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TITLE: ORGANOTIN PIEZO- AND PYROELECTRIC POLYMER FILMS

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ORGANOTIN PIEZO- AND PYROELECTRIC POLYMER FILMS

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ABSTRACT

The synthesis of a new class of piezo- and pyroelectrically active materials of various co- and terpolymers of tributyltin methacrylate (TBTM) and trimethyltin methacrylate (TMTM) is described. A description of sample preparation, poling techniques, and measurement system is given in some detail. Films of the various polymer compositions were evaluated for tin content, glass transition temperature (Tg), crystallinity or "ordering" of the amorphous phase and piezo- and pyroelectric activity. Experimental results on 25-30 mol% TBTM/methyl methacrylate copolymers, which possessed good piezoelectric activity, antifouling properties and paint-formulation characteristics, are discussed in detail. Solvent-induced orientation effects that lead to piezoelectric activity in amorphous, unpoled, polymers are also described.

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INTRODUCTION

Since the early work on the piezoelectric effect in polymeric materials, many types of polymers have been shown to be piezoelectrically active.[1] Of the synthetic polymers, poly(vinylidene fluoride) (PVF_2) in β and δ crystal forms, has the highest piezoelectric constant, $d_{31} = (2 - 5) \times 10^{-11} CN^{-12}$. The piezoelectricity in polymers may also be roughly related to the dielectric constant.[2] The dielectric constant for PVF_2 is 8.0 for the β and δ crystal forms. In the β crystal form the dipoles can be oriented to a sufficiently high degree, whereas in the δ crystal form the chain has a small dipole moment, the overall dipole moment in a unit cell is zero, and no piezoelectric activity is found.

In amorphous polymers, such as poly(methyl methacylate), the piezoelectricity is explained on the basis of the freezing

mechanism.[3] The semipermanent dipoles are oriented under the influence of a high dc field applied above the glass transition temperature (T_g) and maintained during cooling toward T_g.

The work reported here involved designing polymers that in addition to being piezoelectrically active also possessed antifouling properties and could be formulated into a paint. The polymer systems investigated consisted of various tributyltin and trimethyltin methacrylate (TBAM and TMTM, respectively) homo-, co-, and terpolymers. These polymers are known to be antifouling, and alignment of the strong tin-oxygen dipoles by poling procedures was expected and later found to be possible also by medium hydrogen bonding solvents without the poling procedures.

EXPERIMENTAL

MONOMERIC MATERIALS

Bis(tri-n-Butyltin)oxide (TBTO)

This material was used in the synthesis of the tin-containing methacrylates as received from Alfa Division of Ventron Corp.

Tributyltin Methacrylate (TBTM)

TBTM (312.9g, 0.525 mol) and ligroin (750mL) are added to a 2-L, one-necked flask equipped with a stir bar and liquid-addition funnel; the freshly distilled methacrylic acid (MAA) (93.10 g 1.0825 mol) is then placed in the addition funnel. The flask is cooled to ca. 4°C in an ice bath and the MAA is added at a rate of ca. 3 mL/min so that the flask temperature will not rise above 15°C. After addition the ice bath is removed and the mixture is stirred for about 1 h.

The reaction mixture is poured into a separatory funnel and washed extensively with H_2O to remove the excess MAA. (Note: Excess MAA is used because TBTO is more difficult to remove; also, do not wash with $NaHCO_3$ solution because it causes product decomposition.) The ligroin solution is dried (on 3-Å molecular sieves or with $MgSO_4$) filtered, and concentrated on a Rotovac (by removing 600 mL of ligroin). The solution is then stoppered and placed in a freezer to induce crystallization. The liquid is poured off the crystals, the crystals are warmed to room temperature, more ligroin is added, and the solution is stoppered and refrozen. This freeze-thaw procedure should be carried out until the yellowish product yields colorless crystals on freezing (2-4 cycles; mp 18°C). The yield of crystallized product is typically ca. 95%.

Trimethyltin Methacrylate (TMTM)

This monomer was synthesized according to the general procedures of Koton et al.[4,5] and Shostakovskii et al.[6] from trimethyltin hydroxide (used as received) and MAA in benzene. The product was recrystallized from a 50-50 mixture of petroleum ether and carbon tetrachloride to yield fine white needles with a mp of 117°C as determinded in a differential scanning calorimeter at a heating rate of 20°C/min. The melting points reported in the literature ranged from 100 to 122°C.[6-8] The yield of the recrystallized material was 69%.

