Polyimidothioether polymers*

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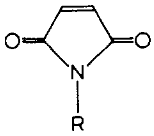
Bismaleimides undergo rapid and exothermic polymerization with hydrogen sulphide and polythiols in the presence of a proton donor to yield linear, thermoplastic polyimidothioether polymers. A number of polyimidothioether polymers and copolymers were synthesized from two arylenebismaleimide and four glycol bis(thioglycolates), and some of their properties were studied.

INTRODUCTION

In recent years, new interest and enthusiasm have been shown in the study of some new thermoplastic polymers which have, as an integral part of the backbone, alternating 'hard' and 'soft' domains. The former units arise from high melting monomers, while the latter units are from low melting or liquid monomers. Since such polymers are generally not crosslinked, they exhibit typical thermoplastic behaviour. Typical of this class are the polyimidothioether polymers (PITE) first reported by Crivello and Juliano[1] in 1975.

The interest in polyimidothioether polymers stems from the fact that the double bond in maleimides, being flanked on either side by C=O groups,



show pronounced reactivity towards a variety of nucleophiles, Diels–Alder reactions and 1,3-dipolar additions. Among the most powerful nucleophiles known are the thiolate anion and thiols, and the literature furnishes ample examples of thiol addition to maleimide[2-6]. Crivello and Juliana[1] reported the synthesis of PITE polymers from bismaleimides and thiol-terminated polysulphide liquid polymers, and Crivello[7] in 1976 reported the use of simple aliphatic dithols for PITE polymer synthesis.

The present work was undertaken to investigate the possibility of using diol bis(thioglycolates) and polyol bis(thioglycolates) in the PITE polymer synthesis, and characterization of the resulting products.

EXPERIMENTAL

General remarks

Infra-red spectra were recorded either as nujol mulls or liquid film on Perkin–Elmer Model 137E infracord Spectrophotometer, n.m.r. spectra were recorded on a Varian T-60 spectrometer in CF$_3$COOH with TMS reference. Melting points are uncorrected.

The 'work up', referred to frequently, means the following:

The reaction mixture was poured into methanol (500 ml) containing glacial acetic acid (5–10 ml). The precipitated polymer was filtered, washed with fresh portions of methanol, and dried in vacuum. When the product did not separate, it was recovered by distilling off all organic liquids under reduced pressure, washed with little dry ether and dried in a vacuum.

Materials

All amines were purified by distillation or recrystallization. Crude maleic anhydride was purified by mixing with a little acetic anhydride and distilling at normal pressure. The fraction boiling at 195°–6°C was collected and used. All organic solvents were purified by standard methods.

Synthesis of monomers

(a) *Bis(thioglycolates) of ethylene glycol (EG) and Polyethylene glycols (PEG)-200, 400 and 600.* These were synthesized according to the modified procedure of Cameron and Duke[8]. A toluene or xylene solution of the glycol (0.1 mol), thioglycolic acid (0.25 mol) and *p*-toluene sulphonic acid (1.5% w/w of the glycol), as catalyst, was refluxed in a three-necked flask equipped with a stirrer, and a Dean–Stark equipment for azeotropic removal of water. After all the water was removed, the contents were refluxed for a further 8–10 h. The cooled reaction mixture was washed with hot water several times, dried over anhydrous Na$_2$SO$_4$ and filtered. The solvent was distilled off under reduced pressure to yield the product. Only EG bis(thioglycolate) could be purified by vacuum distallation. b.p. 141°–5°/3–4 torr.

Characteristics of all these compounds are recorded in *Table 1*.

(b) *Synthesis of aromatic bismaleimides.* These were synthesized using a slight modification of Searle's method[9].

