Preparation of block copolymers using a new polymeric peroxycarbamate

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(Received 8 July 1985)

Block copolymers of poly(styrene-*b*-methyl methacrylate), poly(styrene-*b*-n-butyl methacrylate) and poly(methyl methacrylate-*b*-styrene) have been prepared via chemical reactions. A new polymeric peroxycarbamate is synthesized by reacting equimolar amounts of an aliphatic diisocyanate with a dihydroperoxide. This compound is an effective polymerization initiator, and is used to prepare active prepolymers containing fragments of polymeric peroxycarbamate. A second vinyl monomer is then incorporated to produce various block copolymers. Styrene contents, intrinsic viscosities and chemical and mechanical properties of the copolymers were determined.

(Keywords: preparation; block copolymers; poly(styrene-*b*-methyl methacrylate); poly(styrene-*b*-n-butyl methacrylate); poly(methyl methacrylate-*b*-styrene); polymeric peroxycarbamate)

INTRODUCTION

Synthesis and characterization of various polymeric peroxycarbamates were described earlier[1]. There have been several attempts to prepare block copolymers via chemical reactions using certain intermediate prepolymers and other monomeric compounds. Various modes of preparation and the properties of the block copolymers have been described[1-3].

In this work a new polymeric peroxycarbamate is prepared by reacting equimolar amounts of an aliphatic diisocyanate (bis(4-isocyanatocyclohexyl)methane) with a dihydroperoxide (2,5-dimethyl-2,5-dihydroperoxyhexane). The material is isolated, purified and characterized by physicochemical methods and used as an initiator to polymerize certain vinyl monomers. The polymeric product obtained with this procedure contains peroxycarbamate groups from the initiator, and it is called an 'active' prepolymer. Subsequently, polymerization of a second monomer is initiated by the prepolymer obtained in this way.

Using the above sequence of reactions tri-block copolymers of the following structures have been prepared: poly(styrene-*b*-methyl methacrylate), poly(styrene-*b*-n-butyl methacrylate) and poly(methyl methacrylate-*b*-styrene). Chemical, spectroscopic, mechanical and physical characterization of the products were carried out.

EXPERIMENTAL

Materials

Bis(4-isocyanatocyclohexyl)methane (H-MDI) was a product of DuPont de Nemours and Co. It was distilled under reduced pressure before use. Its purity, determined by isocyanate analysis, was better than 99%.

2,5-Dimethyl-2,5-dihydroperoxyhexane (Luperox-2,5-2,5) was a product of Lucidol Division, Penwalt Corp. It was recrystallized twice from carbon tetrachloride. Peroxygen content was 99% of the theoretical value.

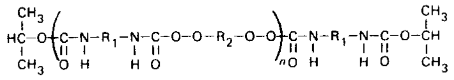
Dibutyltin dilaurate (T-12) was a product of Cincinnati Milacron Chemical Inc. and was used without any purification.

Styrene (S), methyl methacrylate (MMA) and n-butyl methacrylate (nBMA) were washed with 10% aqueous NaOH solution, dried over $CaCl_2$ and freshly distilled under reduced pressure.

Procedure

Preparation of polymeric peroxycarbamate (PPC). Equimolar amounts of diisocyanate (H-MDI) and dihydroperoxide (Luperox-2,5-2,5) were reacted in methylene chloride at room temperature under a dry nitrogen atmosphere in the dark for 72 h. Chain extension reaction was carried out in the presence of T-12 as catalyst. An excess of H-MDI was then added to this solution to cover both ends of peroxycarbamate with isocyanate end groups. Subsequently the isocyanate end groups were capped with isopropyl alcohol by reacting for 24 h at room temperature. The white powder was precipitated in petroleum ether, filtered, washed with a mixture of petroleum ether/methylene chloride (5/1 by volume) and dried in vacuum. Overall yield was 61.3% by weight. Peroxygen content of the product was 12.5%.

The chemical structure of PPC can be represented as follows:



$$(CH_3)_2CH{-}O{-}\left(\underset{\underset{O}{\|}}{C}{-}\underset{\underset{H}{|}}{N}{-}R_1{-}\underset{\underset{H}{|}}{N}{-}\underset{\underset{O}{\|}}{C}{-}O{-}O{-}R_2{-}O{-}O\right)_n\underset{\underset{O}{\|}}{C}{-}\underset{\underset{H}{|}}{N}{-}R_1{-}\underset{\underset{H}{|}}{N}{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH(CH_3)_2$$

PPC

where R_1 and R_2 represent the hydrocarbon backbone in

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H-MDI and Luperox-2,5-2,5 respectively, and $n=6$. The molecular weight of PPC was $\sim 3000\ \mathrm{g\ mol^{-1}}$.

Preparation of active polymers and copolymers. Active polymers were obtained by polymerization of vinyl monomers using PPC as initiator. Weighed amounts of the PPCs were dissolved in predetermined amounts of vinyl monomers. Benzene was sometimes added to the mixture as polymerization solvent. The mixture was then degassed on the vacuum line. Bulk or solution polymerization was carried out in evacuated and sealed Pyrex tubes for appropriate reaction times in a thermostatted oven at 80°C. The active polymer, which contains segments of the initiator, was then precipitated with a large amount of methanol, filtered and dried in a vacuum oven for 24 h. Peroxygen content of the product was subsequently determined.

Since prepolymers of active polystyrene or active poly(methyl methacrylate) contain percarbamate groups in their chains, block copolymer of vinyl monomers were prepared by using active prepolymers as initiators for free-radical copolymerization reactions.

Initiation of styrene or methyl methacrylate polymerization by PPC. Kinetics of bulk polymerization of styrene and solution polymerization of methyl methacrylate were studied using PPC as initiator. The polymerization procedure is described above.

