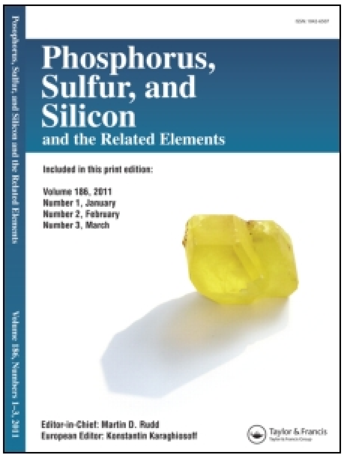

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POLY(IMIDE)S BASED ON FURFURYL-DISULFIDE

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POLY(IMIDE)S BASED ON FURFURYL-DISULFIDE

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Poly(disulfido-imide)s were prepared by Diels-Alder (DA) reaction of furfuryl-disulfide (FDS) with the various bismaleimides. The DA reaction was carried out in xylene as solvent, as well as in bulk, followed by aromatization of tetrahydropthalimide intermediates in the presence of acetic anhydride. All the poly(disulfido-imide)s (PDSI)s were characterized by elemental analyses, IR spectral data, and thermogravimetry. The poly(disulfido-imide)s (PDSI)s exhibit moderate thermal stability. Preliminary test for glass reinforcement of the poly(disulfido-imide) (PDSI) indicates that laminates with good mechanical strength can be obtained.

Key words: Diels-Alder reaction; furfuryl disulfide; bismaleimides; poly(imide)s, poly(disulfidoimide)s, IR spectral study, thermogravimetry.

