

Synthesis and Characterization of Polyimidothioethers

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SYNOPSIS

Polyimidothioethers were synthesized as possible polymers for evaluation as X-ray resists. These polymers were varied in the ratio of the monomers and in their structures. Aliphatic thiols, bismaleimides, and iodonium monomers were used. The composition was varied using ratios of the bisimide to iodonium of 9 : 1, 8 : 2, 7 : 3, 6 : 4, 5 : 5, and 0 : 1. The ratio of the thiols, containing 6 to 10 $-\text{CH}_2-$ groups, to the monomers was 1 : 1. The synthesis and characterization of the intermediate compounds and polymers are described in detail.

INTRODUCTION

The polymers selected for synthesis were investigated with anticipation of developing a material sensitive to X-ray radiation. Incorporation of iodonium groups would increase the sensitivity of the polymer, and aromatic structures would enhance the etch-resistant characteristics of the material. A possible candidate to meet these requirements is the polymer, containing diphenylmethane, dithiol, and bismaleimide groups, shown in Figure 1. The structure of the bismaleimide was selected to optimize the characteristics of the anticipated resist formulated from these polymers. The well-known reaction of the facile addition at the double bonds of the maleimide compounds by nucleophiles has been used for the polymerization of monomers containing two nucleophilic functional groups. The dithiols serve this purpose, either aromatic or aliphatic. The maleimides chosen were bifunctional in anticipation of producing linear, long-chain polymers. The bismaleimides were prepared by cyclodehydration based essentially on the method of Searle.¹ The synthesis and characterization of this polymer are detailed in this work.

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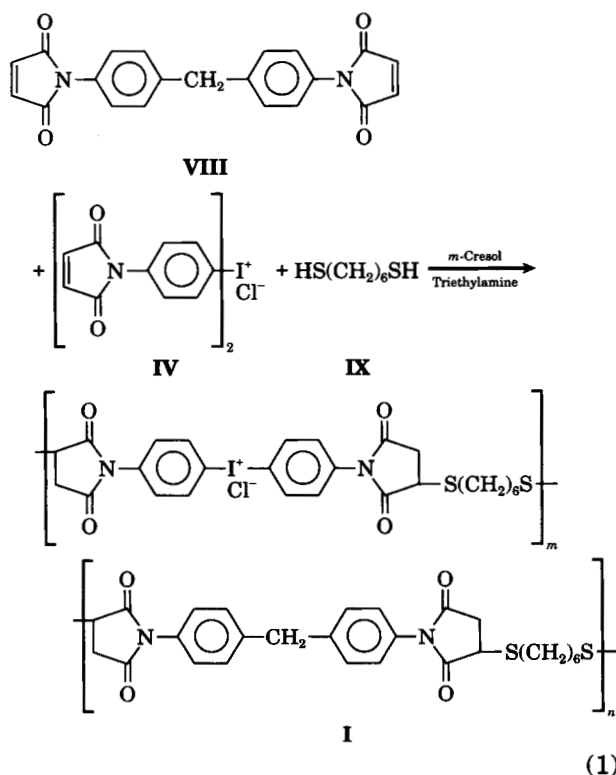
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EXPERIMENTAL

Syntheses

The polymers synthesized were polyimidothioethers (I), Eq. (1). The thiols were purchased and purified by fractional distillation. The imide and iodonium monomers were synthesized just prior to polymerization.²⁻²⁰