Rate, R_p, and average degree of polymerization, $\bar{P}_n$, were calculated from the conversion–time data and dilute solution viscosity measurements respectively. The intrinsic viscosities were converted to $\bar{P}_n$ by means of the following equations:

Polystyrene in benzene at 30°C[4]

$$[\eta]=4.61\times10^{-3}\times\bar{P}_n^{0.73} \tag{1}$$

Poly(methyl methacrylate) in benzene at 30°C[5]

$$[\eta]=5.2\times10^{-3}\times\bar{P}_n^{0.76} \tag{2}$$

Analysis. Isocyanate analyses were performed by reacting a weighed amount of the material with standard di-n-butylamine solution in toluene and back-titrating the excess with standard HCl[6].

Peroxygen analyses of PPC and active polymeric samples were determined by iodometric titration[7].

Styrene content of the copolymers was determined by u.v. spectroscopy at 269 nm. This method is based on measuring the absorbance of pure polystyrene, peroxycarbamate and copolymer at 269 nm (refs. 3 and 8).

The copolymerization products contained the copolymer and the homopolymers of the parent monomers. Homopolymers of polystyrene, poly(methyl methacrylate) and poly(n-butyl methacrylate) were determined by extracting copolymeric samples with boiling cyclohexane, acetonitrile and isopropyl alcohol, respectively. Extracted homopolymers were recovered from their solutions by precipitating with methanol. They were then dried and weighed.

For mechanical tests, samples were compression moulded and annealed at 105°C for 24 h. Stress–strain tests were carried out on an Instron machine at room temperature with a rate of elongation of $3.1\ \mathrm{mm\ min^{-1}}$. Torsional modulus–temperature relationships of the copolymers were established by means of a Gehman Torsional Tester.

I.r. spectra of thin films or methylene chloride solutions of samples were taken on a Perkin–Elmer 177 grating spectrophotometer.

U.v. spectra of chloroform solutions of block copolymers were taken on a Varian 635D spectrophotometer.

RESULTS AND CONCLUSIONS

In this study we first prepared and characterized a new polymeric peroxycarbamate (PPC) by reacting equimolar amounts of a cycloaliphatic diisocyanate and an aliphatic dihydroperoxide. We used this oligomeric polyfunctional initiator to initiate free-radical polymerization of vinyl monomers. Subsequently, we used this initiator as a starting material for the synthesis of various block copolymers.

Kinetics of low-conversion polymerization

PPC was utilized as a free radical initiator for the polymerization of styrene and methyl methacrylate at 80°C. Conversions were kept below 13% for proper analysis of the kinetic results. The results for bulk polymerization of styrene and solution polymerization of methyl methacrylate are given in *Tables 1* and *2* respectively. R_p values were calculated by subtracting the purely thermal rates of polymerizations for both monomers.

Table 1 Bulk polymerization of styrene initiated by polymeric peroxycarbamate at 80°C

Run	$[\mathrm{I}]_0\times10^3$ (mol l^{-1})	$[\mathrm{M}]_0$ (mol l^{-1})	Time (min)	Yield (wt%)	$R_p\times10^5$ (mol l^{-1} s^{-1})	$(1/\bar{P}_n)\times10^4$
1	0.17	8.19	116	2.02	1.27	2.14
2	0.26	8.18	120	2.71	1.97	1.97
3	0.82	8.16	120	5.00	4.57	4.50
4	1.32	8.15	120	7.49	7.40	5.14
5	2.72	8.13	120	9.53	9.71	6.48
6	3.89	8.10	120	10.90	12.40	8.86
7	5.79	8.09	120	13.53	15.35	11.14
8	6.04	8.08	130	12.97	13.58	8.14
9	6.31	8.07	90	11.78	16.68	13.30
10	16.79	8.00	90	10.53	22.80	18.80
11	18.03	7.86	40	6.90	22.37	21.40
12	33.60	7.56	40	9.33	30.71	27.63
13	40.81	7.42	44	10.74	32.21	31.36

Table 2 Solution polymerization of methyl methacrylate initiated by polymeric peroxycarbamate at 80°C

Run	$[I]_0 \times 10^3$ (mol l^{-1})	$[M]_0$ (mol l^{-1})	Time (min)	Yield (wt%)	$R_p \times 10^5$ (mol l^{-1} s^{-1})	$(1/\bar{P}_n) \times 10^4$
1	0.14	7.066	115	6.49	5.64	1.20
2	0.71	7.037	50	4.84	10.35	1.94
3	1.63	7.257	54	6.82	14.27	4.25
4	2.67	7.237	52	7.53	16.46	3.70
5	6.06	7.298	35	7.30	24.37	12.62
6	8.37	7.277	30	6.84	26.65	7.14
7	14.70	7.259	38	9.09	27.94	18.93
8	23.09	7.340	32	12.95	48.51	22.20
9	40.16	7.278	15	8.43	67.20	50.19
10	51.39	7.268	13	11.30	104.35	82.12
11	83.15	7.248	14	11.30	96.42	82.12
12	92.10	7.228	11	11.03	119.75	94.33

