

Polymerization of *N,N'*-bismaleimido-4,4'-diphenylmethane with arenedithiols. Synthesis of some new polyimidosulphides

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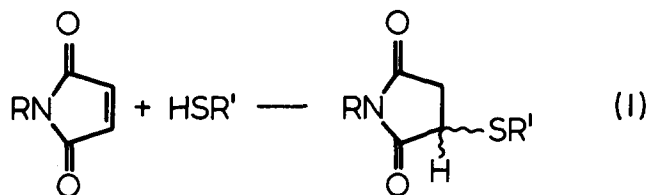
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Two new polyimidosulphides were prepared in 94% yield or higher and with inherent viscosities as high as 1.45 dl g^{-1} (0.5 g polymer/100 ml dimethyl sulphoxide; 25°C) by the addition of 4,4'-dimercaptodiphenylether or 4,4'-dimercaptobiphenyl to *N,N'*-bismaleimido-4,4'-diphenylmethane. Formation of soluble species requires a solvent that is or contains a proton source, since crosslinked products result otherwise. The polymers are amorphous thermoplastics with rigid backbones, reflected by their high glass transition temperatures ($T_g = 185^\circ\text{--}212^\circ\text{C}$) as well as by their insolubility in all but highly polar media, such as dimethyl sulphoxide or *N,N*-dimethylformamide. Both polyimidosulphides, when heated under nitrogen or air (thermogravimetric analysis), show no weight loss up to about 350°C , but the polymers degrade catastrophically (apparently via base-catalysed thiol elimination) within minutes at room temperature when dissolved in aprotic solvents containing secondary or tertiary amines.

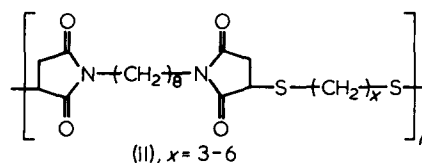
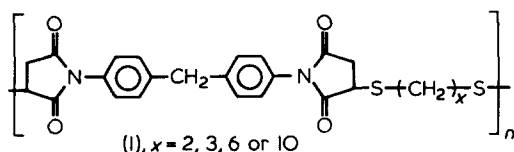
(Keywords: polyimidosulphides; polyamides; step-growth polymers; bismaleimides; dithiols)

INTRODUCTION

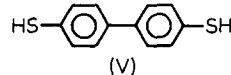
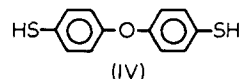
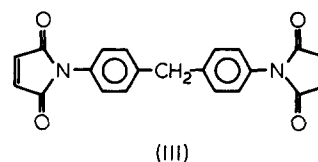
The Michael-type addition of thiols to the electrophilic carbon-carbon double bonds of *N*-alkyl- or *N*-arylmaleimides (equation (1))¹ has recently been adapted to syntheses of step-growth polymers formed via reactions of alkanedithiols with *N,N'*-bismaleimidoarenes²⁻⁴ or *N,N'*-bismaleimidoalkanes^{4,5}



Examples of these polymerizations include Crivello's preparation² of polyimidosulphides (I) and our synthesis⁵ of structurally related polymers (II). While (I) reportedly² undergo melting transitions (T_m) at $100^\circ\text{--}192^\circ\text{C}$, the far more flexible polyimides (II) are generally amorphous, elastomeric materials with glass transition temperatures (T_g) of $6.5^\circ\text{--}13^\circ\text{C}$;⁵ an exception, polyimidosulphide (II) ($x = 6$), is a leather-like, crystalline ($\sim 37\%$) thermoplastic that exhibits $T_g = 35^\circ\text{C}$ and $T_m = 77^\circ\text{C}$.



In order to exploit further the well established chemistry of equation (1) for the generation of polyimidosulphides with polymer chains less mobile than those of (II) and perhaps most (I), we studied the first polymerizations of a bismaleimide, *N,N'*-bismaleimido-4,4'-diphenylmethane (III), with arenedithiols (4,4'-dimercaptodiphenylether (IV) and 4,4'-dimercaptobiphenyl (V)) to afford polymers (VI) and (VII).



