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THERMAL FUNCTIONAL POLYMERIC "INIFERTERS" BASED ON PHOSPHORUS-CONTAINING POLY(THIURAM DISULFIDES); SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

Secondary amine end-terminated oligomeric poly(phosphonamides) and poly(phosphorylamides) were synthesized by the condensation reaction of phenylphosphonic dichloride, ethyl dichlorophosphate, 2,2,2-tribromoethyl dichlorophosphate, and 2,2,2-trichloroethyl dichlorophosphate with an excess of piperazine or *N,N'*-dimethyl-1,6-hexanediamine. The macrodiamines were chain extended by reaction with CS_2 to the macrobis(dithiocarbamates) followed by oxidative coupling to the corresponding poly(thiuram disulfides) bearing the phosphorus functions. The diamine precursors and their polythiuram disulfides were characterized by elemental analysis, spectral analysis, thermal analysis, and viscosity measurements. The thermal stabilities of the prepolymers were correlated with their structures. The composition of the thiuram disulfide functions could be

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determined by TGA, whereas the kinetics of their thermal decomposition in the solid state was studied by DSC analysis. The activation energy varied with the chemical structure of the backbone but was quite independent of the chain length. Alternatively, oligomeric polythiuram disulfides containing phenyl phosphonate groups were synthesized by the condensation reaction of phenylphosphonic dichloride with *N,N'*-diethyl-*N,N'*-bis(2-hydroxyethyl)thiuram disulfide.

INTRODUCTION

Tetraalkylthiuram disulfides have of late emerged as thermal and photo "iniferters" for the preparation of α,ω-functional vinyl polymers and in the synthesis of vinyl block copolymers through a living radical mechanism [1-3]. This type of compounds, possessing comparatively good initiating capacity and leading to a great extent of primary radical termination and chain transfer reaction ("iniferters"), appeared ideal for the terminal functionalization of vinyl polymers. Although a good deal of work on the application of simple thiuram disulfides is available [4-7], not much work has been reported in the literature on the synthesis or applications of poly(thiuram disulfides). Recently, Maiti et al. [8] reported a synthesis using aliphatic diamine (primary) and that they obtained insoluble polymers by it.

It is known, and our own experience has revealed, that the thiuram disulfides based on primary amines are highly unstable, especially in solutions where they undergo slow dehydrosulfurization to the thioisocyanate.

In view of our interest in the functionalization of vinyl polymers by the radical method, it appeared that the thiuram disulfide moiety is an excellent carrier for the required functional group since radical polymerization in their presence would help to incorporate the functional group in the polymer chain by an "iniferter" mechanism. Incorporation of phosphorus functionality warranted synthesis of P-containing poly(thiuram disulfides). To meet this requirement α,ω-diamine end-terminated oligomeric phosphonamides and phosphorylamides were synthesized by the reaction of phenylphosphonic dichloride, ethyl dichlorophosphate, 2,2,2-trichloroethyl dichlorophosphate, 2,2,2-tribromoethyl dichlorophosphate with one of the diamines piperazine or *N,N'*-dimethyl-1,6-hexanediamine. The prepolymers (macrodiamines) were eventually transformed to the corresponding poly(thiuram disulfides) by reaction with CS_2 and iodine. This paper describes the synthesis and characterization by elemental, spectral, and thermal analysis of the P-containing poly(thiuram disulfides) and their precursors. Studies on model compounds without phosphorus are also included. Viscosity and molecular weight studies of a selected series of compounds are also described.

EXPERIMENTAL

Materials

Phenyl dichlorophosphonate (phenylphosphonic dichloride), ethyl dichlorophosphate, 2,2,2-trichloroethyl dichlorophosphate, and 2,2,2-tribromoethyl dichlorophosphate (from Aldrich Chemical Co.) were purified by vacuum distillation and stored over argon. Piperazine and *N,N'*-dimethyl-1,6-hexanediamine were used as received. Triethylamine and $CHCl_3$ were purified by refluxing over CaH_2 and then distilling from it. Carbon disulfide and I_2 (Aldrich) were used without further purification. *N,N'*-Diethyl-*N,N'*-bis(2-hydroxyethyl)thiuram disulfide was synthesized by a known procedure [3].

Instruments

Proton NMR spectra were recorded with a Bruker AW-60 spectrometer. IR spectra were taken with a Perkin-Elmer Model P83 spectrometer. ^{31}P-NMR spectra were obtained with a Bruker 90 MHz spectrometer, with H_3PO_4 as external reference. Viscosity measurements were done with a capillary-type viscometer at 25°C in $CHCl_3$ solutions. TGA was performed with a Mettler TC10 thermal analyzer, and DSC analysis was carried out on a Perkin-Elmer DSC II thermal analyzer equipped with a thermal analysis data station.

Syntheses

Poly(Thiuram Disulfides) of *N,N'*-Dimethyl-1,6-hexanediamine (1a), Piperazine (1b), and *N,N'*-Diethylethylenediamine (1c)

Diamine (0.025 mol) was dissolved in 50 mL $CHCl_3$ and cooled to 10°C. To this was added 7 mL triethylamine followed by 2 g CS_2. The mixture was stirred for 30 min. The solution became yellow. I_2 (6.45 g, 0.05 mol) was then added until its characteristic color persisted. A yellow precipitate started forming for 1a and 1c. It was filtered under suction and thoroughly washed with ethanol. For 1b, precipitation was achieved by adding ethanol. Drying was done under vacuum at room temperature. Quantitative yields were obtained. The elemental analysis is presented in Table 1.

TABLE 1. Elemental Analysis of Compounds 1a, 1b, and 1c

Compounds		C	H	N	S
1a: $(C_{10}H_{18}N_2S_4)_n$	Calculated	40.81	6.12	9.52	43.54
	Found	40.55	6.20	9.32	43.73
1b: $(C_6H_8N_2S_4)_n$	Calculated	30.51	3.39	11.86	54.24
	Found	30.48	3.30	11.70	54.50
1c: $(C_8H_{14}N_2S_4)_n$	Calculated	36.09	5.26	10.52	48.12
	Found	36.20	5.20	10.71	48.36

Phosphonamides 2a

Various oligomers of differing molecular weights were prepared by varying the mole ratios of phenylphosphonic dichloride and piperazine. In a representative reaction, 3.2 g (0.037 mol) piperazine was dissolved in 50 mL dry $CHCl_3$. Dry triethylamine (8 mL) was added, followed by 4 mL (5 g, 0.028 mol) phenylphosphonic dichloride drop by drop over a period of 20 to 25 min under argon. The system warms to about 40°C. The initially formed white precipitate slowly vanishes in the course of the reaction. The system was stirred at room temperature for 24 h. The amine hydrochloride was washed out with ice-cold water, and the solution was dried over anhydrous $MgSO_4$. The high molecular weight products were isolated by precipitating the chloroform solution into ether. The white precipitate was filtered, washed with ether, and dried under vacuum. Characterization was done by chemical analysis, $[\eta]$, ^1H NMR, ^{31}P NMR, and end-group analysis (see Results and Discussion).

Phosphonamide 2e

In a typical synthesis, 0.04 mol freshly distilled phenylphosphonic dichloride was slowly added to 0.1 mol *N,N'*dimethyl-1,6-hexanediamine dissolved in 50 mL $CHCl_3$. A white precipitate formed immediately. The mixture was stirred for 24 h. The precipitate was filtered off, and the filtrate was washed with ice-cold water. The solution, after drying over $MgSO_4$, was concentrated by evaporating $CHCl_3$ and then poured into a large excess of ether to isolate the polyphosphonamide. A brown resinous hygroscopic product was obtained after drying in vacuum.

Phosphorylamides 2b, 2c, and 2d

The phosphorylamides were synthesized by reaction of the corresponding dichlorophosphates with piperazine. A representative preparation is as follows: 0.06 mol piperazine dissolved in 50 mL dry $CHCl_3$ containing 14 mL TEA was reacted with 0.05 mol of the corresponding dichlorophosphate under argon. The system started warming up. After the addition the system was maintained at room temperature overnight. The triethylamine hydrochloride was washed out with ice-cold water. The solution, after drying over anhydrous $MgSO_4$, was added to diethyl ether to precipitate the high molecular weight fraction of the polyamide. The white precipitates were filtered and dried at 40°C under vacuum. The polymers were characterized by elemental analysis, NMR (^1H and ^{31}P) and end-group analysis (see Results and Discussion).

Phosphorylamides 2f and 2g

In a 250-mL three-necked flask under argon was placed 0.06 mol *N,N'*-dimethyl-1,6-hexanediamine and 5 mL dry triethylamine. The system was cooled to 10°C, and 0.02 mol of the respective dichloride was added dropwise over 15 min. The mixture was allowed to warm up to room temperature and kept stirred for 20 h. The precipitated hexanediamine hydrochloride was filtered off; the residue was thoroughly washed with ice-cold water and dried over $MgSO_4$; and the solvent was evaporated. A resinous mass was obtained. Yield: 30%. Characterization was done by ^1H NMR, elemental, and end-group analysis.

Poly(Thiuram Disulfides) 3a-3g

In a typical synthesis, the diamine precursor (5 g) was dissolved in 50 mL chloroform and cooled to 10°C. Triethylamine (2 mL) was added, followed by 1 mL CS_2. A solution of I_2 in $CHCl_3$ was added to the pale yellow solution until the violet color persisted. The solution was washed 3 times with ice-cold water, dried over $MgSO_4$, and poured into diethyl ether to precipitate the yellow fine powder (for 3a-3e) or brown resinous masses (for 3f and 3g). They were dried at room temperature under vacuum. The polymeric compounds were analyzed by spectral, elemental, thermogrametric, and DSC analysis.

TABLE 2. Elemental Analysis of Compound 3h

$C_{16}H_{23}N_2O_3PS_4$	C, %	H, %	N, %	O, %	P, %	S, %
Calculated	42.66	5.11	6.22	10.67	6.88	28.4
Found	42.32	5.27	5.59	11.88	6.39	27.22

Poly[*N,N*′-Diethyl-*N,N*′-bis(2,2′-phenylphosphonoethyl)thiuram Disulfide] 3h

To 8.2 g (0.025 mol) of *N,N*′-diethyl-*N,N*′-bis(2-hydroxyethyl)thiuram disulfide dissolved in 25 mL $CHCl_3$ taken in an amber-colored RB flask under argon atmosphere was added 7 mL (0.05 mol) triethylamine and 4.92 g (0.025 mol) phenylphosphonic dichloride. The system was stirred at 0°C for 24 h. The viscous solution was washed twice with ice-cold water, dried over anhydrous $MgSO_4$, and the polymer was precipitated with ether. A brown tacky polymer was obtained, which was dried in vacuum at room temperature. Yield: 4 g (35%). Characterized by elemental analysis and ^1H NMR. The elemental analysis is presented in Table 2.