POLYMERIC MATERIALS

Poly(tri-n-Butyltin Methacrylate)

The glassware used was always dried overnight at 100°C. Azoisobutyronitrile (AIBN) was used as the initiator at a ratio of

1:1000 mol of monomer. Toluene was used as the solvent. The monomer-toluene mixture was degassed on a vacuum line (10^{-4} torr) in three freeze (liquid N_2)-thaw cycles. The polymerization vessel was then sealed, warmed to RT, and placed in an oven at a constant temperature of 80°C for at least 16 h. The flask was shaken occasionally during this time. The polymer was isolated from methanol as a yellowish, somewhat tacky, rubbery mass. Films cast from toluene were elastic but not very strong. The yield was above 95%.

Copolymers of TBTM and TMTM

The general procedure was the same as that for the polymerization of poly(TBTM). Both benzyol peroxide and AIBN were used as the initiators, with the AIBN giving the higher yields. The amount of toluene was always equal to the weight of the monomers. The copolymers were isolated from their viscous toluene solutions by pouring the solution slowly into a 10 times larger volume of ligroin. The isolated material was dried in a vacuum oven at 50°C/16 h. Typically, a 29 mol% TBTM/MMA copolymer was obtained in a 90% yield with an inherent viscosity in dimethylformamide as high as 1.2.

Sample Preparation

Films for piezo- and pyroelectric activity measurements were cast from dilute toluene or cyclohexanone solutions having typical concentrations of 10% or less. The films were cast in a clean-air hood on specially cleaned, large (~ 15.25 by 25.4 cm) glass plates in at least three layers, each < 10 μm thick. The individual layers were only partially dried and were soft to the touch before the next layer was cast. The final, multilayered films were dried overnight in a vacuum oven at 323 K (50°C). The films were then floated off the

glass plates in tanks filled with distilled, deionized water, and were dried again in a vacuum oven at 50°C for about 16h. Typical film thicknesses for activity evaluations were 30 ± 5 m. Electrodes of tin were vacuum evaporated onto the films. Electrode thicknesses ranged from 750 to 1100 Å. Experimented film samples were cut into rectangles of typically 1.3 x 12.7 cm. The electrodes were offset at opposite ends and wires were attached with a silver epoxy (Emerson and Cummings, Inc., Eccobond Solder 57C).

Poling Technique

Films were routinely poled for 30 min. at 800 - 850 kV/cm, at 15 - 20 K above the T_g of the particular polymer film. The films supported fields of 1000 kV/cm at room temperature for short periods of time (long-term studies were not performed). The length of time required to pole films adequately was first established for a specified length of time, measuring the activity, and then depolarizing the films by heating to ∿ 20 K above their Tg with the leads shorted for 1 h. This cycle was repeated for increasing lengths of time until essentially constant activity was reached. Each cycle started from zero activity after depolarization. Using this procedure it was found that the maximum activity was usually developed after 20 - 25 min. of poling at 800 - 850 kV/cm, 20 K above the T_g.

Piezoelectric Activity Measurements

The measurement system was similar to that of Hayakawa and Wada.[1] A thin strip of film is clasped between jaws, one of which is immovable whereas the other is attached to the impedance head of a B&K instruments, Model 8001 joined to an electromechanical shaker. A

sinusoidal current drives the shaker's movable coil producing linear oscillations of the impedance head and attached jaw.

The piezoelectric output from the film is measured as an open-circuit voltage by an electrometer (Kiethley Model 610B) as the unity gain amplifier with an input impedance of $> 10^{12}$ ohms. Care was taken to ensure that the film's operating frequency was within the amplifier's unity gain frequency response. The output from the electrometer can be connected either to an oscilloscope for visual display or to a lock-in amplifier for accurate voltage measurement. The reference signal to the lock-in amplifier was provided by the oscillator of the system.

RESULTS AND DISCUSSION

Polymer Synthesis

Organotin esters of acrylic and methacylic acids have been polymerized by a variety of free-radical initiators as well as thermally in bulk, solution or equeous emulsion phases.[9-12] Because of the superior paint formulation properties of TBTM polymers a series of co - and terpolymers were prepared.

Under identical polymerization conditions for charged 21-mol%, TBTM-comonomer compositions and a copolymerization time of 16 h the isolated yield of MMA copolymer was 90%, of acrylonitrile copolymer, 40%, of methacrylonitrile copolymer, 30%, and of styrene copolymer, 25%. Numerous attempts at copolymerizing α-methylstyrene were unsuccessful. This failure apparently is an example of steric hindrance due to the tributyltin group because copolymerization of a α-methylstyrene with MMA was successful.

Five TBTM terpolymer compositions were also prepared and are summarized in Table I. Most interesting was the fact that methacrylic acid in the TBTM/MMA terpolymerizations acted as a polymerization "sensitizer." Polymerizations with methacrylic acid were complete (100% conversion) in less than 1 h and the inherent viscosity of the terpolymers in dimethylformamide was always above 0.7.