This paper details the synthetic approaches to (VI) and (VII) (cf. Table 1) along with fundamental properties of these materials that are, in fact, characteristic of

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Table 1 Polymerization of *N,N'*-bismaleimido-4,4'-diphenylmethane (III) with 4,4'-dimercaptodiphenyl ether (IV) in *m*-cresol

Expt no.	Solids (%) ^a	Temp. (°C)	Time (h)	η_{inh}^b (dl g ⁻¹)	$\bar{M}_w \times 10^{-5}^c$	$\bar{M}_n \times 10^{-5}^c$	\bar{M}_w/\bar{M}_n
1	22	~25	48	0.39	—	—	—
2	22	105	1	0.31	0.7	0.2	3.5
3	22	105	2	0.53	—	—	—
4	22	105	3	0.68	2.1	0.5	4.2
5	22	105	4	1.45	4.5	0.8	5.6
6	22	80	6	0.57	1.4	0.4	3.5
7	22	80	21	0.72	—	—	—
8	22	80	48	1.35	2.7	0.6	4.5
9	16 ^d	105	6	0.43	—	—	—
10	16 ^d	105	18	0.50	—	—	—
11	22	140	6	0.50	—	—	—

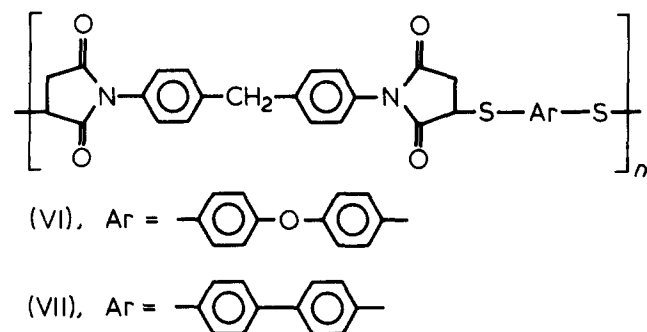
^a Concentration corresponds to 0.44 mol l⁻¹ in each monomer

^b Values determined for 0.50 g (VI)/100 ml DMSO at 25°C

^c Values determined relative to those of polystyrene standards using g.p.c. (see 'Experimental')

^d Concentration corresponds to 0.34 mol l⁻¹ in each monomer

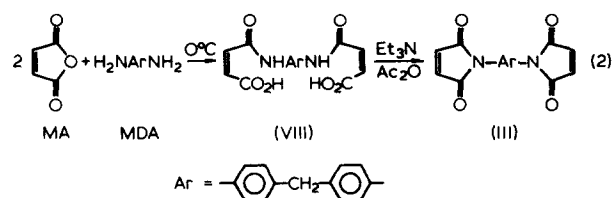
amorphous polymers with inflexible backbones. In addition, other features of polyimidosulphides (VI) and (VII), including their propensity to degrade in basic media, are described.



RESULTS AND DISCUSSION

Monomer synthesis

N,N'-Bismaleimido-4,4'-diphenylmethane (III) was prepared by a modification⁶ of a previously reported⁷ method in which methylenedianiline (MDA) reacts rapidly and essentially quantitatively with 2 mol of maleic anhydride (MA) in chloroform (CHCl₃) at ~0°C to produce bismaleamic acid (VIII) (equation (2)). Cyclo-dehydration of (VIII) at room temperature in acetone, containing triethylamine (Et₃N) and acetic anhydride (Ac₂O; a water scavenger), gives bisimide (III) in 51% yield.