RESULTS AND DISCUSSION

Synthesis and Characterization of Poly(Phosphonamide) and Poly(Phosphorylamide)

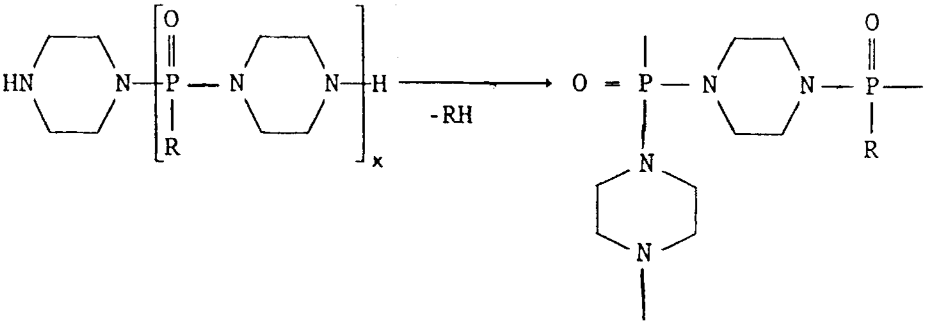
In view of the stringent requirements for flame-retardant polymeric materials and the known flame-retardant action of the phosphorus-containing groups, polyphosphonamides and polyphosphorylamides have an important position among the P-containing polymers. Some of these polymers have found use as flame-retardant additives, while others with amine terminals have been chemically incorporated into a variety of polymers with built-in flame retardancy [9, 10].

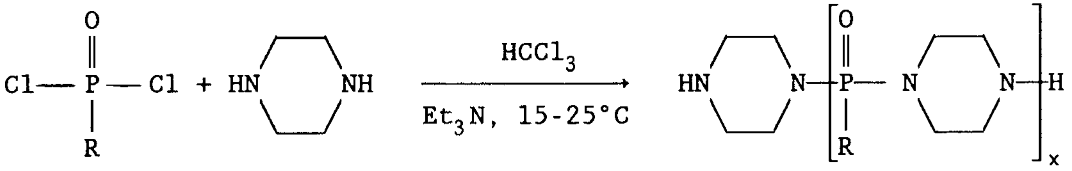
Phosphonamides based on the reaction of aryl or alkyl dichlorophosphonate with aliphatic and aromatic diamines have been cited in the literature. The synthesis is often effected by solution or interfacial condensation polymerization reactions.

In order to synthesize stable poly(thiuram disulfides) bearing P-functions, it was necessary for us to envisage secondary-diamine-terminated polyphosphonamide or phosphorylamide structures. Their synthesis was effected by condensation reaction in solution between phenylphosphonic dichloride, ethyl dichlorophosphate, 2,2,2-trichloroethyl dichlorophosphate, and 2,2,2-tribromoethyl dichlorophosphate with excess quantities of piperazine or *N,N'*-dimethyl-1,6-hexanediamine according to the following reaction schemes. Reaction of the diamines like *N,N'*-diethylethylenediamine with the phosphonic dichloride did not give rise to any insoluble polymer owing to cyclization. For the above two diamines, the possibility for cyclizations is minimized by geometrical factors. (See diagram on page 1096.)

Since the reactivity of the amine toward the acid chloride is very high and since the former is always in excess, the resulting polymers were expected to have an amine functionality of 2. The oligomers 2a, 2b, 2c, and 2d were white fine powders, insoluble in ether, THF, and acetone, but soluble in alcohols and chloroform. 2e, 2f, and 2g were resinous masses with the same solubility characteristics.

The synthesis of 2a was studied in detail. Polymers with varying $\overline{DP}$ could be prepared by changing the molar ratio of the reactants. Since the very low molecular weight fractions were extracted with ether, a direct correlation between the $\overline{DP}$ and the molar ratio could not be arrived at. However, in general, $\overline{DP}$ decreased with an increasing ratio of the reactants. Relatively high molecular weight polymers are produced in good yields even at high reactant ratios, contrary to the general rule of condensation polymerization. This points out the fact that the apparent stoichiometry is altered by the flanking of the amine groups by the liberated HCl. The characteristics of the various polymers and their reaction conditions are given in Table 3. Under comparable conditions a relatively high molecular weight for 2b, 2c, and 2d vs 2a may be due to some adventitious crosslinking reactions involving the amine and the alkoxygroup on the P atom:

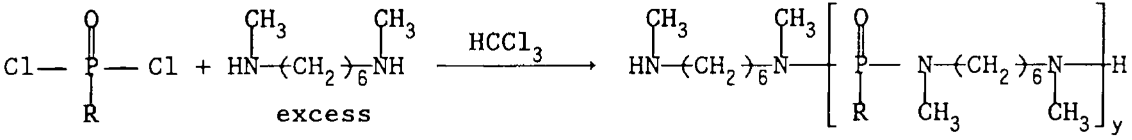




2a - 2d

2a when R = Ph, 2b when R = OC_2H_5,

2c when R = $O\text{-}CH_2\text{-}CCl_3$, 2d when R = $O\text{-}CH_2\text{-}CBr_3$.



2e , 2f, 2g

2e when R = Ph, 2f when R = $O\text{-}CH_2\text{-}CCl_3$,

2g when R = $O\text{-}CH_2\text{-}CBr_3$.

The oligomers were characterized by ^{1}H and ^{31}P NMR, IR, elemental analysis, and end-group analysis. The spectral details of the phosphonamides and phosphorylamides are given in Table 4. The chemical shifts of the methylene protons in 2a, 2b, and 2c did not change appreciably with the chemical environment of the phosphorus atom. However, a downward drift was observed when the phenyl group was replaced by the electron-withdrawing alkoxy and haloalkoxy groups. ^{31}P NMR of all the compounds prepared by solution condensation contained only one singlet. This shows that practically all the chains are terminated by amine groups. The ^{31}P spectrum of a sample of 1a prepared by an interfacial technique (with aqueous NaOH solution and $CHCl_3$ as the immiscible phases) showed additional peaks resulting from terminal P–Cl, P–OH, and P–ONa groups. A representative ^{31}P-NMR spectrum of one such polymer is shown together with that of a polymer prepared in solution in Fig. 1. The chemical shift values of the different P atoms are compiled in Table 4. The lower chemical shift when the phenyl group is replaced by an alkoxy group is a consequence of the increased *d*-orbital occupation through $d\pi$-$n\pi$ back-bonding involving the electron on the oxygen atom. Replacement of piperazine by dimethylhexamethylenediamine led to increased deshielding of the P atom. The IR spectra of all the compounds showed characteristic absorption bands at around 1200 cm^{-1} (P–N–C symmetric stretch) and 950 cm^{-1} (P–N–C asymmetric stretch). The major absorption peaks are listed in Table 2, and a representative IR spectrum is shown in Fig. 2. The elemental analyses of the polymers were consistent with those calculated for a given molecular weight.

Intrinsic Viscosity and Molecular Weight

The intrinsic viscosity $[\eta]$ of the various oligomers prepared under different conditions, shown in Table 3, decreases as the ratio of the reactants increases. The molecular weights of the polymers were determined by analysis of the terminal NH-groups by the perchloric acid titration method. They were in the range 2000-8000 and are comparable to the molecular weights reported for similar compounds [11]. From $[\eta]$ and the molecular weights, the Mark-Houwink constants K and a were calculated by the well-known relation $[\eta] = KM^{a}$. A plot of ln $[\eta]$ versus ln M gave an excellent straight line (Fig. 3). The value of $a = 0.68$ is slightly higher than that reported for a similar phosphonamide [12]. In contrast to several organic polymers, a low value of the constant a is indicative of the strong dipolar interactions of the polymer. The value of K was obtained as 2.608×10^{-4} dL/g.

TABLE 3. Details of the Synthesis of the Phosphon(ryl)amides and the Corresponding Poly(Thiuram Disulfides)

Refs.	Acid chloride	Diamine[a]	Molar ratio (amine/$-PCl_2$)	Yield of high products, %	$\bar{M}_w$ (end-group analysis)
2a	$C_6H_5-P(O)-Cl_2$	1	1.075	97	8 290
	"	1	1.15	95	6 240
	"	1	1.2	95	4 240
	"	1	1.25	90	4 138
	"	1	1.4	89	3 021
	"	1	1.5	82	2 347
2b	$C_2H_5O-P(O)Cl_2$	1	1.4	38	7 614
2c	$CCl_3CH_2O-P(O)Cl_2$	1	1.4	97	6 120
2d	$CBr_3CH_2O-P(O)Cl_2$	1	1.35	91	12 240
2e	$C_6H_5-P(O)Cl_2$	2	3.0	65	2 720
2f	$CCl_3CH_2O-P(O)Cl_2$	2	3.0	50	2 240
2g	$CBr_3CH_2O-P(O)Cl_2$	2	3.0	73	2 950

TABLE 3 (continued)

Refs.	Intrinsic viscosity, $[\eta]$, dL/g	Amount of CS_2 consumed per 100 g	Concentration of thiuram disulfide (TGA), wt%	$[\eta]$ of the polythiuram disulfide	$\bar{M}_n$
2a	0.1245	2	2.3	0.170	14 000
	0.10	2.5	2.4	0.175	14 300
	0.078	3.7	3.5	0.160	12 500
	0.07	4.0	4.0	0.140	10 300
	–	4.9	5.2	0.213	19 100
	0.0535	7.0	6.7	0.13	9 250
2b	0.09	2.3	2.5	0.237	22 400
2c	–	3.00	2.8	–	–
2d	–	1.8	–	–	–
2e	–	9.5	9.0	–	–
2f	–	7.0	7.4	–	–
2g	–	8.1	–	–	–

[a] 1 = piperazine; 2 = *N,N'*-dimethyl-1,6-hexanediamine.

