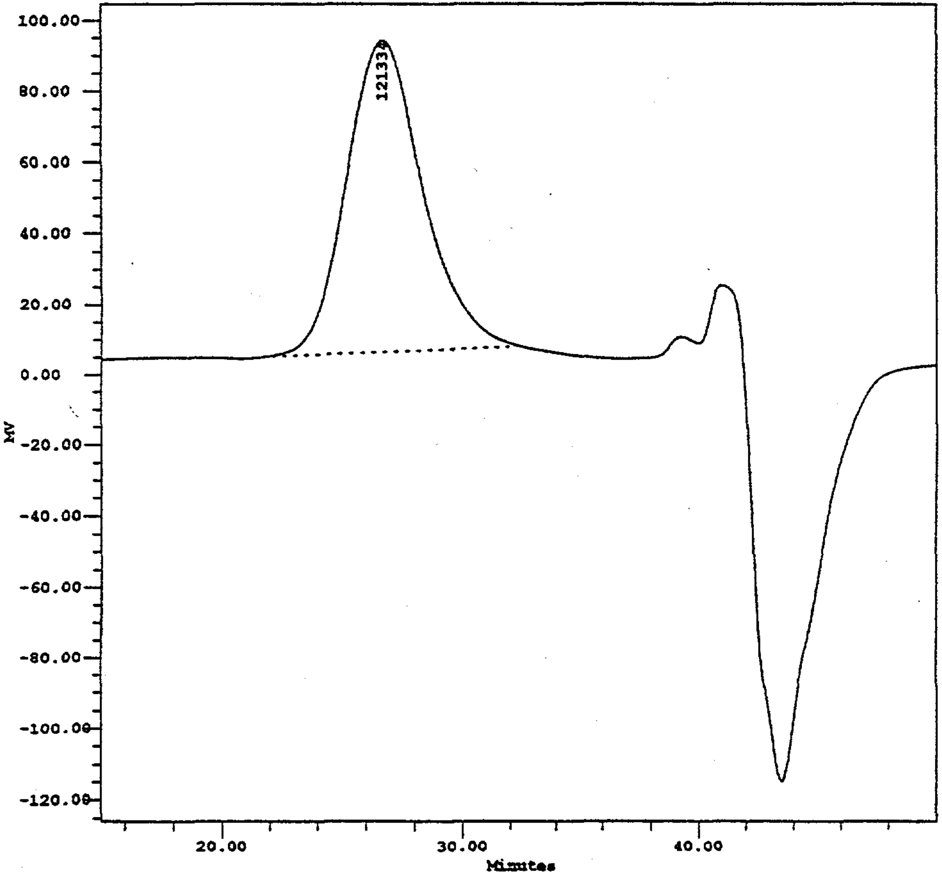


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99081
Vial: 7
Injection: 1
Channel: 410
Date Acquired: 05/25/99 08:00:19 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Trout

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 05/26/99 07:45:18 AM
Dilution: 1.00000

MP: 121334 Mw: 140811 Mn: 81199 Polydispersity: 1.734132
Retention Time: 26.683

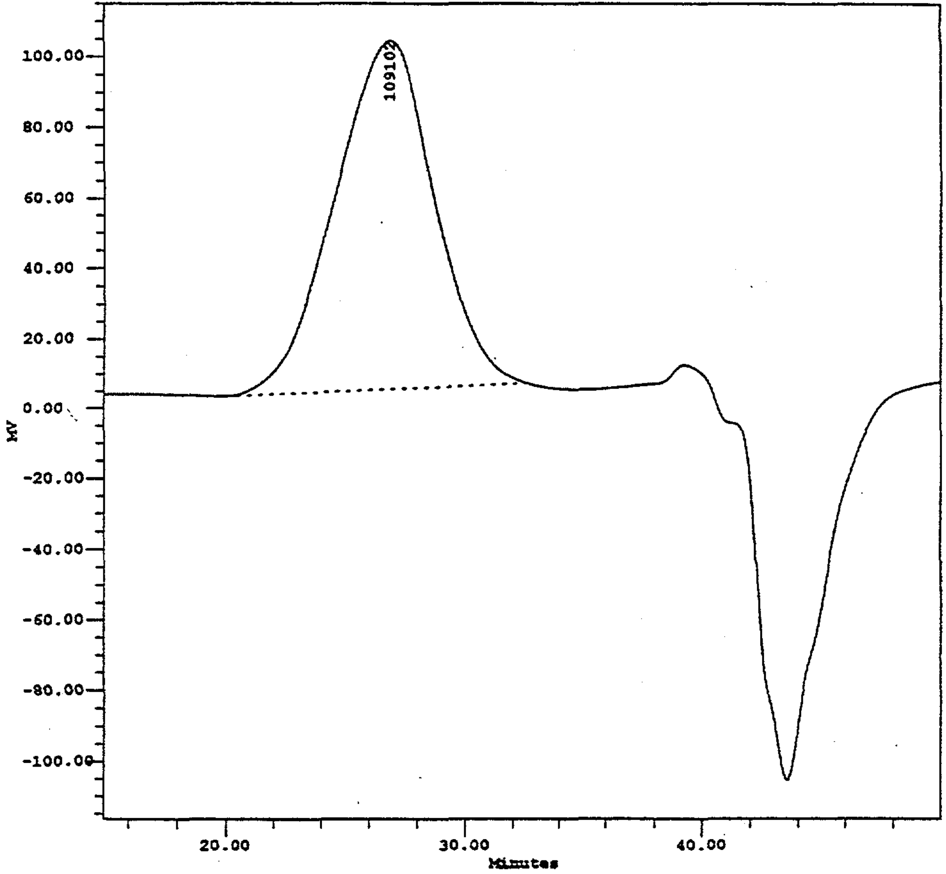


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99082
Vial: 8
Injection: 1
Channel: 410
Date Acquired: 05/25/99 08:54:04 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Trout

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 05/26/99 07:45:46 AM
Dilution: 1.00000

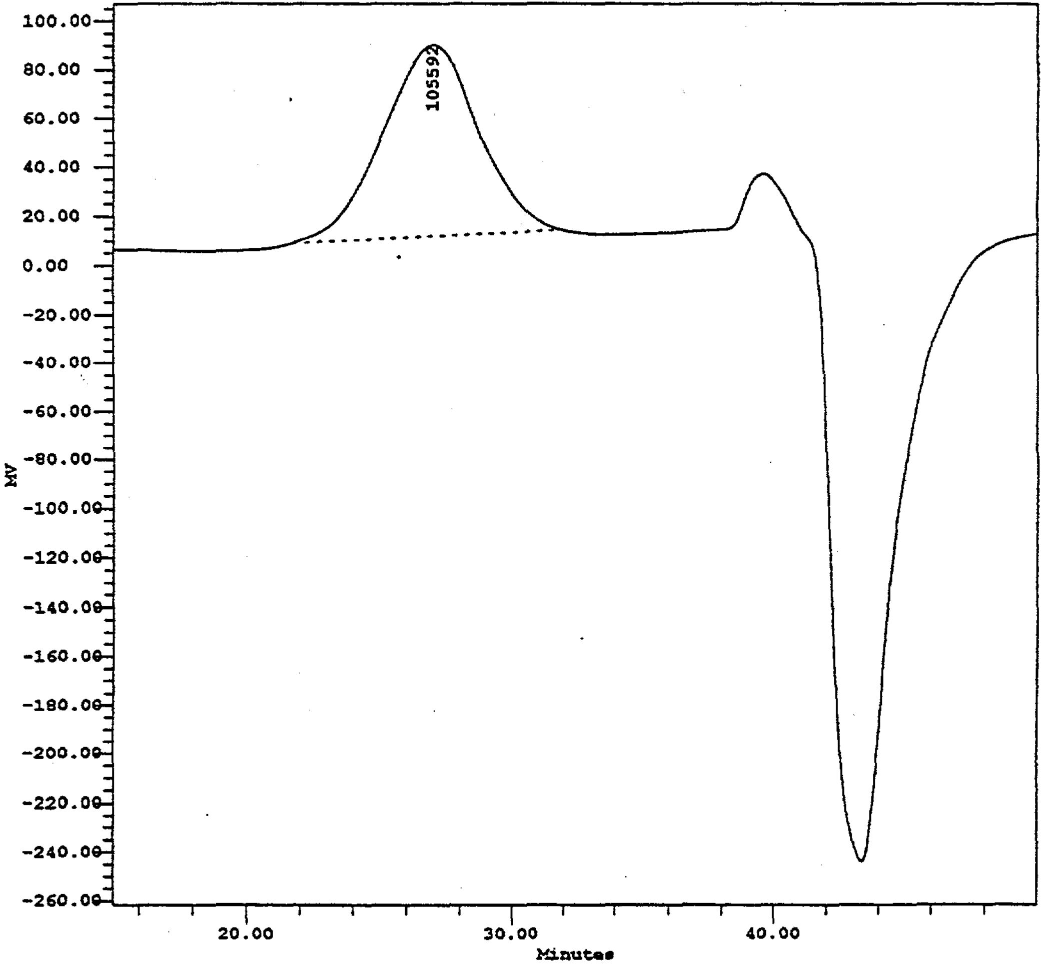
MP: 109102 Mw: 187196 Mn: 82052 Polydispersity: 2.281436
Retention Time: 26.900



Millennium Sample Information

Project Name:	Paul99		
Sample Name:	jy99083		
Vial:	9	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	05/25/99 09:47:49 PM	Date Processed:	05/26/99 07:46:14 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	Trout		