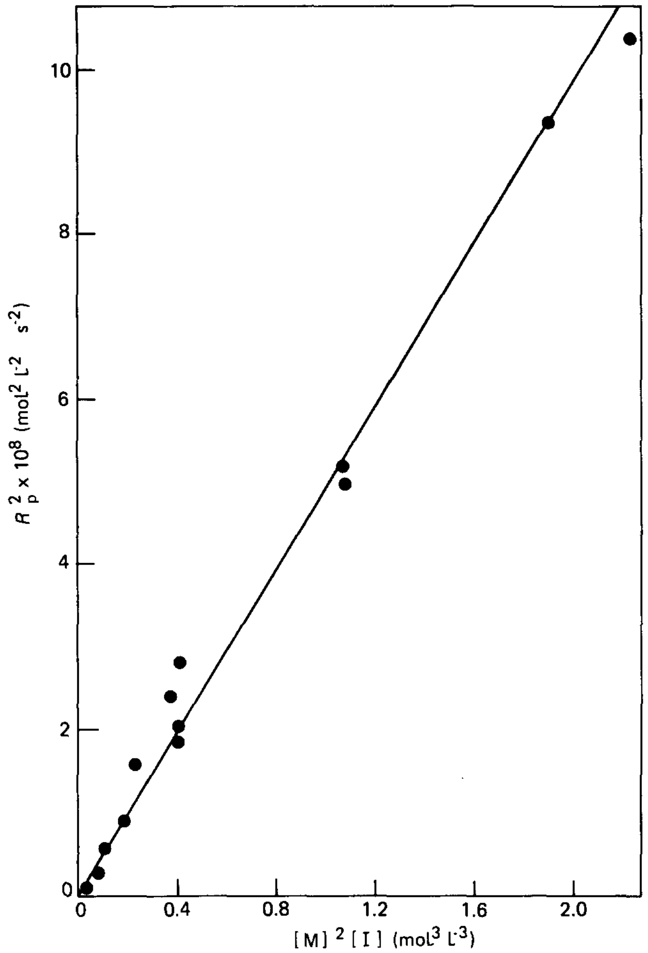

Figure 1 Plot of R_p^2 *versus* $[I][M]^2$ for styrene polymerization in bulk at 80°C, initiated by PPC

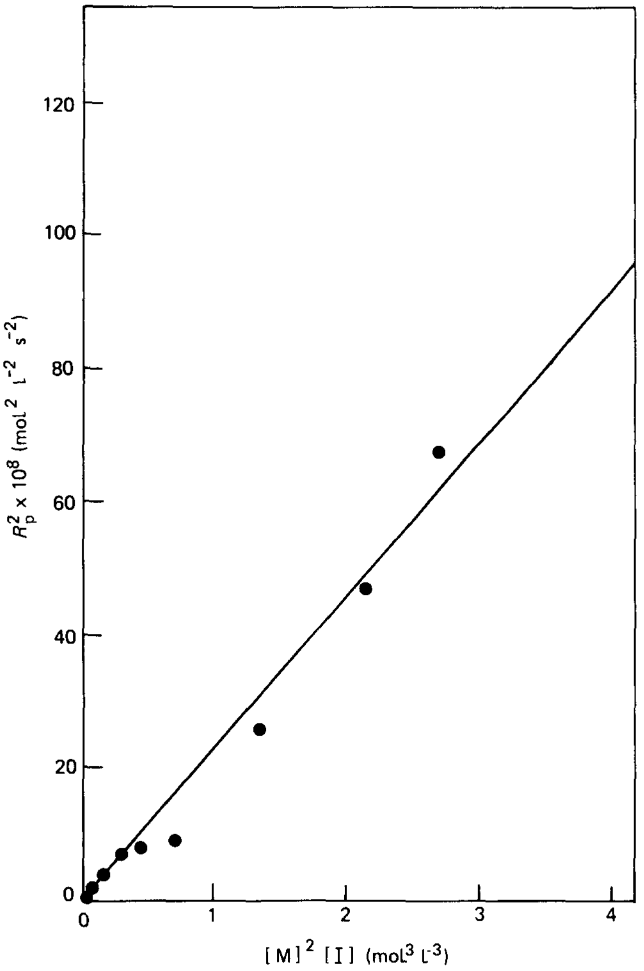

Figure 2 Plot of R_p^2 *versus* $[I][M]^2$ for solution polymerization of methyl methacrylate at 80°C, initiated by PPC

The rate of initiation (R_i) and rate of polymerization (R_p) of a free-radical polymerization reaction are given by[4,9,10]

$$R_i = 2fk_d[I] \tag{3}$$

and

$$R_p = k_p[M](fk_d[I]/k_t)^{1/2} \tag{4}$$

where [I] and [M] are the initiator and monomer concentrations, k_d, k_p and k_t are the thermal decomposition, propagation and termination rate constants respectively, and f is called the initiator efficiency. The term $k_p^2(fk_d/k_t)$ is often denoted K^2 and is a measure of the initiator reactivity[10]. The value of K^2 can be obtained from the slope of the plot of R_p^2 *versus* $[I][M]^2$ as can be seen from equation (4). For our systems the values of K^2 are estimated from *Figures 1* and *2* as 5.00×10^{-8} l mol^{-1} s^{-2} and 2.33×10^{-7} l mol^{-1} s^{-2} for styrene and methyl methacrylate respectively.

For free-radical polymerization, average degree of polymerization ($\bar{P}_n$) is related to the rate of polymerization (R_p) via the following equation[4,9,10]:

$$\frac{1}{\bar{P}_n} = C_M + C_S\frac{[S]}{[M]} + \frac{k_t}{k_p^2[M]^2}R_p + \frac{C_I}{K^2[M]^3}R_p^2 \tag{5}$$

Here C_M, C_I and C_S represent the chain transfer constants to monomer, initiator and solvent respectively. For bulk ($[S]=0$) polymerization if $C_I=0$, a plot of $1/\bar{P}_n$ *versus* R_p should yield a straight line. These plots are shown for styrene and methyl methacrylate in *Figures 3* and *4* respectively. The straight lines represent the monoradical lines. The slopes and intercepts of these lines are calculated from literature values[9-12]. The curvatures observed at high $R_p/[M]^2$ values for both monomers result from chain transfer to initiator. The intercepts of these curves with the $1/\bar{P}_n$ axis gives C_M. The values of chain transfer constants for styrene and methyl methacrylate monomers are determined to be 7.5×10^{-5} and 3.0×10^{-5} respectively. They are in good agreement with literature values[9,11,13].

In order to determine C_I, equation (5) was rearranged and $1/\bar{P}_n - C_M - C_S[S]/[M] - k_tR_p/k_p^2[M]^2$ was plotted against $R_p^2/K^2[M]^3$ for both monomers. These plots are represented in *Figures 5* and *6*. From the slopes C_I values are determined as 0.44 and 0.71 for polymerization of styrene and methyl methacrylate respectively. (The literature value[14] for the chain transfer constant to chloroform, $C_S=1.14\times10^{-4}$, is used in evaluation of MMA polymerization. For bulk polymerization, $[S]=0$.)

