

Functionalization of vinyl polymers through polymeric iniferters: synthesis of poly(methyl methacrylate-*b*-phosphonamide) and poly(styrene-*b*-phosphonamide)

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New thermal polymeric iniferters based on poly(thiuram disulphides) bearing polyphosphonamide blocks have been synthesized and characterized. This was realized by synthesizing bis(secondary amine)-terminated polyphosphonamides by reaction of phenyl phosphonic dichloride with piperazine. Chain extension of the resulting macrodiamines through a dithiocarbamylation reaction followed by oxidative coupling gave poly(thiuram disulphides) bearing the phosphonamide function. Thermal polymerization of methyl methacrylate (MMA) and styrene in the presence of these iniferters led to the formation of their block copolymers with phosphonamide through an 'iniferter' mechanism. The kinetics of polymerization of MMA over a limited iniferter concentration range were determined at 70, 78, 85 and 95°C and those of styrene at 78°C. The various kinetic parameters pertaining to initiation and primary radical termination were evaluated. In the case of styrene, normal polymerization behaviour was observed. The 'iniferter' efficiency was found to increase with temperature. The nature and block length of the resulting copolymers were found to be dependent on the monomer/polymeric iniferter ratio and on the extent of monomer conversion. Some of the physical properties of the copolymers were evaluated.

(Keywords: polymeric iniferter; poly(thiuram disulphide); functionalization; block copolymer; polyphosphonamide; flame-retardant polymer)

INTRODUCTION

The classical methods of deriving di-, tri- and multi-block copolymers are based on the anionic technique involving deactivation of the living anion using suitable electrophiles. A few radical techniques, needing less rigorous polymerization conditions, have also been introduced to realize this end. The radical methods are mostly based on the use of prepolymeric backbones with azo and/or peroxy initiator groups incorporated in them acting as macroinitiator for the polymerization of a second vinyl monomer¹⁻³. A recent addition to this technique is due to Crivello *et al.*⁴ It makes use of bis(silyl pinacolate) incorporated in a polysiloxane backbone acting as macroinitiator for vinyl monomers and gives rise to siloxane block copolymers. Another means to achieve this is to use aromatic polysulphides as macrochain transfer agents for vinyl polymerizations, exploiting the mild chain transfer property of the aromatic disulphide linkage^{5,6}. In all these cases, the efficiency of the technique depends solely on the initiating or chain transferring property of the prepolymer used. Recently Otsu *et al.*^{7,8} have reported the use of dithiocarbamyl-terminated prepolymers as photo-iniferters for vinyl polymerization, leading to copolymers through a living radical mechanism. Equally interesting is

the work of Niwa *et al.*⁹ based on xanthate-terminated prepolymers as photoiniferters to meet the same end. Tetraalkyl thiuram disulphide compounds are well recognized for their radical initiating, chain transferring and primary radical terminating (*iniferter*) properties^{7,10,11} and we have recently reported the use of this kind of compound as thermal functional iniferters to derive α,ω end functional vinyl polymers¹². In our desire to confer flame-retardant characteristics to poly(methyl methacrylate) and polystyrene, we wanted to design block copolymers of these systems with phosphonamide, since the flame-retardant action of phosphorus-containing compounds is well known. To realize this, it was necessary to envisage synthesis of polymeric iniferters containing the required phosphonamide function in the backbone, so that vinyl polymerization of methyl methacrylate (or styrene) in their presence should lead to block copolymers through an extension of the principle of simple iniferters. In recent work we have reported the synthesis and characterization of a variety of phosphorus-containing prepolymer-based polythiuram disulphides as potential functional polymeric iniferters¹³.

In this paper we describe the synthesis and characterization of one such polymeric iniferter and the application of it to derive block copolymers of methyl methacrylate (MMA) and styrene with phosphonamide. The kinetics of polymerization of MMA and styrene using it over a limited concentration range at different temperatures have been described. The characterization of

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the resulting block copolymers and some of their physical properties are also reported.

EXPERIMENTAL

Materials

MMA and styrene were purified by distillation from CaH₂ under a reduced pressure of argon. Phenyl phosphonic dichloride (Aldrich) was purified by vacuum distillation. Piperazine (Aldrich), I₂ (Aldrich) and CS₂ (Aldrich) were used as supplied. HCCl₃, triethylamine and 2-methoxyethanol were distilled and stored under dry conditions before use.

Methods

¹³C n.m.r. spectra were recorded using a Bruker 200 MHz spectrometer. D.s.c. experiments were done on a Perkin-Elmer DSC II thermal analyser equipped with a data acquisition system. T.g.a. were carried out on a Mettler TC10A thermal analyser under N₂ atmosphere. Viscosity measurements were carried out on a capillary-type viscometer.

Synthesis of phosphonamide-based poly(thiuram disulphide) (polymeric iniferter)

In a typical experiment, to 11.9 g (0.138 mol) of piperazine and 30 ml of triethylamine dissolved in 150 ml of dry CHCl₃ was added at 5–10°C 19.2 g (0.0958 mol) of phenyl phosphonic dichloride over a period of 15–30 min. The system was stirred at room temperature overnight. The triethylamine hydrochloride was rapidly washed out using ice-cold distilled water and the solution was dried using Na₂SO₄. The polymer was isolated by dropping the solution into ether. The macrodiamine so obtained was characterized by end-group analysis and intrinsic viscosity.

The chain extension reaction was carried out as follows. To 15 g of the above poly(phosphonamide) dissolved in 100 ml of CHCl₃ was added 2 ml of triethylamine and 1 ml of CS₂. To this, a solution of I₂ was added until the end point. The CHCl₃ solution was washed with ice-cold water, dried and the polymer isolated by precipitating it with ether. Characterization was done by elemental analysis, intrinsic viscosity and t.g.a.

Polymerization

The polymerizations were carried out in sealed evacuated glass tubes. Since the polymeric iniferter was insoluble in the monomer, 2-methoxyethanol was used as the homogenizing medium. Solvent (5 ml), containing the required quantity of the polymeric iniferter, was pipetted out into a Pyrex glass tube of 110 × 140 mm containing 10 ml of the monomer. The contents were deaerated by at least three cycles of freezing, evacuation and thawing and were sealed off at a pressure of 0.1 mmHg. The tubes were immediately wrapped in aluminium foil and polymerization was carried out in an electrically controlled oil bath at the required temperature. After polymerization for the desired length of time the tubes were chilled in a dry ice/isopropanol mixture and the polymer was isolated by precipitating the contents, diluted with CHCl₃, dropwise into methanol. The precipitate was collected in a sintered glass crucible, dried and weighed.