TABLE 4. Spectral Characteristics of the Polyphosphon(ryl)amides and Their Thiuram Disulfides

Refs.	^{1}H NMR ($CDCl_3$), δ in ppm[a]					
	$-\underset{\Phi}{\underset{\mid}{\overset{\parallel}{P}}}-$ $-\underset{OCH_2R}{\underset{\mid}{\overset{\parallel}{P}}}-$	$-\underset{\parallel}{\overset{\mid}{P}}-\overset{CH_3}{\overset{\mid}{N}}-$	$-\underset{\parallel}{\overset{\mid}{P}}-\overset{\mid}{N}-CH_2-$	$-\underset{\parallel}{\overset{\mid}{P}}-\overset{\mid}{N}-\underset{\mid}{\overset{\mid}{C}}-(CH_2)_4-$	$-CH_2-\underset{\mid}{N}-\overset{S}{\overset{\parallel}{C}}-S-$[b]	$-\overset{CH_3}{\overset{\mid}{N}}-\underset{S}{\underset{\parallel}{C}}-S-$[b]
2a/3a	7.38 (m)		2.96 (b)		4.15	
2b/3b	3.99 (q) 1.28 (t) $J = 12$ Hz		3.04 (b)		4.15[c]	
2c/3c	4.47 (d) $J = 7$ Hz		3.14 (b)		4.20[c]	
2d/3d	4.57 (d) $J = 7$ Hz		3.16 (b)		4.20	
2e/3e	7.4 (m)	2.5 (d) $J = 16$ Hz	2.80 (m)	0.9-1.6 (b)	3.95 (b)	3.45 (s)
2f/3f	4.40 (d) $J = 7$ Hz	2.6 (d) $J = 16$ Hz	3.04 (b)	1.2-2 (b)	3.98 (b)	3.53 (s)
2g/3g	4.55 (d) $J = 7$ Hz	2.64 (d) $J = 16$ Hz	30 (b)	0.95-1.71 (b)	3.93 (b)	3.50 (s)
3h	$\delta = 7.2\text{-}7.8$ (b) Φ;		4.0 (q, $-N-\underline{CH_2}-CH_3$)		3.6 (t, $-N-\underline{CH_2}-CH_2-O-$)	

TABLE 4 (continued)

	IR			
Refs.	ν_{PNC} (sym), cm^{-1}	ν_{PNC} (asym), cm^{-1}	Others, cm^{-1}	Chemical shift of the P-atom ^{31}P ($CDCl_3$), ppm
2a/3a	1200	960	1440 (C=C aromatic) 1120 (C–C–N) 720 (CH_2 bend)	25.0
2b/3b	1220	960	1450, 720 (CH_2) 1100 (C–C–N) 1380 (CH_3)	13.7
2c/3c	1240	965	1450 (CH_2) 1100 (C–C–N) 880 (C–Cl_3)	13.3
2d/3d	1230	970	1450, 730 (CH_2) 1090 (C–C–N) 865 (C–Br_3)	12.6
2e/3e	1205	960	1450 (C=C aromatic) 1110 (C–C–N) 720 (CH_2 bend)	26.1
2f/3f	1210	965	1460 (C=C, CH_2) 1120 (C–C–N) 870 (C–Cl_3)	18.6
2g/3g	1220	980	1460, 720 (CH_2) 1100 (C–C–N) 880 (C–Br_3)	17.8
3h	3.2 (q, P–O–CH_2–)		1.08 (t, –CH_3)	

[a] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad.
[b] Signals found only in compounds in Series 3.
[c] Observed as a part of the signals on column 2.

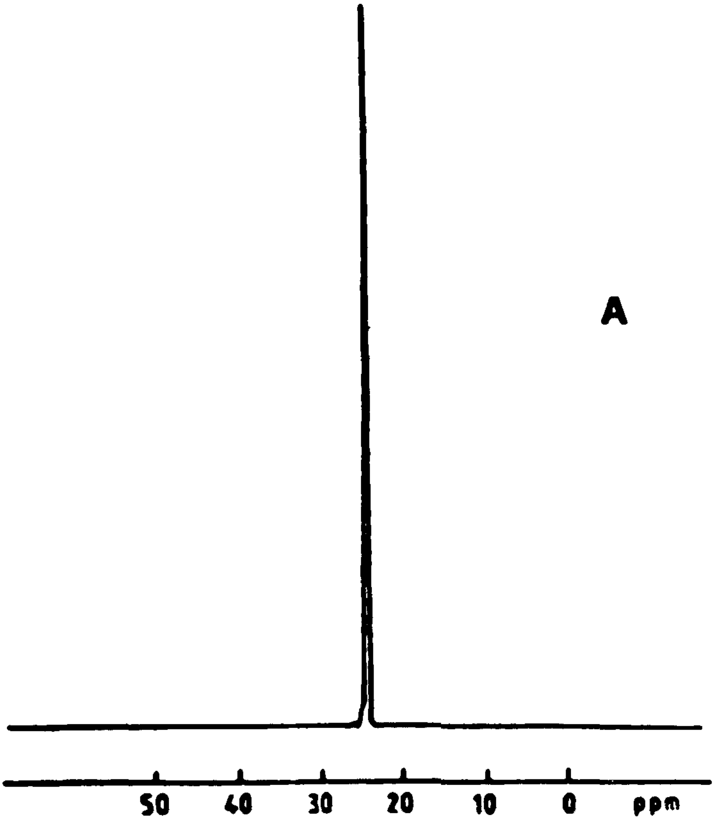
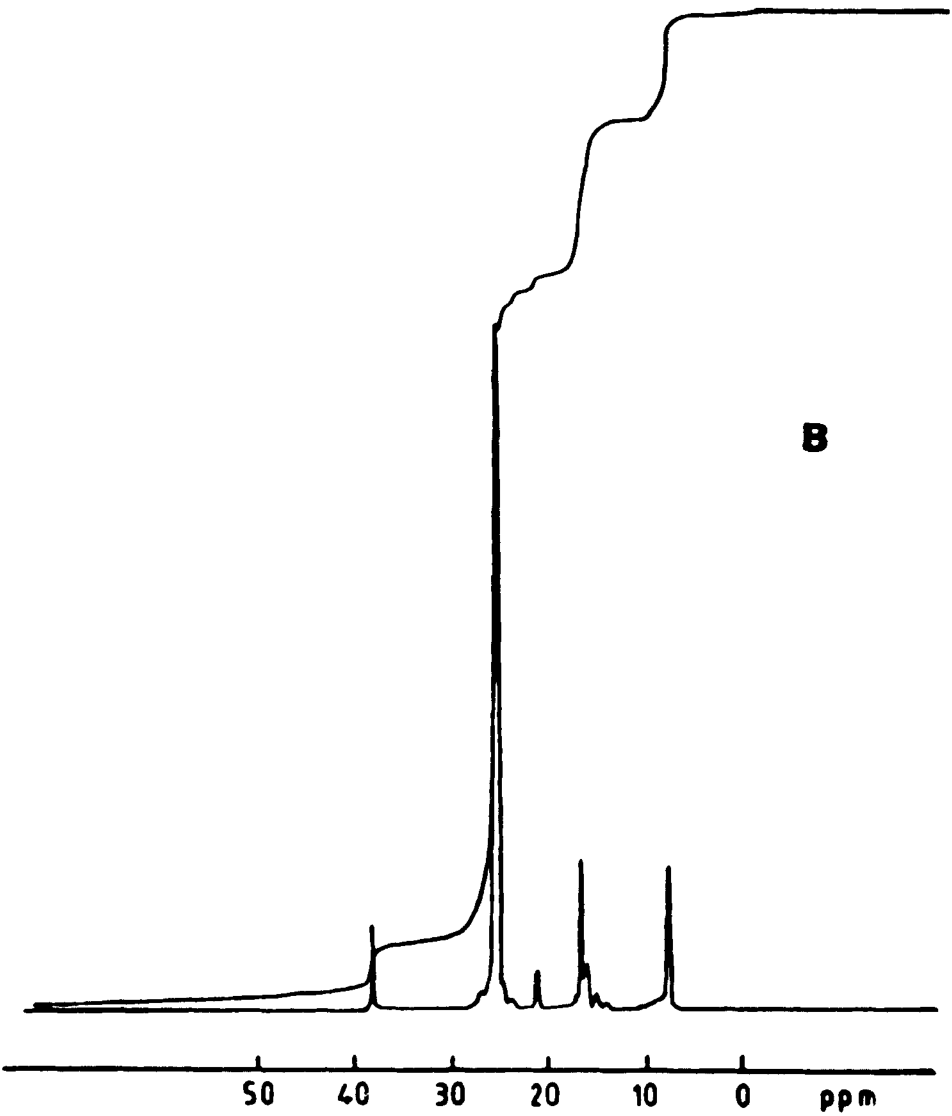


FIG. 1. ^{31}P-NMR spectra of the polyphosphonamide 2a prepared (A) in solution and (B) interfacially.


B
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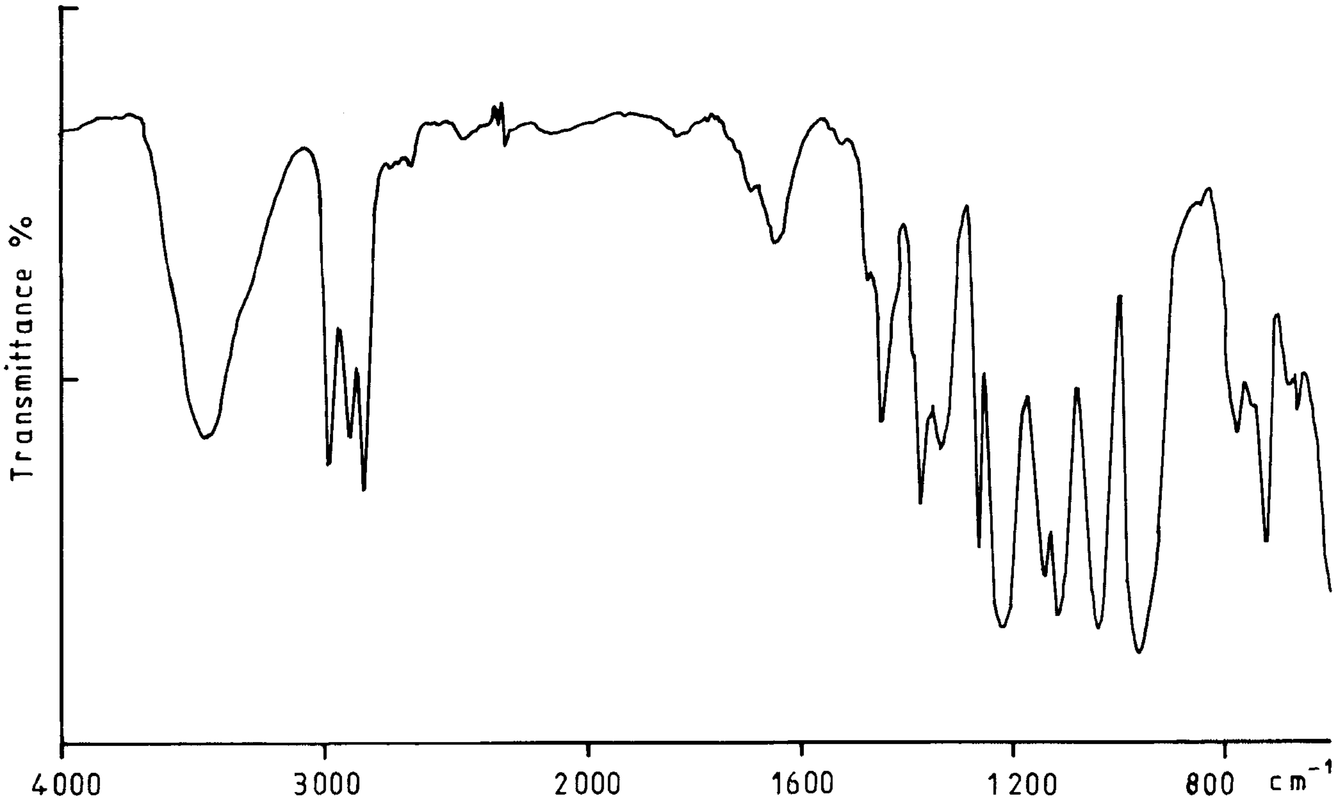


FIG. 2. IR (KBr) spectrum of the polyphosphorylamide <u>2f</u>.