Values of K^2 and $R_i/[I]$ for various initiators are tabulated in *Table 3*. It should be noted that the first two initiators listed in this table contain more than one decomposing peroxygen bond per molecule. Therefore $R_i/[I]$ values must be divided by this number for a reliable comparison. Such a comparison indicates that PPC studied in this work shows a slower initiation at 80°C.

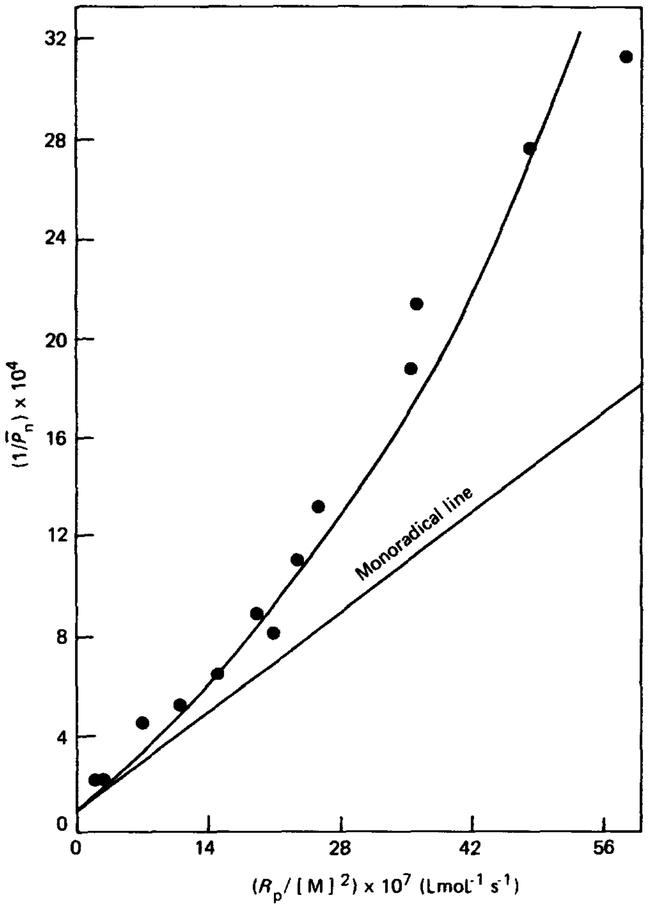

Figure 3 Plot of $1/\bar{P}_n$ *versus* R_p for styrene polymerization at 80°C, initiated by PPC

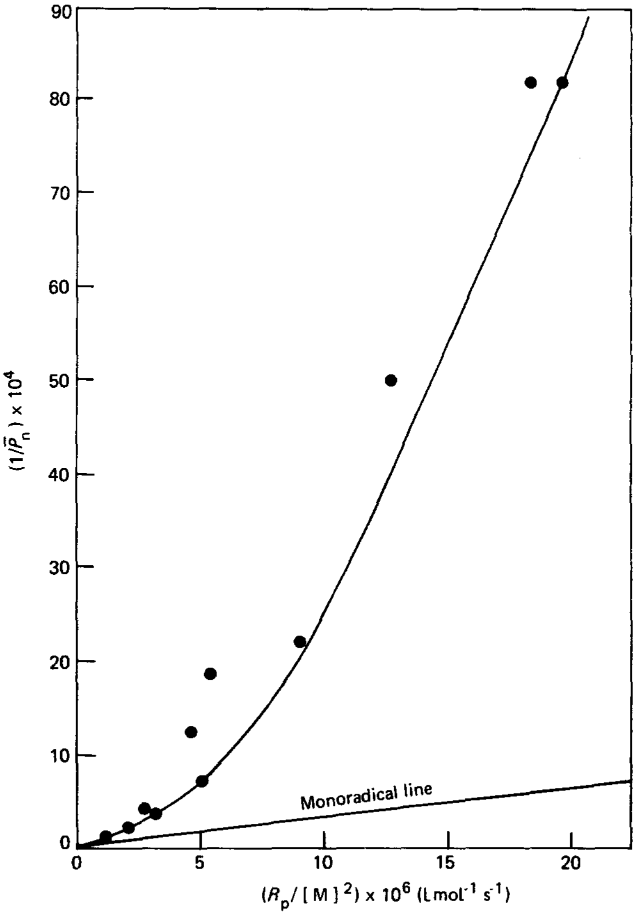

Figure 4 Plot of $1/\bar{P}_n$ *versus* R_p for methyl methacrylate polymerization at 80°C, initiated by PPC