TABLE I

TBTM Terpolymer Compositions[a]

Composition, charged (mol%)						Yield
TBTM	MMA	MAA	α-MeSty	AN	MAN	(%)
40	30	30	---	--	---	100
40	50	10	---	--	---	100
40	30	---	---	--	30	5
30	35	---	35	--	---	1
30	---	---	31.5	38.5	---	51

[a]MMA = methylmethacrylate; α-MESty = -methylstyrene; MAA = Methacrylic acid; AN = acrylonitrile; MAN = methacrylonitrile.

Corresponding copolymers without the methacrylic acid, would require at least 16 h for an 80% conversion. Terpolymerization of α-methylstyrene in the compositions tried was not possible. The use of methacrylic acid in a terpolymerization of α-methylstyrene may be more promising.

Tin Content in TBTM/MMA Copolymers

Qualitatively, TBTM, hence the tin content, could be monitored by IR spectroscopy--specifically the tin-ester carbonyl absorption at 6.1 μm. Thus we observed that the tin-ester carbonyl absorption increased in the copolymer with increasing conversion. Chemical analysis for tin in a series of different TBTM/MMA copolymers, polymerized to about the same conversion (80-85%), also confirmed the observation that TBTM is the slower polymerizing comonomer. The data are summarized in Table II. Thus in the initial stages of polymerization the copolymer is low in the tin comonomer and the tin concentration approaches that of the charged

TABLE II

Tin Content in TBTM/MMA Copolymers

Composition, charged (mol%)	Sn found (%)	Sn found (mol%)	Sn difference (mol%)
10	7.5	9	1
21	14.5	18	3
30	17.5	25	5
35	19.0	29	6
40	21.0	32	8

concentration only if the polymerization is conducted essentially to completion. Furthermore, this difference in tin concentration between

that charged and that found in the copolymer is more pronounced with increasing TBTM concentration in the charged composition.

Glass Transition Temperature versus Composition

Because of the importance of the relationship between stability of the dipole alignment (after poling), piezoelectric activity, and T_g in amorphous polymers, we determined the T_gs on most of the materials prepared. They were determined on vacuum-dried films cast from various solvents and measured in a Perkin-Elmer differential scanning calorimeter at a heating rate of 20°C/min. Some representative copolymer T_gs are listed in Table III. By extrapolating the available TBTM/MMA data to 100 mol% TBTM we obtained a T_g of -70°C for TBTM.

TABLE III

Glass Transition Temperature of Various Polymers

Polymer	T_g (°C)
MMA	105
TBTM/Sty (50:50 wt%)	55
TBTM/MMA (18 mol% TBTM)[a]	71
TBTM/MMA (29 mol% TBTM)[a]	56
TBTM/MMA (41 mol% TBTM)[a]	32
TBTM/AN (30 mol% TBTM)	20
TMTM/MMA (50:50 mol%)	75

[a] These particular compositions were established analytically; the others represent the charged compositions.

X-Ray Diffraction Analysis

The crystallite size and/or perfection of the crystals can be estimated from the breadth of reflections. Crystallite size and perfection may play a role in the piezoelectric behavior of a polymer and would be expected to be affected by the choice of solvent and the rate at which the polymer is cooled down during poling.

Because of the considerable piezoelectric activity in the 30-mol % TBTM/MMA copolymers, we investigated the crystallizing and/or orientation effects of these materials. Guinier x-ray diffraction photographs and microdensitometer traces of the photographs were obtained on the copolymer films, unpoled and poled, while being formed. The poled and unpoled films indicated the existance of crystals. A more detailed study is needed to elucidate the extend of "ordering" of the amorphous phase.

X-ray diffraction photographs and microdensitometer traces of the photographs were also obtained on the 50:50 mol % (charged) TMTM/MMA copolymer. Again the photographs indicated the existance of crystals in the unpoled copolymer film. However, a comparison of the 50:50 mol % TMTM:MMA and 30 mol % TBTM:MMA copolymer microdensitometer traces revealed apparent difference in the "ordering" of the amorphous phases in the two polymers. The broad peaks in the microdensitometer traces of the two copolymers had 2θ maxima at the following positions:

	Position of 2θ maxima (deg)		
30 mol % TBTM/MMA	11	17	30 (poled only)
50 mol % TMTM/MMA	--	16	--

The fact that the 11° maximum was not observed in the 50-mol % TMTM/MMA unpoled copolymer, coupled with the fact that the maximum at 16-17° was observed, is a strong indication that we are seeing certain "orientation" effects in these largely amorphous materials. The x-ray reflection at $2\theta = 30^{\circ}$ is weak and seen only in the poled TBTM/MMA copolymer. Interestingly, recently, vinylidene cyanide/vinyl acetate copolymer was also shown to be piezoelectrically active and from the weak and broad x-ray reflections at $2\theta = 15^{\circ}$ and 30° was interpreted as possessing of crystals in the copolymer.[13]

Piezoelectric Activity

Piezoelectric activity data here will be reported only on the 25- to 30-mol % TBTM/MMA copolymers because they represent the best compromise between reasonably long-term piezoelectric activity at room temperature, antifouling properties, and paint formulation characteristics.