The rate of polymerization was determined

gravimetrically from the time-conversion plots. The conversions were limited to less than 10% for the kinetic studies.

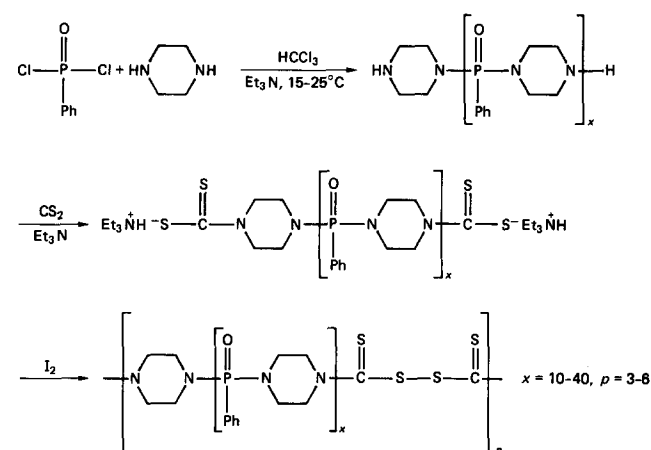
RESULTS AND DISCUSSIONS

The kinetics of polymerization of MMA and styrene initiated by tetraalkyl thiuram disulphides have already been reported¹⁰⁻¹². Apart from acting as initiator, they possess excellent chain transfer properties and bring about a great deal of primary radical termination, with the result that all the polymer molecules are invariably end-capped with the fragments resulting from these molecules (or 'iniferters'). By virtue of these three properties, it appeared to us that thiuram disulphide is an excellent vehicle for carrying the functional groups to be imparted to the polymer chain ends. An extension of this principle led us to envisage polymeric iniferters bearing the thiuram disulphide along the polymer chain by means of which a block copolymer can be realized when vinyl polymerization is carried out in their presence.

We were interested in improving the flame-retardant properties of PMMA and polystyrene through synthesis of their block copolymers with polyphosphonamides. This necessitated synthesis of thiuram disulphide-based polymeric iniferters containing the polyphosphonamide blocks for use as functionalizing agents for these monomers.

Synthesis and characterization of the polymeric iniferter

α,ω-Diamine-terminated polyphosphonamides were synthesized by the condensation reaction of phenyl phosphonic dichloride with an excess of piperazine. The macrodiamines were characterized by end-group analysis. They were transformed to the poly(thiuram disulphide) by reaction with CS₂ followed by oxidation with I₂. The synthetic scheme and the mechanism are depicted as follows:



The polymeric iniferter was characterized by n.m.r. and elemental analysis. The composition of the thiuram disulphide function could be determined by thermo-gravimetric analysis, by noting the weight loss between 160 and 215°C (due to evolution of CS₂). The molecular weights of the prepolymers were determined from end-group analysis. From the viscosity-molecular weight relation for the prepolymers and by extending the same Mark-Houwink constants *k* and *a* to the polymeric iniferter, the molecular weights of the latter could be

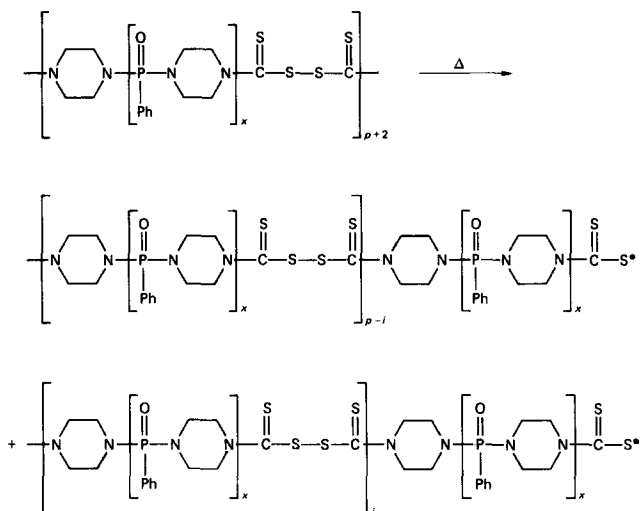
determined from their intrinsic viscosity. The relation used is¹³:

$$[\eta] = 2.608 \times 10^{-4} M^{0.69}$$

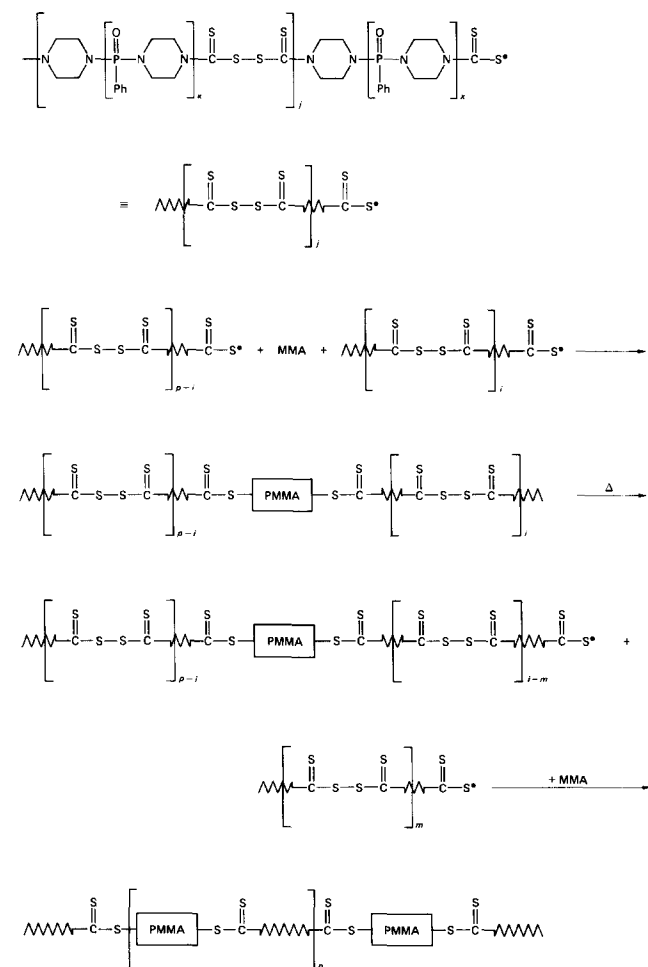
More details regarding synthesis and characterization can be found in ref. 13.