MP: 105592 Mw: 151108 Mn: 77999 Polydispersity: 1.937312
Retention Time: 26.967

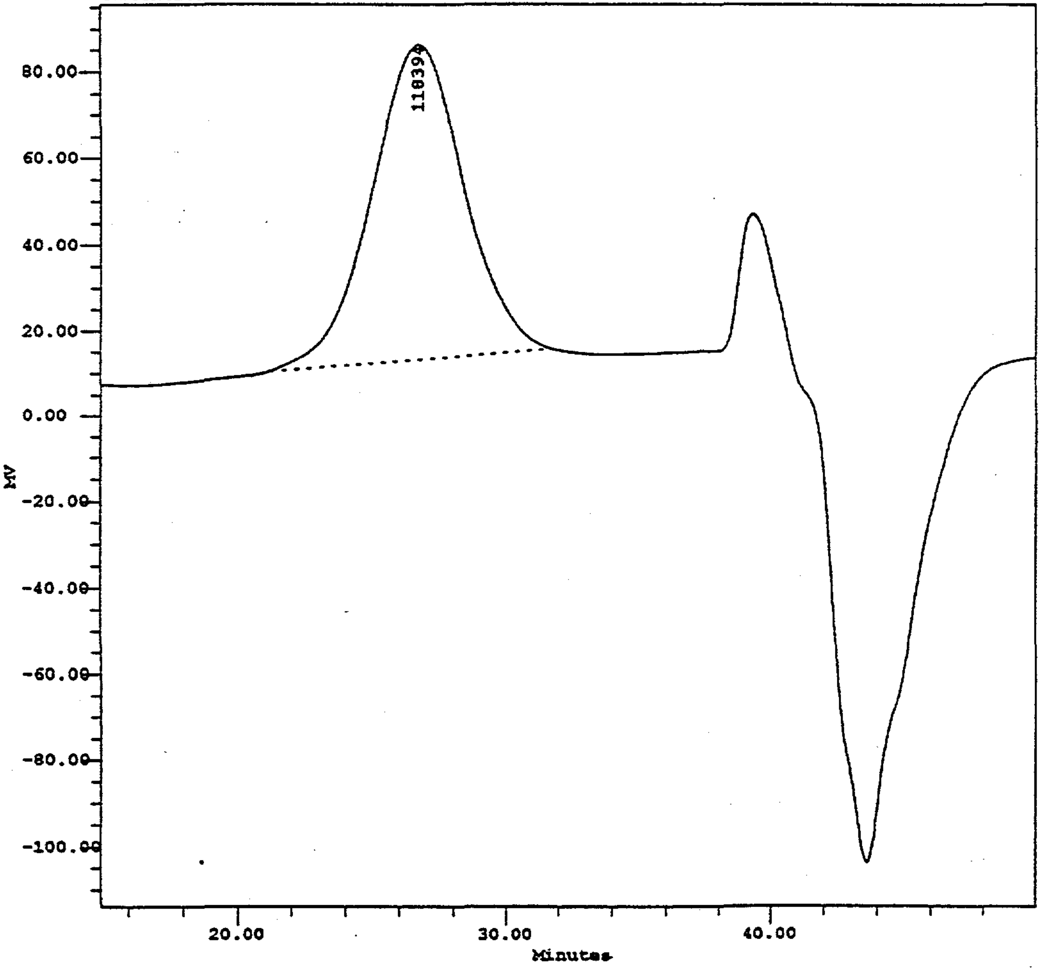


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99084
Vial: 10
Injection: 1
Channel: 410
Date Acquired: 05/25/99 10:41:34 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Trout

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 05/26/99 07:46:52 AM
Dilution: 1.00000

MP: 118394 Mw: 162706 Mn: 87326 Polydispersity: 1.863208
Retention Time: 26.733

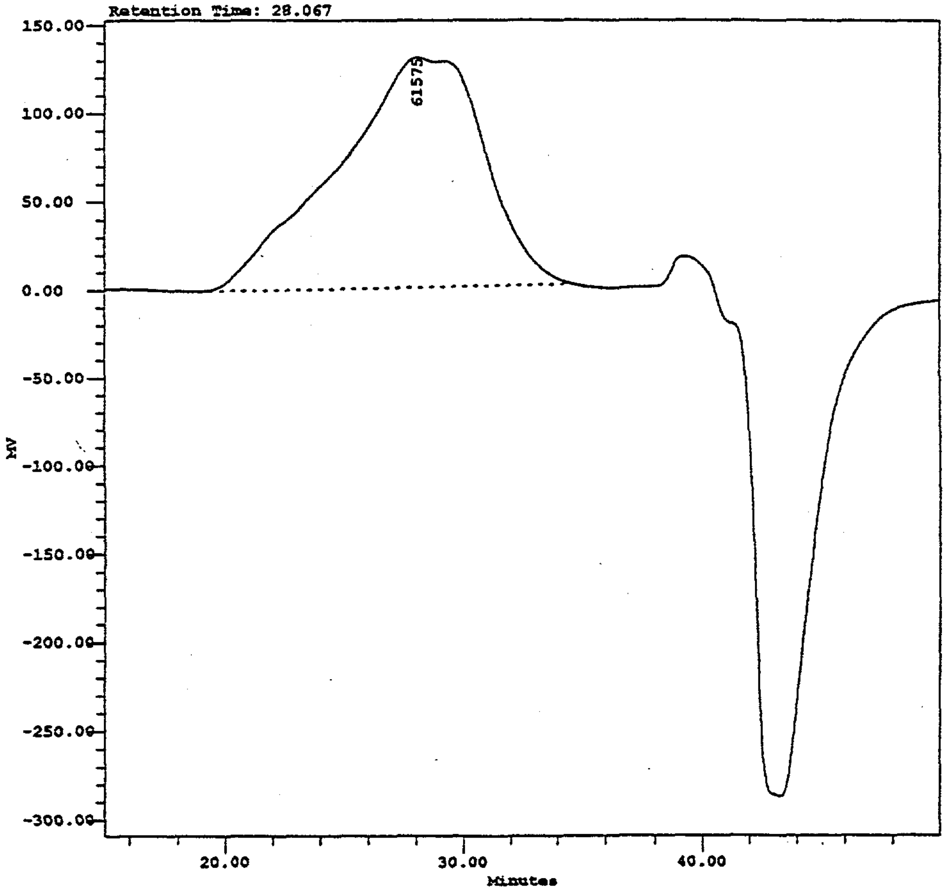


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99095
Vial: 2
Injection: 1
Channel: 410
Date Acquired: 05/30/99 10:55:20 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Trout

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 05/31/99 07:07:06 AM
Dilution: 1.00000

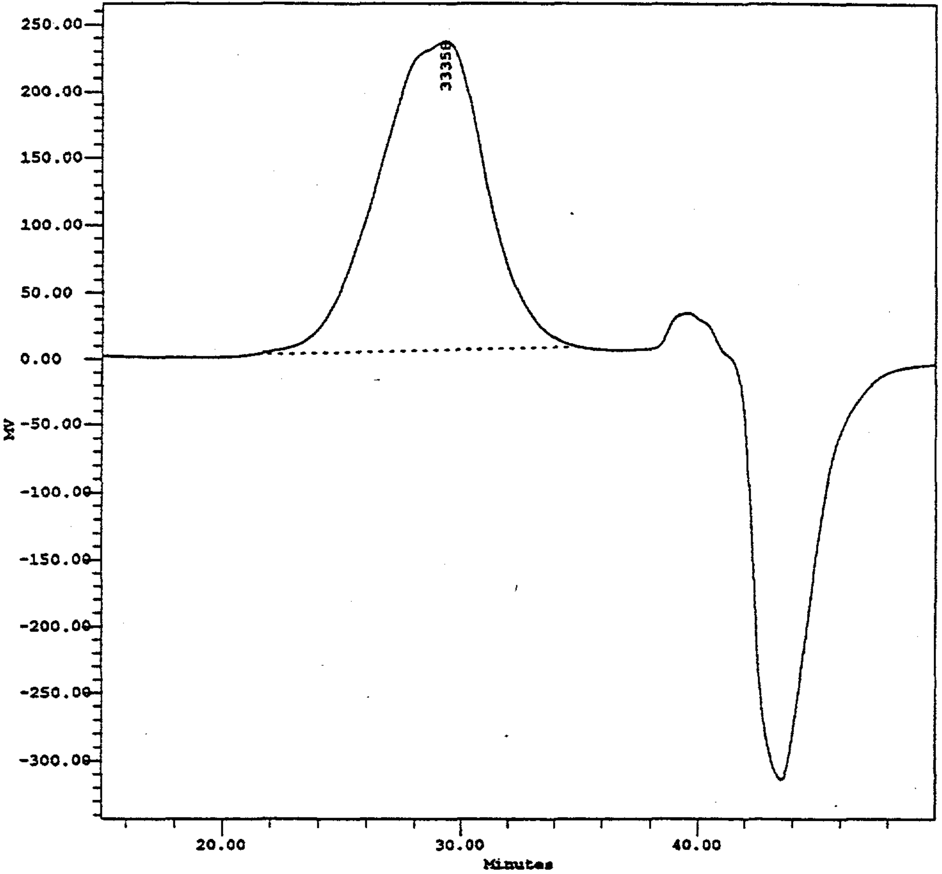
MP: 61575 Mw: 164357 Mn: 36563 Polydispersity: 4.495172
Retention Time: 28.067



Millennium Sample Information

Project Name:	Paul99		
Sample Name:	jy99096		
Vial:	3	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	05/30/99 11:49:04 PM	Date Processed:	05/31/99 07:06:39 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	Trout		

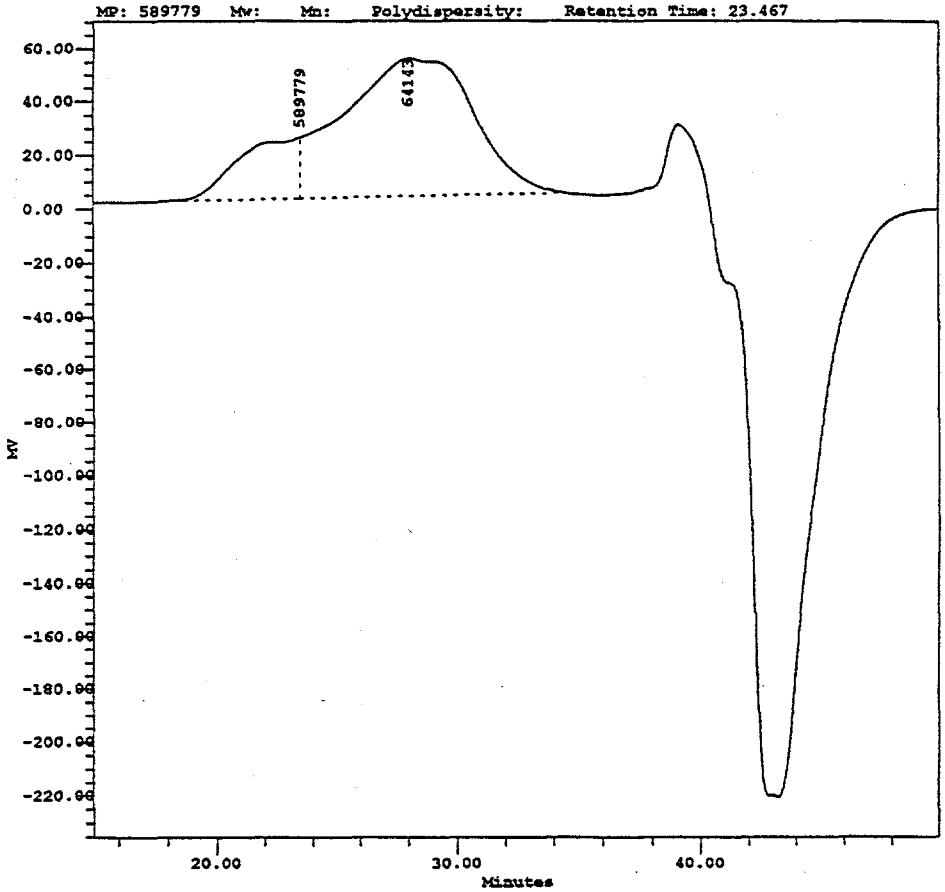
MP: 33358 Mw: 76242 Mn: 28631 Polydispersity: 2.662882
Retention Time: 29.317



Millennium Sample Information

Project Name: Paul99
Sample Name: jy99097
Vial: 4
Injection: 1
Channel: 410
Date Acquired: 05/31/99 12:42:50 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Trout