A solution of the diamine (0.05 mol) in toluene (250 ml) was added with good stirring to a warm solution of maleic

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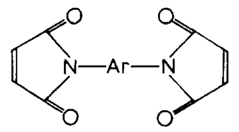
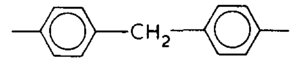
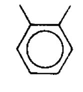
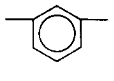
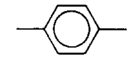
Table 1 Characteristics of poly(thioglycolates)

Bis(thioglycolate) of	b.p. (°C/mm Hg)	d^{25}	η_D^{25}		Analysis %C	%H	%S
Ethylene glycol	148/3	1.33	1.514	Calculated:	34.28	4.76	30.4
				Found:	34.81	5.14	29.9
PEG*-200	–	1.26	1.494	Calculated:	42.1	6.49	18.71
				Found:	42.07	7.01	18.8
PEG-400	–	1.227	1.492	Calculated:	46.92	7.4	11.39
				Found:	47.13	7.72	11.6
PEG-600	–	1.2265	1.489	Calculated:	48.7	7.05	8.6
				Found:	48.93	7.43	8.89

* Polyethylene glycol

Table 2 Characteristics of aromatic bismaleimides



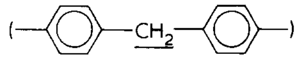
Number	Aromatics	m.p. (°C)		Analysis %C	%H	%N
1		158	Calculated:	70.39	3.91	7.82
			Found:	69.25	4.47	7.95
2		241	Calculated:	62.68	2.95	10.44
			Found:	62.90	3.16	10.58
3		198	Calculated:	62.68	2.95	10.44
			Found:	62.75	3.28	10.60
4		>345	Calculated:	62.68	2.95	10.44
			Found:	62.83	3.21	10.57

anhydride (0.11 mol) in toluene (100 ml) maintained at 50–60°C. The reaction was exothermic and the precipitation of the bismaleamic acid was immediate. After the complete addition of the amine, the reaction mixture was kept for 30 min and filtered. The solid was washed several times with hot toluene and air dried.

This maleamic acid was transferred to a 500 ml round-bottomed glask into which dry acetic anhydride (150 ml) and fused sodium acetate (5–6 g) were added. The contents were heated with stirring for 80–90 min, cooled and poured into 3 litres of ice-water with vigorous agitation. The separated bismaleimide was filtered, washed with several fresh portions of ice-water, and recrystallized from a benzene–EtOH mixture.

N-phenylmaleimide was synthesized similarly from aniline (0.1 mol) and maleic anhydride (0.11 mol). In *Table 2* are presented the characterization of the bismaleimides synthesized.

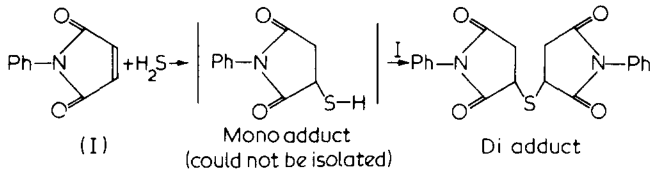
I.r.: 1720 cm^{-1} (C=O); 690, 840–850, 3100 cm^{-1} (C=C), NMR ((*N*,*N*′-bismaleimido-4,4′-diphenylmethane (DMB)): δ 4.1 HC=CH in maleimide ring) δ2.2



Maleimide–thiol reactions

Before the polymer syntheses were attempted, we examined the addition of H_2S to *N*-phenyl-maleimide, and thiophenol addition to DMB, as described below:

Addition of H_2S to N-*phenylmaleimide.* A solution of *N*-phenylmaleimide (1.0 g) in *m*-cresol (15 ml) containing 2–3 drops of tri-n-butylamine was bubbled with H_2S gas along with stirring. The reaction was exothermic. After 30 min, the H_2S passage was stopped and the product obtained after the 'work up' of reaction mixture (for 'work up' procedure see 'General remarks' in Experimental section).



The product obtained was diadduct. m.p. 202°C (Ref 7: 202°C).