There was indirect evidence that the polymeric iniferter contains an appreciable amount of macrocyclics.

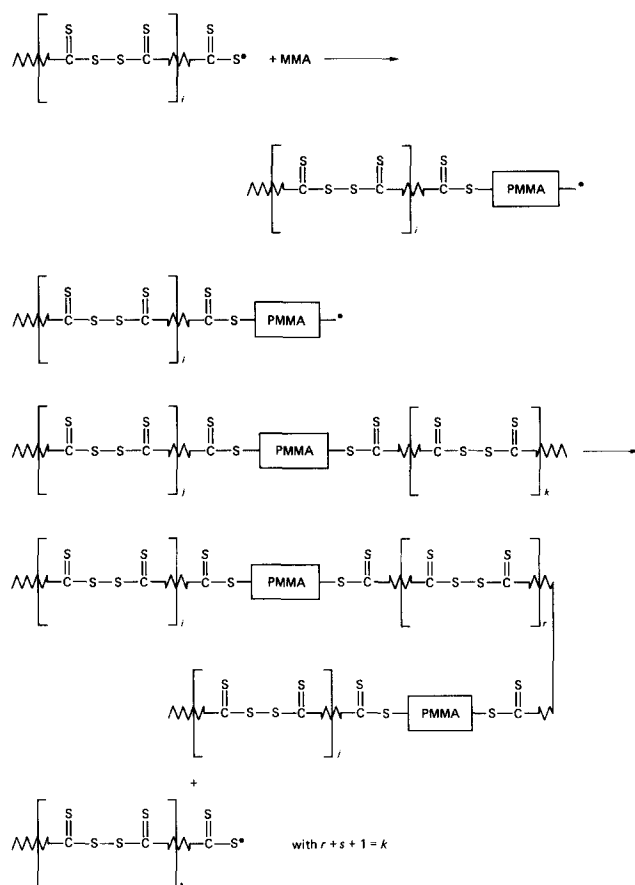
The mechanism by which the block copolymer is formed in an ideal case of polymerization can be depicted as follows:



For ease, the above structure can be symbolized as follows:



and in the case of transfer:

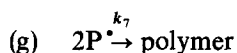
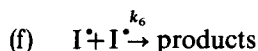


The conventional radical methods of block copolymer synthesis using polymeric initiators or chain transfer agents lead also to the formation of considerable amounts of homopolymers. Since thiuram disulphides function in all three ways, it is to be expected that all the polymer chains must carry the initiator (poly)fragments by virtue of one or more of its properties. Evidently the structure, molecular weight and composition of the final copolymer will be dependent on the relative ratios of the polymeric iniferter and the monomer and the percentage conversion. Macro-photoiniferters bearing pendant dithiocarbamyl groups have recently been reported by Otsu *et al.*¹⁴. Photopolymerization of vinyl monomers in their presence gives rise to graft copolymers.

Kinetics of polymerization

The various kinetic phenomena that take place when vinyl polymerization is carried out in the presence of an iniferter are as follows:

- $I_2 \xrightarrow{k_1} 2I^\bullet \quad R_i = 2fk_1[I] \quad \text{where } I_2 = \text{PI}$
- $I^\bullet + M \xrightarrow{k_2} M^\bullet$
- $M^\bullet + nM \xrightarrow{k_3} P^\bullet$
- $P^\bullet + I_2 \xrightarrow{k_4} I-P + I^\bullet$
- $P^\bullet + I^\bullet \xrightarrow{k_5} I-P$



The reactions (a), (b), (d) and (e) confer the iniferter property to the initiator. The global rate of polymerization in such cases is¹²:

$$R_p^2 = \frac{R_{p0}^2 + (k_3^2/k_7)M^2R_i}{1 + 2 \frac{k_5k_4}{k_7k_2} \frac{I}{M} + \frac{k_6k_4^2}{k_7k_2^2} \left(\frac{I}{M}\right)^2} \quad (1)$$

where R_{p0} is the rate of thermal polymerization in the absence of the catalyst. Equation (1) can be simplified to:

$$R_p^2 = \frac{R_{p0}^2 + A^*I}{1 + 2B^*I/M + C^*(I/M)^2} \quad (2)$$

where A^* , B^* and C^* are complex constants and $I = [PI]$ is the concentration of the polymeric iniferter:

$$A^* = \frac{k_3}{k_7^{1/2}} k^{1/2} M$$

(M remains constant for small conversions)

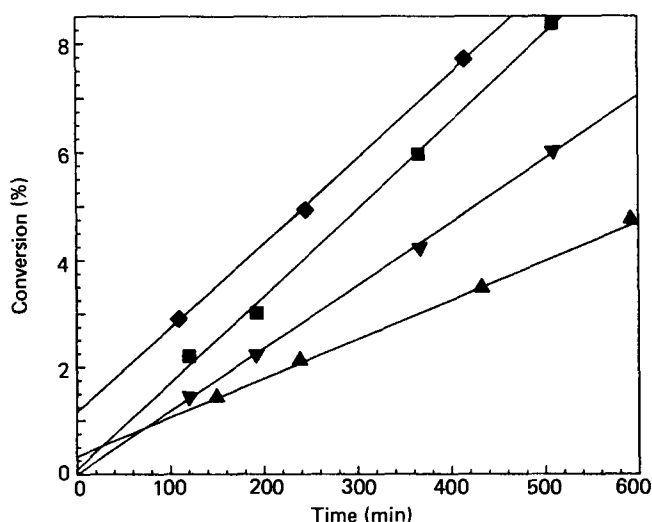


Figure 1 Time-conversion plots for the polymerization of MMA and styrene: (■) MMA, 70°C, $[PI] = 3.68 \times 10^{-3} \text{ mol l}^{-1}$; (▼) MMA, 70°C, $[PI] = 9.2 \times 10^{-4} \text{ mol l}^{-1}$; (◆) styrene, 78°C, $[PI] = 5.26 \times 10^{-3} \text{ mol l}^{-1}$; (▲) styrene, 78°C, $[PI] = 1.32 \times 10^{-3} \text{ mol l}^{-1}$