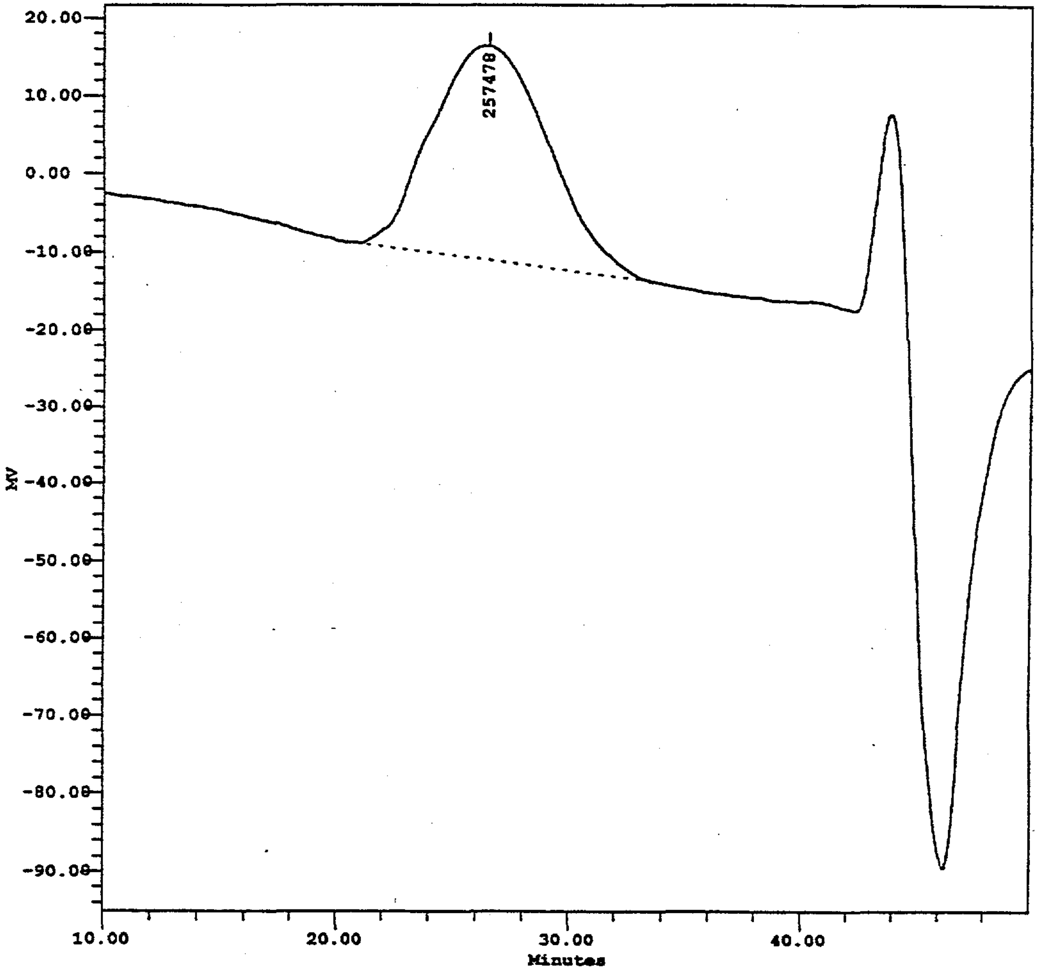
Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 05/31/99 07:06:06 AM
Dilution: 1.00000



Millennium Sample Information

Project Name:	LOWMW		
Sample Name:	jy99-150		
Vial:	7	Sample Type:	Broad Unknown
Injection:	1	Volume:	200.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	09/07/99 03:28:56 PM	Date Processed:	03/09/00 03:02:14 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	sept299		

MP: 257478 Mw: 312806 Mn: 130477 Polydispersity: 2.397405
Retention Time: 26.550

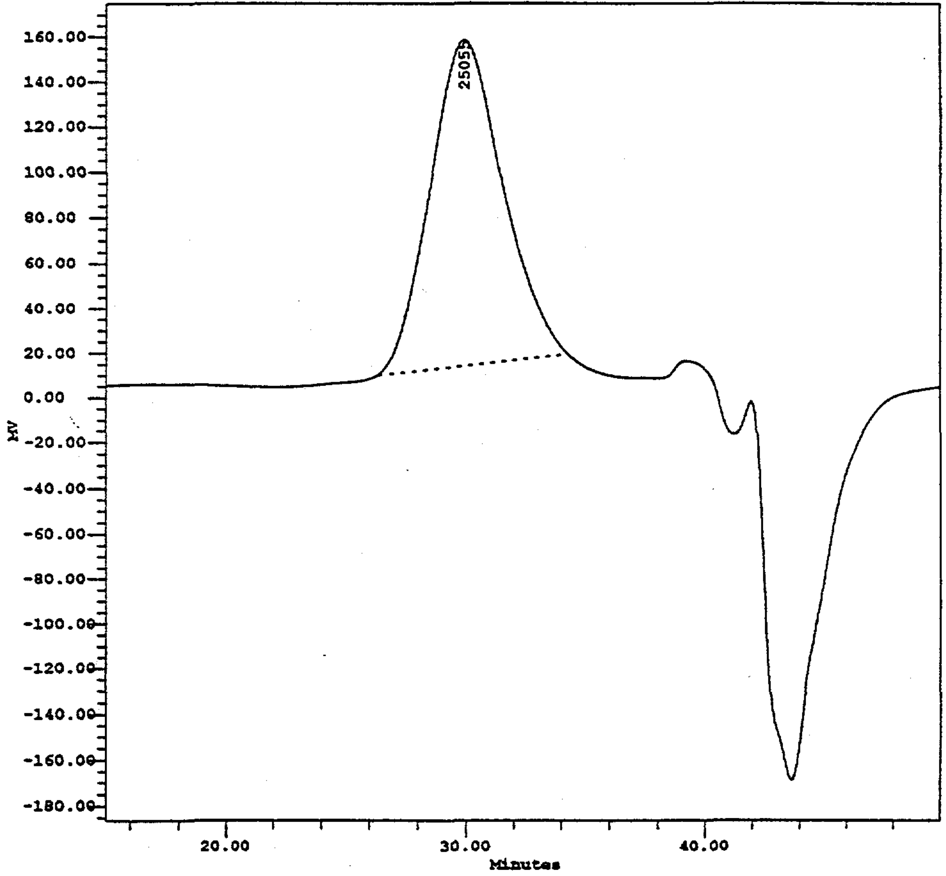


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99093
Vial: 18
Injection: 1
Channel: 410
Date Acquired: 05/26/99 05:51:34 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Trout

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 05/26/99 07:52:20 AM
Dilution: 1.00000

MP: 25055 Mw: 28062 Mn: 17739 Polydispersity: 1.581943
Retention Time: 29.900

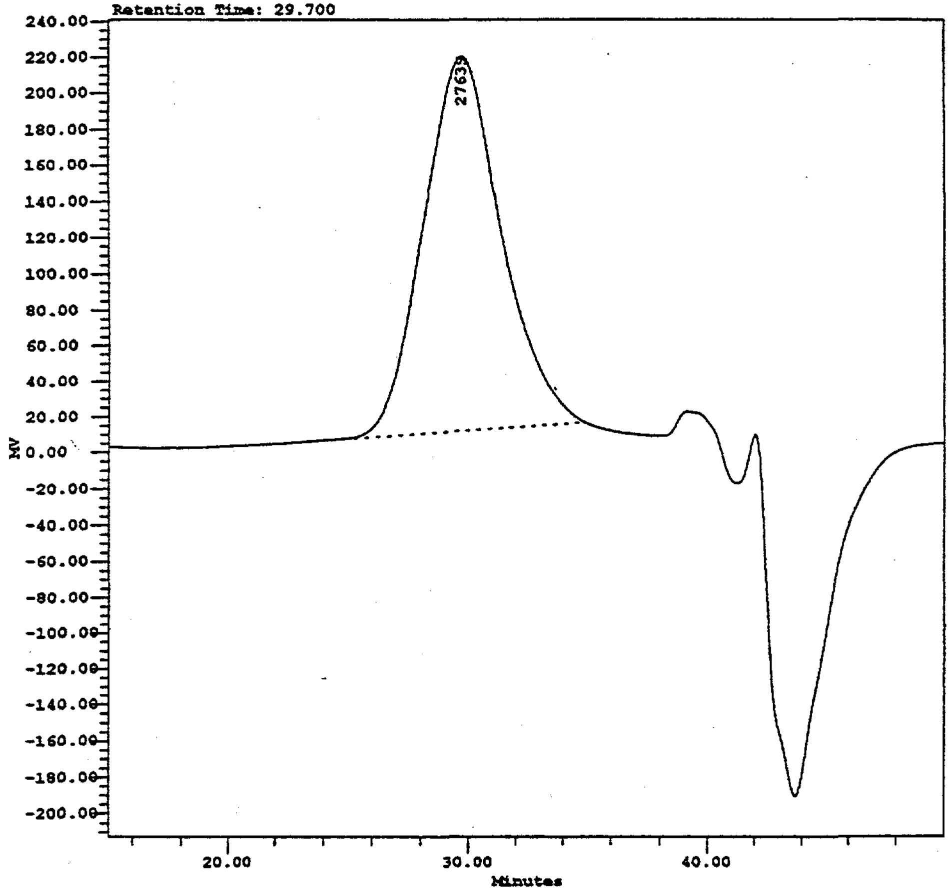


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99090
Vial: 15
Injection: 1
Channel: 410
Date Acquired: 05/26/99 03:10:18 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: Trout

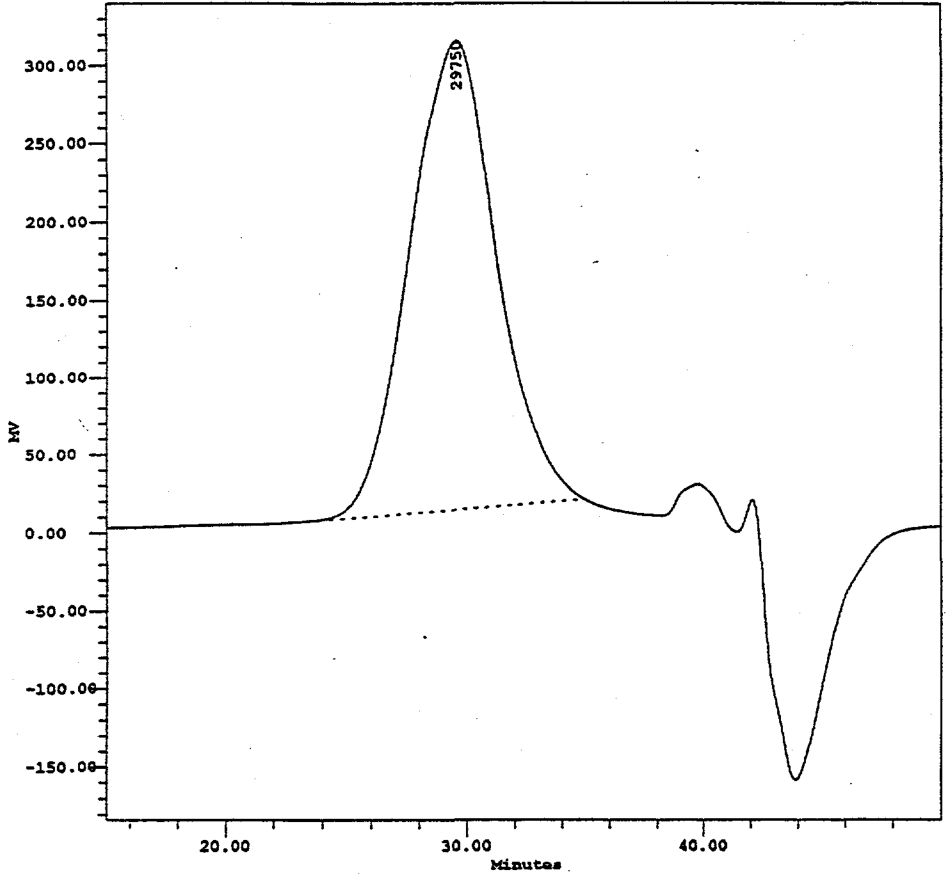
Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 05/26/99 07:50:22 AM
Dilution: 1.00000