Analysis: Calculated for monoadduct ($C_{10}H_9O_2NS$): C, 57.97, H, 4.34%; for diadduct ($C_{20}H_{16}O_4N_2S$): C, 63.15, H, 4.24%; Found: C, 63.42, H, 4.43%.

Addition of thiophenol to DMB. Thiophenol (1.1 g) and DMB (1.8 g) were stirred together in *m*-cresol (20 ml) containing 2–3 drops of tri-n-butyl amine for 3 h at room temperature. The product, after the work up, was a white, solid m.p. 142°C. Yield 1.6 g.

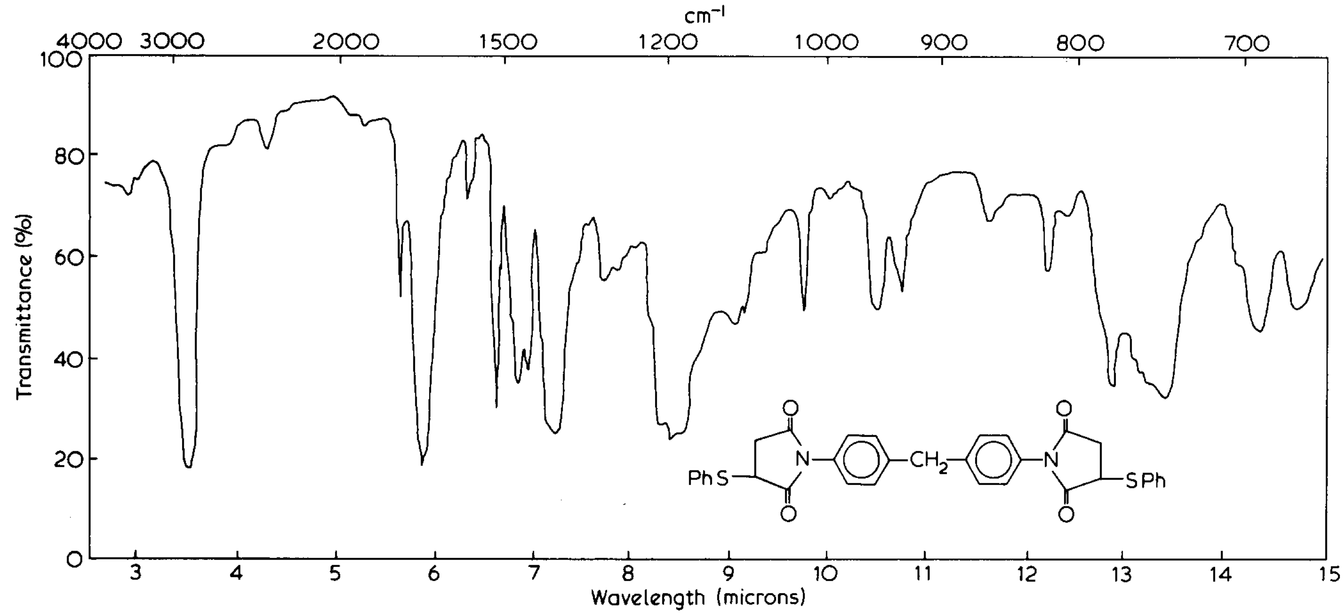
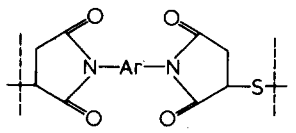
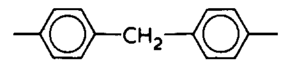
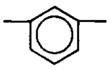
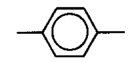


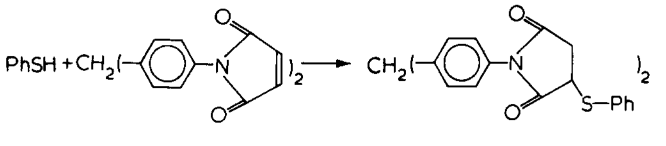
Figure 1 I.r. spectrum of DMB-thiophenol adduct