Table 1 Rate of polymerization of MMA and styrene

Concentration of the iniferter ^a [PI] × 10 ⁴ (mol l ⁻¹)	MMA				Styrene, 78°C	
	Rate of polymerization × 10 ⁵ (mol l ⁻¹ s ⁻¹)				Concentration of the iniferter ^a [PI] × 10 ⁴ (mol l ⁻¹)	$R_p \times 10^6$ (mol l ⁻¹ s ⁻¹)
	70°C	78°C	85°C	95°C		
0	0.31	0.98	2.33	3.45	0	4.00
1.38	0.52	1.24	2.71	4.75	1.974	4.92
2.76	0.70	1.57	3.11	6.25	3.95	6.00
5.52	—	—	4.04	7.45	6.58	7.09
9.20	1.30	2.02	4.62	8.08	13.16	7.80
18.40	1.56	2.50	6.23	10.50	26.32	12.79
36.80	1.83	3.18	6.84	11.85	52.64	16.94
55.20	—	—	6.91	—	—	—
73.60	—	—	7.14	—	—	—

^a Expressed in terms of the molar concentration of the thiuram disulphide groups

with $k = R_i/I = 2fk_1$

$$B^* = \frac{k_5k_4}{k_7k_2} \quad \text{and} \quad C^* = \frac{k_6k_4^2}{k_7k_2^2}$$

Equation (2), depicting the polymerization behaviour, shows that R_p is no longer a linear function of the square root of the initiator concentration, unlike for radical polymerization using azo and peroxy initiators. On the other hand, R_p increases with $[I]$, reaches a maximum depending on C^* and then decreases.

Polymerization of methyl methacrylate

MMA was polymerized thermally in the presence of a polymeric iniferter (PI) of phosphonamide block length 3450 and polymer molecular weight 18 500. This corresponds to an average of 5.4 polyphosphonamide units per polymer chain. 2-Methoxyethanol was used as the homogenizing medium, keeping the monomer concentration constant at 6.26 mol l^{-1} . The rate of polymerization was determined at various concentrations of the PI at 70, 78, 85 and 95°C; R_p was determined from time-conversion plots. A representative plot is shown in Figure 1. It can be seen that as the concentration of PI increases, the plots possess intercepts corresponding to the PI incorporated into the polymer. The details of the R_p values and the PI concentration are cited in Table 1. In the kinetic calculation it was assumed that the reactivity of the once reacted PI is unaltered by its incorporation into the polymer chain. Equation (2) was used to describe the polymerization behaviour of MMA. A computerized multiple regression analysis was used to resolve the constants A^* , B^* and C^* . In this limited concentration range C^* was found to be zero. In this case, equation (2) becomes further simplified to:

$$R_p^2 = \frac{R_{p0}^2 + A^*I}{1 + 2B^*I/M} \quad (3)$$

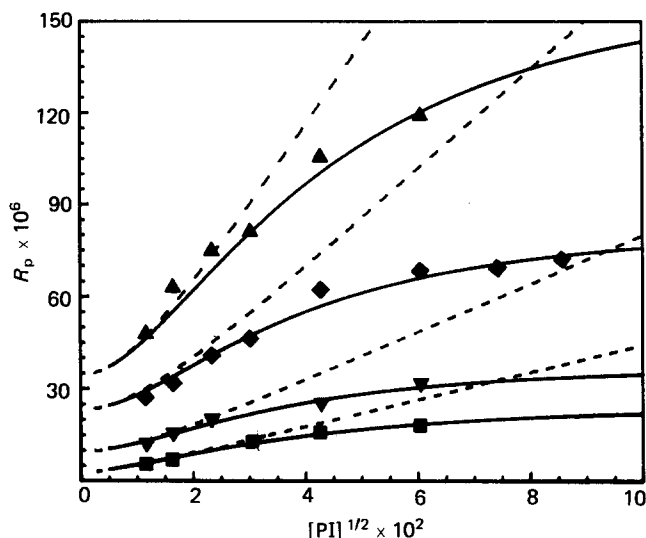
The constants A^* and B^* determined by the computer analysis for MMA at the four different temperatures are quoted in Table 2. Figure 2 shows the plot of R_p vs. $I^{1/2}$ using equation (3), and a satisfactory fit between the regression curves and the experimental points can be found. The broken curves are represented by the simple kinetic behaviour expressed as:

$$R_p^2 = R_{p0}^2 + A^*I \quad (4)$$

Evidently the constant A^* (a measure of the initiating

Table 2 Various kinetic parameters pertaining to the polymerization of MMA and styrene

Constants	MMA				Styrene, 78°C
	70°C	78°C	85°C	95°C	
$A \times 10^4$ ($\text{mol}^{1/2} \text{l}^{1/2} \text{s}^{-1}$)	4.44	7.93	16.52	27.73	2.30
B	960	1370	1230	900	0
$k = 2fk_1$ ($\text{s}^{-1} \times 10^6$)	0.182	0.476	1.65	3.40	0.71


Figure 2 Variation of R_p with $[PI]^{1/2}$ for MMA polymerization at 70, 78, 85 and 95°C (from bottom upwards): (—) theoretical curves from equation (3); (● etc.) experimental points; (---) theoretical curves for a simple kinetic scheme

efficiency) increases with temperature but B^* was found to be almost a constant, i.e. $B^* = 1100 \pm 200$. B^* is a measure of the extent of primary radical termination, which in the concentration range studied does not vary much with temperature. Both A^* and B^* were found to be considerably less than those for simple thiuram disulphides^{1,2}.