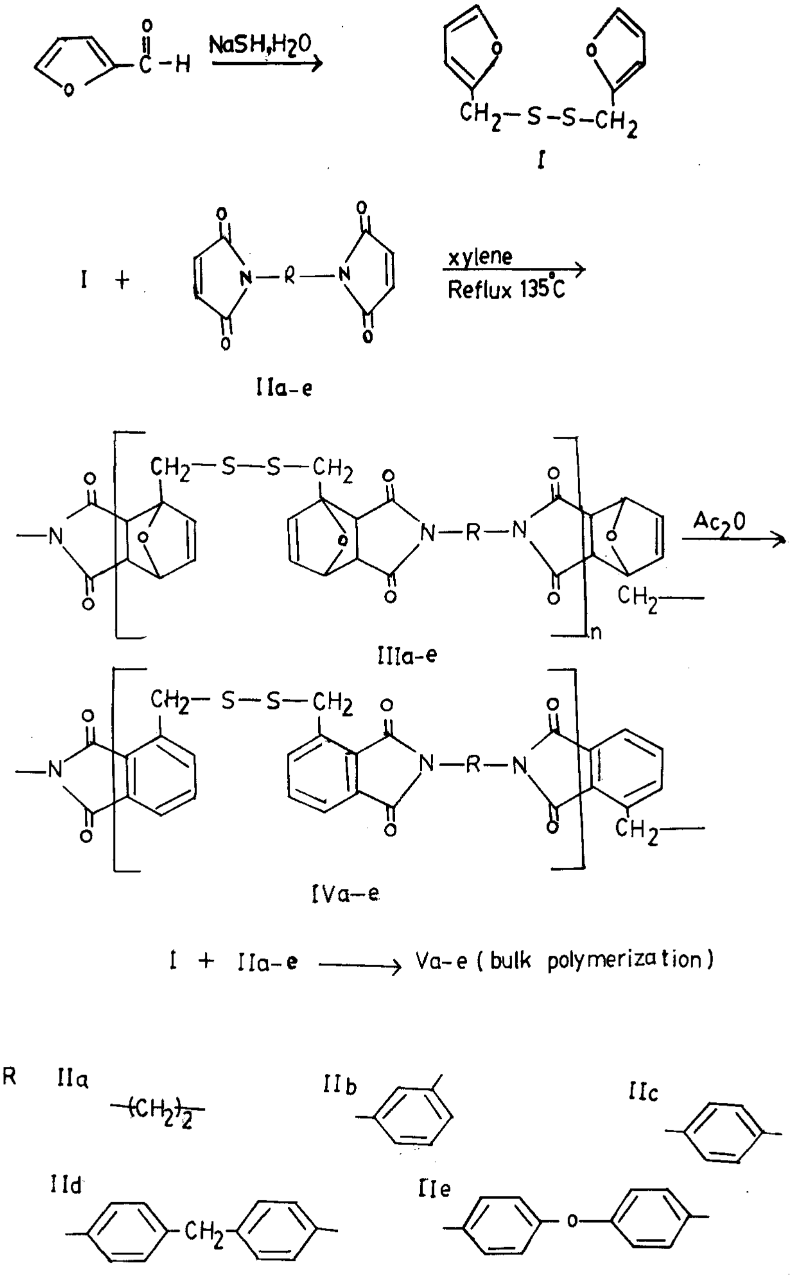
INTRODUCTION

The introduction of flexible linakages such as —O— and —Si—O— to improve processibility of poly(imide)s without major sacrifice in thermo-oxidative stability has received great attention both industrially and academically.[1–5] Copoly(imide)s are suitable for preparation of interlaminar flexible composites that could exhibit the desired properties described above. One of the approaches considered is the introduction of the —S— or —S—S— linkage in the poly(imide) chain. This approach has received little attention.[6,7] Formerly, modified copoly(imide)s containing —CH_2—S—S—CH_2— linkage have been prepared by condensation polymerization. However, evolution of volatile by-product is considerable.[6,7] They yield porous structures with reduced strength compared to the addition-type polymerization process which do not produce volatile by-products.[8]

Hitherto the Diels Alder (DA) intermolecular addition polymerization of furfuryl disulfide (FDS)(**I**) (Scheme I) with various bismaleimides (**IIa–e**) has received no attention in spite of the ease of synthesis of (FDS)(**I**) from furfural, an agricultural waste, and ease of processing of [PDIS] from (FDS)(**I**). Hence it was thought interesting to study (PDSI)s based on furfuryl disulfide (FDS).

RESULTS AND DISCUSSION

Furfuryl disulfide (FDS) was prepared by the modification of the method reported in the patent literature.[9] The sulfur content of FDS is consistent with the molecular formula of FDS. The important IR spectral characteristics of FDS are a weak band at 2850 and 2930 cm^{-1} due to asymmetrical and symmetrical stretching vibrations at —CH_2—, the bands 925, 880, 785, and 720 arise from 2-furanyl ring[10] and the bands at 730–680 cm^{-1} are attributed to the —S—S— linkage. The structure of



SCHEME I

FDS was also confirmed by its reduction reaction. On reduction of FDS(I) by zinc/HAC̄ yield furfuryl mercaptan (70%). Its boiling point was 153–156°C.[11]

The synthesis of (FDS)(I), all the poly(disulfido-imide)s [PDSI]s (**III**, **IV**, **V**) form FDS(**I**) and bismaleimides **IIa–e** are shown in Scheme I. The non-aromatized products **IIIa–e** are first formed and then aromatized by treatment with acetic

TABLE I

Characterization of non-aromatic poly(disulfido-imide)s **IIa–e**

Table : 1 Characterization of Non-aromatic poly(disulfido-imide)s IIIa-e

Polymer Sample	Molecular Formula (molar mass)	Elemental analysis calcd (Wt %)	found	Yield (%)	IR Spectral features				Weight loss (%) at various temperatures (°C)						
					-CH2-S-	-C=C-	imide	aromatic	200	300	400	500	600	700	775
IIIa	$[C_{20}H_{18}N_2O_6S_2]n$	C 53.81	53.91	75	2945	1500	1780		3	12	15	40	60	70	80
	(446)n	H 4.04	4.14		2885	1610	1700								
		N 6.22	6.12		705		1100								
		S 14.35	13.25				730								
IIIb	$[C_{24}H_{18}N_2O_6S_2]n$	C 58.3	58.35	79	2950	1500	1780	3030	5	11	14	42	62	72	90
	(494)n	H 3.64	3.69		2840	1600	1710	780							
		N 5.67	5.57		710		1100								
		S 12.96	12.92				730								
IIIc	$[C_{24}H_{18}N_2O_6S_2]n$	C 58.3	58.4	83	2935	1520	1770	3020	4	13	16	43	63	74	87
	(494)n	H 3.64	3.75		2870	1600	1700	820							
		N 5.67	5.05		700		1100								
		S 12.96	13.02				720								
IIId	$[C_{31}H_{24}N_2O_6S_2]n$	C 63.70	63.80	72	2940	1500	1790	3040	3	14	17	41	61	75	85
	(584)n	H 4.11	4.21		2860	1600	1710	830							
		N 4.79	4.69		695		1100								
		S 10.96	10.86				730								
IIIe	$[C_{30}H_{22}N_2O_7S_2]n$	C 61.43	61.53	80	2930	1500	1780	3030	5	12	18	42	66	76	89
	(586)n	H 3.75	3.79		2845	1600	1700	820							
		N 4.78	4.68		710		1100								
		S 10.92	11.00				730								