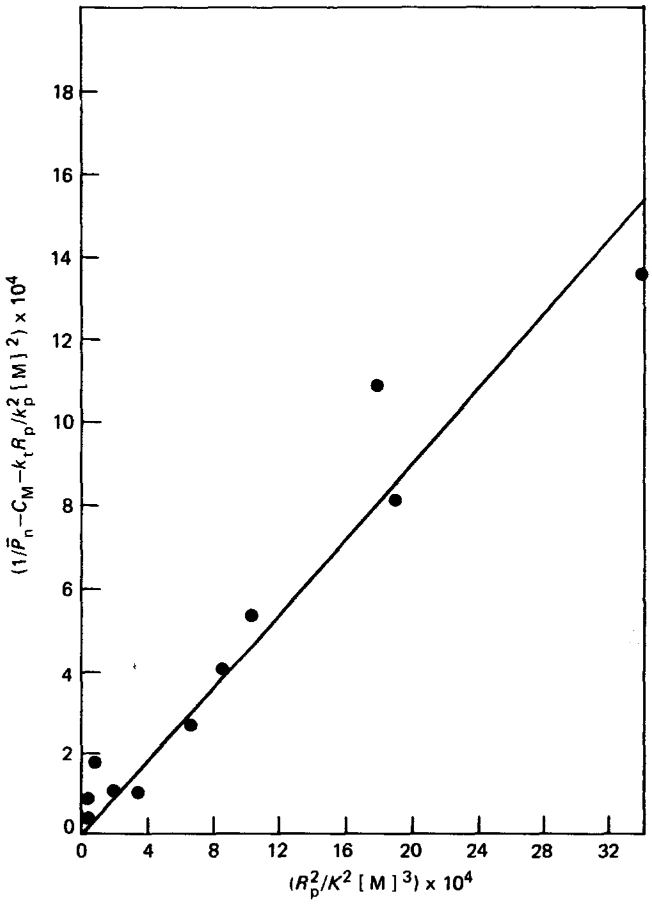

Figure 5 Plot of $1/\bar{P}_n - C_M - k_tR_p/k_p^2[M]^2$ *versus* $R_p^2/K^2[M]^3$ for styrene polymerization in bulk at 80°C, initiated by PPC

This may indicate that PPC can be used as an effective high-temperature initiator.

Decomposition of active polymers

Preparations of 'active' PS and 'active' PMMA by using PPC as initiator were described in the Experimental section. Peroxygen contents (wt%) and intrinsic viscosities of these polymers are given in *Tables 4–6*. The number of peroxide groups in the 'active' polymers can be regulated by changing the concentration of PPC and of vinyl monomers and the polymerization temperature.

To determine the positions of peroxide groups in the 'active' polymers, we have studied the reduction of intrinsic viscosities of these chains. *Figure 7* shows the variation of intrinsic viscosity of an 'active' PS sample in chlorobenzene and in toluene solutions at 80°C. We have shown that thermal decomposition of 'active' PS in the presence of a free-radical scavenger (iodine) considerably reduces the intrinsic viscosity of the initial macromolecule. This observation indicates that peroxide groups are located in isolated positions along the main PS chain.

Preparation and characterization of block copolymers

Experimental data on preparation of poly(styrene-*b*-methyl methacrylate), poly(styrene-*b*-n-butyl methacrylate) and poly(methyl methacrylate-*b*-styrene) block copolymers are included in *Tables 4, 5* and *6* respectively.

Examination of the data recorded in *Tables 4–6* leads

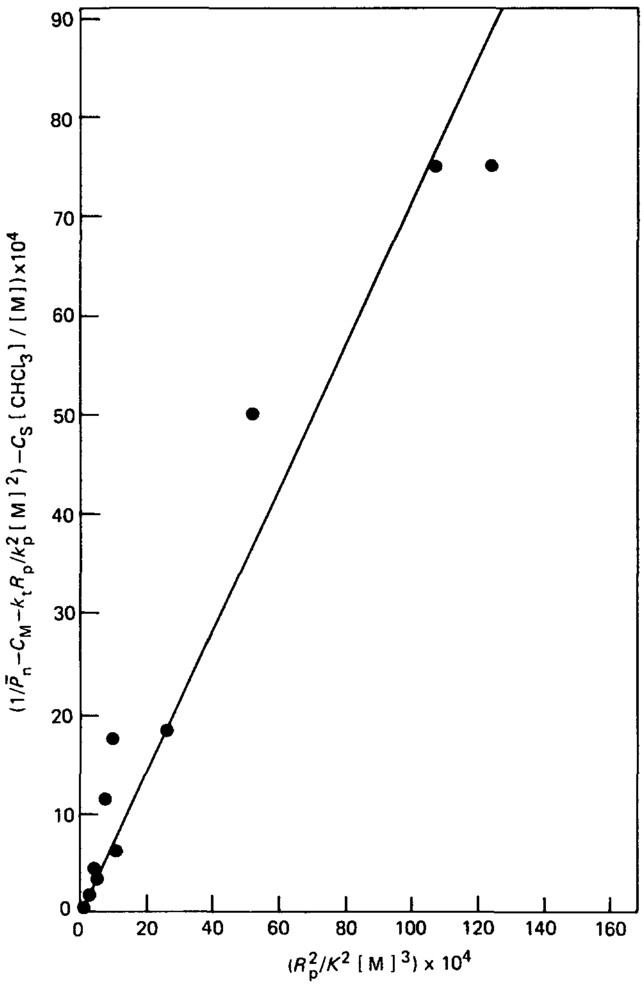

Figure 6 Plot of $1/\bar{P}_n - C_M - C_S[S]/[M] - k_t R_p/k_p^2[M]^2$ *versus* $R_p^2/K^2[M]^3$ for methyl methacrylate polymerization at 80°C, initiated by PPC