Film cast from hydrocarbon solvents, such as toluene, supported poling fields up to 1000 kV/cm. Poling increased g_{31} activity from barely detectable in the unpoled film to better than 10% of poled PVF_2 activity:

	d_{31} Activity (C/N)	
Casting Solvent	25 mol% TBTM/MMA	PVF_2*
Cyclohexanone	1.7×10^{-12}	20×10^{-12}
Toluene	0.53×10^{-12}	---
	g_{31} Activity (Vm/N)	
	30 mol% TBTM/MMA	
Toluene	16.1×10^{-3}	150×10^{-3}

* Kureha KF Piezofilm; sample obtained from NBS

These d_{31} and g_{31} values are not the highest obtainable in this class of materials, rather, these polymer compositions represent the compromise of activity, anti-fouling properties, and paintability characteristics. The activity in these materials increased with increasing TBTM content and we have not established the maximum activity obtainable. The g_{31}-constant of the TBTM polymer films is comparable to that of ceramics.

Pyroelectric Activity

Initial pyroelectric activity evaluation on 30-mol% TBTM/MMA films with a pyroelectric detector was done at NASA/Langley Research Center, VA.[14] Unfortunately, the films supplied were 50 μm thick or about 10 times thicker than desirable for a good pyroelectric response.

To obtain a figure of merit for a pyroelectric detector, one must also consider thermal noise and intrinsic noise of the system due to dielectric loss. These considerations lead to a figure of merit, called the normalized detectivity, D*:[15]

$$D^* = \frac{p\eta}{2c\rho} \left[\frac{1}{t\omega\varepsilon\tan\delta\kappa T} \right]^{1/2} ,$$

where ρ is the pyroelectric coefficient, η is the efficiency with which the incident radiation is absorbed, t is the detector thickness, ε is the dielectric constant, tan δ is the dielectric dissipation factor, k is Boltzmann's constant, and T is the absolute temperature. The normalized detectivity D*, obtained with our films, was 1.5×10^5 cm.$Hz^{1/2}$/W. This value is low, for reasons indicated before,

and compares with D* for PVF_2 as follows: 1×10^8 cmHz ½/W.

Solvent Induced Orientation Effects

Films cast from certain solvents, most notably cyclohexanone and methyl ethyl ketone, possessed piezoelectric activity in the unpoled state, whereas films of equal composition but cast from other solvents, for example, toluene, possessed no activity in the unpoled state:

	d_{31} Activity (C/N)	
Casting Solvent	25 mol% TBTM/MMA	PVF_2*
Cyclohexanone	1.5×10^{-12}	0
Toluene	near noise level	-

*Commercial sample of an unpoled film.

Ketone solvents have medium hydrogen bonding characteristics, which we believe are important. The presence of activity is attributed to a unique combination of an inherent chain orientation in cast thin (< 10 μm) films[16-18] and an oxygen-tin dipole orientation by the ketone solvents as they evaporate during film deposition. The ketone molecules would be expected to coordinate with the tin-oxygen dipole because of their medium-strong hydrogen bonding parameter value. Also, it is extremely difficult to remove the last traces of cyclohexanone from a polymer film; and thus any remnants would act as a solvent plasticizer and facilitate the dipole orientation. Further study is needed especially because this dipole orientation eliminates the possibility of charge injection during film poling, a mechanism that has been frequently cited as possibly causing piezoelectric activity in polymeric films.

CONCLUSION

A 30-mol% TBTM/MMA copolymer possessed good piezoelectric activity, antifouling properties, and paint formulation characteristics. The polymers could be made piezoelectrically active in thin films by preferentially dipole-orienting solvents or by poling procedures. Unpoled 25-mol % TBTM/MMA film, cast from cyclohexanone, possessed the d_{31} piezoelectric activity of 1.5×10^{-12} C/N. Whereas poled 30-mol% TBTM/MMA film, cast from toluene, possessed a g_{31} activity of 16.1×10^{-3} Vm/N. For pyroelectric activity evaluation a very thick (50- μm) 30-mol% TBTM/MMA film in a pyroelectric detector had a normalized detectivity, D*, of 1.5×10^{5} $cmHz^{1/2}/W$. To our knowledge this is the first evaluation piezo- and pyroelectric activity in organotin polymers and of orientation effects induced by solvents.

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