Extent of primary radical termination

The deviation of the kinetic behaviour from the simple square-root law is a consequence of polymer radical termination caused by the primary radicals. The proportion of primary radicals in the termination excluding reaction (f) can be expressed as the rate ratio:

$$\phi = \frac{k_5[P\cdot][I\cdot]}{k_5[P\cdot][I\cdot] + k_2[I\cdot][M\cdot]} \quad (5)$$

After adaptation and simplification the equation takes the form:

$$\phi = \frac{1}{2}(1 - R_p^2/A^*I) \quad (6)$$

The values of ϕ calculated from equation (6) using the experimental values of R_p and A^* at various temperatures and concentration of I are compiled in Table 3. Obviously ϕ increases with increase in concentration of the iniferter. The R_p value used in the calculation is corrected for the contribution from thermal polymerization as:

$$R_{p,corr} = (R_{pi}^2 - R_{p0}^2)^{1/2}$$

where $R_{pi} = R_p$ initiated and $R_{p0} = R_p$ thermal.

Formal reaction order

Participation of the primary radicals in the termination reactions causes a decrease in the order of the reaction with respect to the concentration of the initiator, i.e. deviation from the usual square-root dependence. The formal reaction order with respect to the initiator is given as $d \ln R_p / d \ln I$. From equation (3):

$$R_p^2 = \frac{R_{p0}^2 + A^*I}{1 + 2B^*I/M}$$

At higher PI concentration, R_{p0}^2 can be neglected with respect to R_p^2 , and therefore:

$$R_p^2 \approx \frac{A^*I}{1 + 2B^*I/M} \quad (7)$$

Differentiating the equation gives:

$$n = \frac{d \ln R_p}{d \ln I} = \frac{1}{2} \left(\frac{1}{1 + 2B^*I/M} \right) \quad (8)$$

The values of n calculated using equation (8) are tabulated in Table 4. Naturally n decreases as I increases.

Thermal dissociation of the initiator

From the expression for A^* it becomes evident that:

$$A^* = 2fk_1 \frac{k_3^2}{k_7} M^2$$

if it is assumed that addition of a small amount of the homogenizing medium does not alter the ratio of the rate of propagation k_3 and rate of conventional termination k_7 , i.e. k_3^2/k_7 , by much, it is possible to calculate the factor $2fk_1$, the overall rate constant for the thermal dissociation of the initiator, by adopting the literature value of k_3^2/k_7 , since M remains constant for small conversion. The factor $2fk_1$ thus calculated at the four different temperatures is given in Table 1. The Arrhenius plot for this constant is shown in Figure 3. An excellent linearity within experimental error indicates that f does

Table 3 Degree of primary radical termination for MMA

Concentration of iniferter $\times 10^4$ (mol l^{-1})	Fraction of primary radicals in termination reaction			
	70°C	78°C	85°C	95°C
2.76	—	0.06	0.12	0
5.52	—	0.05	0.14	0
9.20	0.06	—	0.17	0.12
18.40	0.18	0.27	0.28	0.15
36.80	0.28	0.30	0.30	0.27
55.20	—	—	0.36	—
110.40	—	—	0.39	—

Table 4 Formal reaction order with respect to the concentration of PI for MMA

[PI] $\times 10^4$ (mol l^{-1})	70°C	78°C	85°C	95°C
2.76	0.461	0.446	0.460	0.450
5.52	0.427	0.403	0.424	0.430
9.20	0.392	0.356	0.386	0.395
18.40	0.319	0.277	0.314	0.327
36.80	0.234	0.192	0.230	0.242
55.20	0.185	0.146	0.181	0.193
73.60	0.153	0.118	0.150	0.160

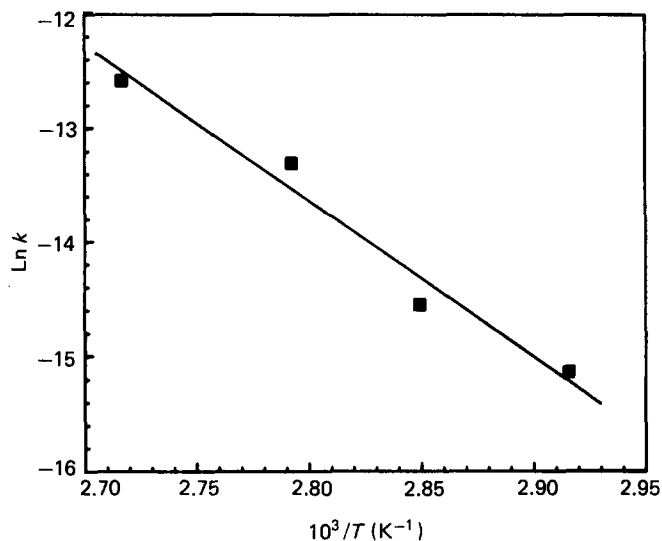


Figure 3 Arrhenius plot for the overall thermal dissociation constant of the PI for the polymerization of MMA

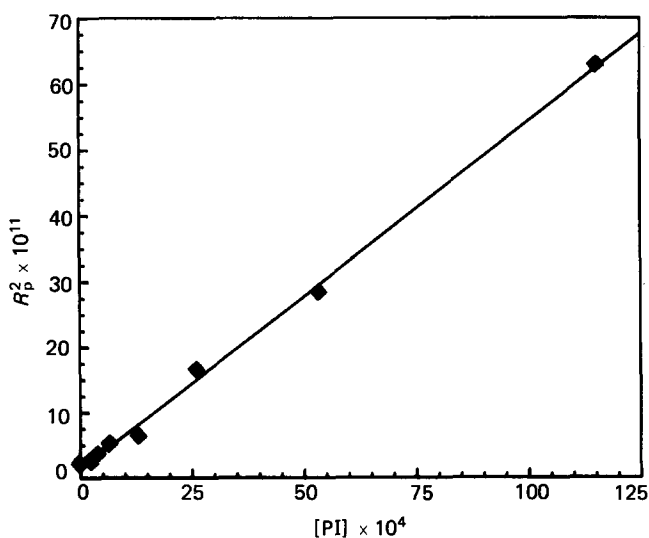


Figure 4 R_p^2 versus $[PI]$ plot for styrene polymerization

not vary significantly with temperature. The activation energy for the overall decomposition corresponds to 138 kJ mol^{-1} , which is practically the same as for simple thiuram disulphides¹². This shows that incorporation of this functional group into a polymer backbone does not impose any extra energy requirement for their decomposition. However, the rate constants for initiation were about 20 times less than those for their microanalogue¹², showing that incorporation into a polymer chain does slow down the rate of dissociation and hence the rate of initiation. A decrease in B^* can also be attributed to the same cause.