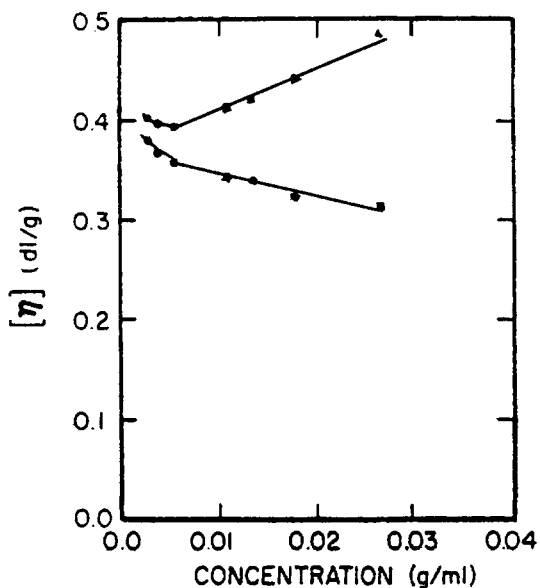
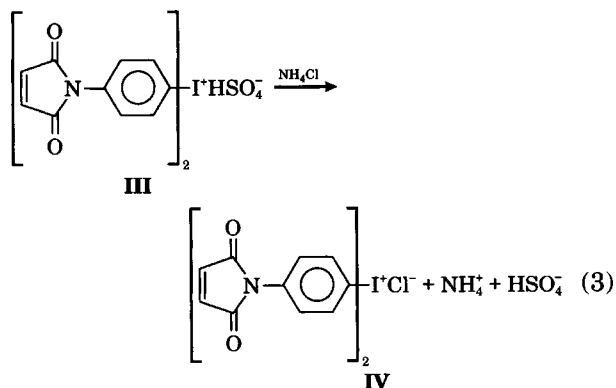
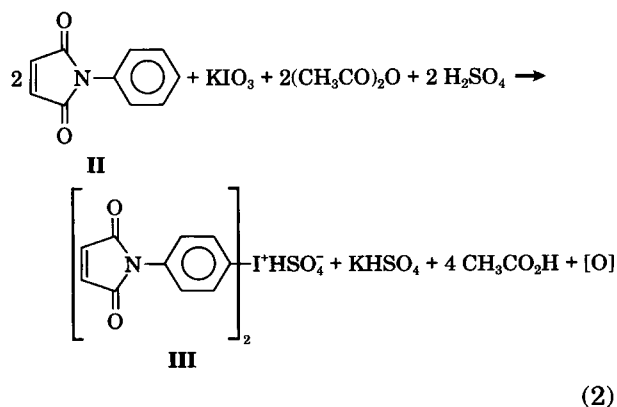


Figure 1 Typical intrinsic viscosity plot of the polymer.

Iodonium Salt

The synthesis [Eqs. (2) and (3)] was carried out in a three-necked 250-mL flask fitted initially with a condensing column and an argon inlet adapter. Stoichiometric amounts of potassium iodate (4.28 g) and maleimide (II) (6.907 g) were added to the flask with acetic anhydride (30 mL) at ambient temperature under argon. The system was placed in a cryogenic bath to lower the mixture temperature to -12°C . The color of the mixture was whitish yellow. The argon inlet was exchanged for a pressure-equalizing funnel to introduce sulfuric acid (9 mL) dropwise. The color changed to orange-brown. Stirring continued for 64 h.



After the 64-h period, deionized water (30 mL) was added dropwise while maintaining a temperature below -5°C . The color changed to pale yellow. The precipitate, 4,4'-(*N*-maleimido)diphenyliodonium bisulfate (III), was filtered in a Buchner funnel. The precipitate was dissolved in methanol (250 mL) and gravity filtered. A saturated aqueous solution of ammonium chloride (6–7 g) was added to the filtrate and placed in the cryogenic bath (-12°C) to encourage flocculation. The precipitate was filtered and washed with methanol (1 L) to remove traces of sulfuric acid. The product, 4,4'-(*N*-maleimido)diphenyliodonium chloride (IV), was dried overnight in a vacuum oven. The yield was about 46% by weight.

ANAL: Calcd: C, 47.41%; H, 2.39%; N, 5.53%; Cl, 7.00%; I, 25.05%. Found: C, 46.38%; H, 2.89%; N, 5.96%; Cl, 6.74%; I, 23.90%.

Bismaleamic Acid

The synthesis was carried out in a 1000-mL three-necked flask immersed in an ice bath and fitted with an argon inlet and condensing column. The maleic anhydride (34.5 g) was pulverized and stirred in acetone (50 mL) until dissolved and cooled. The diaminodiphenylmethane (34.5 g) was added to acetone (100 mL) in an Erlenmeyer flask and swirled until dissolved. The diaminodiphenylmethane solution was added dropwise from a pressure-equalizing funnel into the maleic anhydride solution. Rapid reaction occurred forming the bismaleamic acid precipitate, which was a pale yellow color. The reaction mixture temperature rose significantly. After addition was complete and the temperature dropped, the ice bath was removed. After 30 min, the mixture was filtered and the precipitate was dried at ambient temperature in a vacuum oven. The yield based on diaminodiphenylmethane was about 97% by weight.