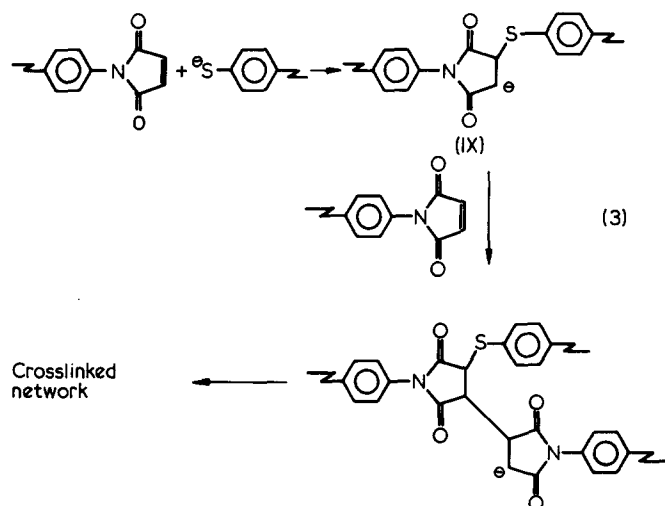
Polymer synthesis and characterization

Polyimidosulphides (VI) and (VII) were prepared in $\geq 94\%$ yield by allowing 4,4'-dimercaptodiphenylether (IV) or 4,4'-dimercaptobiphenyl (V) to react with an equivalent of bismaleimide (III) in *m*-cresol, containing a catalytic amount of tri(*n*-butyl)amine (Bu₃N) to initiate thiolate (ArS⁻) formation and thus promote the polymerization (illustrated for dithiol (IV) in Table 1). Inherent viscosities (η_{inh}) of isolated (VI) (measured for the polymer in dimethylsulphoxide (DMSO)) indicate that the reaction of (III) with (IV) responds predictably to changes in monomer concentration, reaction temperature and polymerization time. Low-molecular-weight ($\eta_{inh} = 0.31$ dl g⁻¹) but clearly polymeric (VI) is formed when the monomers (22% solids) are allowed to stir in *m*-cresol (containing Bu₃N) at ~25°C for 48 h (Expt 1, Table 1). At 105°C, an identical solution of (III) and (IV) affords (VI) having $\eta_{inh} = 0.31$ –1.45 dl g⁻¹ within only 1–4 h (Expts 2–5), but high-molecular weight (VI) is produced more slowly at a lower temperature (80°C; Expts 6–8) or with a lower monomer concentration (16% solids; Expts 9 and 10). A high reaction temperature of 140°C yields (VI) with η_{inh} of only 0.50 dl g⁻¹ after 6 h (Expt 11); polymerization at 140°C may be limited by the onset of the addition of weakly nucleophilic *m*-cresol to unconsumed maleimido end groups, terminating growth of the polymer chain.

Polyimide (VII), having $\eta_{inh} = 0.56$ –0.70 dl g⁻¹, was obtained by reaction of bisimide (III) with dithiol (V) under the conditions of Expts 4 and 5 in Table 1.

Beyond its role as a reaction medium, *m*-cresol promotes formation of soluble (VI) and (VII) by acting as a proton source, capable of neutralizing anionic intermediates (IX), which, in aprotic solvents, serve as branching sites that ultimately produce crosslinked, insoluble products *via* equation (3)². Such crosslinked polymers are formed exothermically and instantaneously

when (III) is treated with dithiols (IV) or (V) in *N,N*-dimethylformamide (DMF), and similar gelatinous materials were reported as products of the reactions of bisimide (III) with alkanedithiols or hydrogen sulphide in DMF or DMSO². Addition of acetic acid (AcOH) obviates crosslinking by neutralizing (IX) (as does *m*-cresol) and allows generation of soluble (VI) or (VII) ($\eta_{inh} \geq 0.3 \text{ dl g}^{-1}$).

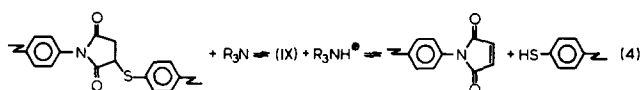


The primary structures of polymers (VI) and (VII) were verified by routine spectral and analytical methods (Table 2). Along with the complete loss of the weak S-H absorptions at 2560 cm^{-1} present in the i.r. spectra of starting dithiols (IV) and (V), spectra of the polyimidosulphides (including crosslinked (VI) prepared in DMF) exhibit the expected²⁻⁵ imide carbonyl stretching bands at ~ 1780 (weak) and $1705\text{--}1720 \text{ cm}^{-1}$. Infra-red spectra of (VI) and (VII) also contain absorptions at 1170 (VI) and 1185 (VII) cm^{-1} that are not apparent in spectra of monomers (III), (IV) and (V) and are near those previously assigned to C-S-C stretching vibrations ($1165\text{--}1180 \text{ cm}^{-1}$) in polyimidosulphides such as (I)². High-temperature ¹H n.m.r. spectra of soluble (VI) and (VII) ($\eta_{inh} = 1.45 \text{ dl g}^{-1}$ and 0.56 dl g^{-1} , respectively) display multiplets centred near 4.5 ppm , due to absorption of the ring methine proton (H^a , Table 2) adjacent to sulphur, along with unsymmetrical quartets at $\sim 3.3\text{--}3.5$ and $2.7\text{--}2.8 \text{ ppm}$ corresponding to the two non-equivalent ring methylene protons, H^b . Other signals in the n.m.r.

spectra of (VI) and (VII) are consistent with the structures shown, and despite the potential for degradation of (VI) and (VII) in DMF (*vide infra*), samples in DMF-*d*₇ showed absolutely no spectral changes after 20 min at 100°C . Elemental analyses of linear (VI) and (VII), as well as of crosslinked (VI), agree well with compositions calculated for the polyimidosulphides.