Kinetics of polymerization of styrene

The kinetic study was extended to the case of styrene also over a limited concentration range and in the presence of 2-methoxyethanol. The R_p values were determined as a function of the concentration of the PI at 78°C and are compiled in Table 1. Evaluation of the data by the use of equation (3) revealed that in this case $B^* = 0$, which means that the system behaves exactly as in any conventional initiated polymerization. The rate

expression becomes:

$$R_p^2 = R_{p0}^2 + A^*2I$$

Figure 4 shows a plot of R_p^2 versus $[I]$, resulting in a straight line. This observation is quite consistent with that of Beniska *et al.*¹¹, who found that the degree of primary radical termination in the case of styrene is inferior to that of MMA even in extended concentration ranges when tetraalkyl thiuram disulphides are used as initiators. In this limited concentration range it is found to be absent. In the case of MMA, the electron-deficient reactive polymer radicals have a greater affinity towards the soft, electron-rich dithiocarbamyl radical, whereas the polystyryl radicals are substantially stable and have a reduced affinity for the same.

Copolymer synthesis and characterization

The polymerizations were carried out in the presence of 2-methoxyethanol as homogenizing medium. The block copolymers were isolated by precipitating them in methanol in which the unreacted polymeric iniferter dissolved. Their compositions were determined from the percentage of phosphorus content. Copolymers of varying composition were prepared by varying the concentration of the polymeric iniferter. It was found that when the percentage of phosphorus exceeded 2.3% ($\approx 15\%$ by weight of the phosphonamide) in the case of MMA and 3.5% ($\approx 25\%$ by weight of phosphonamide) in the case of styrene, the copolymers tend to be soluble in methanol and were hence difficult to purify by precipitation in methanol. Hence only the copolymer of low phosphonamide content could be isolated in the pure form. Naturally the phosphonamide composition of the resulting copolymer increased when the PI concentration was increased, and it decreased when the conversion was increased. Figures 5 and 6 demonstrate the variation of composition of the copolymer as a function of the PI concentration and conversion in typical cases. At higher temperature, the efficiency of the functionalization (incorporation of P moiety) increased owing to the enhanced iniferter activity. Polymers containing more than 1% phosphorus were found to gel in solvents like tetrahydrofuran (THF), benzene, acetone, etc. Thus their isolation in pure form posed a problem. The swelling was

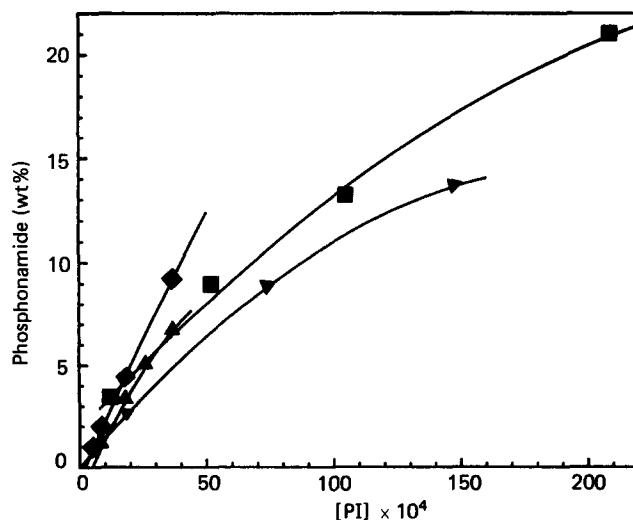


Figure 5 Variation of copolymer composition with $[PI]$ at conversion $3.5 \pm 0.5\%$: (\blacktriangle) MMA, 78°C ; (\blacktriangledown) MMA, 85°C ; (\blacklozenge) MMA, 95°C ; (\blacksquare) styrene, 78°C

caused by the strong dipolar interaction of the phosphonamide blocks, which are in fact insoluble in these solvents. The swollen polymers were isolated and their ^{13}C n.m.r. spectra are shown in Figures 7 and 8.

The signals corresponding to the aromatic carbons on the phosphonamide can be seen clearly in both spectra at 131.6 and 128.4 ppm, whereas that corresponding to piperazine is merged with the signals characteristic of the parent polymers. The assignments of the carbon atoms can be seen in the spectra. The signals due to the

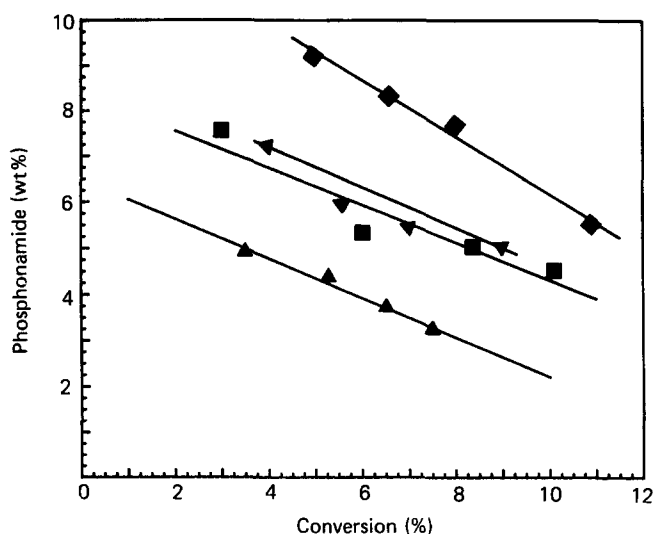


Figure 6 Variation of copolymer composition with conversion: (■) 70°C, (▼) 85°C, (◆) 95°C for MMA, $[\text{PI}] = 3.68 \times 10^{-3} \text{ mol l}^{-1}$; (▲) 78°C, styrene, $[\text{PI}] = 2.63 \times 10^{-3} \text{ mol l}^{-1}$