Bismaleimide

The synthesis was carried out in a 250-mL three-necked flask fitted with an argon inlet and a condensing column. The bismaleic acid (13.25 g) and nickel II acetate tetrahydrate (3.07 g) were placed in the flask. The acetic anhydride (6.87 g) and acetone (30.6 g) were added and stirred. The triethylamine (2.24 g) was added and stirring under argon was continued. The initial reaction color was pale yellow-green. After a few hours, the bismaleamic acid dissolved and the reaction mixture color turned pale green. Stirring continued for 48 h. The bismaleimide precipitate, yellow-white in color, had formed during the stirring.

Water (90 mL) was added to the reaction mixture before filtering. The precipitate was treated with a 1 : 1 solution of $\text{CHCl}_3/\text{MeOH}$ and filtered. The yield was about 35% by weight.

ANAL: Calcd: C, 70.37%; H, 3.94%; N, 7.82%. Found: C, 69.72%; H, 3.98%; N, 7.74%.

Polyimidothioethers

The dithiols and *m*-cresol were vacuum distilled immediately before use.

The bismaleimido and iodonium were used in mole ratios of 9 : 1, 8 : 2, 7 : 3, 6 : 4, 5 : 5, and 0 : 1. These are referred to as B9, B8, B7, B6, B5, and B0, respectively. These mixtures are added to the dithiols in a 1 : 1 mole ratio.

The bismaleimidothioethers were polymerized in a 250-mL three-necked flask fitted with a stirrer, condensing column, and argon inlet adapter. Monomers were added in stoichiometric amounts. The following experimental procedure is for the polyimidothioether synthesized in a ratio of 9 : 1 for *N,N*-bismaleimido-4,4-diphenylmethane to 4,4-*N*-maleimidodiphenyliodonium chloride dihydrate. *N,N*-Bismaleimido-4,4-diphenylmethane (3.22 g) and maleimidodiphenyliodonium chloride (0.506 g) were dissolved in an *m*-cresol (10 mL) in a reaction vessel. 1,6-Hexane dithiol (1.491 g) was added to the mixture and stirred for 10 min. The mixture was a transparent amber color. Four drops of triethylamine were added as a catalyst. After 20 min, the temperature rose slightly and the viscosity increased. Stirring continued for 5 h. The polymer was precipitated in a methanol solution (1 L) acidified with HCl (4 mL).

As the reaction solution was poured into the methanol solution, stiff, long white fibers formed. The *m*-cresol was extracted from the polymer by

Soxhlet extraction for 8 h using methanol. The polymer was vacuum dried overnight. The yield was about 95% by weight.

Instrumentation

Melting points were determined on an Electrothermal Engineering, Ltd., capillary melting point apparatus, Model IA6304, and are uncorrected.

Intrinsic viscosity measurements were done at 30°C using dimethyl sulfoxide as the solvent with a Canon Ubbelohde viscometer.

FTIR spectras were recorded on a Perkin-Elmer 1750 FTIR spectrometer with either KBr pellets or a film cast from CHCl_3 solution or on thin films spun on silicon wafers that had been polished on both sides. Weight-average molecular weight (\bar{M}_w) and number-average molecular weight (\bar{M}_n) were determined by means of gel permeation chromatography (GPC) using polystyrene calibration on a Waters Associates Model 6000A; column, 60 cm mixed bed at 50°C; eluent, dimethyl formamide containing 0.1 mol/L of lithium bromide.

Differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermogravimetric analysis were performed with a Perkin-Elmer 7/4 thermal analyzer controller, Perkin-Elmer DSC 4 differential scanning calorimeter, and a Perkin-Elmer TGS-2 thermogravimetric analyzer.

The polymers were tested for solubility in various solvents. Solubility studies assume importance since a proper solvent is needed for spinning a clear film for lithography purposes. The choice of a proper developer also depends on solubility of polymer in various solvents.