Table 3 Properties and elemental analysis data of polyimidothioethers from bimaleimides and hydrogen sulphide. General structure of these polymers:



Polymer	Aromatics	Yield (%)	Melting point (°C)	Inherent viscosity *dl/g****		Analysis C%	Analysis H%
1		95	272	0.493	Calculated: Found:	64.23 63.96	4.02 5.29
2		97	307	0.047	Calculated: Found:	55.62 55.04	3.31 4.38
3		96	260	0.097	Calculated: Found:	55.62 56.37	3.31 4.15
4		95	272	0.297	Calculated: Found:	55.62 55.39	3.31 4.08

*** 1% solution in DMF at 30°C



Analysis: Calculated for $C_{33}H_{26}O_4N_2S_2$: C, 68.51, H, 4.5%. Found: C, 68.83, H, 4.8%.

This is a new compound. Its i.r. spectrum is shown in *Figure 1*. Characteristic i.r. bands are: 1710, 1780 cm^{-1} (C=O), 1180–1190 cm^{-1} (C–S–C) and 700 cm^{-1} (C_6H_5).

Polymerization methods

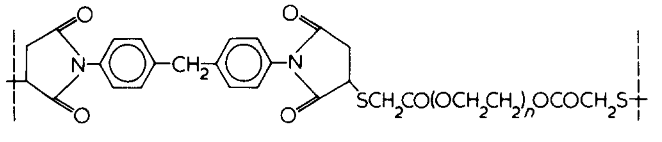
Polymers from H_2S and bismaleimide. These were synthesized according to the method of Crivello[7]. Characteristics of all these polymers are recorded in *Table 3*.

Characteristic infra-red bands present in the i.r. spectra of these polymers: 1730 cm^{-1} (C=O) and 1190 cm^{-1} (C–S–C). Bands due to unsaturation were absent in their i.r. spectra.

Polymers from bismaleimides and glycol bis(thioglycolates). In this class, the synthesis of the title polymers was performed using DMB and *o*-phenylene bismaleimide (OPBM).

(a) from bismaleimide and bis(thioglycolate) (1:1 molar proportion). DMB (1.79 g) and *m*-cresol (25 ml) were gently stirred together in a 3-necked flask to effect solution. EG bis (thioglycolate) (1.05 g) was added followed by 2–3 drops of tri-n-butylamine. The reaction was slightly exothermic. The reaction mixture was stirred at room temperature for 3 h. The product was obtained after the 'working up' of reaction mixture.

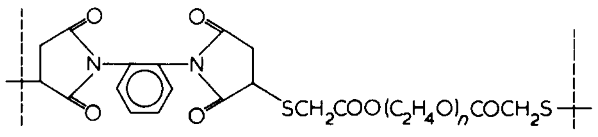
Table 4 Characteristics of polyimidothioethers from DMB and various glycol bis(thioglycolates). General structure of the polymers:



Polymer	Bis(thio-glycolate)	n = (in the structure)	Melting point (°C)	η_{inh} dl/g*		Analysis	
						C%	H%
5	EG[a]	1	73	0.155	Calculated:	57.04	3.87
					Found:	57.69	4.20
6	PEG-200[b]	4	VL[c]	0.234	Calculated:	56.55	5.15
					Found:	55.84	6.16
7	PEG-400	9	VL	0.093	Calculated:	56.10	6.08
					Found:	56.00	6.11
8	PEG-600	13	VL	0.050	Calculated:	55.83	6.56
					Found:	54.58	6.83

[a] Ethylene glycol
[b] Polyethylene glycol
[c] Viscous brown liquid
* 1% solution in DMF at 30°C

Table 5 Characteristics of polyimidothioethers from OPBM and glycol bis(thioglycolates). General structure of polymers:



Polymer	Bis(thio-glycolate) of	n = (in the structure)	Melting point (°C)	η_{inh}, dl/g**		Analysis	
						C%	H%
9	EG*	1	55–58	0.123	Calculated:	50.2	3.76
					Found:	49.9	4.43
10	PEG-200	4	VL*	0.156	Calculated:	51.14	4.91
					Found:	50.96	5.23
11	PEG-400	9	VL	0.080	Calculated:	52.04	6.02
					Found:	51.13	6.29
12	PEG-600	13	VL	0.038	Calculated:	52.48	6.56
					Found:	51.98	6.97

* See *Table 3*
** 1% solution in DMF at 30°C

Polymers from DMB and other bis(thioglycolates) were prepared similarly. Characteristics of all these polymers are recorded in *Table 4*.

Polyimidothioether polymers from OPBM and the glycol bis(thioglycolates) were parepared similarly and their characteristics are recorded in *Table 5*.

I.r. spectra of all these polymers conclusively showed addition to the double bond. In *Figure 2* the i.r. spectrum of DMB-PEG 400 bis(thioglycolate) polymer is shown.

(b) Polyimidothioether polymers from DMB and glycol bis(thioglycolate) (in 10:1 molar proportion) and H_2S. DMB (3.58 g) and *m*-cresol (25 ml) were placed in a 3-necked flask equipped with a stirrer and gas inlet tube. EG bis(thioglycolate) (0.21 g) and 2–3 drops of n-Bu_3N were added into the flask and the mixture stirred for 30 min. H_2S gas was then slowly bubbled into the reaction mixture with stirring. H_2S passage was continued for a period of 60 min and stopped. The reaction mixture was stirred for further 60 min and the product isolated after working up the reaction mixture.

Similarly polymers from DMB and bis(thioglycolates) of PEG-200, 400 and 600 were prepared by the above method.

Physical characteristics of these block polymers are reported in *Table 6*.

Synthesis of polyimidothioether copolymers

Two types of copolymers were synthesized:

(a) from DMB and two glycol bis(thioglycolates);

(b) from the mixture of DMB-OPBM and a glycol bis(thioglycolate).

(a) From DMB and two glycol bis(thioglycolates). Into a solution of DMS (3.58 g, ;.01 mol) in *m*-cresol (25 ml) were added with stirring, a mixture of DG bis(thioglycolate) (1.05 g, 0.005 mol) and PEG-200 bis(thioglycolate) (1.71 g, 0.005 mol) and 2–3 drops of n-Bu_3N. The reaction was slightly exothermic. The reaction mixture was stirred for 3 h at room temperature and the product isolated by the usual work up porcedure.