MP: 27639 **Mw:** 33021 **Mn:** 18693 **Polydispersity:** 1.766527
Retention Time: 29.700



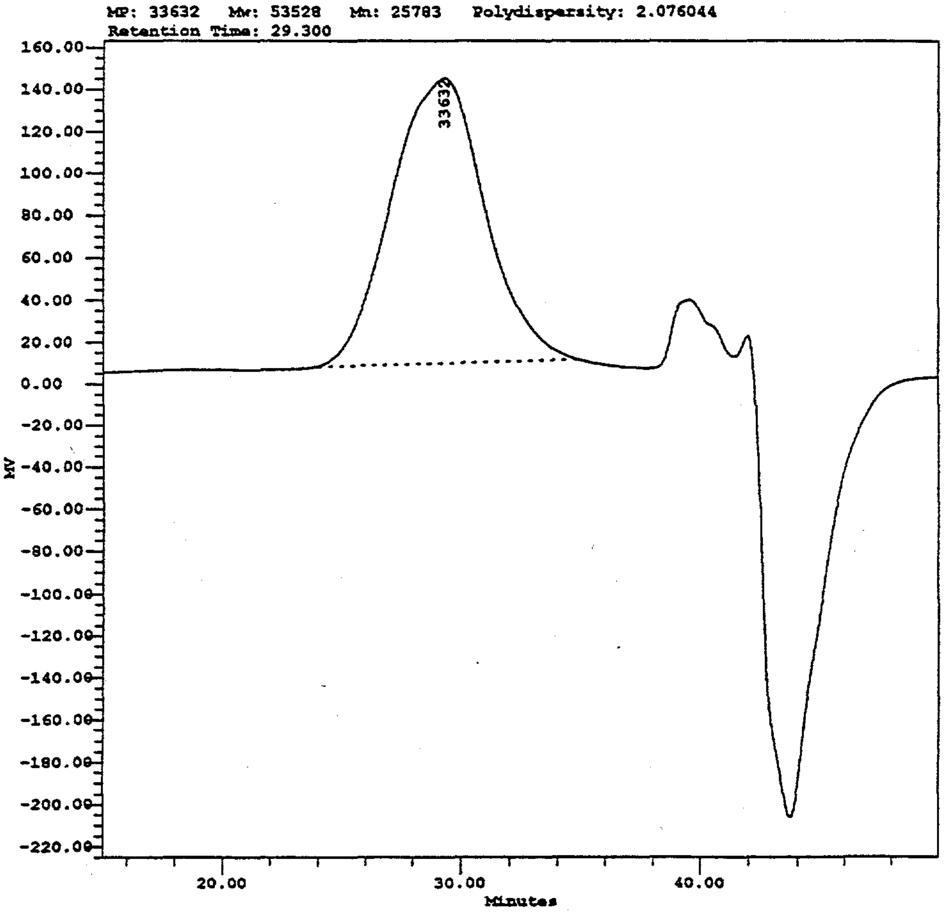
```
                    Millennium Sample Information

Project Name:        Paul99
Sample Name:         jy99091
Vial:                16                          Sample Type:      Broad Unknown
Injection:           1                           Volume:           300.00
Channel:             410                         Run Time:         50.0 min
Date Acquired:       05/26/99 04:04:04 AM        Date Processed:   05/26/99 07:51:03 AM
SampleWeight:        1.00000                     Dilution:         1.00000
Acq Meth Set:        meth_set1
Processing Method:   Trout
```

MP: 29750 Mw: 42596 Mn: 21581 Polydispersity: 1.973766
Retention Time: 29.550



Millennium Sample Information

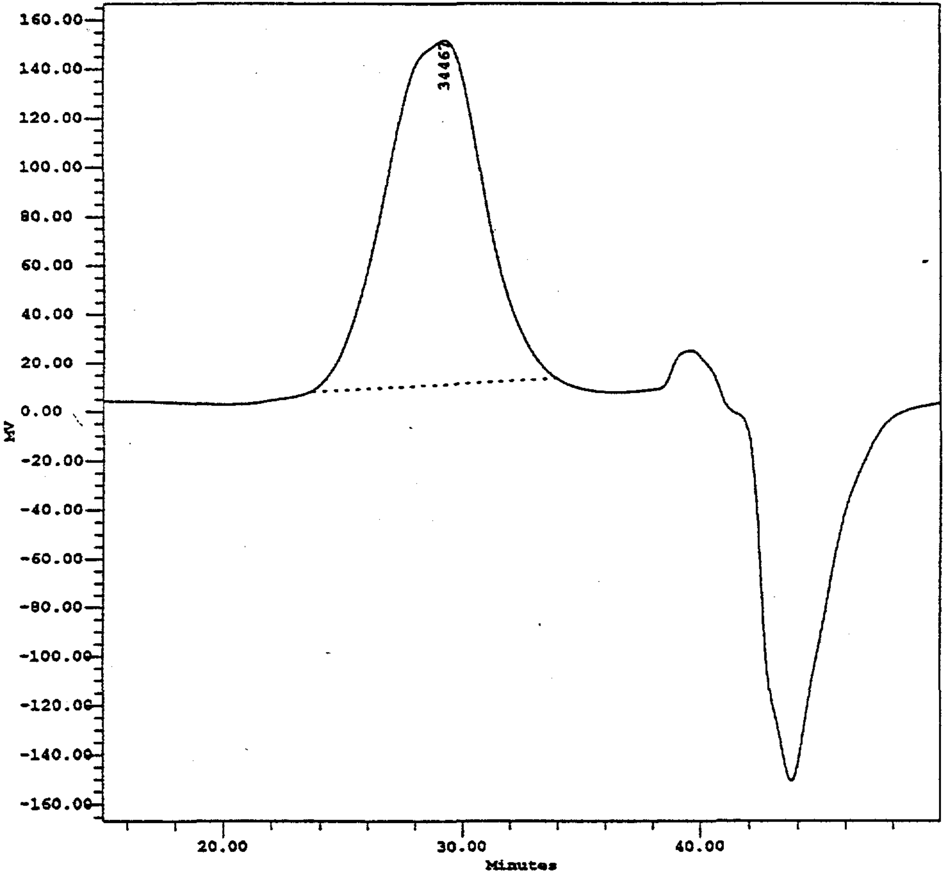
Project Name:	Paul99		
Sample Name:	jy99092		
Vial:	17	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	05/26/99 04:57:49 AM	Date Processed:	05/26/99 07:51:43 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	Trout		



Millennium Sample Information

Project Name:	Paul99		
Sample Name:	jy99094		
Vial:	19	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	05/26/99 06:45:19 AM	Date Processed:	05/26/99 07:53:00 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	Trout		

MP: 34467 Mw: 62320 Mn: 29639 Polydispersity: 2.102589
Retention Time: 29.250

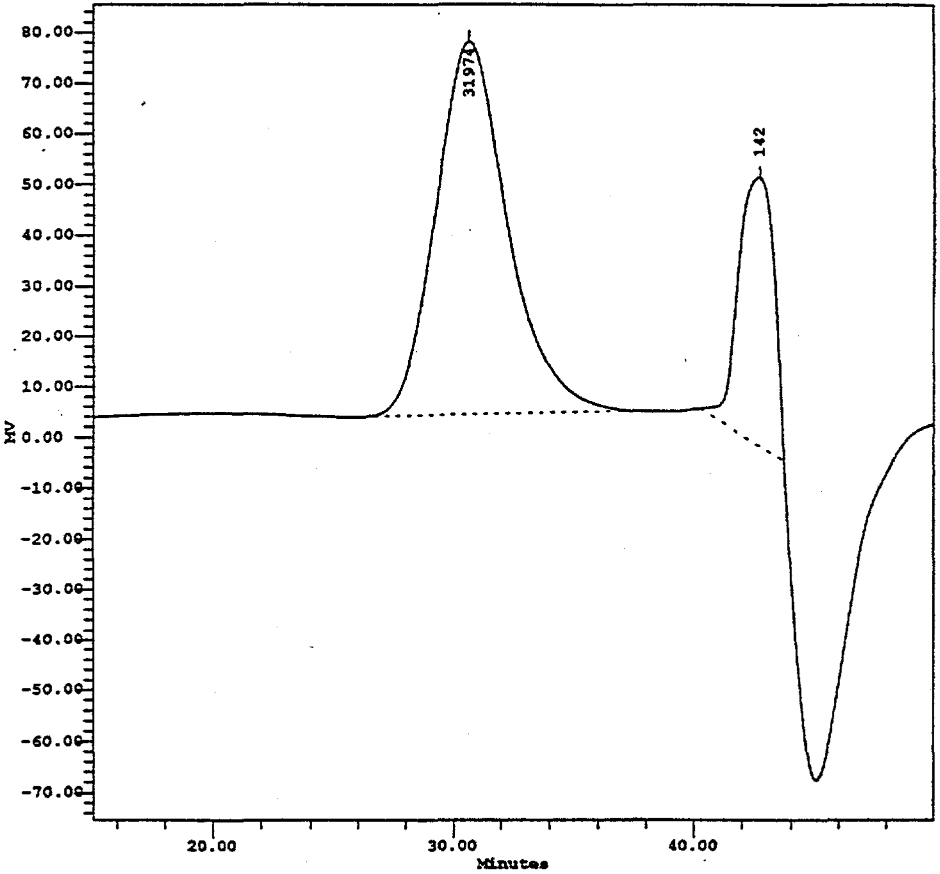


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99108
Vial: 31
Injection: 1
Channel: 410
Date Acquired: 06/13/99 09:38:40 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: 61299

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 06/13/99 02:01:39 PM
Dilution: 1.00000