anhydride to yield **IVa–e**. In the absence of **IIa–e**, heating of (FDS)(**I**) in xylene at 135°C does not alter the properties of (FDS)(**I**). It was also observed that heating of bismaleimides in xylene at 135°C does not induce the addition polymerization of **IIa–e**. This has been shown to be only possible either at elevated temperature or in the presence of initiator.[12,13] This indicates that in the DA reaction of FDS and bismaleimides, it does not exhibit self polymerization or degradation of FDS bismaleimides. All the polymer samples were obtained in high yields in the form of dark brown solid powders. They are insoluble in common organic solvents and not affected by concentrated mineral acid and formic acid. The elemental analysis of all poly(imide)s sample are shown in Tables I–III and are consistent with their predicted structures (Scheme I).

TABLE II

Characterization of aromatic poly(disulfido-imide)s **IVa–e**

Polymer Sample	Molecular Formula (molar mass)	Elemental analysis calcd (Wt %)	found (Wt %)	Yield (%)	IR Spectral features				Weight loss (%) at various temperatures (°C)						
					-CH2-S-	-C=C-	imide	aromatic	200	300	400	500	600	700	775
IVa	$[C_{20}H_{14}N_2O_4S_2]n$	C 58.54	58.64	82	2950	1500	1780	3030	3	13	16	45	65	75	78
	(410)n	H 3.41	3.42		2880	1610	1710	730							
		N 6.83	6.80		705		1100	830							
		S 15.1	15.00				720								
IVb	$[C_{24}H_{14}N_2O_4S_2]n$	C 62.88	62.95	87	2960	1500	1770	3030	4	12	17	44	68	80	85
	(458)n	H 3.05	3.09		2870	1600	1700	780							
		N 6.11	6.05		710		1100								
		S 13.97	12.91				730								
IVc	$[C_{24}H_{14}N_2O_4S_2]n$	C 62.88	63.00	89	2945	1520	1780	3020	4	11	14	45	66	81	87
	(458)n	H 3.05	3.56		2880	1610	1700	790							
		N 6.11	5.75		700		1100	830							
		S 13.97	14.25				720								
IVd	$[C_{31}H_{20}N_2O_4S_2]n$	C 67.88	67.85	72	2955	1500	1770	3030	5	15	16	47	61	82	86
	(548)n	H 3.65	3.69		2860	1610	1700	780							
		N 5.11	5.01		690		1100	830							
		S 11.68	11.58				730								
IVe	$[C_{30}H_{18}N_2O_2S_2]n$	C 65.45	65.55	85	2940	1500	1770	3020	5	10	15	46	68	83	88
	(550)n	H 3.27	3.37		2845	1600	1710	790							
		N 5.09	5.00		710		1100	820							
		S 11.64	11.54				720								

Typical IR spectra of poly(disulfido-imide)s are shown in Figure 1. Examination of IR spectra of all poly(disulfido-imide)s reveals that all the spectra contain prominent characteristic bands of the imide and sulfide group. The bands around 1,700, 1,620, 1,050, and 720 cm^{-1} are contributions from imides **I**, **II**, **III**, and **IV**, respectively. Bands around 2,950, 2,880, 1,450, 1,270, and 715 cm^{-1} (Shoulder) correspond to sulfide linkage group. The IR spectrum of poly(disulfido-imide) **IIIa** does not show a distinct band at 3,030 cm^{-1} because of the aromatic of monomer **I**, but shows a band at 830 cm^{-1} due to C—H bending vibration of the two adjacent hydrogen atoms. The IR spectrum of aromatized (PDSI)s **IIIa** (i.e., **IVa**) show the distinct aromatic band at 3,030 cm^{-1} as well as multiple absorption bands in the region 800–1,200 cm^{-1}. They may be assigned to the C—H in plane and out of plane bending vibration character of aromatic systems. The band at 780 cm^{-1}