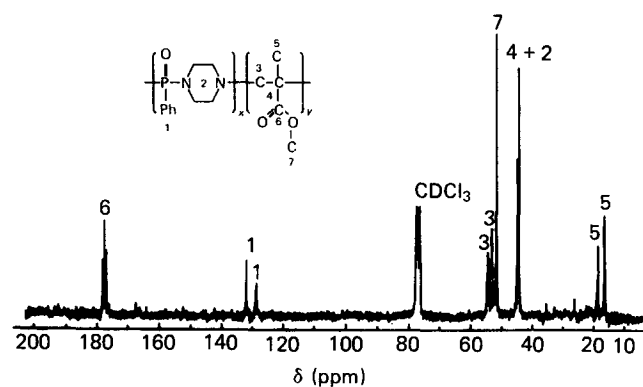


Figure 7 ^{13}C n.m.r. (CDCl_3) of poly(MMA-*b*-phosphonamide)

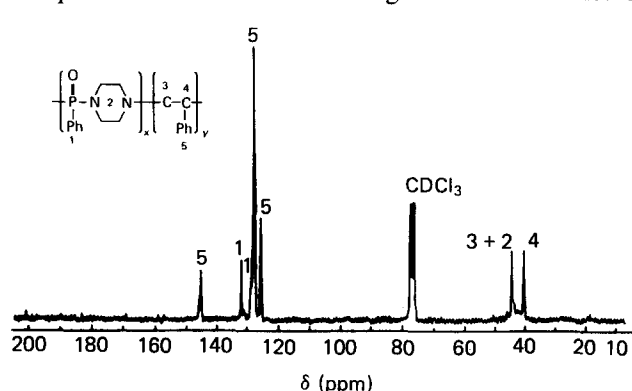


Figure 8 ^{13}C n.m.r. (CDCl_3) of poly(styrene-*b*-phosphonamide)

dithiocarbamyl carbon, however, could not be seen, owing to its very low population in the chain.

In general, for the same concentration of the PI, and more or less the same conversion, polystyrene was found to be more enriched in phosphonamide blocks. This is because of the shorter polystyryl blocks between the phosphonamide blocks. This shortening of the chain is an inherent property of polystyrene (low k_2^2/k_7) aided by its high chain transfer property towards the thiuram disulphide groups. It is quite possible that in spite of all the three functions there may be some amount of the non-functional polymer present. The amount could not be determined exactly owing to the lack of special solvent extraction techniques, since the polymers bearing less than 1% of phosphorus have similar solubility characteristics to that of PMMA homopolymer. G.p.c. analysis of the copolymers with less than 10% conversion did not give any evidence for the presence of homopolymer, which would have appeared as a separate peak in the high-molecular-weight range.

Copolymer composition and structure

Knowledge of the overall composition of the polymer calculated from the phosphorus content and the molecular weight allowed us to gain an idea of the structures of the copolymers and their variation with conversion. The molecular weights were determined from their $[\eta]$ values in CHCl_3 by assuming that a small proportion of the phosphonamide does not bring significant alterations to the chain conformation in a good solvent like CHCl_3 (good for both segments) and the values are only approximate. Table 5 lists the compositions and molecular weights of a few series of

Table 5 Variation of the structure and molecular weight of the copolymer with conversion

Monomer	Polymerization conditions	Phosphonamide block mol. wt	Conversion (%)	Phosphonamide (wt%) in the polymer	Molecular weight	Average mol. wt of the vinyl block per block of phosphonamide
MMA	$T = 85^\circ\text{C}$ $[\text{PI}] = 7.36 \times 10^{-3}$ (mol l^{-1})	4100	3.3	9.00	89 700	45 500
			5.5	8.05	113 200	50 930
			8.0	7.18	130 000	57 100
			9.8	6.70	153 000	61 190
	$T = 85^\circ\text{C}$ $[\text{PI}] = 3.68 \times 10^{-3}$ (mol l^{-1})	4100	4.0	7.20	217 800	57 000
			5.6	5.90	231 300	69 490
			7.0	5.43	250 200	75 500
			9.1	5.03	288 400	81 500
Styrene	$T = 78^\circ\text{C}$ $[\text{PI}] = 2.63 \times 10^{-3}$ (mol l^{-1})	2700	3.5	4.90	219 000	55 000
			5.3	4.36	284 500	61 930
			6.5	3.70	421 800	73 000
			7.5	3.20	492 000	84 300

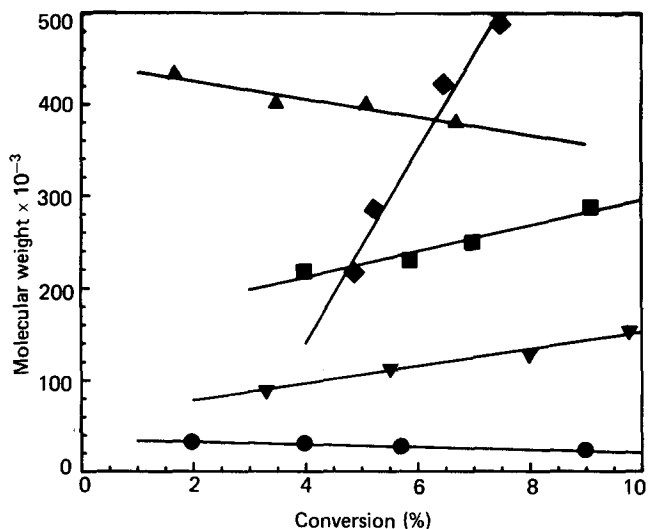


Figure 9 Variation of polymer molecular weight* with conversion: (■) MMA, 85°C, $[PI] = 3.68 \times 10^{-3} \text{ mol l}^{-1}$; (▼) MMA, 85°C, $[PI] = 7.36 \times 10^{-3} \text{ mol l}^{-1}$; (●) MMA, 70°C, DHTD initiated, $[DHTD] = 9.14 \times 10^{-2} \text{ mol l}^{-1}$; (▲) MMA, 70°C, DHTD initiated, $[DHTD] = 2.04 \times 10^{-2} \text{ mol l}^{-1}$; (◇) styrene, 78°C, PI initiated, $[PI] = 2.63 \times 10^{-3} \text{ mol l}^{-1}$. *Viscosity-average molecular weight for (■), (▼) and (◇); weight-average molecular weight for (▲); number-average molecular weight for (●)