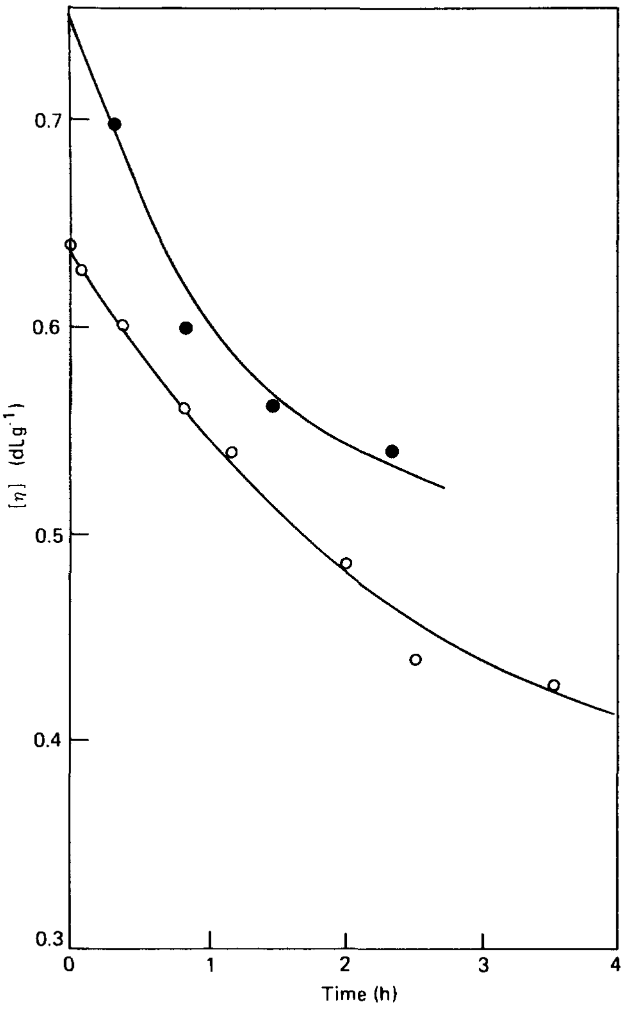

Figure 7 Reduction of intrinsic viscosity of an 'active' PS sample as a function of time at 80°C: ●, in toluene; ○, in chlorobenzene solution

Table 3 Polymerization of styrene and methyl methacrylate at 80°C by various free-radical initiators

Initiator	K^2 (l^2 mol^{-2} s^{-4})	$R_i/[I]$ (s^{-1})	Number of decomposing bonds per molecule	Ref.
(a) Styrene				
PPC	5.00×10^{-8}	2.92×10^{-5}	~6	this work
Luperox-2,5-2,5	6.00×10^{-9}	3.52×10^{-6}	2	15
Benzoyl peroxide	11.02×10^{-8}	6.42×10^{-5}	1	10, 16
(b) Methyl methacrylate				
PPC	2.33×10^{-7}	1.62×10^{-5}	~6	this work
Luperox-2,5-2,5	1.77×10^{-8}	1.23×10^{-6}	2	15
Benzoyl peroxide	1.34×10^{-6}	9.20×10^{-5}	1	10.16

Table 4 Preparation of poly(styrene-*b*-methyl methacrylate) block copolymers (active polymer, PS; second monomer, MMA)

	Active polymer			Copolymerization				Homopolymers in block copolymer		
Run	Initial (wt%)	Peroxygen content (%)	$[\eta]$ (dl g^{-1})	Temp. (°C)	Time (h)	Conversion of comonomer (wt%)	PS in block copolymer (%)	PS (%)	PMMA (%)	$[\eta]$ final (dl g^{-1})
1	7.0	0.29	0.45	60	1.33	4.1	64.3	–	–	1.12
2	16.3	0.74	0.30	60	4.50	30.7	37.6	–	–	2.42
3	22.5	0.67	0.28	60	1.87	35.0	41.2	–	–	2.42
4	22.9	0.74	0.30	60	3.00	66.8	37.5	–	–	2.60
5	24.0	0.21	0.56	60	2.00	34.6	48.3	–	–	1.71
6	27.5	0.14	0.66	60	2.00	9.9	78.0	–	–	1.22
7	16.9	0.12	0.49	80	1.50	36.9	37.9	–	–	1.75
8	19.7	0.35	0.47	80	2.00	71.0	26.4	–	–	2.25
9	24.5	0.12	0.49	80	1.50	76.0	33.7	–	–	2.36
10	25.8	0.50	0.58	80	2.50	83.0	31.5	4.1	1.5	1.38
11	26.0	0.40	0.52	80	1.45	87.5	25.8	–	–	3.00
12	31.1	0.21	0.56	80	2.00	84.0	39.8	–	–	2.20
13	35.2	0.12	0.49	80	2.00	81.4	40.7	–	–	1.80
14	39.2	0.33	0.41	80	2.50	85.0	44.3	5.1	1.8	1.73
15	43.0	0.33	0.41	80	2.50	79.0	50.0	6.0	1.0	1.50
16	50.6	0.12	0.49	80	3.00	77.0	42.0	–	–	1.60
17	51.0	0.40	0.52	80	1.33	98.2	48.1	4.2	1.1	1.65
18	67.0	0.40	0.52	80	1.47	97.6	68.2	–	–	1.40
19	68.0	0.40	0.48	80	1.66	98.0	69.5	8.4	3.6	1.26

Table 5 Preparation of poly(styrene-*b*-n-butyl methacrylate) block copolymers at 80°C (active polymer, PS; second monomer, nBMA)

	Active polymer			Copolymerization			Homopolymers in block copolymer		
Run	Initial (wt%)	Peroxygen content (%)	$[\eta]$ (dl g^{-1})	Time (h)	Conversion of comonomer (wt%)	PS in block copolymer (%)	PS (%)	PMMA (%)	$[\eta]$ final (dl g^{-1})
20	10.6	0.33	0.41	20.00	58.0	18.0	1.1	4.5	1.95
21	21.2	0.36	0.38	3.00	98.4	23.0	–	–	1.70
22	27.2	0.42	0.30	2.00	64.7	43.0	–	–	1.20
23	28.0	0.33	0.41	3.75	66.0	35.0	1.4	1.0	1.40
24	37.0	0.33	0.41	2.75	77.5	49.3	1.8	0.6	1.63
25	47.0	0.40	0.52	2.50	79.5	53.0	–	–	1.24
26	49.5	0.45	0.30	2.00	76.0	57.0	–	–	0.80
27	64.4	0.35	0.38	1.25	43.3	76.3	–	–	0.87

Table 6 Preparation of poly(methyl methacrylate-*b*-styrene) block copolymers at 80°C (active polymer, PMMA; second monomer, styrene)