TABLE III

Characterization of bulk phase poly(disulfido-imide)s Va–e

Polymer Sample	Molecular Formula (molar mass)	Elemental analysis calcd (Wt %)	found	Yield (%)	IR Spectral features -CH2-S-	-C=C-	imide	aromatic	Weight loss (%) at various temperatures (°C) 200	300	400	500	600	700	775
Va	$[C_{20}H_{14}N_2O_4S_2]n$ (410)n	C 58.54 H 3.41 N 6.83 S 15.1	58.64 3.40 6.80 15.00	80	2950 2880 700	1500 1600	1770 1700 1100 730	3030 730 830	3	13	17	49	66	74	80
Vb	$[C_{24}H_{14}N_2O_4S_2]n$ (458)n	C 62.88 H 3.05 N 6.11 S 13.87	62.94 3.06 6.05 13.95	85	2960 2880 710	1500 1610	1780 1700 1100 720	3030 780	5	14	18	45	67	75	82
Vc	$[C_{24}H_{14}N_2O_4S_2]n$ (458)n	C 62.88 H 3.05 N 6.11 S 13.97	65.85 3.54 6.00 14.00	90	2940 2860 705	1500 1610	1780 1710 1100 730	3020 780 830	4	13	17	47	66	78	85
Vd	$[C_{31}H_{20}N_2O_4S_2]n$ (548)n	C 67.88 H 3.65 N 5.11 S 11.68	67.85 3.66 5.06 11.65	82	2965 2870 685	1500 1600	1780 1700 1100 720	3040 790 830	3	14	15	46	69	86	88
Ve	$[C_{30}H_{18}N_2O_5S_2]n$ (550)n	C 65.48 H 3.27 N 5.09 S 11.64	65.55 3.29 5.05 11.60	82	2950 2865 705	1500 1610	1770 1710 1100 730	3030 780 820	6	12	16	45	68	75	86

might be due to C—H bending vibration of the adjacent hydrogen atoms of pthalimide moiety arising from the aromatization of the poly(tetrahydropthalimide) intermediate (**IIIa**). This indicates the aromatization of the poly(tetrahydropthalimide) **IIIa**. These bands could not be observed separately for the aromatic system already present in monomer and the aromatic system in poly(tetrahydropthalimide) (unaromatized PDSIs **IIIa–e** in the spectra of PDSI **IVb–e**). A medium band around 2,950–2,930 appeared in all the spectra of (PDSI), attributed to —CH_2—S—.

Typical TG curves are shown in Figure 2. The TG data show that the produced (PDSI) samples exhibited <4% weight loss at 225°C probably corresponding to residual solvents and that they decompose in two stages. The first stage, between 225 and 300°C depends upon the nature of the PDSI. The first step in degradation of the PDSI is may be due to degradation at —S—S— linkage. The second stage