RESULTS AND DISCUSSION

Syntheses

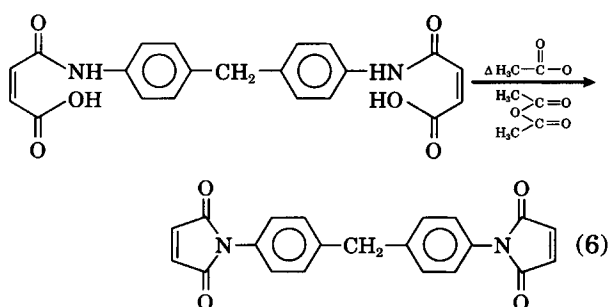
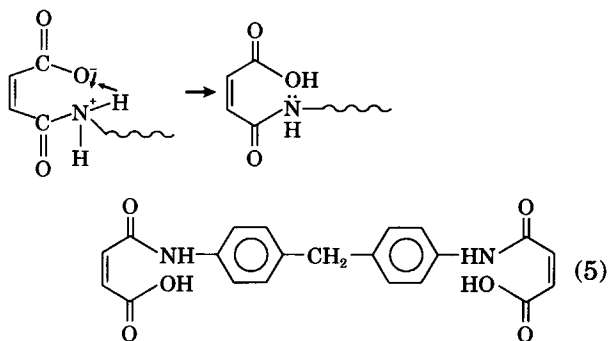
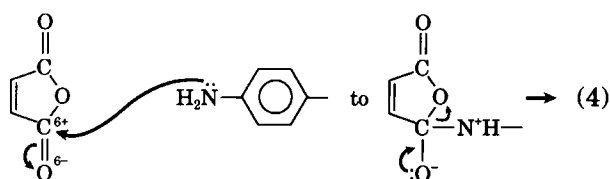
Bismaleimide

Various methods to synthesize bismaleimide were attempted, many resulting in low yield upon purification. All of those attempted with heating to accomplish ring closure resulted in brown precipitates accompanied by much product loss during recrystallizations.

The bismaleic acid syntheses were attempted in chloroform, methylene chloride, and acetone. Several different buffers were also tried: sodium acetate, potassium acetate (with heat), and nickel (II) acetate tetrahydrate (without heat).

Using a one-step procedure with nickel (II) acetate tetrahydrate as a buffer with triethylamine as a catalyst and acetone as the solvent gave the best yield of crude product, easiest purification, and largest final yield (42%).

The mechanism for synthesis of the bismaleamic acid involves the attack of the $C^{\delta+}$ of the carbonyl group by the lone pair electrons of the nucleophilic amine group, as shown in eqs. (4) and (5). The mechanism for the bismaleimide synthesis is shown in eq. (6). Again, the nucleophilic nitrogen attacks the carbonyl carbon. The water released reacts with the acetic anhydride (water scavenger) to form acetic acid. To maintain conditions so that ring closure continues, nickel (II) acetate tetrahydrate is added as a buffer.



Iodonium Salt

The synthesis involves electrophilic aromatic substitution to form a diaryliodonium bisulfate salt,

which is highly nucleophilic in nature. This is converted to a chloride salt, which is less nucleophilic by a direct metathesis (substitution of one charged group for another) with a salt containing the desired anion.⁵

The reaction does not proceed with ease at temperatures below -16°C or above -8°C . For this reason reactions were run very close to -12°C . The conversion of the bisulfate salt to the chloride salt has been found to facilitate increase of the ultimate molecular weight of the polymer. If the monomer is synthesized using an excess of water, i.e., not a saturated solution of $\text{NH}_4\text{Cl}/\text{H}_2\text{O}$, the yield of monomer also drops.

Polyimidothioether

Both monomers contain two maleimide groups that are the basis for the copolymerization. The double bond on the maleimide is electrophilic since the flanking double-bonded oxygens are highly electronegative. These oxygen atoms withdraw electrons from the ring double bond, decreasing the electron density.

The highly electrophilic nature of the ring double bond causes it to be susceptible to anionic polymerization in polar media, which would produce cross-linked polyimides. To avoid this, the anionic species can be protonated so that a high molecular weight linear polymer may be obtained. For this reason *m*-cresol is used as both the solvent and the protonating agent. The reaction is base-catalyzed using a tertiary amine.

Since thiols are strong nucleophiles, bistiols are used to polymerize cationically the bismaleimide monomers. Several aliphatic thiols were used, ranging from 6 to 10 $-\text{CH}_2-$ groups, and all were capable of polymerizing the monomers. The triethylamine initiates thiolate formation ($-\text{CH}_2\text{S}^-$). The *m*-cresol serves as a solvent and a proton source to neutralize the resonance-stabilized anionic intermediate, eq. (6).