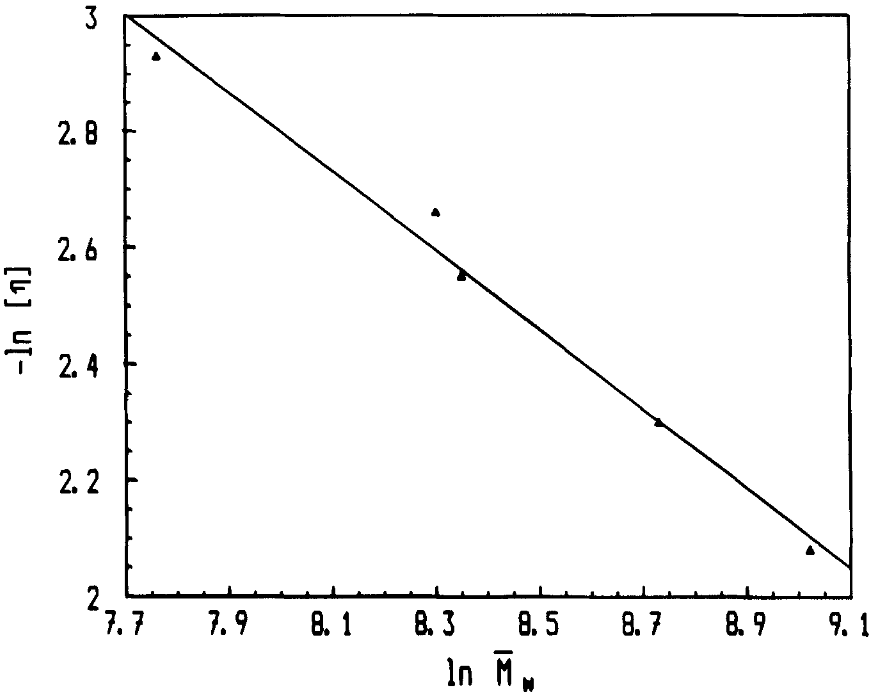


FIG. 3. Determination of the Mark-Houwink constants for the Polymer 2a in $HCCl_3$ at 25°C.

Thermogravimetric Analysis

The thermal behavior of the various P-containing polymers have been extensively studied [13-17]. In general, although phosphorylation does not improve the initial decomposition behavior, they have been found to decrease the overall rate of decomposition and leave behind a good amount of char. Char-yielding polymers are desirable for use in flame-retardant formulations [15-21]. Some of the polymers of the above type have already been utilized in flame-retardant formulations and in copolymerization. Since the flame-retardant action of the P-containing polymer can arise either by their interaction in the condensed phase or in the vapor phase through the decomposition products [22], a study of the thermal behavior of these polymers can furnish some information on their mechanism of flame-retardant action.

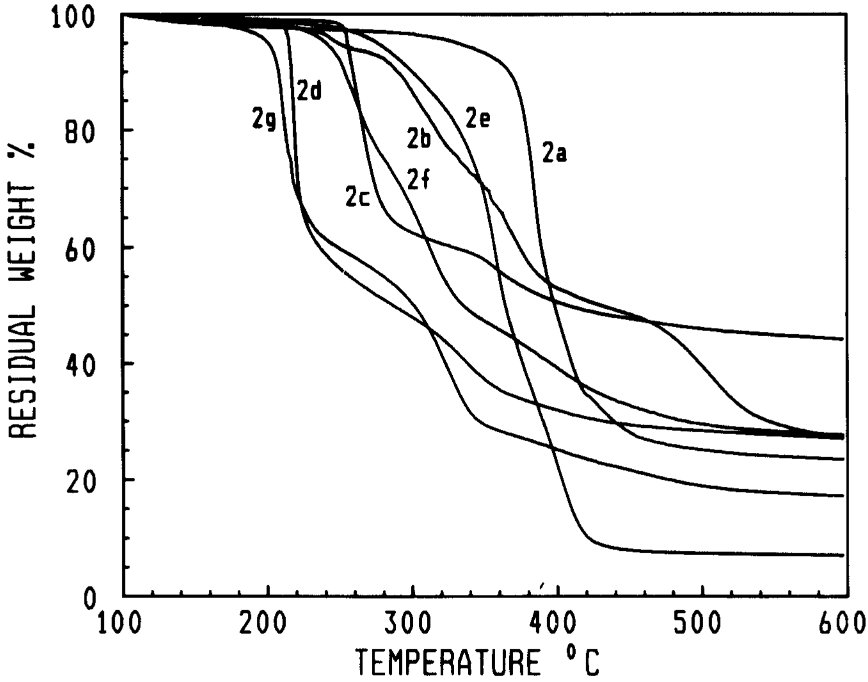


FIG. 4. TGA of the various polyphosphon(ryl)amides. Heating rate, 10°C. Atmosphere, N_2.

Thermogravimetric analysis of the polymers was done under N_2 at a heating rate of 10°C/min. The thermograms are shown in Fig. 4 for the various polyamides. The polymers based on phenylphosphonic dichloride had the highest thermal stability. The phosphorylamides were found to be the least stable, the stability decreasing catastrophically when the ester group contains halogens. In these cases the thermal decomposition of the polyamide must be expected to be triggered by rupture of the P—N bond. In phenylphosphonamides this bond is stabilized by a possible *dπ-nπ* back-bonding involving the nonbonding electron on N with the *d*-orbitals on P, which can be favored through extended conjugation with the phenyl group. In phosphorylamides this extended delocalized back-bonding is not possible. Further, replacement of the phenyl group by an alkoxy group can result in a reduction in the stability of the P—N bond, owing probably to the competition between the oxygen and the N-atom for back-bonding. The bulkier halogen atoms on the alkoxy groups probably disrupt sterically the geometrical requirement to favor the

TABLE 5. Thermal Decomposition Characteristic of the Poly(Phosphonamide) and Poly(Phosphorylamide)[a]

Refs.	Initial decomposition temperature, °C	% Char at 600°C	E_A,[b] kJ/mol
2a	380	34	395
2b	275	40	61.5
2c	255	49	179.7
2d	215	27	800
2e	330	15	154.6
2f	250	29	125.4
2g	200	18	188.1

[a] Heating rate 10°C/min, atmosphere N_2.
[b] For initial stage of decomposition.

back-bonding, thereby causing a reduction in the bond stability. Electron-withdrawing substituents on the alkoxy group can help reduce the interaction between the oxygen and the P-atom, thereby stabilizing the P—N bond. This may explain the decreased stability of the tribromoethyl phosphorylamide over the trichloroethyl phosphorylamide. In general, the steric hindrance to the stabilization of the P—N bond dominates over the electron-withdrawing effect.

From the thermal decomposition characteristics of the polymers (Table 5) and the thermograms (Fig. 3), the following conclusions can be drawn.

The polymers based on phenylphosphonamides are the most stable ones. For a given polymer, better stability results when piperazine is the diamine compared to dimethylhexanediamine. This is quite obvious in view of the cyclic structure of the former. Higher char yield is obtained for piperazine-based polymers at higher temperature. The relatively high char yield in spite of their lower thermal stability for 2b and 2c must be due to crosslinking involving the amine and the ester or chloroalkyl group on the P atom. For 2d and 2g, the first-stage decomposition probably involves loss of the tribromoethyl group. From the thermal studies it appears that 2a-based polymers can show better flame-retardant action in the condensed phase. The activation energy for the major thermal decomposition step was calculated from the