MP: 31974 Mw: 35954 Mn: 20675 Polydispersity: 1.739029
Retention Time: 30.650

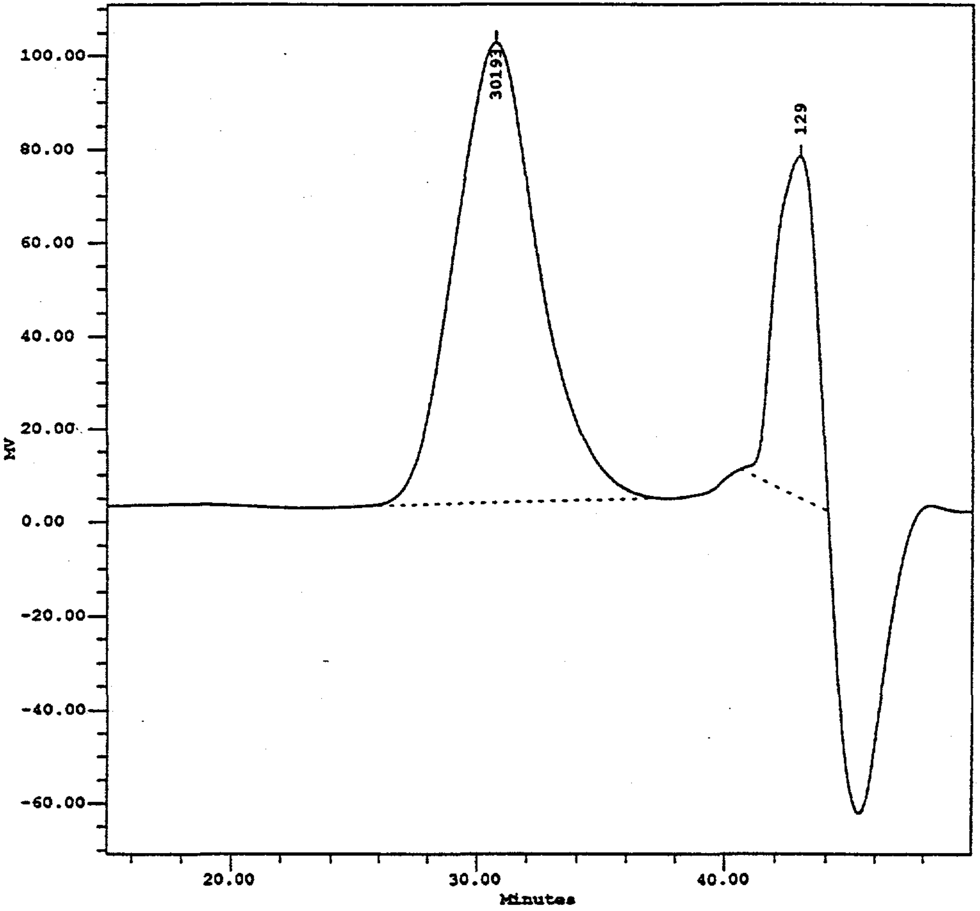


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99109
Vial: 32
Injection: 1
Channel: 410
Date Acquired: 06/13/99 10:32:25 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: 61299

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 06/13/99 02:02:16 PM
Dilution: 1.00000

MP: 30193 Mw: 38016 Mn: 19918 Polydispersity: 1.908680
Retention Time: 30.767

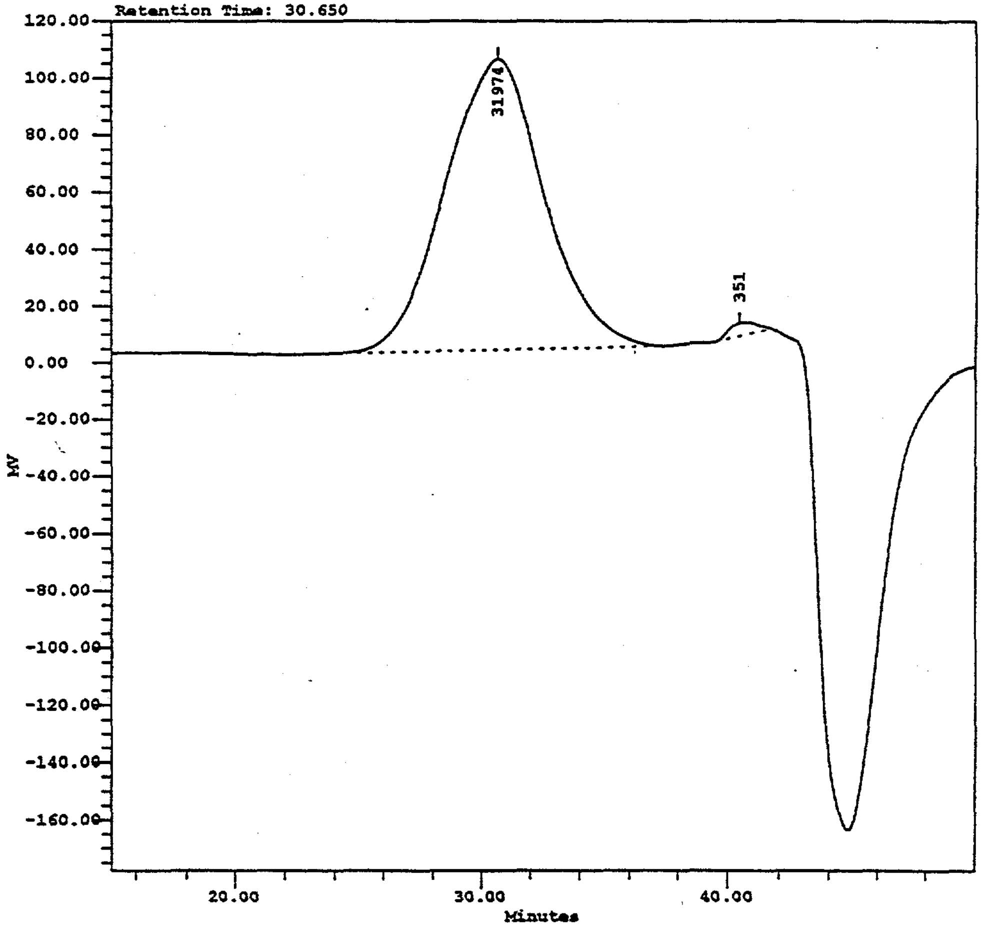


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99104
Vial: 27
Injection: 1
Channel: 410
Date Acquired: 06/13/99 06:03:46 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: 61299

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 06/13/99 07:01:12 AM
Dilution: 1.00000

MP: 31974 Mw: 50464 Mn: 21699 Polydispersity: 2.325625
Retention Time: 30.650

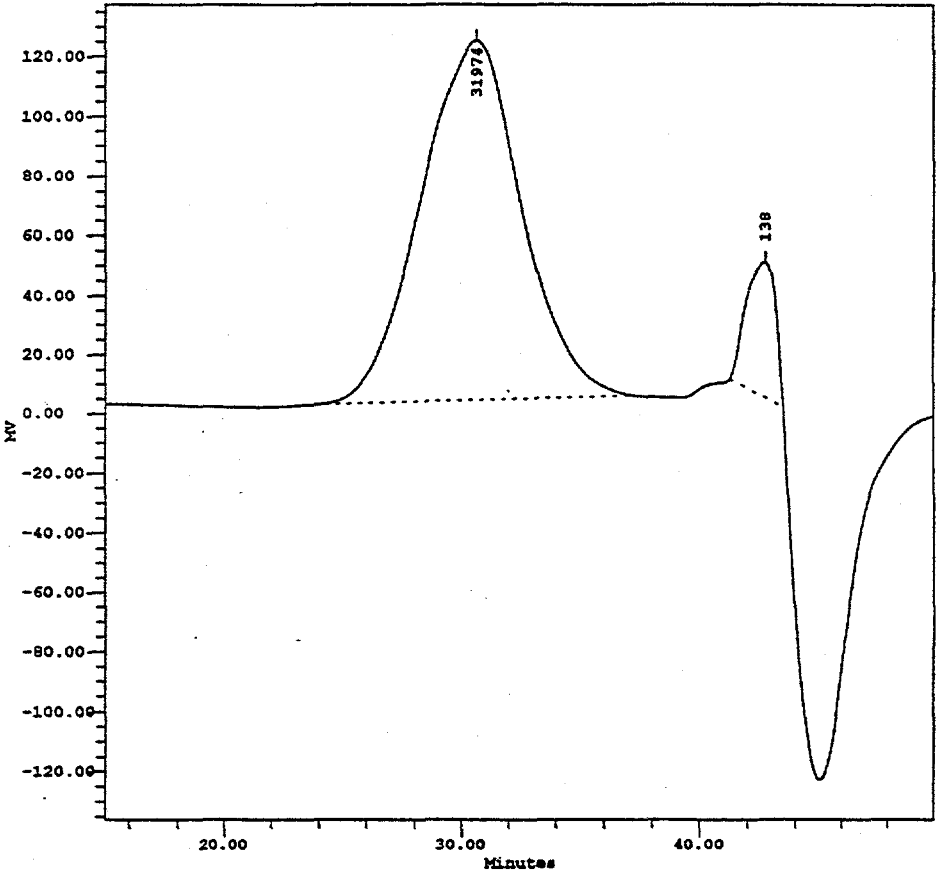


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99110
Vial: 33
Injection: 1
Channel: 410
Date Acquired: 06/13/99 11:26:09 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: 61299

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 06/13/99 02:02:46 PM
Dilution: 1.00000

MP: 31974 Mw: 55249 Mn: 21919 Polydispersity: 2.520620
Retention Time: 30.650

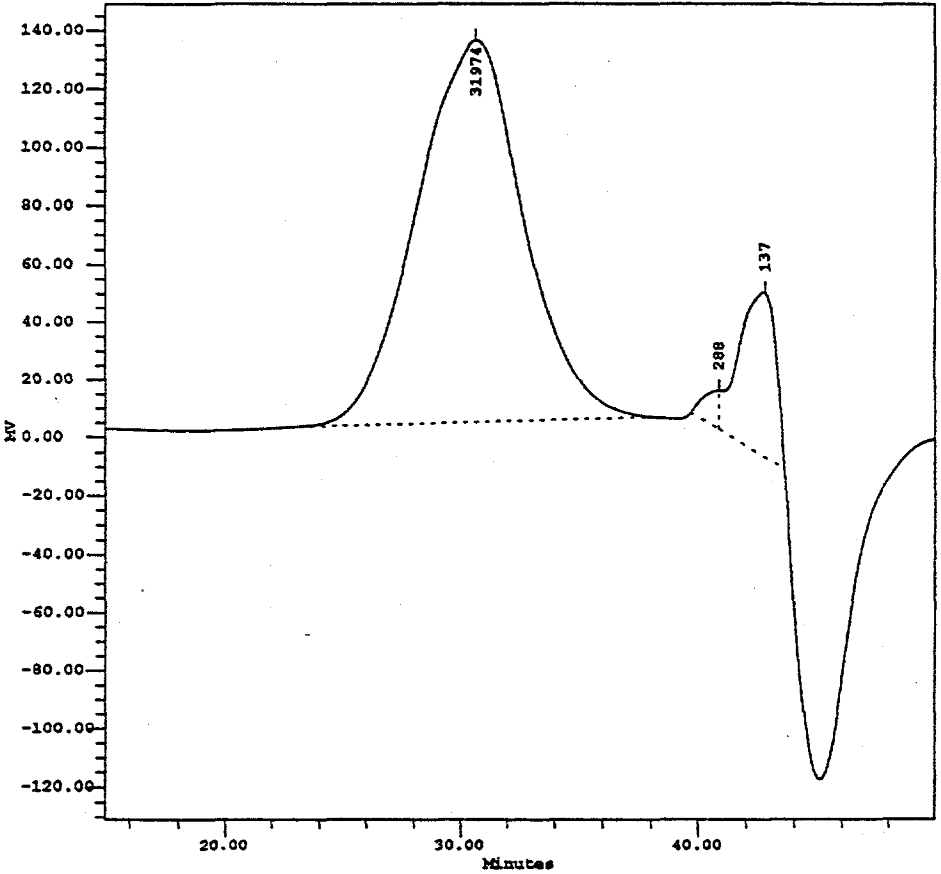


111

Millennium Sample Information

Project Name:	Paul99		
Sample Name:	jy99111		
Vial:	34	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	06/13/99 12:19:54 PM	Date Processed:	06/13/99 02:03:34 PM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	61299		