polymers and their variation with conversion. In a typical case of PMMA polymerization using a polymeric iniferter of molecular weight 19 800 containing phosphonamide of block length 4100 (i.e. average of 4.83 units per polymer chain) at a concentration of $7.26 \times 10^{-5} \text{ mol l}^{-1}$, it can be seen that the molecular weight almost doubles as the conversion goes from 3 to 10% while the P content does not decrease considerably. In this conversion range and at high PI concentration, a steady-state situation can be expected which should give rise to a constant molecular weight. But a two-fold increase points towards the mechanism of chain growth by successive additions of the monomer unit into the PI chain as proposed in the preceding section. Table 5 also contains the average block molecular weight of the PMMA moiety per unit of phosphonamide block, which increases with increase in conversion. If it is assumed that the copolymer does not bear any more disulphide linkages, at 10% conversion, the polymer has a multi-block structure containing 2.5 units each of the blocks. At a PI concentration of $3.68 \times 10^{-5} \text{ mol l}^{-1}$, the length of PMMA block per block of phosphonamide increases from 57 000 at 4% conversion to 81 500 at 9% conversion. And if the same assumptions are made, the multi-block copolymer at 9% conversion contains an average 3.5 A–B units per chain. In a typical case of polystyrene, there was a tremendous increase in molecular weight with increase in conversion (Table 5). The interference of homopolymer in the molecular-weight increase can be ruled out since at these limited conversion levels appreciable amounts of PI remain in the system. A g.p.c. analysis of the resultant copolymer (with low phosphorus content) did not reveal any bimodal distribution due to the presence of homopolymer. Interestingly, when a simple iniferter like *N,N'*-diethyl-*N,N'*-bis(2-hydroxyethyl) thiuram disulphide (DHTD) was used as the initiator, the molecular weight of the resultant polymer decreased slightly with conversion. Hence the proposed mechanism of chain growth by successive insertion of the monomer in the PI chain as depicted in the preceding section holds good. The

variation of molecular weight with conversion in all these cases is shown in Figure 9.

In one case when a MMA–phosphonamide block copolymer (7% phosphonamide by weight) of molecular weight 103 000 was hydrolysed with 1.2% NaOH in 2-methoxyethanol for 24 h at room temperature, the isolated polymer was found to have a reduced molecular weight of 69 790, showing that hydrolysis of the dithiocarbamate bond in the block copolymer had taken place, causing chain degradation. This observation further substantiates the existence of multi-block structure.

Glass transition temperatures

The copolymers were subjected to differential scanning calorimetric examinations. They showed only one T_g , implying that the sequences were compatible. The T_g values increased with increase in phosphorus content of the polymer. However, a systematic variation of T_g with composition could not be observed. This may be due to the fact that T_g is determined not only by the composition but also by the distribution of the blocks. For PMMA, T_g increased tremendously to 126°C with increasing phosphorus content and thereafter it was not found to vary with composition. A similar trend was observed for polystyrene also. The maximum T_g was observed to be 110°C. The increase in T_g is a consequence of the enhanced rigidity of the chain caused by the strong dipolar interaction of the phosphonamide blocks.

Flame and thermal resistance of the polymers

The flame resistance of the polymers was measured by their limiting oxygen index (LOI) values. It was found that the LOI increased with increase in phosphorus content. The details of the LOI and the mechanism of flame-retardant action will be reported separately.

Thermogravimetric analysis of the block polymers was carried out in a nitrogen atmosphere. The samples used were sufficiently leached with THF to remove any homopolymer present. The THF swollen samples were squeezed and dried. The thermograms of the homopolymers along with those of their block copolymers are shown in Figure 10. The copolymeriza-

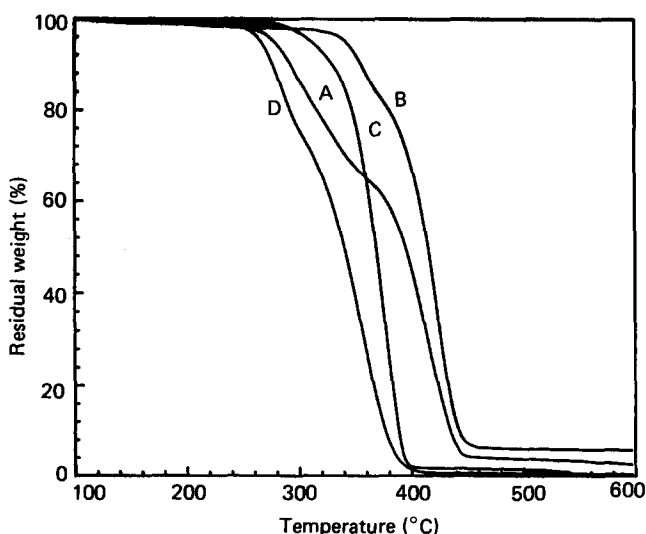


Figure 10 Thermograms of the phosphonamide block copolymers of MMA and styrene with those of the homopolymers: A, poly(MMA-*b*-phosphonamide), $P = 2\%$; B, poly(styrene-*b*-phosphonamide), $P = 3.3\%$; C, PMMA, AIBN initiated; D, polystyrene, thermal non-catalysed, N_2 atmosphere. Heating rate $10^\circ\text{C min}^{-1}$

tion adversely affected the thermal stability of PMMA in the initial stage of decomposition, whereas an improvement in the later stages can be observed in its thermograms. The presence of phosphorus is known in some cases to cause induced decomposition of polymers, leading to char formation, which accounts for their enhanced flame resistance^{15,16}. Probably a similar mechanism of flame retardation must be operative in this system also. A substantial increase in the thermal stability of polystyrene was observed by copolymerization. The copolymers left behind some char residue at higher temperatures when the homopolymers underwent complete depolymerization. Char formation can augment the flame resistance of polymeric materials by acting as a barrier to heat.

CONCLUSIONS

Polymerization of MMA and styrene in the presence of phosphonamide-containing poly(thiuram disulphide) (polymeric iniferter) resulted in new block copolymers, viz. poly(phosphonamide-*b*-MMA) and poly(phosphonamide-*b*-styrene), through an iniferter mechanism. The composition and molecular weight of the block copolymer can be regulated by a proper choice

of the monomer/polymeric iniferter ratio and the extent of polymerization.

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