	Active polymer			Copolymerization			Homopolymers in block copolymer		
Run	Initial (wt%)	Peroxygen content (%)	$[\eta]$ (dl g^{-1})	Time (h)	Conversion of comonomer (wt%)	PS in block copolymer (%)	PS (%)	PMMA (%)	$[\eta]$ final (dl g^{-1})
28	12.1	0.34	0.70	5.0	12.5	50.5	–	–	1.20
29	13.1	0.63	0.60	4.7	14.7	48.7	–	–	0.65
30	13.1	0.53	0.28	5.5	6.9	58.0	–	–	0.90
31	15.0	1.62	0.45	4.5	16.5	54.0	–	–	0.80
32	18.0	1.40	0.22	5.5	33.3	64.5	0.5	6.4	1.00
33	21.2	0.26	3.50	6.5	6.2	21.0	–	–	3.10
34	24.0	0.28	1.30	20.0	80.0	76.0	0.6	8.7	4.00
35	25.0	0.18	1.30	20.0	34.6	57.5	–	–	1.75
36	31.6	0.26	3.50	5.6	11.6	23.6	–	–	2.00
37	50.0	0.18	1.30	20.0	89.0	52.7	–	–	2.25

to some general features of this mode of block copolymer preparation. 'Active' polymers used as initiators for block copolymerization show the conventional properties of peroxidic initiators. This conclusion is also supported by the low-conversion polymerization studies given in the initial part of this work. Extended polymerization times led to copolymer production in high yields. In addition, total homopolymer contents of copolymeric samples were less than 7%. The agreement between stoichiometrically calculated and experimental values of PS residue in block copolymeric samples proves that nearly all 'active' PS (or 'active' PMMA) is incorporated into block copolymers. Intrinsic viscosities of copolymeric products depend on the type of component taking part in block copolymerization. Intrinsic viscosities are generally increased with the addition of second blocks on 'active' polymeric component. Identical values of intrinsic viscosities or even a decrease are observed if relatively long PS blocks were added on 'active' PMMA chains (*Table 6*, runs 2, 4 and 5).

This method of block copolymer preparation yields products that contain only a few per cent homopolymers of related monomers. This is confirmed by selective solution and fractional precipitation behaviour[17] of copolymeric samples, in addition to the careful analysis of i.r. spectra.

Fractional precipitation experiments provide definite evidence for the formation of block copolymers. *Figure 8* shows the fractional precipitation curves for two poly(S-*b*-MMA) copolymers (runs 14 and 15). Percentages of precipitated amounts of polymers were plotted against increasing volume ratios γ of precipitant to solvent. Precipitation results of a blend of PS and PMMA (50 wt% of each polymer) are also included in this figure. It will be seen that precipitation curves of block copolymers are located between precipitation curves of PS and PMMA components of the blend. Since the PS content of run 15 was higher than of run 14, precipitant having higher γ values was necessary to precipitate this sample from THF solution as is shown in *Figure 8*. *Figure 9* shows the fractional precipitation curves for poly(S-*b*-nBMA) copolymers (runs 20, 23 and 24). For this system, run 24, which contains the highest percentage of PS, is precipitated with least amount of precipitant from THF solution as was expected.

The preparation of block copolymers using diacyl oligoperoxide initiators has been described earlier[18]. Block copolymers of A–B, B–A–B and –B–A–B–A–B– types could be formed from polymeric peroxycarbamate or oligomeric peroxide initiators. However, since active polymers contain several peroxycarbamate groups the formation of A–B type block copolymers would be relatively low.

Three samples of poly(S-*b*-MMA) (*Table 1*, runs 7, 17 and 18) were studied in various solvents by using a light scattering technique[19]. The copolymer compositions, determined from the additivity of the refractive index

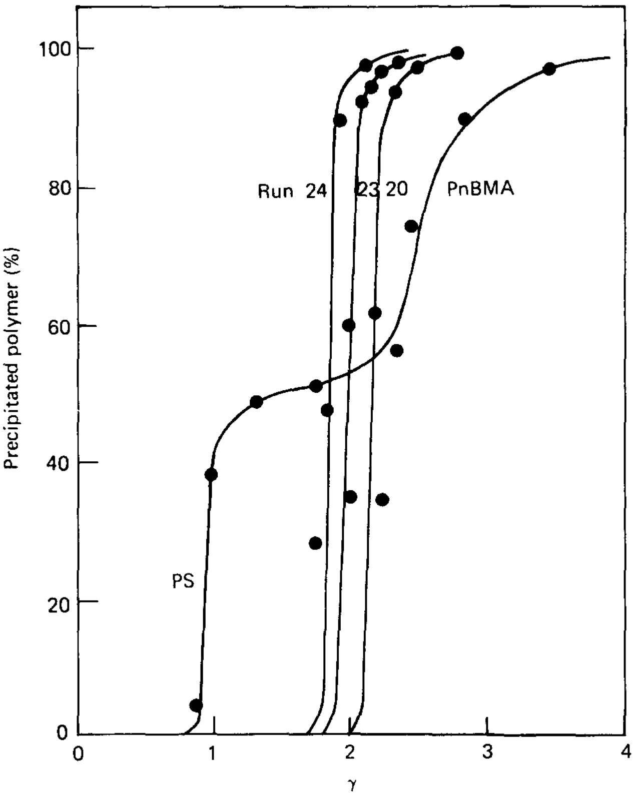

Figure 9 Fractional precipitations of a PS–nBMA blend and poly(S-*b*-nBMA) block copolymers (*Table 5*, runs 20, 23 and 24). γ indicates the volume ratio of precipitant to solvent. Precipitant, methanol; solvent, THF