MP: 31974 Mw: 59652 Mn: 20552 Polydispersity: 2.902497
Retention Time: 30.650

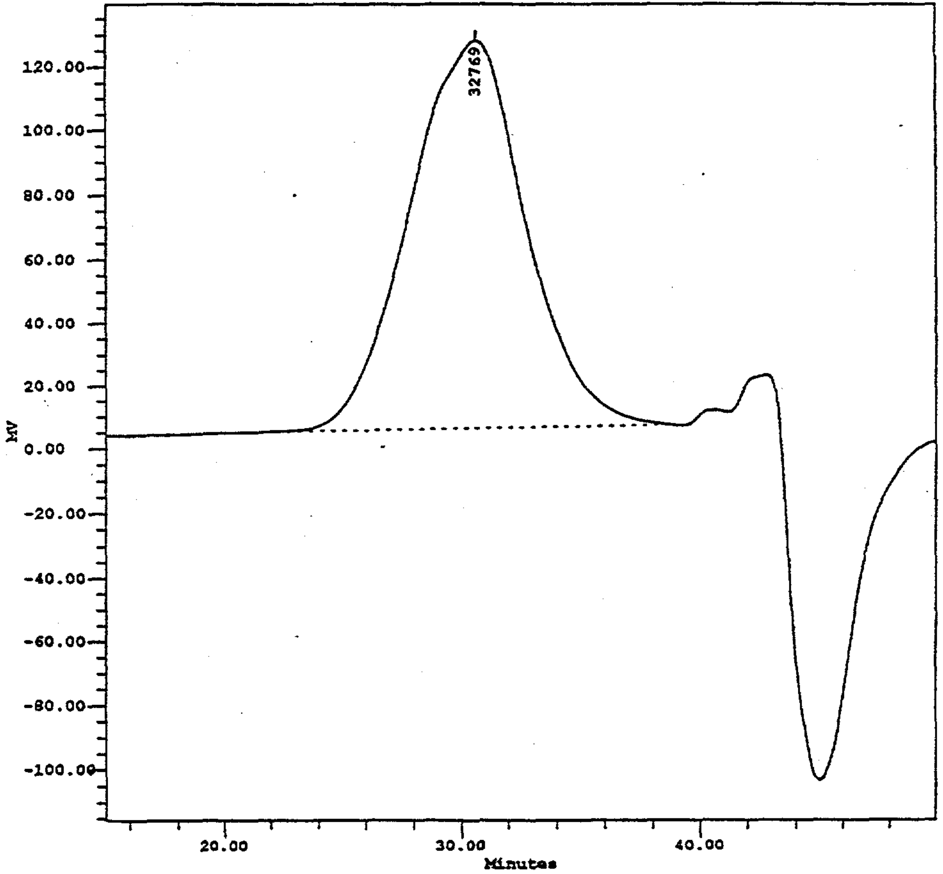


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99107
Vial: 30
Injection: 1
Channel: 410
Date Acquired: 06/13/99 08:44:55 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: 61299

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 06/13/99 02:00:53 PM
Dilution: 1.00000

MP: 32769 Mw: 68078 Mn: 20203 Polydispersity: 3.369756
Retention Time: 30.600

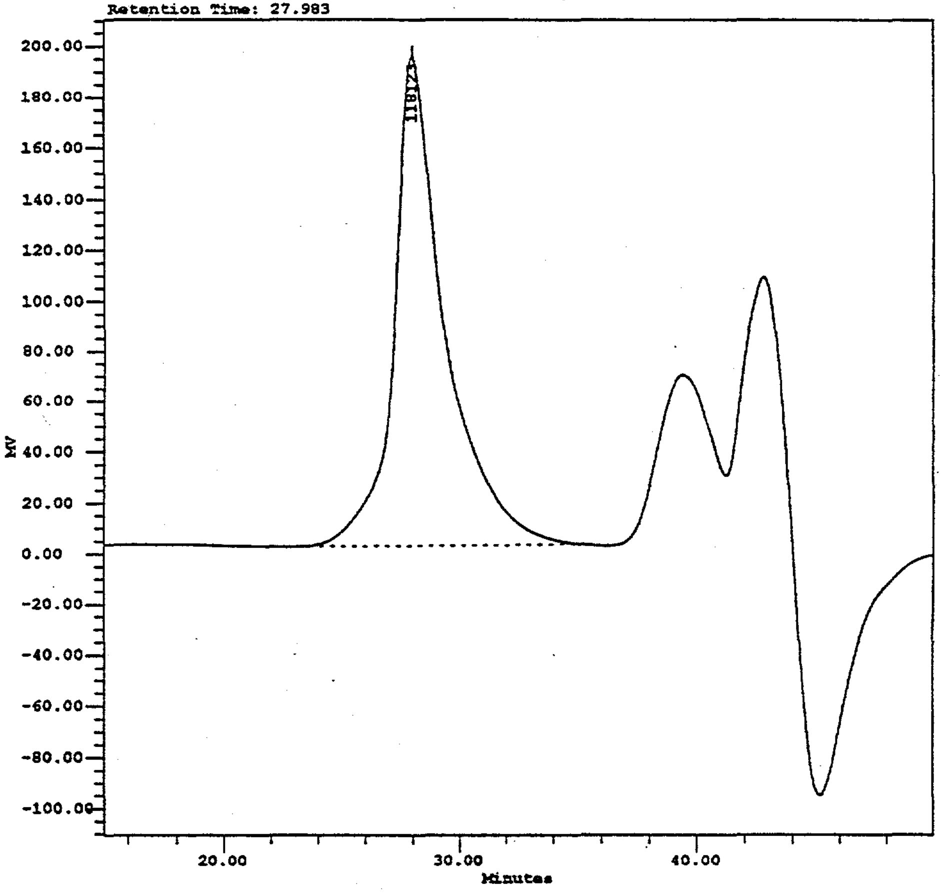


Millennium Sample Information

Project Name: Paul99
Sample Name: jy99118
Vial: 6
Injection: 1
Channel: 410
Date Acquired: 06/24/99 09:26:54 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: 61299

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 06/28/99 11:51:32 AM
Dilution: 1.00000

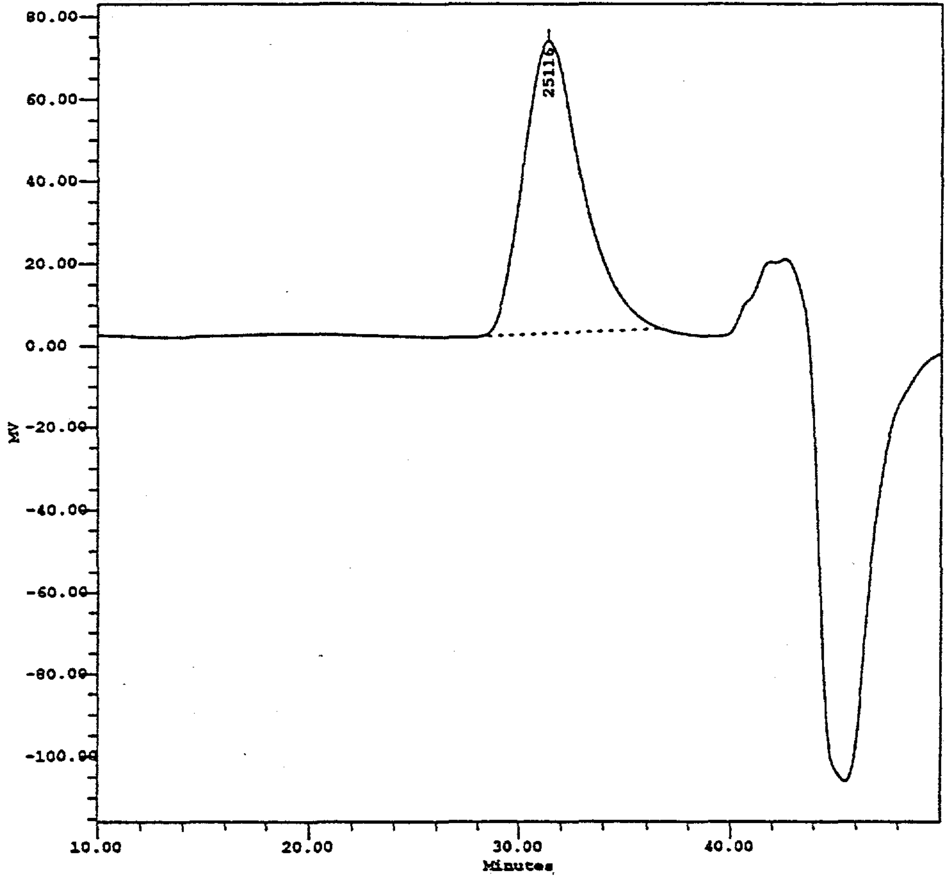
MP: 118123 Mw: 109752 Mn: 64316 Polydispersity: 1.706449
Retention Time: 27.983



Millennium Sample Information

Project Name:	LOWMW		
Sample Name:	jy99161		
Vial:	13	Sample Type:	Broad Unknown
Injection:	1	Volume:	200.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	12/03/99 09:05:55 AM	Date Processed:	12/08/99 10:46:38 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	sept299		