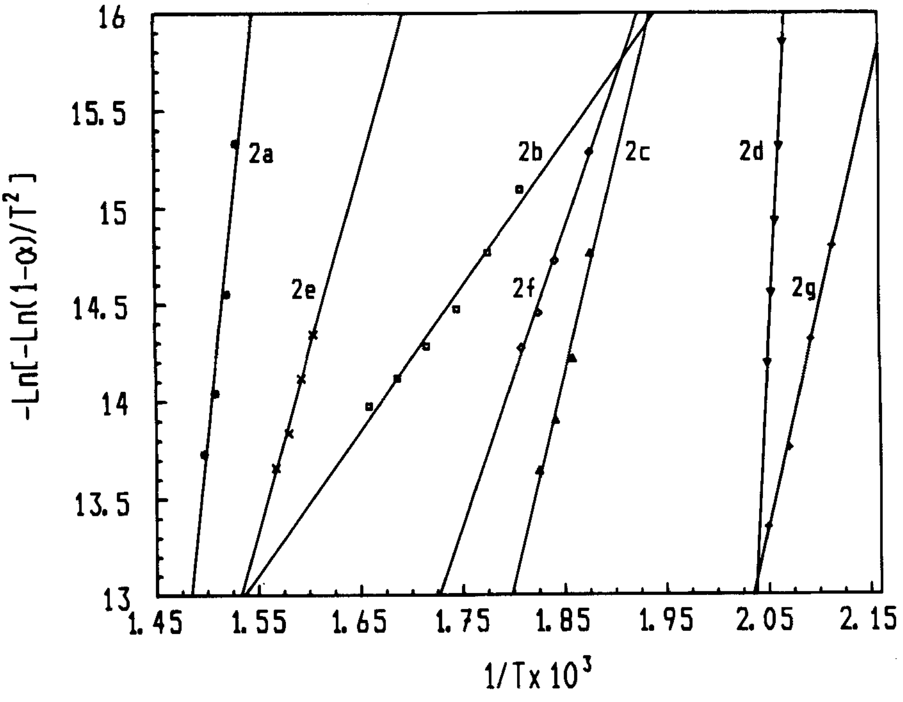
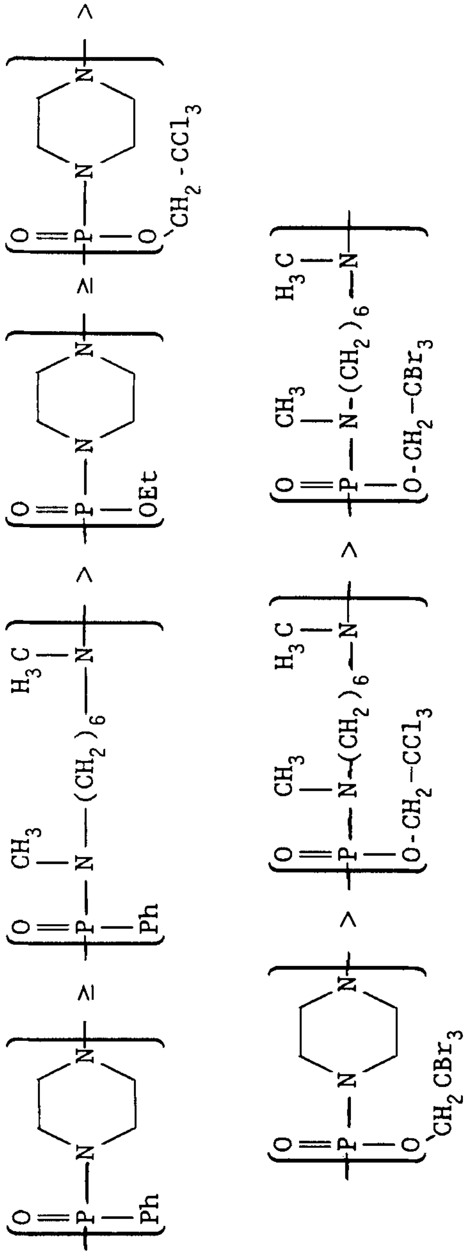


FIG. 5. Coats-Redfern plot for determination of the activation energy for the thermal decomposition of various polymers.

weight loss-temperature profile by the equation of Coats and Redfern [21]:

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]=\ln\left[\frac{\mathrm{AR}}{\phi}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT}, \tag{1}$$

where α is the fraction decomposed at temperature T, ϕ is the heating rate, and E is the activation energy. E was calculated by a plot of the left-hand side of Eq. (1) versus $1/T$ by assuming a first-order reaction. Representative kinetic plots are shown in Fig. 5. In general, the thermal stability decreased in the order shown on page 1109.



Glass Transition Temperature

The glass transition temperatures of the prepolymers can give useful information on the T_g of their blends and of polymers bearing them as functional groups. The most thermally stable system, 2a, was chosen for this study. The T_g of 2a of varying molecular weight was determined by DSC analysis. The values were corrected by using indium as standard. As expected, the T_g was found to increase with increasing molecular weight. Applying the Fox-Loshaek relation [24] for the variation of T_g with molecular weight,

$$T_g = T_{g_\infty} - K/M, \tag{2}$$

where T_{g_∞} is the T_g for the polymer of infinite molecular weight. Figure 6 shows the plot of Eq. (2) for Polymer 2a. K was found to be 1.12×10^5 and T_{g_∞} was determined from the intercept as 209.5°C. The low K value shows the rigid nature of the polymer chain.

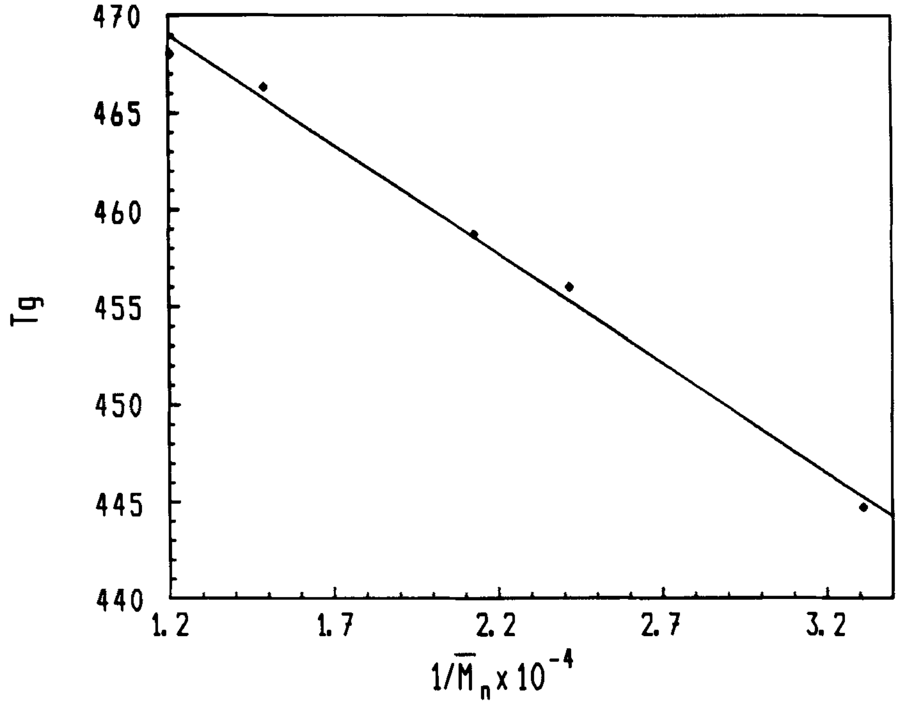


FIG. 6. Variation of T_g with molecular weight for the Polymer 2a.

Physical Characteristics

In general, the prepolymers were soluble in alcohols, $CHCl_3$, and DMF but insoluble in ketones, ethers, esters, and hydrocarbon solvents, with the exception of 2c which was partially soluble in a variety of solvents. They were highly hygroscopic. The hygroscopicity was severe in the case of 2b; 2a and 2b were swollen by water. 2a, 2b, 2c, and 2d were fine white powders, whereas the rest were tacky resinous products.

Synthesis and Characterization of Polythiuram Disulfides Bearing Phosphonamide and Phosphorylamide Blocks

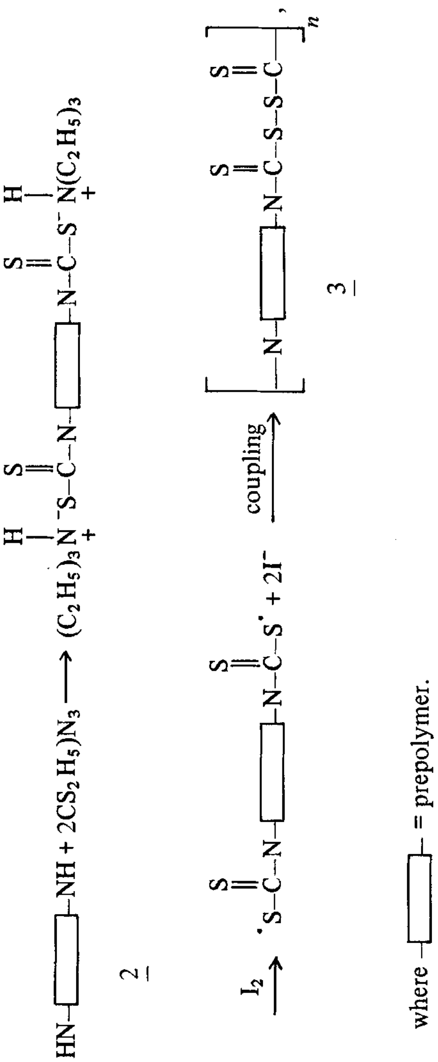
Tetraalkylthiuram disulfides are generally prepared by the simple addition reaction of the corresponding amine with CS_2 to give the dithiocarbamate, followed by oxidation to the thiuram disulfide. Recently, Maiti et al. reported the synthesis of polythiuram disulfides by an extension of the above reaction to diamines and obtained insoluble poly(thiuram disulfides). The insolubility arises from the presence of a large proportion of the highly polar dithiocarbamyl groups.

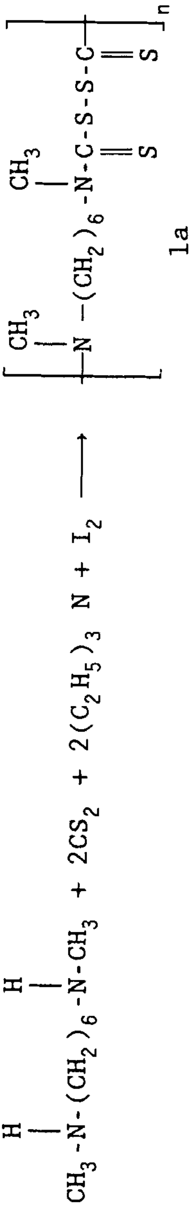
Our recent study on the functionalization of PMMA by using a functional thiuram disulfide as "iniferter" [3] has given evidence that they are excellent vehicles for placing functional groups on vinyl polymers. In line with our interest to synthesize vinyl polymers containing phosphorylamide and phosphonamide blocks, we synthesized poly(thiuram disulfides) containing those phosphorus functionalities. The above described amine-terminated polymers (2a-2g) were reacted with CS_2 to the bis(dithiocarbamates), which were subsequently oxidized by I_2 to the poly(thiuram disulfides). The reaction scheme and the mechanism of the reaction can be depicted as shown on page 1112. The products 3a, 3b, 3c, 3d, 3e, 3f, and 3g correspond to the precursors 2a, 2b, 2c, 2d, 2e, 2f, and 2g, respectively. The polymerization occurs by coupling of the radicals. Termination may be occurring by coupling with monoradicals resulting from adventitious monofunctional prepolymers or by the cyclization of the macrodiradical.

Synthesis of Model Poly(Thiuram Disulfides)

In order to obtain insight into their synthesis and characteristics, we synthesized model poly(thiuram disulfides) based on three typical secondary diamines, *N,N'*-diethylethylenediamine, piperazine, and *N,N'*-dimethyl-1,6-hexanediamine, as expressed on page 1113.