Polymer properties

During attempts to measure the relative (to polystyrene (PS)) weight (M_w) and number (M_n) average molecular weights of polymers (VI) and (VII) by gel permeation chromatography (g.p.c.), we found that in DMF (the only suitable chromatographic eluent that is a good solvent both for (VI) and (VII) and for PS calibration standards), polyimidosulphides (VI) and (VII) can degrade significantly at room temperature. This behaviour appears to be promoted by an impurity in the solvent rather than being due to any direct involvement of DMF *per se*, since the rate and extent of the degradation depend upon the purity of the DMF in which the polymers are dissolved. For instance, the η_{inh} of one sample of (VI) (0.5% w/v) in 'reagent' grade DMF dropped from 0.72 to $<0.3 \text{ dl g}^{-1}$ within 4 h while in the 'spectral' grade solvent, the η_{inh} of an identical sample remained above 0.6 dl g^{-1} after 24 h. It seems reasonable to suspect that adventitious, relatively basic ($\text{p}K_a = 10.73$)⁸ dimethylamine could catalyse degradation of (VI) or (VII) in DMF through the thiolate elimination depicted in equation (4). Indeed, the



validity of equation (4) is supported by the observation that in DMSO, in which (VI) or (VII) alone is stable indefinitely, polyimidosulphide (VI) ($\eta_{inh} = 1.45 \text{ dl g}^{-1}$) degrades catastrophically at 25°C to a material with $\eta_{inh} < 0.1 \text{ dl g}^{-1}$ within 30 min after treatment with diethylamine (Et_2NH , $\text{p}K_a = 11.09$)⁸ or Et_3N ($\text{p}K_a = 11.01$)⁸, indicating that an amine acts to promote degradation as a base and not as a nucleophile. Further, the i.r. spectrum of (VI) in DMSO showed little change after addition of excess Et_2NH other than the rapid appearance of a weak band at 2480 cm^{-1} , a characteristic absorption of the S-H stretching vibration for thiols in the presence of an amine.⁹

Table 2 Characterization of polyimidosulphides (VI) and (VII)

No.	I.r. (cm^{-1}) ^a		¹ H n.m.r. (ppm) ^b		Anal: found (calcd) (%)			
	C=O	C-S-C	H ^a	H ^b	C	H	N	S
(VI)	1780, 1705	1170	4.5	3.5, 2.8 ^c	66.7 (66.87)	4.14 (4.10)	4.91 (4.73)	11.2 (10.82)
(VI) (crosslinked)	1175, 1705 ^d	1170 ^d	—	—	66.5	4.18	4.97	10.6
(VII)	1780, 1720	1185	4.4	3.3, 2.7 ^c	68.9 (68.72)	4.29 (4.20)	5.20 (4.86)	11.5 (11.12)

^a Values determined for films cast from DMSO onto sodium chloride plates

^b Values determined at 90 MHz for samples in DMF-*d*₇ at 100°C

^c Upfield absorptions were partially obscured by those of the solvent

^d Values determined for sample as a potassium bromide pellet

Clearly, the elimination depicted in equation (4) is reversible, since, as noted above, treatment of bisimide (III) in DMF with dithiol (IV) leads to crosslinked polymer (VI), the insolubility of which drives the reaction to the left (i.e. towards the Michael linkage). Of course, during synthesis of linear (VI) and (VII), the moderately acidic solvent, *m*-cresol, neutralizes (IX) (cf. also equation (3)) and therefore limits the role of the basic catalyst (Bu_3N) to one of thiolate formation and precludes depolymerization through equation (4).