Table I Intrinsic Viscosity and Molecular Weight Distribution of the Polymers

Polymer	Intrinsic Viscosity (dL/g)	\bar{M}_n (10^{-3})	\bar{M}_w (10^{-3})	\bar{M}_w/\bar{M}_n
B9	0.64	107	159	1.49
B8	0.52	90	125	1.39
B7	0.535	76	106	1.39
B6	0.415	53	73	1.38
B5	0.425	65	89	1.37

The copolymer was precipitated by quenching in methanol acidified with hydrochloric acid. The acid neutralized the thiolate ion. The copolymer was Soxhlet extracted with warm methanol so as to remove *m*-cresol incorporated during quenching.

Table I gives the intrinsic viscosities and molecular weight distributions of the polymers. The polymers are polyelectrolytes, which is evident from the viscosity analysis (Fig. 1). The $[\eta]$ values vary from 0.415 dL/g to 0.64 dL/g. The polyelectrolytic nature is due to the presence of charged species that repel each other in the chain, leading to an expanded chain and hence an increase in viscosity as the solution is diluted.²¹

\bar{M}_n , \bar{M}_w , and \bar{M}_w/\bar{M}_n ratios are given in Table I. A decrease in molecular weight occurs with an increase in the content of the iodonium monomer in the polymer. The GPC analysis is done using *N,N*-dimethylformamide (DMF)/LiBr as the solvent. The LiBr suppresses the electrolyte behavior of the polymer. The decrease in both \bar{M}_n and \bar{M}_w values is probably not due to the increased rigidity associated with the chains as the iodonium content increases. Instead, it is quite possible that the molecular weight is restricted during polymerization as the iodonium content increases due to the repulsion produced from

nearby units, thus restricting the chain length and the molecular weights.

Table II shows the solubility of polymers in various solvents. The polymers were soluble in 1,1,2,2-tetrachloroethane (TCE), *m*-cresol, dimethyl sulfoxide (DMSO), and DMF. Hence, for lithography purposes, we chose TCE as the solvent since *m*-cresol, DMSO, and DMF all have high boiling points.

The thermograms show that the polymers are all stable to 300°C. Figure 2 shows a typical primary thermogram of the bismaleimidothioether polymer. From these primary thermograms, it is obvious that decomposition occurs in one stage and no stable intermediates are formed during decomposition. Thus, no crosslinking occurs during the polymer degradation. Table III gives the initial decomposition temperatures of the polymers. It is evident from the table that the temperature values decrease with an increase in iodonium monomer content. Polymers with higher imide content and lesser iodonium monomer seem to be slightly more stable. The bond strength of the C-I bond is 60 kcal/mol, I-Cl is 51 kcal/mol. These prove to be weak sites where degradation can begin and are responsible for the lower thermal stability as the iodonium content increases.

The DTA, Table IV, lists the endothermic and

Table II Results of Solvency Tests

Solvents	Polymer ^a					
	B9	B8	B7	B6	B5	B0
1,1,2,2-Tetrachloroethane	+	+	+	+	+	Swells
Methanol	-	-	-	-	-	-
<i>m</i> -Cresol	+	+	+	+	+	+
Dimethyl sulfoxide	+	+	+	+	+	+
<i>N,N</i> -Dimethylformamide	+	+	+	+	+	Swells
Acetone	Swells				-	-
<i>N,N</i> -Dimethylacetamide	+				Swells	-
γ -Butyrolactone		+			Swells	
Chloroform	+	+	Swells		Swells	-
2-Butanone	-				-	-
1-Methyl-2-pyrrolidinone	+ Yellow			+	+	+
4-Methyl-2-pentanone	-				-	-
Waycoat	-	-	-	-	-	-
2-Methoxyethyl acetate	-				-	-
2-Ethoxyethyl acetate	-				-	-
5-Methyl-2-hexanone	-	-			-	-
Toluene	-				-	-
2-Propanol	-				-	-
Isoamyl Acetate	-				-	-
Butyl Acetate	-				-	-

^a + = soluble; - = insoluble.