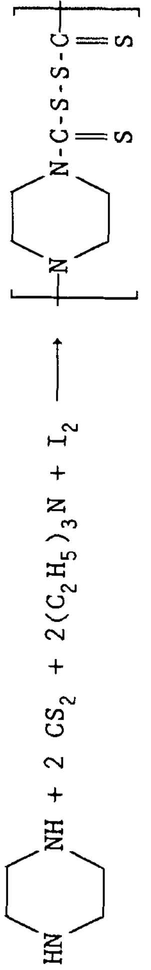
We preferred to choose secondary amines since the thiocarbamates of


2
3
I2
coupling
where
= prepolymer.

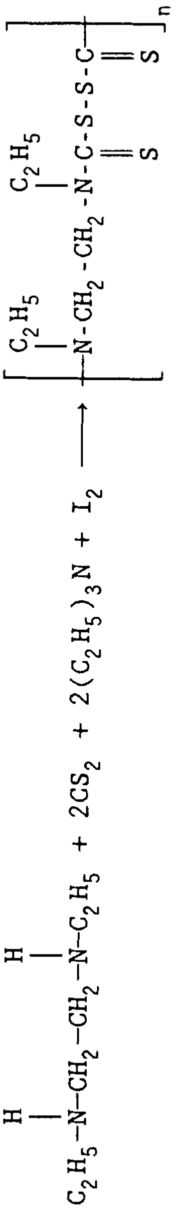


$$CH_3\text{-}\overset{H}{N}\text{-}(CH_2)_6\text{-}\overset{H}{N}\text{-}CH_3 + 2CS_2 + 2(C_2H_5)_3N + I_2 \longrightarrow \left[\text{-}\overset{CH_3}{N}\text{-}(CH_2)_6\text{-}\overset{CH_3}{N}\text{-}\underset{S}{\underset{\|}{C}}\text{-}S\text{-}S\text{-}\underset{S}{\underset{\|}{C}}\text{-}\right]_n$$

1a



1b



$$C_2H_5\text{-}\overset{H}{N}\text{-}CH_2\text{-}CH_2\text{-}\overset{H}{N}\text{-}C_2H_5 + 2CS_2 + 2(C_2H_5)_3N + I_2 \longrightarrow \left[\text{-}\overset{C_2H_5}{N}\text{-}CH_2\text{-}CH_2\text{-}\overset{C_2H_5}{N}\text{-}\underset{S}{\underset{\|}{C}}\text{-}S\text{-}S\text{-}\underset{S}{\underset{\|}{C}}\text{-}\right]_n$$

1c

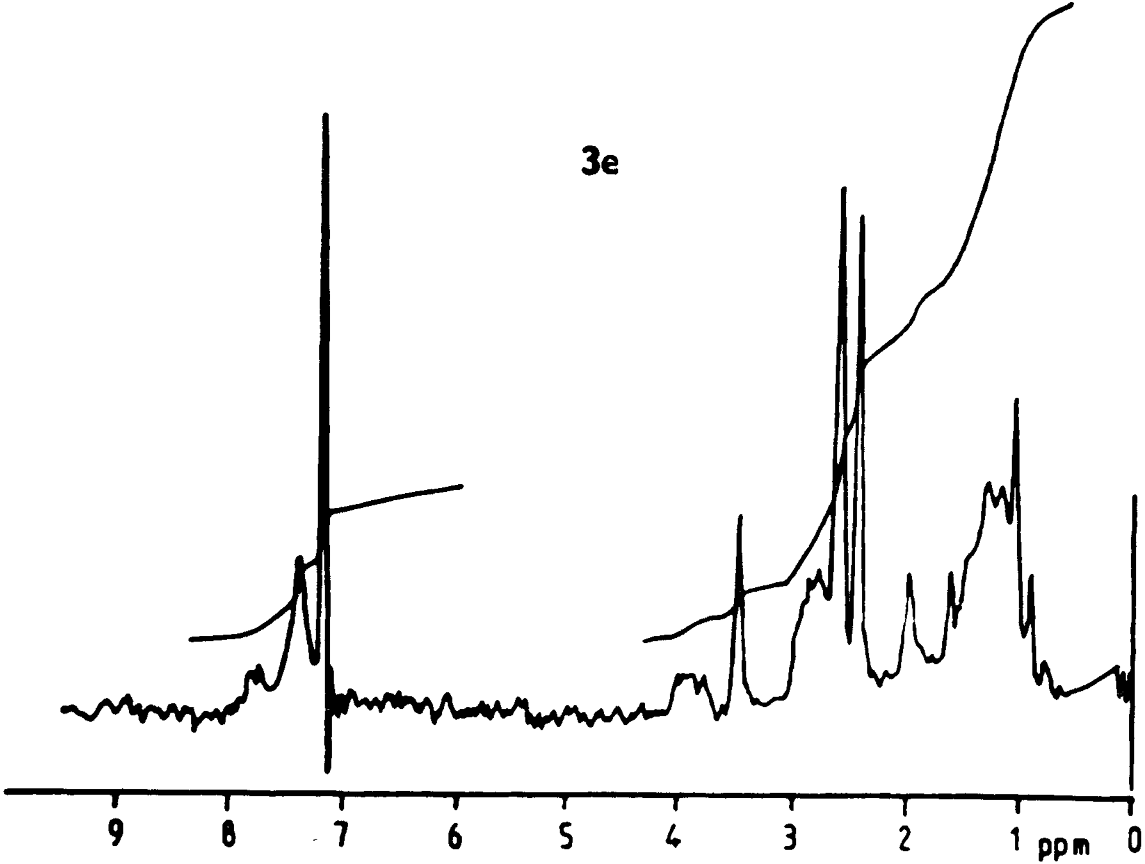
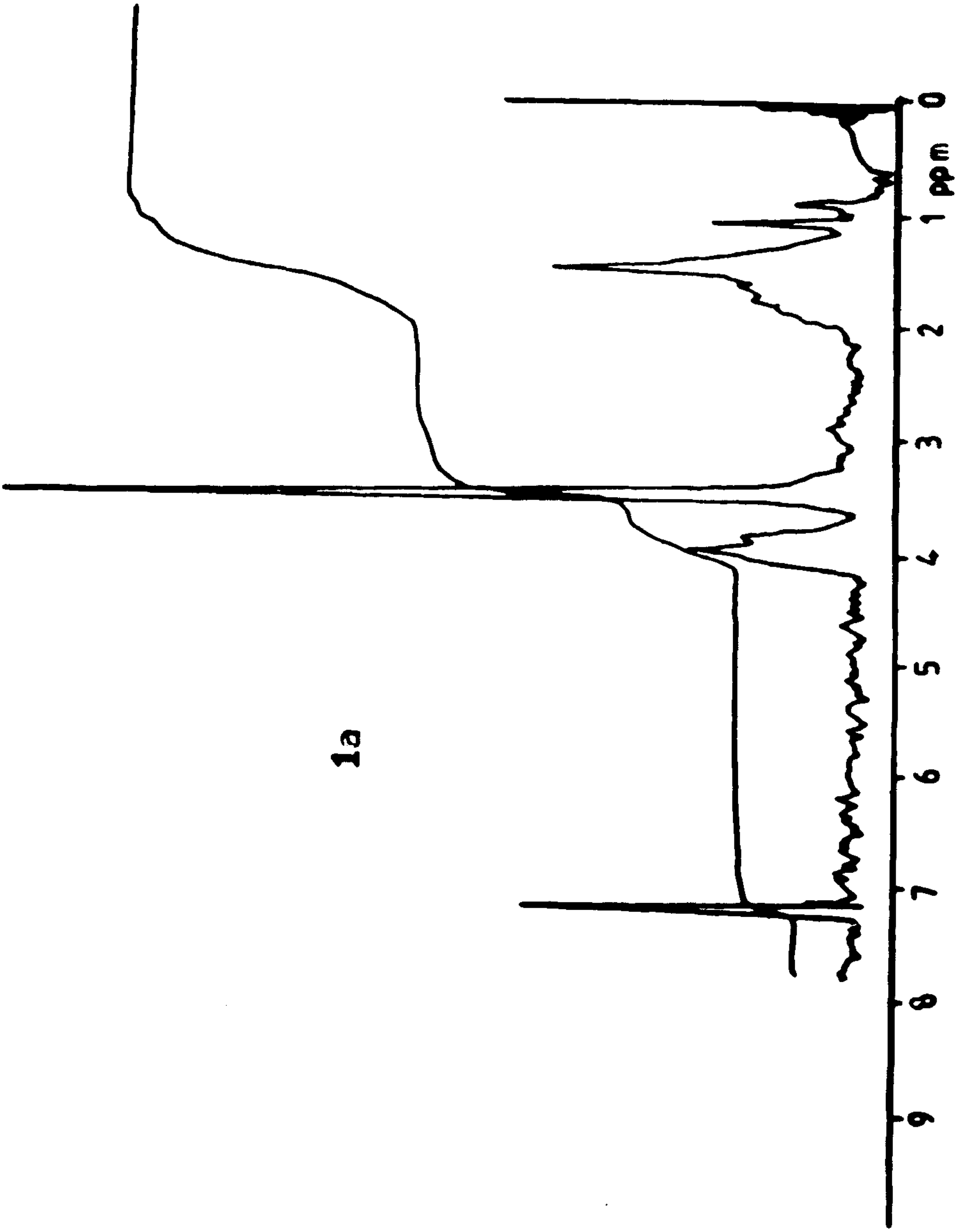
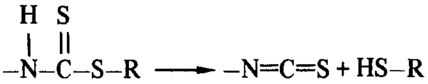


FIG. 7. Proton NMR spectra of 3e and 1a in $CDCl_3$.



1a

primary amines are comparatively less stable due to their tendency for easy dehydrosulfurization in solution to give isothiocyanates:



$$-\overset{\overset{H}{|}}{N}-\overset{\overset{S}{\|}}{C}-S-R \longrightarrow -N{=}C{=}S + HS-R$$

Further, possible intermolecular H-bonding through the –NH groups can render the polymers less intractable.

The above model compounds were characterized by IR, NMR (1a only), and elemental analysis. The characteristic IR absorption was observed at 1500 cm^{-1} (CH_2 bend), 1380 cm^{-1} (CH_3 bend), 1175 cm^{-1} (C=S stretch), and 720 cm^{-1} (CH_2 bend).