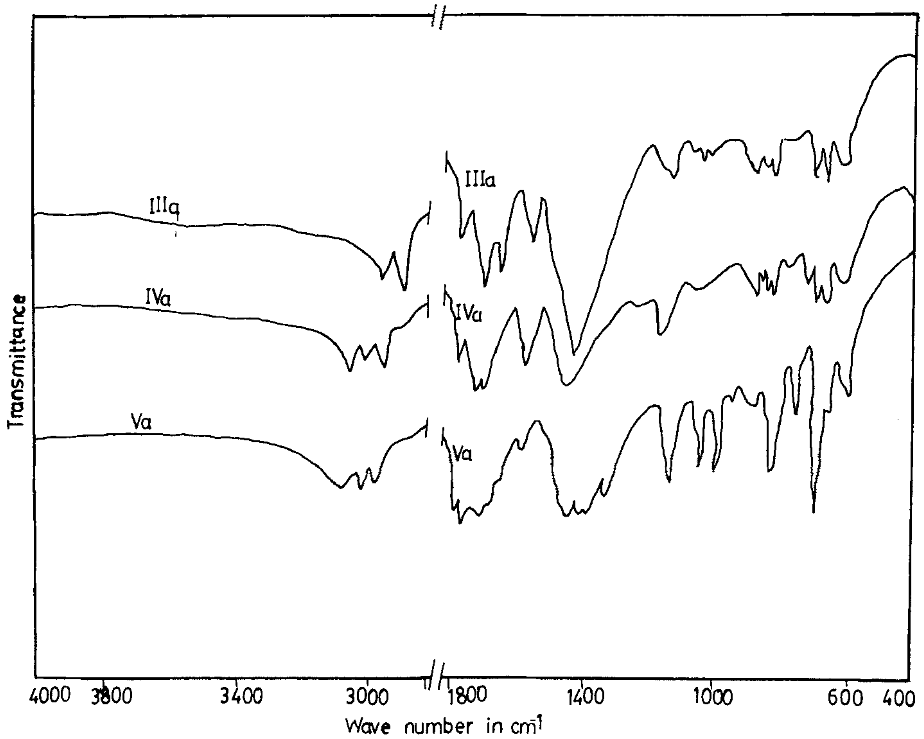


FIGURE 1 IR Spectra (KBr) of poly(disulfido-imides) **IIa**, **IVa**, **Va**.

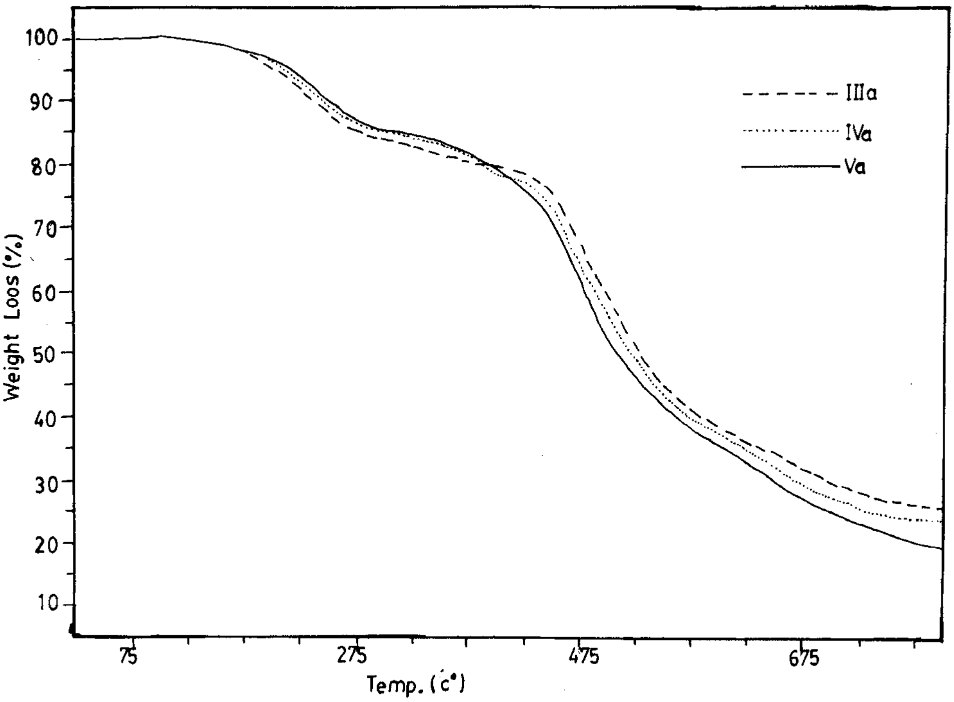


FIGURE 2 TG Curves (in air) for poly(disulfido-imides) **IIa**, **IVa**, **Va**.

of degradation of PDSIs occurs between 425° and 525°C. The rate of second stage degradation of unaromatized PDSIs is higher than for the aromatized form and also bulk PDSIs. The present (PDSI)s are found to be moderately thermally stable and retain the acid, solvent and weather resistivity.

Because of nonprocessibility of the present insoluble (PDSI)s, qualitative observations were made on "in situ" glass reinforcement using a mixture of FDS(**I**) and bismaleimides (**a**–**e**) in an organic solvent. It was noted that laminate sheets could be made with good mechanical strength (impact strength 211 MPa, flexural strength 295 MPa). The key property of the prepared (PDSI)s is that they can be processed at lower temperatures (140 ± 150°C) than well known poly(imide)s.[14]

EXPERIMENTAL

Materials. Sodium hydrogen sulfide used was obtained from Fluka AG, Switzerland. Furfural was obtained from SDS Fine Chemical Ltd., Boisar, India and was purified by the method reported in the literature.[15] Methanol and various diamines were obtained from SDS chemical, Boisar, India. Other chemicals used were of laboratory grade.