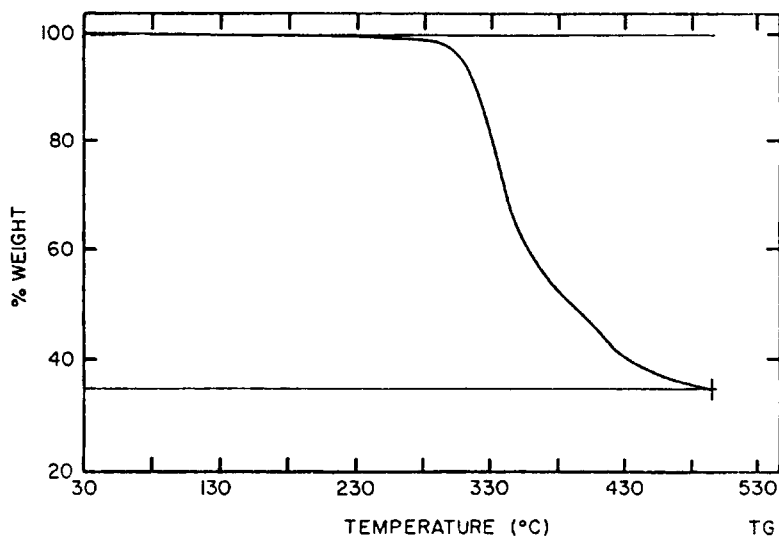


Figure 2 Typical thermogravimetric analysis of the bismaleimidothioether polymer.

exothermic peaks for the polymers according to composition. The exothermic peaks around 150°C may be accounted for partially by the thermal history of the polymer. These peaks may have been caused by a release of energy from the stresses developed during the shock cooling of the polymer upon precipitation. Precipitation was done by pouring a thin stream of polymer into a slowly stirred methanol bath creating a fiber of polymer. This quenching action formed an amorphous polymer

Table III Initial Decomposition Temperatures of the Polymers

Polymer	T (°C)
B9	327
B8	322
B7	315
B6	322
B5	312

Table IV Differential Thermal Analysis

Polymer	T , Onset Temperature of Peak, (°C)	
	Exothermic	Endothermic
B5	157	310
B6	155	332
B7	153	322

with built-in stresses. As the polymer was heated during the analysis, the stresses were released and accompanied by a chemical reaction, possibly release of water molecules, resulting in further imidization.

The endothermic peaks around 300–330°C are a result of decomposition of the polymer. Energy is required to break bonds to eliminate the smaller molecules of the decomposition process. A typical DTA for the polymer is shown in Figure 3.

The DSC (Table V, Fig. 4) also shows peak variations with composition. The broad endotherms, Figure 4, from 40 to 150°C probably indicate evaporation of small amounts of residual nonsolvents and solvents, methanol (bp 65°C) and *m*-cresol (bp 203°C), respectively.

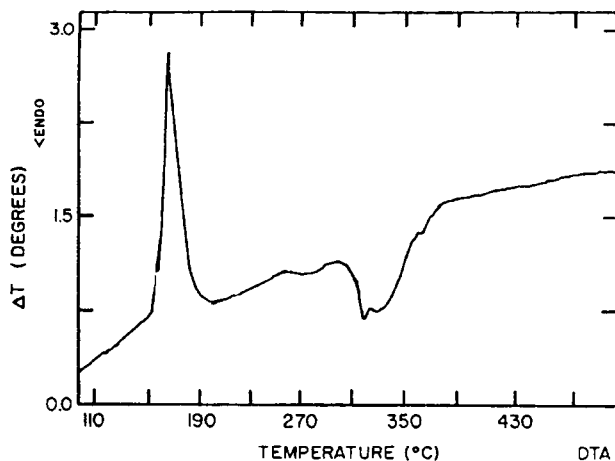


Figure 3 Typical differential thermal analysis of the bismaleimidothioether polymer.

Table V DSC Analyses

Polymer	T , Onset Temperature of Peak, (°C)	
	Exothermic	Endothermic
B5	154	250, 310
B6	146	270, 310, 330
B7	143	270, 315
B8	138	
B9	134	
DSC, after Reheat to 195°C		
B5	None	60, 192

On reheating, the exothermic peaks that occurred around 140–150°C on the DTA were not evident. This may be due to release of stress on softening and occurrence of a reaction. The glass transition temperature, T_g , for amorphous polymers varies with molecular weight since the effect of the chain ends on free volume is proportional to the concentration of the ends. Also, for amorphous polymers, the T_g occurs near the softening temperature just prior to melting. Table VI shows the various physical changes in the polymers.

Both molecular weight and imide content affect the T_g . In general, as the imide content decreases, the softening point decreases. The polymers synthesized with long-chain aliphatic thiols have lower softening and melting points than those with shorter chains. The T_g of the polymer is lowered as the number of CH_2 groups increases.