Similarly, copolymers from DMB and other

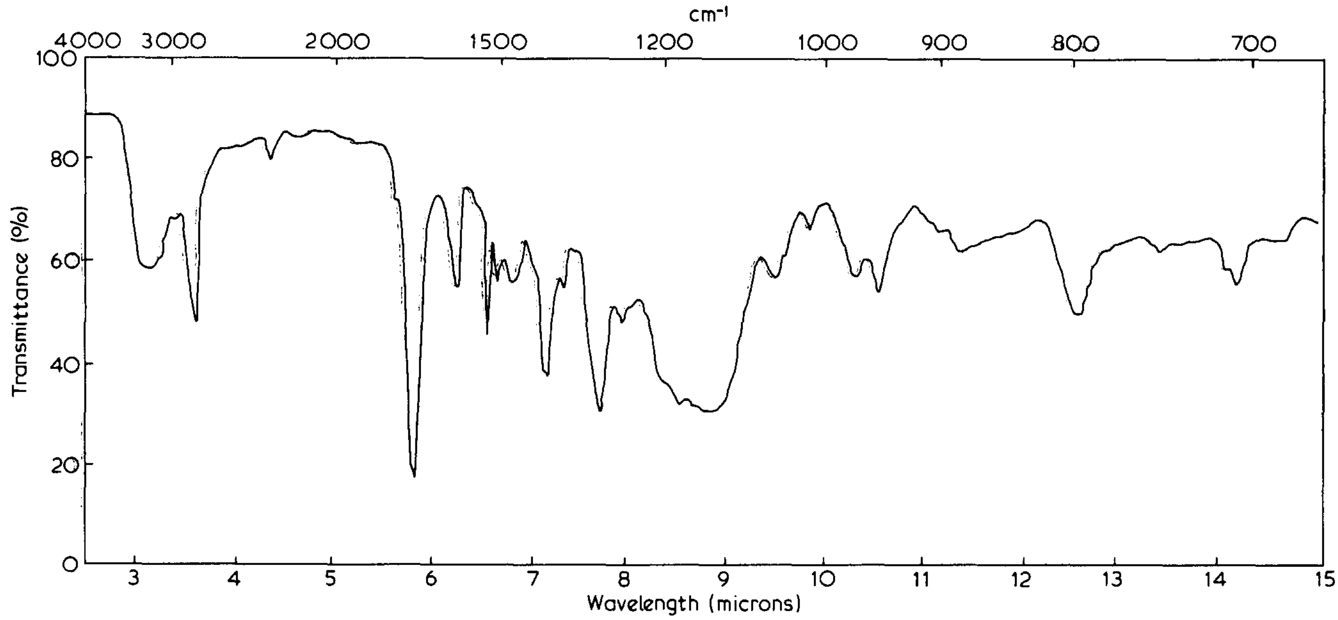
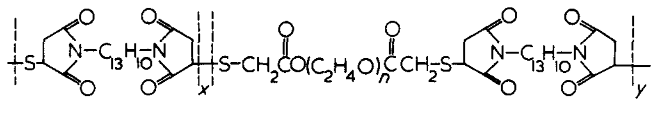


Figure 2 I.r. spectrum of DMB-PEG 400 bis(thioglycolate) polymer (polymer 7)

Table 6 Characteristics of polyimidothioethers from DMB, glycol bis(thioglycolates) and H_2S. General structure of these polymers:



Polymer	Bis(thio-glycolate) of	*n* = (in the structure)	Melting point (°C)	η_{inh}, *dl/g***		Analysis	
						C%	H%
13	EG*	1	65–70	0.181	Calculated: Found:	63.39 62.48	4.19 4.6
14	PEG-200	4	57–61	0.222	Calculated: Found:	63.08 63.73	4.24 4.8
15	PEG-400	9	50–54	0.110	Calculated: Found:	63.74 64.59	4.46 5.36
16	PEG-600	13	45–48	0.103	Calculated: Found:	63.84 65.79	4.6 5.57

* See *Table 3*
** 1% solution in DMF at 30°C

bis(thioglycolates) were synthesized. Characteristics of all these copolymers are shown in *Table 7*. In *Figure 3* the i.r. of DMB-OPBM-EG bis(thioglycolate) copolymer is shown.

(b) From DMB-OPBM mixture and a glycol bis(thioglycolate). A mixture of DMB (1.79 g) and OPBM (1.34 g) was gently stirred in *m*-cresol (25 ml) to effect solution. EG bis(thioglycolate) (2.1 g) was added followed by 2–3 drops of n-Bu_3N and stirred for 3 h at room temperature. The copolymer was obtained after the usual work up.

Copolymers from other bis(thioglycolates) were similarly synthesized.

In *Table 8* the physical characteristics and elemental analysis data of these polymers are shown.

In *Figure 3* the i.r. spectrum of DMB-OPBM-EG bi(thioglycolate) copolymer is shown.

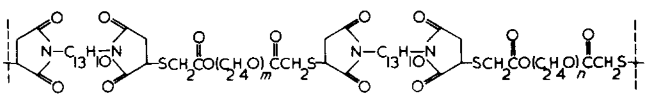
DISCUSSION

Thiol-maleimide addition reactions are highly facile and very general, and thiols or maleimides of widely differing structures can be used.