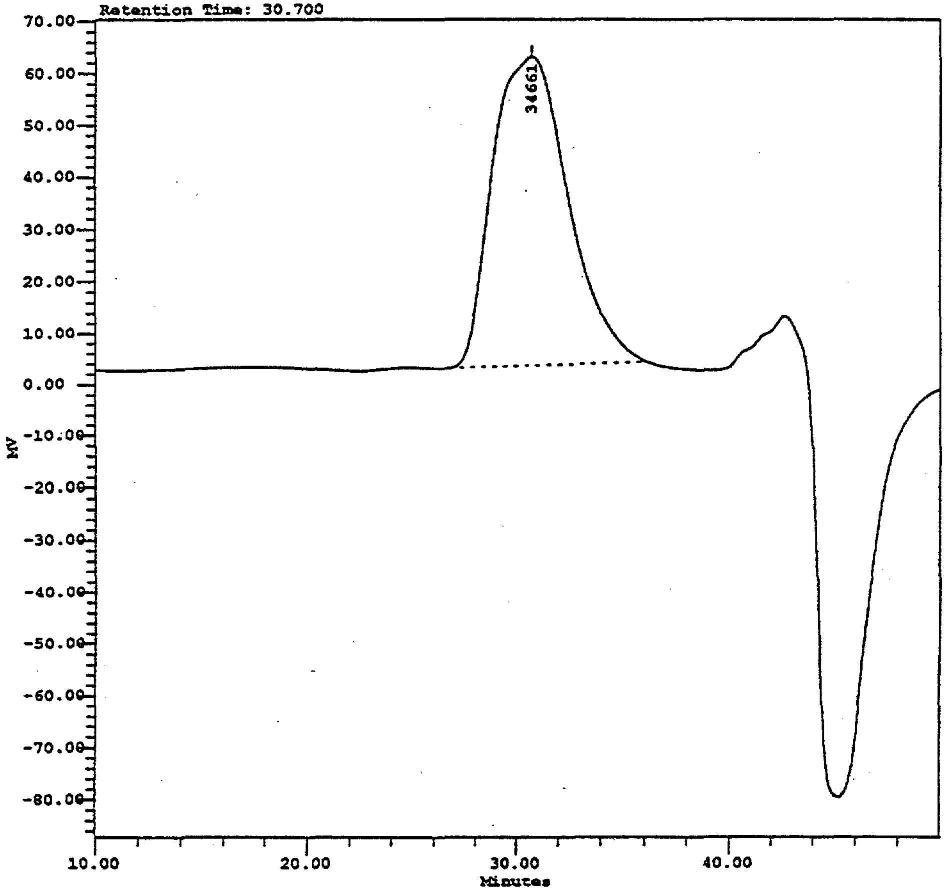
MP: 25116 Mw: 25305 Mn: 16383 Polydispersity: 1.544577
Retention Time: 31.367



Millennium Sample Information

Project Name:	LOWMW		
Sample Name:	jy99162		
Vial:	14	Sample Type:	Broad Unknown
Injection:	1	Volume:	200.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	12/03/99 09:58:58 AM	Date Processed:	12/08/99 10:47:08 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	sept299		

MP: 34661 Mw: 42797 Mn: 24286 Polydispersity: 1.762239
Retention Time: 30.700

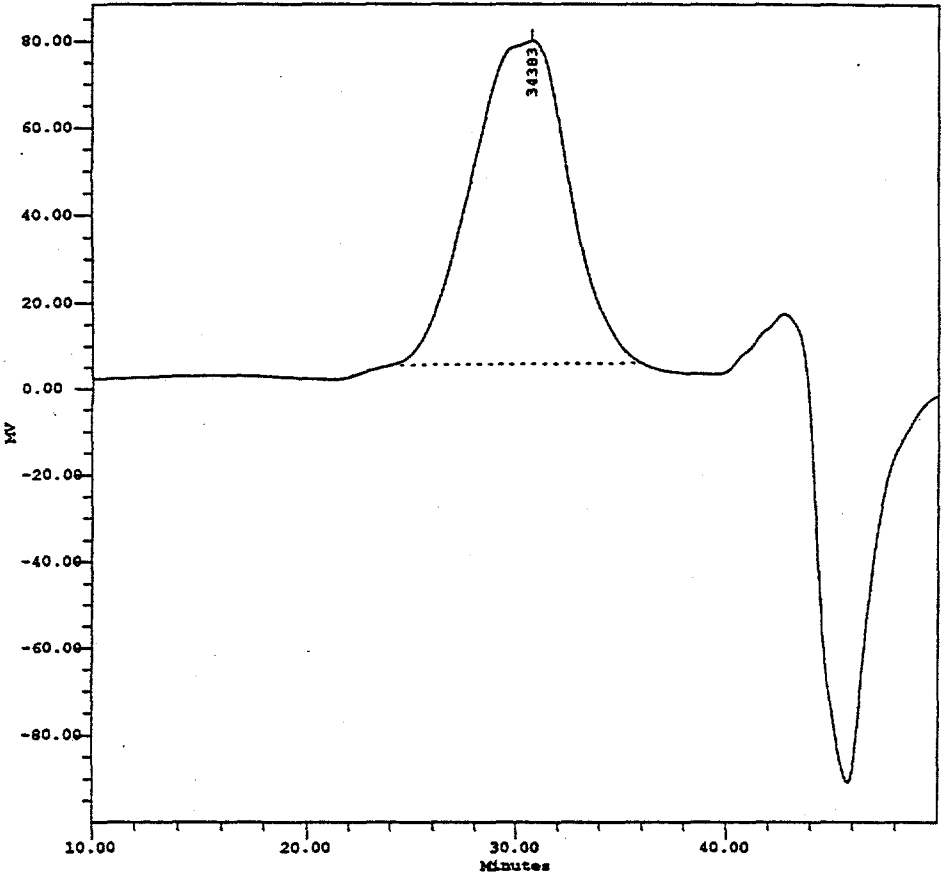


Millennium Sample Information

Project Name: LOWMW
Sample Name: jy99163
Vial: 15
Injection: 1
Channel: 410
Date Acquired: 12/03/99 10:52:00 AM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: sept299

Sample Type: Broad Unknown
Volume: 200.00
Run Time: 50.0 min
Date Processed: 12/08/99 10:47:38 AM
Dilution: 1.00000

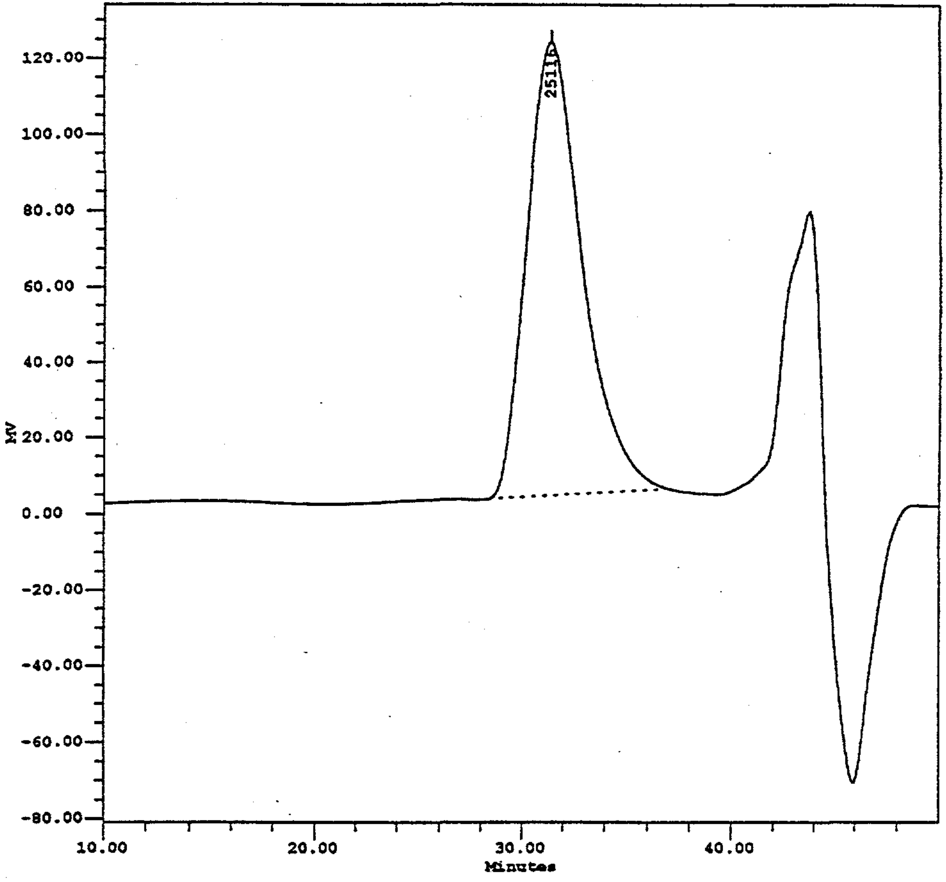
MP: 34383 Mw: 73226 Mn: 29503 Polydispersity: 2.481966
Retention Time: 30.717



Millennium Sample Information

Project Name:	LOWMW		
Sample Name:	jy99164		
Vial:	16	Sample Type:	Broad Unknown
Injection:	1	Volume:	200.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	12/03/99 11:45:06 AM	Date Processed:	12/08/99 10:48:12 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	sept299		

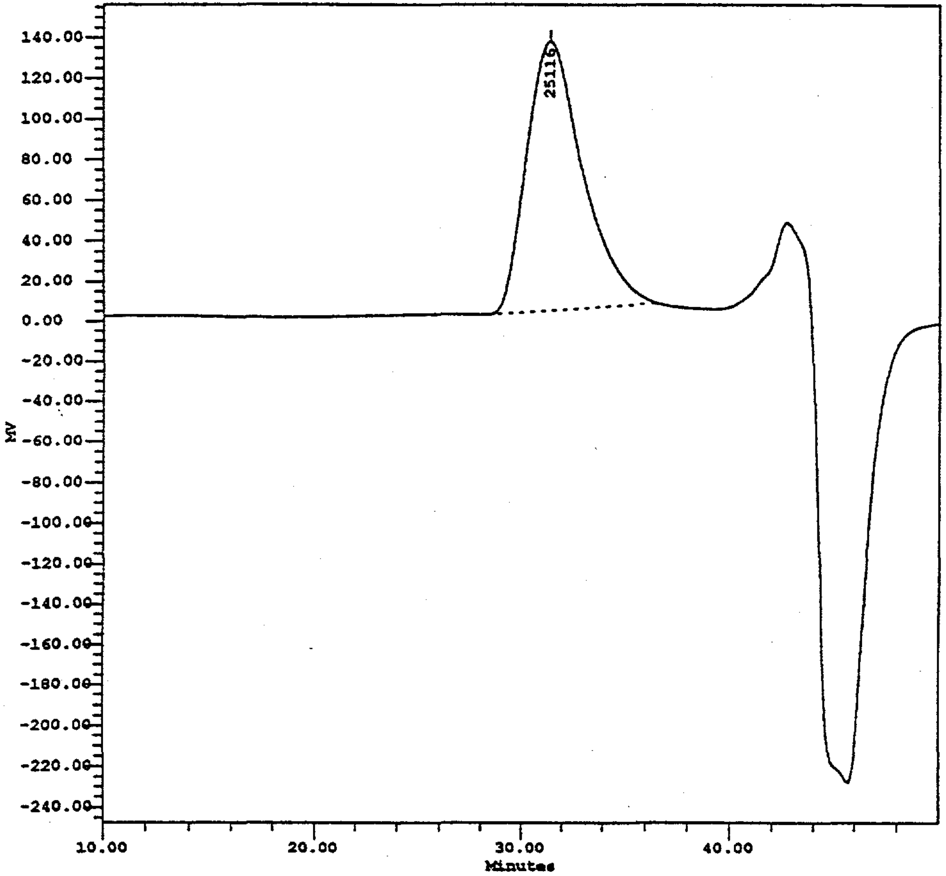
MP: 25116 Mw: 25323 Mn: 16811 Polydispersity: 1.506373
Retention Time: 31.367