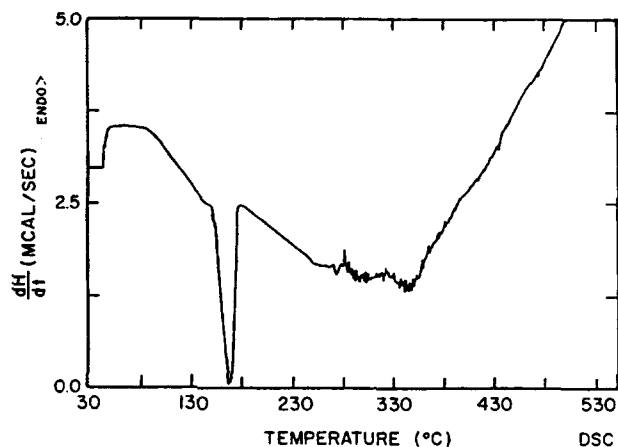


Figure 4 Typical differential scanning calorimeter analysis of the polymer.

Table VI Temperatures of Physical Changes in Polymers

Temperature	Polymers					
	B9	B8	B7	B6	B5	B0
T_{soften}	100	140	70	85	60	40
$T_{\text{shape loss}}$	160	195	135	135	130	135
$T_{\text{deterioration}}$	215	200	220	220	240	240

The fluctuations beyond 270°C are caused by decomposition of the polymer as indicated by the thermogravimetric analysis.

Fourier Transform Infrared Spectroscopy

The infrared spectra of the bisamic acid show a peak around 1710 cm^{-1} , which is the region of imidization vibrations. For this reason a height increase in this peak would indicate cyclodehydration had occurred forming the bisimide (Fig. 5).

The iodonium FTIR is shown in Figure 6.

Polymerization involves breaking the maleimide ring double bond, $\sim =\text{C}-\text{H}$, at $\sim 3106\text{ cm}^{-1}$ in the two monomers (Figs. 5 and 6). This peak is not evident in the polymer FTIRs (Fig. 7).

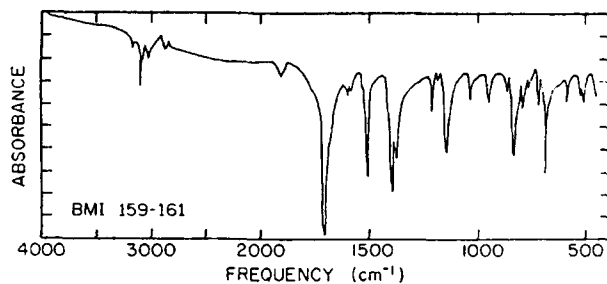


Figure 5 Typical FTIR of bismaleimide.

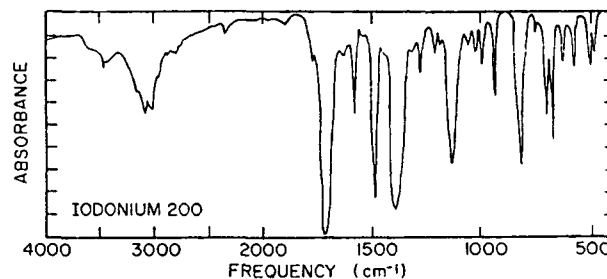


Figure 6 Typical FTIR of iodonium monomer.

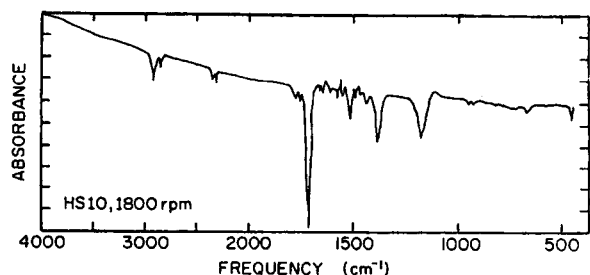


Figure 7 Typical FTIR of polymer.

CONCLUSIONS

Polyimidothioethers have been synthesized by using different imide containing monomers and hexane thiols in the backbone. These polymers behave like polyelectrolytes as is evidenced by the intrinsic viscosity measurements. Molecular weight distributions by GPC analysis show that the \bar{M}_w/\bar{M}_n ratio is 1.6 or less for all the polymers. These polymers are thermally stable up to 300°C and are soluble only in selected organic solvents.

The lithographic behavior of these polymers is the subject of another study.

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Received August 9, 1991

Accepted August 20, 1991