The NMR spectrum of 1a, shown in Fig. 7 along with that of its P-containing analog, is consistent with its structure. While 1b and 1c were insoluble in all solvents, 1a was soluble in $CHCl_3$ and DMF. This is attributed to the presence of a long spacer between the thiuram disulfide groups, reducing the extent of intermolecular interaction. Although the elemental analysis conformed very well to the empitical formula and the polymerization was quantitative as estimated from the amount of I_2 consumed, 1a did not have a very high molecular weight. Since the reaction resembles a polycondensation reaction, the above observation lends support to the fact that a considerable extent of chain cyclization has taken place. Thermogravimetric analysis of these polymers showed a sharp weight loss between 160-240°C, due exclusively to the loss of CS_2. The weight loss was equal to the quantity of CS_2 present. Hence the TGA offered a simple and elegant means for quantitatively determining the composition of thiuram disulfide linkages in the polymers.

The thiuram disulfides of all the phosphorus-containing prepolymers were synthesized. A detailed study on the synthesis of 3a was carried out by preparing diamine precursors of varying $\overline{DP}$. In this case the poly(thiuram disulfides) were synthesized also by the *in-situ* reaction, i.e., without isolation and purification of the diamine precursor. It was found that, under similar conditions, the polythiuram disulfides were soluble until the molar ratio exceeded 1.15 (diamine/PCl_2). The disulfide linkages at this point corresponded to 9% (by TGA; theoretical 9.36%) when the diamine precursor was isolated by precipitation in ether and converted to its thiuram disulfide. The polymers obtained were always soluble, irrespective of the molar ratio (diamine/PCl_2) or $\overline{DP}$ of the precursor. The insolubility of the poly(thiuram disulfides) in the former case could be attributed to the participation of small amounts of unreacted piperazine or very low molecular weight prepolymers in the chain-extension reaction, thereby raising the thiuram disulfide sequences in the chain. (The reaction conditions are shown in Table 3.)

They were characterized by IR, ^1H NMR, ^{31}P NMR, and elemental analysis. IR spectra were similar to those of the precursors. Additional peaks characteristic of the S–C–S linkage could be observed at 1175 cm^{-1} only in polymers containing much of the thiuram disulfide moiety. The ^1H-NMR spectrum of the PTD 3a-3d resembled their diamine precursor, except that an additional peak was observed at 4 ppm due to the proton on the carbon α to the thiocarbamyl group. In the case of 3e the two types of α-proton appeared at 3.95 ppm ($CH_2{-}N{-}C{=}S$) and 3.45 ppm ($CH_3{-}N{-}C{=}S$). Representative spectra are shown in Figs. 7 and 8. The ^{31}P-NMR spectra did not differ from those of the prepolymers. This ruled out the possibility of any side reaction involving the P atom during the thiocarbamylation reaction.

The elemental analysis of the products (Table 6), whose compositions vary with the molecular weight of the prepolymer, confirmed the presence of sulfur. In certain cases the sulfur contents were greater than those calculated or determined by other means (e.g., I_2 consumed, TGA). This discrepancy may be due to the presence of some elemental sulfur formed by the hydrolysis of the thiuram group during the purification (washing with H_2O). The reduction in the bromine content of 3d shows that part of the Br group has been substituted by the amine.

Physical Characteristics of the PTDS

All the polymers were pale yellowish fine powders with the exception of 3d, 3f, and 3g which were tacky brown solids. They were soluble in alcohols, $CHCL_3$, DMF, etc. The exception was 3c which was partially soluble in acetone, THF, and ethyl acetate.

Although 2d is soluble in alcohols, the insolubility of its thiuram disulfide, 3d, may be a consequence of the above-mentioned branching caused through the participation of the bromo groups in the condensation reaction (through amine or dithiocarbamate).

Thermogravimetric Analysis

When the PTDS were subjected to thermogravimetric analysis, an additional sharp weight loss was observed at around 200°C. This was caused by the thermal decomposition of the thiuram disulfide with the release of CS_2 molecules. This was confirmed from the TGA of model compounds 1a, 1b, and 1c, for which weight loss equal to the content of CS_2 was observed at this temperature. This observation led to an easy and precise method for the determina-

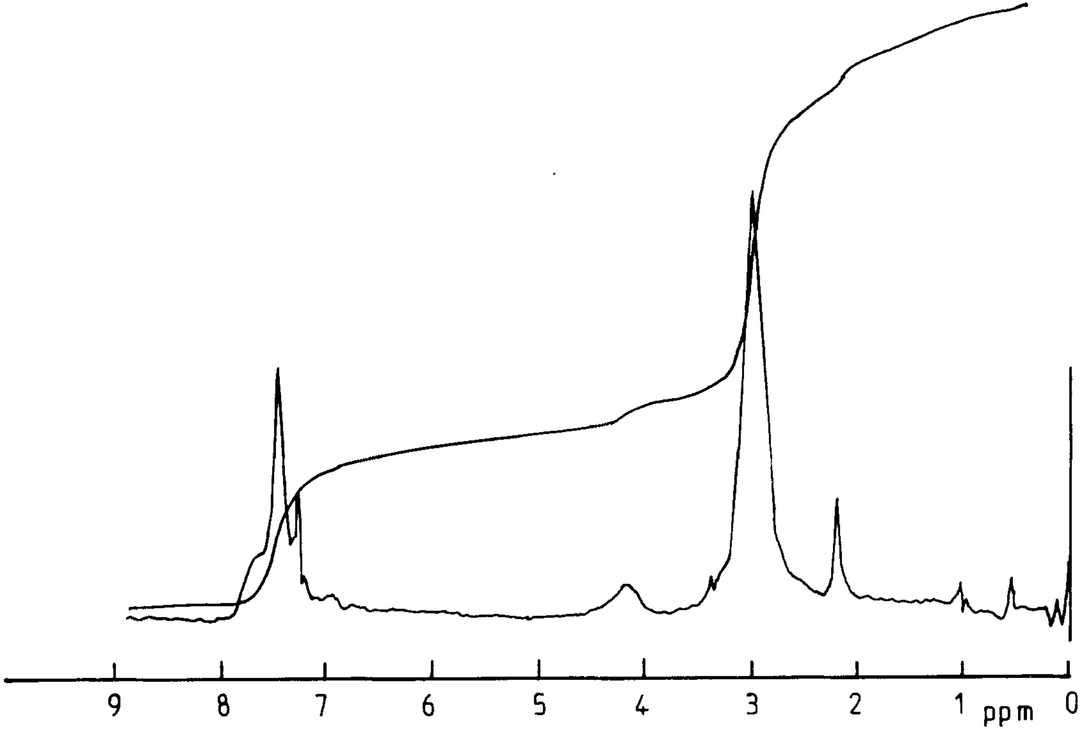


FIG. 8. Proton NMR spectra of 3a in $CDCl_3$.

TABLE 6. Elemental Analysis of the Polythiuram Disulfides

Compound	MW of the diamine segment	C, %		H, %		N, %		O, %		P, %		S, %		Cl/Br, %	
		Calc	Found	Calc	Found	Calc	Found	Calc	Found	Calc	Found	Calc	Found	Calc	Found
3a	4 240	55.65	55.20	6.03	5.91	12.98	13.10	7.43	7.28	14.37	14.16	2.91	3.86	–	–
3b	7 614	40.09	40.15	7.23	7.35	15.60	15.19	17.81	17.23	17.24	17.09	1.65	2.82	–	–
3c	6 000	25.10	24.87	3.39	3.51	9.76	9.74	11.16	10.90	10.81	10.31	2.08	3.62	37.13	36.24
3d	12 240	17.30	17.76	2.40	2.48	6.73	6.60	7.69	6.97	7.45	6.69	1.04	3.01	58.40	55.75
3e	2 720	60.97	61.05	8.40	8.31	10.43	10.29	5.43	5.40	10.52	10.46	4.24	4.71	–	–
3f	2 240	35.20	35.00	5.71	6.43	8.44	8.37	8.38	7.98	8.12	8.05	5.05	7.27	27.90	27.12
3g	2 950	26.86	26.24	4.41	4.52	6.18	6.02	6.27	5.93	5.98	5.50	3.95	5.36	46.33	45.62

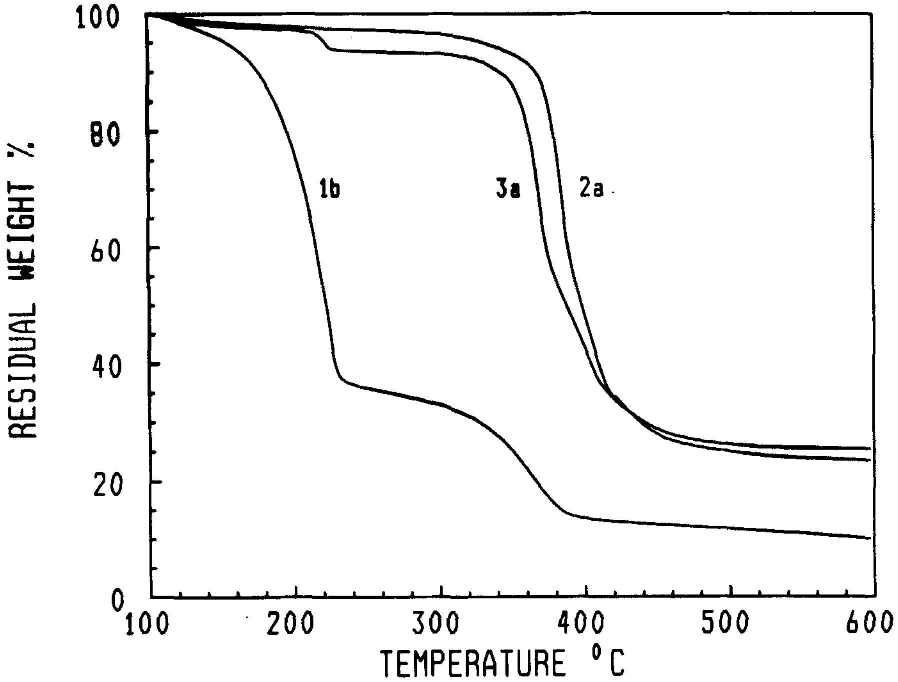


FIG. 9. TGA of 2a, 3a, and 1b. N_2 atmosphere. Heating rate, 10°C/min.

tion of thiuram disulfide concentration in these polymer by TGA. The disulfide concentrations from TGA were in excellent agreement with those calculated from the amount of I_2 consumed during synthesis. The concentrations of thiuram disulfides calculated by the two methods are included in Table 3. The TGA of 3c and 3g did not furnish many details since the diamine precursor also starts to decompose at this temperature. The thermograms of 2a, 3a, and 1b are shown in Fig. 9 for comparative purposes.