From the model reactions, H_2S addition to *N*-phenyl maleimide and that of thiophenol to DMB were found to be spontaneous at room temperature with good yields. This reaction has also been shown to take place in other polar aprotic solvents also[7]. Crivello[7] further found that in the uncatalysed copolymerization of bisthiols and bismaleimides in dipolar aprotic solvents, the self-polymerization of the maleimide to be a seriously competing reaction forming gel-like, insoluble products.

A study of the i.r. spectra and n.m.r. spectra of the monomers and PITE polymers gives an insight into the probable structure of these polymers. The –SH shows a

Table 7 Characteristics of copolymers from DMB and two glycol bis(thioglycolates). General structure of these copolymers:



Polymer	Bis(thioglycolate) of 1	2	Melting point (°C)	η_{inh}, *dl*/g***		Analysis Calculated	Found
17	EG(*m* = 1)	PEG-200(n = 4)	60–65	0.058	C†	56.76	61.53
					H	4.7	5.14
18	EG	PEG-400(n = 9)	NVL*	0.107	C	56.44	56.32
					H	5.37	5.78
19	EG	PEG-600(n = 13)	NVL	0.081	C	56.24	55.25
					H	5.71	5.58
20	PEG-200(*m* = 4)	PEG-400(n = 9)	NVL	0.183	C	56.3	55.81
					H	5.67	6.00
21	PEG-200	PEG-600(n = 13)	VL**	0.255	C	56.1	56.34
					H	6.01	6.32
22	PEG-400(*m* = 9)	PEG-600(n = 13)	VL	0.211	C	55.95	54.72
					H	6.32	6.48

* Non-tacky viscous liquid
** Viscous liquid
† Analysis in duplicate of two samples gave the same value
*** 1% solution in DMF at 30°C

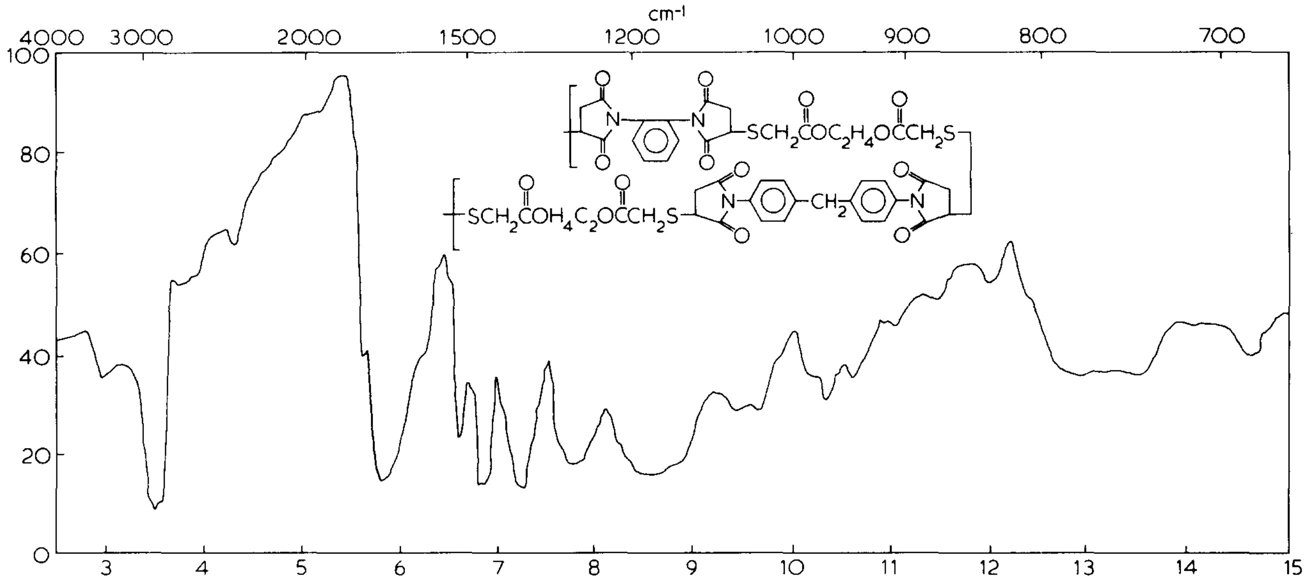
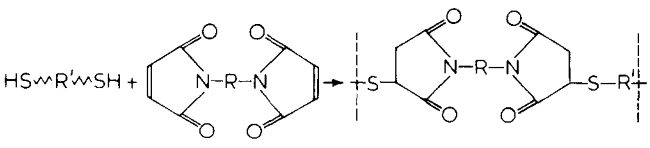