Preparation of monomers. The following bismaleimides (**IIa**–**e**) were prepared according to methods reported.

Sample	Bismaleimides	mp (°C)	Reference
IIa	*N*,*N*′-Ethylene bismaleimide	189–190	16
IIb	*N*,*N*′-1,3-Phenylene bismaleimide	202–203	17–19
IIc	*N*,*N*′-1,4-Phenylene bismaleimide	>300	17–19
IId	1,1′-(Methylene di-4,4-phenylene)bismaleimide	156–158	19–21
IIe	1,1′-(Oxy-di-4,4′-phenylene)bismaleimide	179–182	21

Preparation of Furfuryl Disulfide (FDS). The furfuryl disulfide (FDS)(**I**) was prepared by modification of a method reported in the patent literature.[9] Dry hydrogen sulfide was passed rapidly, over a two-hour period to an ice cold mixture of furfural (28.8 gm, 0.3 mole) in phenol (150 ml) and sodium hydrogen sulfide (25.0 gm, 0.32 mole). After permitting the mixture to stand at room temperature overnight, liquid was separated from the undissolved sodium hydrogen sulfide, refluxed for two hours and then distilled to remove ethanol. The residue was poured into water (400 ml) and extracted with ether (200 ml). The ether was separated, dried over sodium sulfate, and then the remaining trace ether was removed by distillation. The residue of disulfide was then redistilled at 112–115°C under reduced pressure (Ca. 0.5 mm) obtained in 55% yield.

Analysis of FDS: Molecular Weight: $C_{10}H_{10}S_2O_2$ *(226.32).*

% Elemental analysis:

	C%	H%	S%
Calculated:	53.02	4.42	28.28
Found:	52.92	4.55	28.50

I.R. spectral features. Furan ring 1,615 cm^{-1}, 1,510 cm^{-1}, 1,390 cm^{-1} —CH_2—S—: 2,950–2,930 cm^{-1}, 2,880–2,845 cm^{-1},[22] bp 112–115°C 0.5 mm. On reduction of FDS by Zn/HAC yield furfuryl mercaptan 70%. Furfural mercaptan is a colourless liquid, very stable and with an extremely disagreeable odour. Its boiling point was 153–156°C.

The DA reaction of (FDS)(**I**) with various bismaleimides (**IIa**–**e**) were carried out both in solution and in solid phase systems.

Solution phase polymerization. (FDS)(**I**) (2.26 g, 0.01 mole) in 100 ml of dry xylene was mixed with **IIa** (2.24 g, 0.01 mole). 0.1 gm Hydroquinone was added. The solution was stirred and refluxed at 135°C for 24 hours. The resulting solution was cooled and poured into a large volume of dry ether. The precipitated unaromatized polymer (**IIIa**) was filtered off and dried. It was treated twice with hot dimethyl formamide (DMF) to remove unreacted (FDS)(**I**) and **IIa**. Aromatization of polymers **IIIa** was carried out by refluxing 2 gm of the dried polymer in 2 ml of acetic anhydride for 15 hours. The resulting mixture was poured into water. The precipitate of aromatized, polymer **IVa** was filtered off, washed once each with water and methanol.

Bulk polymerization. A mixture of (FDS)(**I**) (1.13 g, 0.005 mole) and **IIa** (1.12 g, 0.005 mole) was suspended in dry tetrahydrofuran (THF) then spread on a petri dish and the THF was evaporated at room temperature. The dried mixture was heated at 135°C for 8 hours and then heated with acetic anhydride (1 ml) at 150 ± 5°C for 8 hours with vigorous agitation. The resulting solidified product **Va** was treated as described above. Polymers formed between **IIb–e** with (FDS)(**I**) were obtained similarly.

Measurements. The C, H, N contents of the all poly(imide)s were estimated by means of Carlo Erba elemental analysis (Italy). Sulfur content of (FDS)(**I**) and all (PDSI)s was determined by the Carius Method.[22] The IR spectra were taken in KBr using a Perkin Elmer 983 spectrophotometer. All polymer samples were subjected to thermogravimetry (TGA) (Du Pont 9900 Thermogravimetry Analyser) in air at a heating rate 10° k/mm, air purge 100 ml/min.

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