DSC Analysis

Thiuram disulfides are known to undergo thermal dissociation to give free radicals capable of initiating vinyl polymerization. In order to study the solid-state thermal decomposition of these compounds, they were subjected to DSC analysis in a N_2 atmosphere. It was found that nearly all compounds based on piperazine showed an exotherm around 140-180°C due to the decomposition and the eventual evolution of CS_2. The decomposition temperatures were

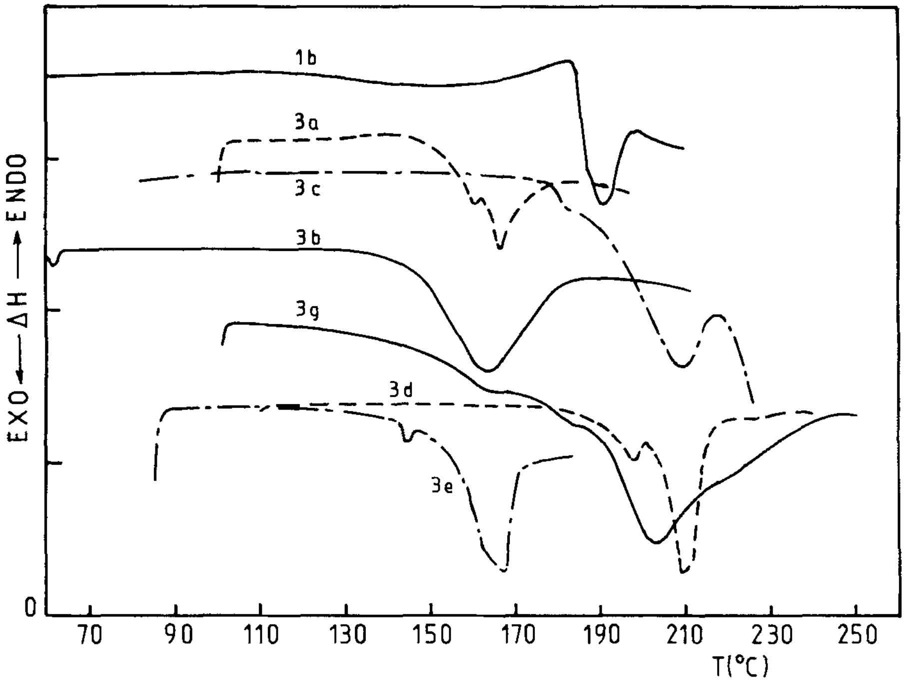


FIG. 10. DSC thermograms of the polythiuram disulfides.

found to vary with the structure of the polymer backbone. A tendency to higher temperatures was observed for the halogenated P backbone. Although the thiuram disulfide groups undergo slow dissociation at temperatures lower than 100°C in solution, the thermograms do not give any evidence for such a reaction in the solid state.

Typical DSC thermograms are shown in Fig. 10. The DSC of 3d and 3g overlapped with the decomposition exotherm of the polyamide itself. From the initial part of the DSC thermograms it was possible to calculate the activation energy for the thermal decomposition of the thiuram disulfide groups by the method of Rogers et al. [25, 26]. A plot of ln d versus $1/T$ gives a straight line whose slope corresponds to E/R, where d is the distance of the peak from its base at temperature T, which is proportional to the heat evolved and in turn to the rate constant for the thermal decomposition at this temperature. The frequency factor A is given by

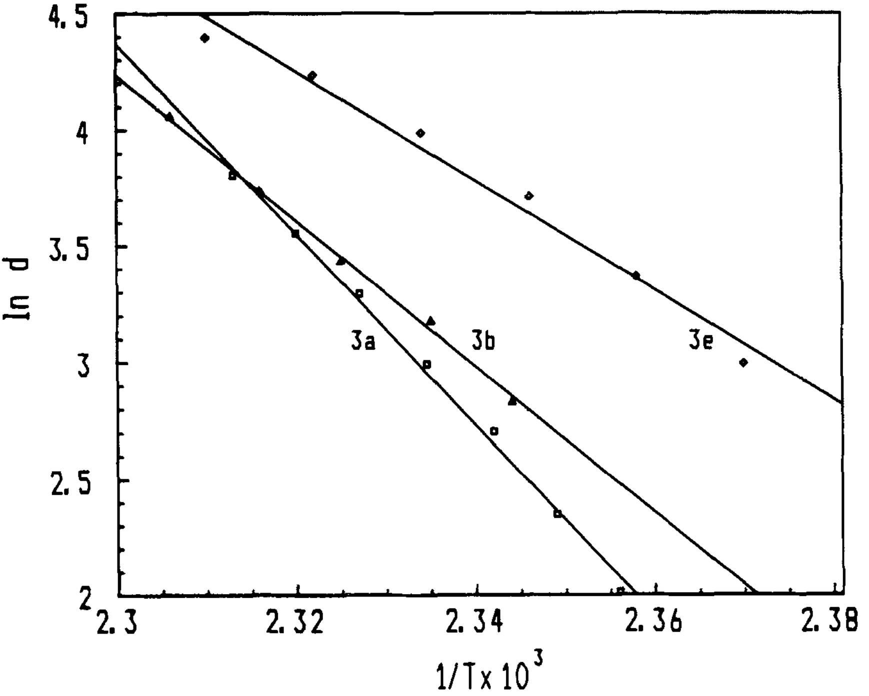


FIG. 11. Arrhenius plots for determining the activation energy for the solid-state thermal decomposition of the thiuram disulfide groups.

$$A = \frac{\Phi e^{E/RT_{max}}}{RT^2_{max}}, \tag{3}$$

where Φ is the linear heating rate and T_{max} is the temperature at the maximum of the exotherm. The activation energy calculated is much higher than that reported for the thermal dissociation of the disulfide in solution [3, 4] (~30 kcal/mol). This high E_A for the thermal dissociation, followed by the decomposition of the CS_2 molecule, must be a consequence of the high stability of the thiuramyl radial $\mathrm{N{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}S}$.

The activation energy calculated for 3a did not vary much with the molecular weight. Figure 11 shows the Arrhenius plots for the determination of

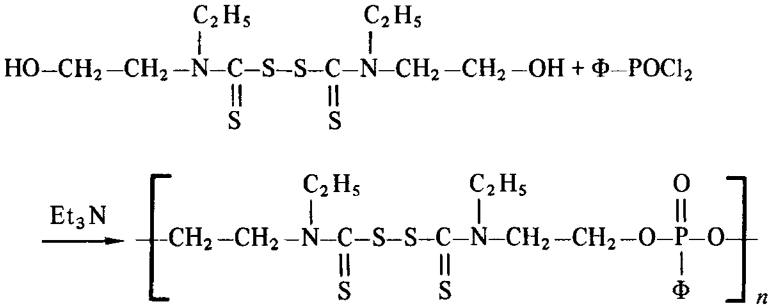
E_A. Those for 3c, 3d, 3f, and 3g could not be determined accurately because of interference of the major decomposition exotherm. The thermal decomposition characteristics of the polymers are collected in Table 7.

Molecular Weights

The molecular weights of the polymers of 3a were calculated from their intrinsic viscosities. The Mark-Houwink constants were taken to be the same as those for their precursors by assuming that the introduction of a small proportion of the thiuram disulfide group may not bring about significant effects on their viscosity characteristics. As expected, chain extension always results in an increase in molecular weight. But it did not increase substantially, contrary to expectation, even up to the complete reaction of all the residual amine during chain extension. This shows that a significant extent of cyclization may be taking place during the oxidative coupling.

Synthesis of Poly(Thiuram Disulfide) Containing Phenyl Phosphonate Groups

Polyphosphates and polyphosphonates are prepared by the condensation reaction of the corresponding dihalide with the diols. A recent study gives some idea as to the conditions to be employed to favor polymerization over cyclization [27]. Use of long-chain diols favors polymerization. An extension of this reaction led to the synthesis of poly(phenyl phosphonates) bearing a large proportion of the thiuram disulfide function, which was effected by the condensation reaction between *N,N′*-diethyl-*N,N′*-bis(2-hydroxyethyl)thiuram disulfide and phenylphosphonic dichloride as follows:



$$HO{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle C_2H_5}{|}}{N}{-}\underset{\underset{\displaystyle S}{\|}}{C}{-}S{-}S{-}\underset{\underset{\displaystyle S}{\|}}{C}{-}\overset{\overset{\displaystyle C_2H_5}{|}}{N}{-}CH_2{-}CH_2{-}OH + \Phi{-}POCl_2$$

$$\xrightarrow{Et_3N} \left[{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle C_2H_5}{|}}{N}{-}\underset{\underset{\displaystyle S}{\|}}{C}{-}S{-}S{-}\underset{\underset{\displaystyle S}{\|}}{C}{-}\overset{\overset{\displaystyle C_2H_5}{|}}{N}{-}CH_2{-}CH_2{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle \Phi}{|}}{P}}{-}O{-}\right]_n$$

3h

The polymer was obtained only in poor yield owing to the solubility of the very low molecular weight products in ether. Elemental analysis and ^1H NMR

TABLE 7. Thermal Decomposition Characteristics of the Thiuram Disulfide Groups in the Polymer from the DSC Analysis[a]

Refs.	Temperature of the onset of decomposition, °C	Temperature of the maximum of the thermograms, °C	Temperature at which decomposition is complete, °C	Activation energy for thermal decomposition (E_d), kJ/mol	Frequency factor (A), s^{-1}
3a[b]	146	166	187	334.4	2.35×10^{38}
3a[c]	147	167	190	311.4	3.28×10^{35}
3a[d]	149	168	195	353.2	2.76×10^{45}
3a[e]	144	167	178	296.9	1.02×10^{34}
3b	140	162	190	194.4	4.76×10^{21}
3e	140	167.5	195	263.3	9.60×10^{34}
1a	163	190	194	—	—

[a] Heating rate 5°C/min.
[b] $\bar{M}_w$ of diamine segments 3200.
[c] $\bar{M}_w$ of diamine segments 4250.
[d] $\bar{M}_w$ of diamine segments 6000.
[e] $\bar{M}_w$ of diamine segments 8000.

were consistent with the expected structure. The polymers underwent catastrophic degradation at 150°C under TGA conditions.

CONCLUSIONS

Chain extension of poly(phosphorylamides) and poly(phosphonamides) through dithiocarbamylation and oxidative coupling results in a new series of thiuram-disulfide-based reactive polymers bearing the required phosphorus function, or functional polymeric "iniferters." These polymers can serve as potential thermal "iniferter" for vinyl polymerization, resulting in a new class of copolymers. This study will be the subject of a subsequent paper [28].

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