Millennium Sample Information

Project Name:	LOWMW		
Sample Name:	jy99165		
Vial:	17	Sample Type:	Broad Unknown
Injection:	1	Volume:	200.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	12/03/99 12:38:11 PM	Date Processed:	12/08/99 10:48:35 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	sept299		

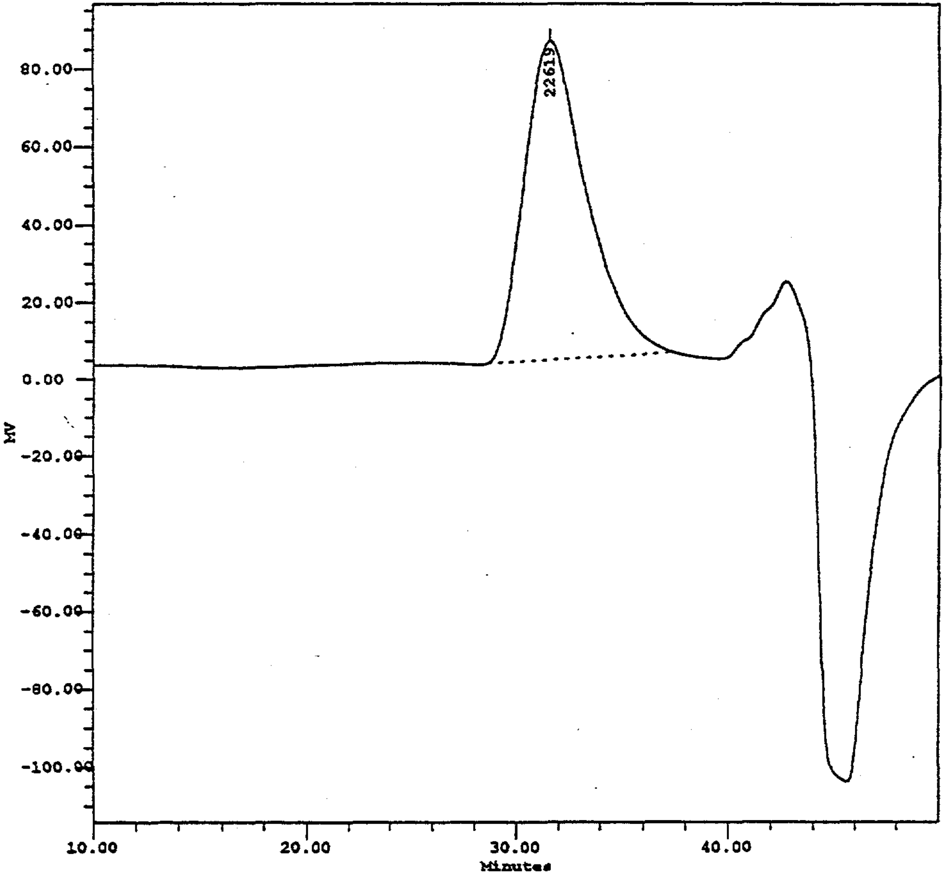
MP: 25116 Mw: 24563 Mn: 16274 Polydispersity: 1.509339
Retention Time: 31.367



Millennium Sample Information

Project Name:	LOWMW		
Sample Name:	jy99166		
Vial:	18	Sample Type:	Broad Unknown
Injection:	1	Volume:	200.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	12/03/99 01:31:18 PM	Date Processed:	12/08/99 10:33:46 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	sept299		

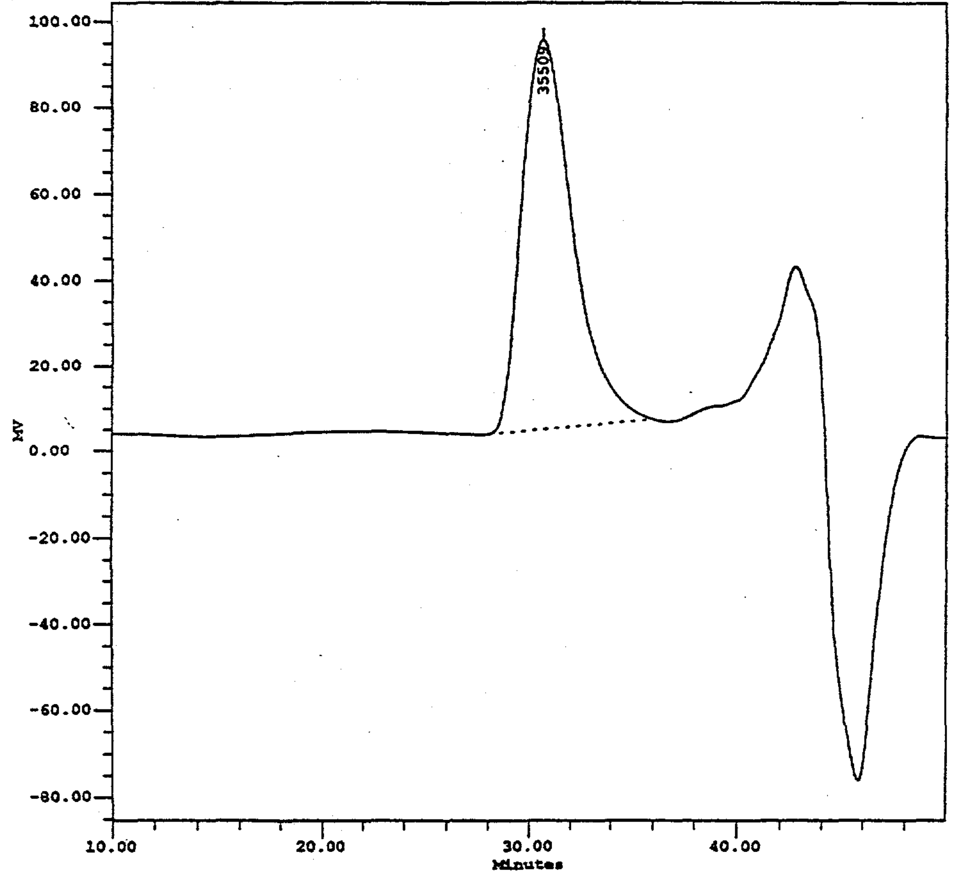
MP: 22619 Mw: 22092 Mn: 13495 Polydispersity: 1.637106
Retention Time: 31.583



Millennium Sample Information

Project Name:	LOWMW		
Sample Name:	jy99168		
Vial:	19	Sample Type:	Broad Unknown
Injection:	1	Volume:	200.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	12/03/99 02:24:22 PM	Date Processed:	12/08/99 10:33:17 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	sept299		

MP: 35509 Mw: 33685 Mn: 23598 Polydispersity: 1.427436
Retention Time: 30.650



REFERENCES

(1) Akelah, A.; Moet, A. *Functionalized Polymers and Their Applications*; Chapman and Hall: New York, **1990**.

(2) Patil, A. O.; Schulz, D. N.; Novak, B. M. Eds. *Functional polymers: Modern Synthetic Methods and Novel Structures*; American Chemical Society: Washington, DC, **1997**.

(3) Jerome, R.; Vanhoorne, P. *Trends in Polymer Science* **1994**, *2*, 382.

(4) Steward, J. M. *Polymer-Supported Reactions in Organic Synthesis*; Wiley, London, **1980**, 343.

(5) Bolto, R. A. *M. Macromol. Sci. Chem.* **1980**, A-14, 107.

(6) Eisenbach, C. D. Ed. *Makromol. Chem. Macromolecular symposia* **1991**, *50.*

(7) Kroschwitz, J. I. Ed. *Concise Encyclopedia of Polymer Science and Engineering* **1990**; 95, 149, 504.

(8) Mark, H. F.; Gaylord, N. G.; Bikales, N. M. Eds. *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons, Inc.: New York, **1964-72**, Vol. 2, 667-678.

(9) Takenaka, K.; Hirao, A.; Hattori, T.; Nakahama, S. *Macromolecules* **1987**, *20*, 2034.

(10) Takenaka, K.; Hattori, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1989**, *22*, 1563.

(11) Takenaka, K.; Hirao, A.; Hattori, T.; Nakahama, S. *Macromolecules* **1992**, *25*, 96.

(12) Hirao, A.; Hiraishi, Y.; Nakahama, S. *Macromolecules* **1998**, *31*, 281.

(13) Penelle, J.; Mayne, V.; Touillaux, R. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 3369.

(14) Penelle, J.; Mayne, V. *Tetrahedron* **1997**, *53*, 15429.

(15) Petzhold, C.; Stadler, R.; Frauenrath, H. *Makromol. Chem., Rapid. Commun.* **1993**, *14*, 33.

(16) Petzhold, C.; Morschhauser, R.; Kolshorn, H.; Stadler, R. *Macromolecules* **1994**, *27*, 3708.

(17) Takenaka, K.; Hirao, A.; Nakahama, S. *Makromol. Chem.* **1992**, *193*, 1943.

(18) Takenaka, K.; Hanada, K.; Shiomi, T. *Macromolecules* **1999**, *32*, 3875.

(19) Petzhold, C.; Stadler, R. *Macromol. Chem. Phys.* **1995**, *196*, 2625.

(20) Mannebach, G.; Bieringer, R.; Morschhauser, R.; Stadler, R. *Macromol. Symp.* **1998**, *132*, 245.

(21) Tomalia, D. A. *Polym. J.* **1985**, *17*, 117.

(22) Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.

(23) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592.

(24) Malmstrom, E.; Hult, A. *J. Macromol. Sci.-Rev. Macromol. Chem. Physc.* **1997**, C37(3), 555.

(25) Turner, S. R. *Polymer News* **1997**, *22*, 197.

(26) Jing, Y.; Sheares, V. V. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.)* **1999**, *80*, 149.

(27) Sheares, V. V.; Li, Y.; Emmick, T. K.; Martin, C. D.; Jing, Y.; Beery, M. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.)* **1999**, *80*, 79.

(28) Blackley, D. C. *Synthetic Rubbers: Their Chemistry and Technology*; Applied Science Publishers: New York, **1983**.

(29) Arlie, J. *Synthetic Rubbers*; Gulf Publishing Company: Houston, Texas, **1992**.

(30) Wei, P. E.; Milliman, G. E. *J. Polym. Sci., Part A-1,* **1969**, *7*, 2305.

(31) Heasley, V. L.; Frye, C. L.; Gore, Jr. R. T.; Wilday, P. S. *J. Org. Chem.* **1968**, *33*, 2342.

(32) Frank, R. L.; Steven, R. P. *Organic Synthesis,* Collective Vol. 3, **1964**, 499.

(33) Mannich, C.; Salzmann, O. *Chem. Ber.* **1939**, *72*, 506.

(34) Mark, H. F.; Gaylord, N. G.; Bikales, N. M. *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons, Inc.: New York, **1964-72**, Vol. 2, 683.

(35) Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Pergamon: New York, **1995**, 159-161.

(36) Odian, G. *Principles of Polymerization*; John Wiley & Sons, Inc.: New York, **1991**, 479, 491.

(37) Brandrup, J.; Immergut, E. H. Eds. *Polymer Handbook*; John Wiley & Sons, Inc.: New York, **1989**, II/153, II/267.

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