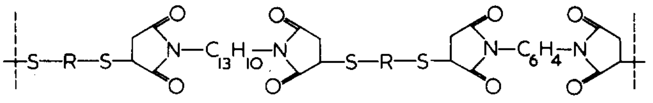
Figure 3 I.r. spectrum of DMB-OPBM-ethyleneglycol bis(thioglycolate) copolymer

medium intensity band at 2530–2900 cm^{-1} in the i.r. In the i.r. of DMB (*Figure 1*), absorptions at 1720 and 1800 cm^{-1} are characteristic of a cyclic dicarbonyl moiety while the bands at 3100 cm^{-1}, 850 and 690–700 cm^{-1} indicate CH = CH form. In the n.m.r spectrum of DMB, the olefinic protons appear at δ 4.10. The –SH protons in ethylene glycol bis(thioglycolate) appear as a triplet centred at δ 2.20. In the i.r. spectra of PITE polymers, the absence of bands due to unsaturation, and –SH functionality and the presence of a strong band at 1180–1200 cm^{-1} (assigned to C–S–C stretching vibrations) indicate thiol addition across the maleimide double bond. This new band at $\sim$1180 cm^{-1} is absent in the i.r. spectra of both the bisfunctional monomers. Crivello[7] has indicated a band due to succinimide ring methylene protons at 1380–1400 cm^{-1}, however, this is overlapped by the band due to C–N–C stretching vibration and thus is difficult for definite assignment. All this evidence indicates the following structure for the PITE polymers.



The physical properties of these polymers show a high degree of dependence on the aliphatic chain length of the thiol as it forms the aliphatic backbone (or the 'soft domain') of the polymer. As the carbon chain length between the thiol groups is increased, the tendency

Table 8 Characteristics of copolymers from DMB, CPBM and a glycol bis(thioglycolate). General structure of these polymers:



Polymer	Bis(thio-glycolate) of, (R)	Physical state	η^{**}_{inh},*dl*/g		Analysis	
					Calculated	Found
23	EG	Solid (mp 78°C)	0.179	C H	52.97 4.01	52.62 4.32
24	PEG-200	VL*	0.250	C H	54.04 5.03	53.92 5.97
25	PEG-500	VL	0.106	C H	54.18 6.05	53.45 5.96
26	PEG-600	VL	0.053	C H	52.24 6.56	53.72 6.93

* Viscous liquid

** 1% solution in DMF at 30°C

towards low viscosity becomes apparent. This trend is evident from the results recorded in *Tables 2–8*. In the present case, this trend with the use of long-chain ethyleneoxide units (i.e. ether units) may be expected to be more pronounced because of the flexible nature caused by ether linkages. This flexibility increases with increasing ether content.

Polyimidothioether copolymers, as mentioned earlier, may be prepared using two different thiols with a bismaleimide or *vice versa*. The copolymers prepared are shown, with their properties, in *Tables 7* and *8*. The i.r. spectra revealed just the basic features—described earlier for PITE polymers—and only the elemental analyses data seem to support the structure assigned to these polymers.

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