Although facile for (VI) and (VII) in DMF or DMSO, the degradation of equation (4) is not general for all polyimidosulphides. The η_{inh} (0.52 dl g^{-1}) of polymer (II) ($n=4$) remains virtually unchanged ($\eta_{\text{inh}}=0.46 \text{ dl g}^{-1}$) after 20 days (25°C) in DMSO containing Et_3N ; one would expect elimination to occur less readily for an alkanethiolate ($\sim\text{CH}_2\text{S}^-$), a relatively poor leaving group, than for a resonance-stabilized arenethiolate. Base-catalysed elimination of phenol from phenoxy-succinimides, a reaction apparently analogous to equation (4), was recently reported by Renner and coworkers¹⁰.

Notwithstanding the at least partial degradation of (VI) and (VII) in spectral grade DMF, relative (to PS) molecular weights for polyimidosulphide (VI) are reasonably proportionate to η_{inh} measured for samples of (VI) prepared under various conditions; for (VI) with $\eta_{\text{inh}}=0.31\text{--}1.45 \text{ dl g}^{-1}$, $\bar{M}_w=(0.7\text{--}4.5)\times 10^5$ and $\bar{M}_n=(0.2\text{--}0.8)\times 10^5$ with \bar{M}_w/\bar{M}_n increasing from 3.5 to 5.6 with increasing molecular weight (Table 1). Polymer (VII) ($\eta_{\text{inh}}=0.56 \text{ dl g}^{-1}$) showed $\bar{M}_w=1.7\times 10^5$, $\bar{M}_n=0.5\times 10^5$ and $\bar{M}_w/\bar{M}_n=3.4$.

The high glass transition temperatures (T_g , Table 3) of (VI) (185°C) and (VII) (212°C) confirm the expected rigidity of the backbones of these materials compared with those of the predictable more flexible polyimidosulphides (I)² and (II)⁵ (see above). However, T_g determined for (VI) and (VII) are somewhat lower than that of the structurally similar polyaspartimide (X) ($T_g=230^\circ\text{--}235^\circ\text{C}$) described some years ago¹¹, probably because intermolecular hydrogen bonding of the amino groups in (X) make associative contributions to chain stiffness in the polyaspartimide that are not possible in (VI) or (VII). Like (X), polyimidosulphides (VI) and (VII) are amorphous and show no indication (differential scanning calorimetry (d.s.c.)) of undergoing first-order, endothermic melting transitions. Both polyimidosulphides can be compression moulded (240°C at 138 MPa) to give tough, flexible films that are easily creased without cracking.

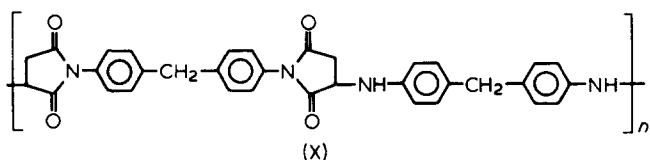


Table 3 Thermal analysis of polyimidosulphides (VI) and (VII)

No.	T_g ($^\circ\text{C}$) ^a	T_d ($^\circ\text{C}$) (N_2) ^b	T_d ($^\circ\text{C}$) (air) ^b
(VI)	185	349	349
(VII)	212	355	350

^a D.s.c.

^b Initial weight loss; t.g.a.

When heated under nitrogen or air (thermogravimetric analysis (t.g.a.)), polymers (VI) and (VII) exhibit initial weight loss (T_d) at $\sim 350^\circ\text{C}$ (Table 3), a value similar to those determined earlier for polyimidosulphides (I) ($T_d\sim 325^\circ\text{C}$)² and (II) ($T_d=336^\circ\text{--}380^\circ\text{C}$)⁵. Thermally induced, homolytic thiol elimination is the likely decomposition pathway for (VI) and (VII), as well as for polyimides (I) and (II)².

EXPERIMENTAL

General

m-Cresol (Aldrich Chemical Co.) was distilled and stored under nitrogen prior to use; dithiols (IV) (m.p. $103^\circ\text{--}104^\circ\text{C}$) and (V) (m.p. $179^\circ\text{--}180^\circ\text{C}$) were obtained from the Parish Chemical Co. and were suitably pure as received. All other materials were purchased from various commercial sources and were used without purification. All reactions were allowed to run in oven-dried glassware under a slow nitrogen flow.

Inherent viscosities of (VI) and (VII) (0.5 g polymer/100 ml solvent) were determined with Cannon-Ubbelohde semi-microviscometer (sizes 50 and 75), maintained at 25°C with a constant-temperature water bath.

Infra-red and ^1H n.m.r. spectra of the polyimidosulphides were obtained as described in Table 2 using, respectively, a Beckman model 4240 spectrophotometer and a Varian model EM 390 spectrometer fitted with a model EM 3940 variable temperature probe.

Glass transitions (T_g) of (VI) and (VII) were measured for bulk samples in closed pans, using a duPont model 990 thermal analyser with Cell Base Module II (d.s.c.) at a heating rate of $10^\circ\text{C min}^{-1}$; T_g were determined at the intersection of tangents to the change in the slope in the trace of relative (to air) heat capacity vs. temperature. Decomposition temperatures (T_d , initial weight loss) were obtained for samples heated at $10^\circ\text{C min}^{-1}$ with a duPont model 951 thermogravimetric analyser (t.g.a.).

Elemental analyses were provided by the Michigan Division Analytical Laboratories, Dow Chemical USA.

Synthesis of bismaleimide (III)

Using a procedure described earlier⁶, MDA (113.8 g, 0.57 mol) and MA (113.8 g, 1.16 mol) were allowed to react in cold (ice bath) CHCl_3 (1.1 l) to afford insoluble bisamic acid (VIII) (223.0 g, 98%). A mixture of the dried (VIII) (160.0 g, 0.41 mol), Ac_2O (82.8 g, 0.81 mol), Nickel(II) acetate tetrahydrate (3.7 g) and Et_3N (27.0 g, 0.27 mol) in acetone (370 ml) was allowed to stir at room temperature for 48 h, during which (III) (90.0 g, 62%) precipitated. Recrystallization of the crude bisimide from 1:1 CHCl_3 /methanol (MeOH) gave (III) as light yellow needles (76.5 g, 52% (based on starting MA and MDA)), m.p. 162°C (d.s.c.), literature value¹¹ 158°C .

Synthesis of polyimidosulphides (VI) and (VII)

Various conditions for preparation of polymer (VI) are outlined in Table 1; the following will serve to illustrate the method. A mechanically stirred mixture of (III) (8.00 g, 0.022 mol), (IV) (5.16 g, 0.022 mol) and *m*-cresol (45 ml) was heated until the monomers completely dissolved. The stirred solution was allowed to cool to room temperature, and Bu_3N (~ 5 drops) in *m*-cresol (5 ml) was added dropwise. After the initial exotherm had subsided (the

solution temperature rose to 45°C), the solution was heated to 105°C and maintained at that temperature, using an infra-red lamp with an I²R Therm-O-Watch Controller, for 4 h, after which the solution was mixed with MeOH (~700 ml) containing AcOH (20 ml), in a Waring Blender. The resulting fibrous (VI) was allowed to stir in fresh MeOH for 24 h, collected and dried *in vacuo* (75°C) for 24 h to give off-white fibrous (VI) (12.60 g, 96%), $\eta_{inh} = 1.45 \text{ dl g}^{-1}$ (Table 1).

Polymer (VII) was prepared similarly by heating (III) (8.00 g, 0.022 mol), (V) (4.80 g, 0.022 mol) and Bu₃N (3 drops) in *m*-cresol (50 ml) at 105°C for 4 h. Isolation and purification as described above for (VI) gave white, fibrous (VII) (12.60 g, 98%), $\eta_{inh} = 0.70 \text{ dl g}^{-1}$ (DMSO).

Gel permeation chromatography

Gel permeation chromatography (g.p.c.) of (VI) and (VII) was performed using a Waters model 244 liquid chromatograph equipped with a Waters model R401 differential refractometer and Hibar-II columns (E. Merck Laboratories), containing Lichrospher (silica gel) 100, 500, 1000 and 4000. Spectral grade DMF (Burdick and Jackson Laboratories, Inc.) containing lithium nitrite (LiNO₂, 0.1 mol l⁻¹) was employed as the eluent and was degassed and passed through a 0.35 µm filter prior to use; viscosity measurements of (VI) in the LiNO₂/DMF

solution showed the salt to have no effect on the rate or extent of polymer degradation in the eluent.

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