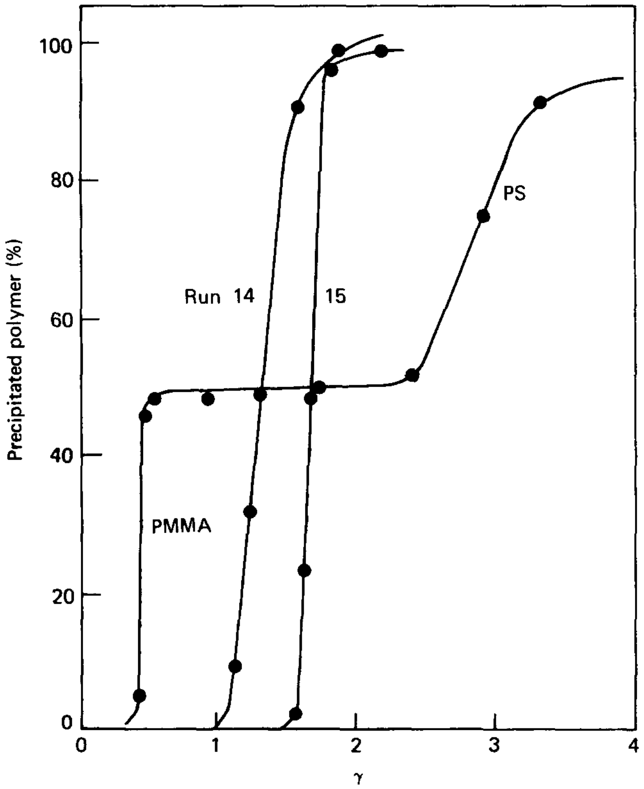

Figure 8 Fractional precipitations of a PS–PMMA blend and poly(S-*b*-MMA) block copolymers (*Table 4*, runs 14 and 15). γ indicates the volume ratio of precipitant to solvent. Precipitant, petroleum ether; solvent, THF

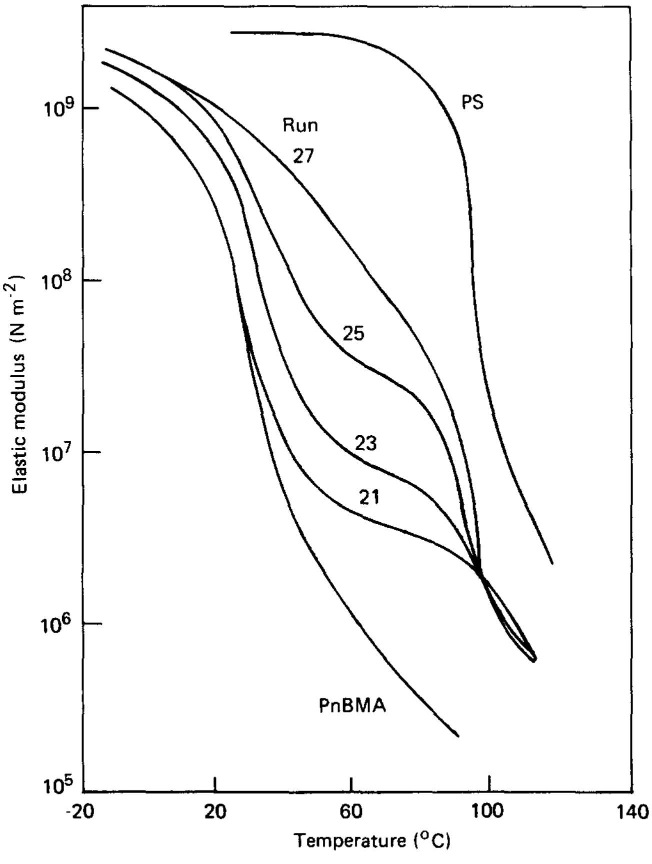

Figure 10 Elastic modulus–temperature relationship for poly(S-*b*-nBMA) block copolymers. Run numbers listed in *Table 5*. Curves for PS and PnBMA are included

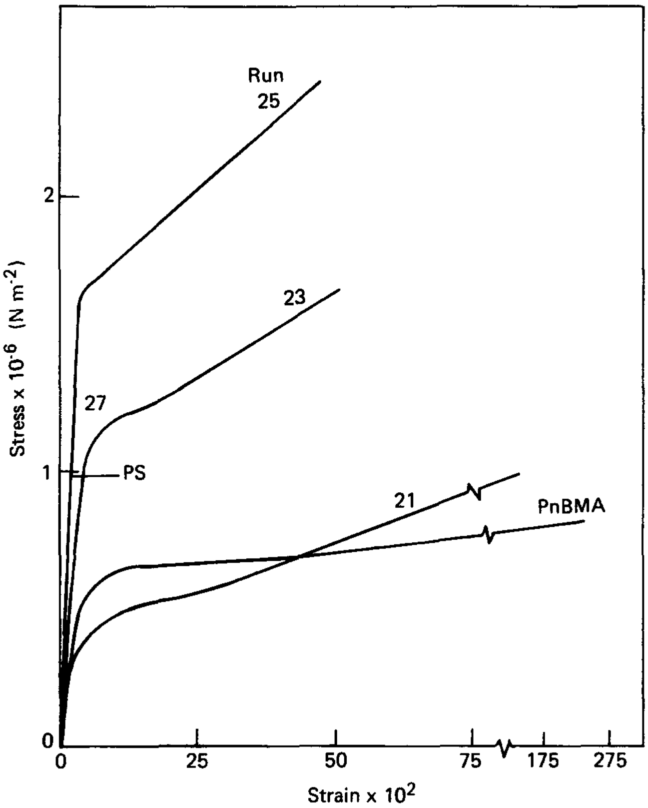

Figure 11 Stress–strain relationship for various copolymers of poly(S-*b*-nBMA). Run numbers listed in *Table 5*

increments of its constituent parts and the copolymer, were in excellent agreement with the results reported in *Table 1*. Block copolymer characters of these samples were confirmed by using light scattering and refractive index data obtained in various solvents[19,20]. However, these results indicate that copolymers obtained with the present method are rather heterogeneous in molecular weight as well as in composition.

In *Figure 10* elastic modulus–temperature relationships of some of the poly(S-nBMA) copolymers are reproduced. This figure also contains the same relationship for pure PS and PnBMA samples. Since T_g values of homopolymers are widely different from each other, elastic modulus–temperature curves present a typical demonstration of a block copolymer for this system.

Figure 11 shows stress–strain relationships for block copolymers together with pure PS and PnBMA. It can be seen that Young's modulus and ultimate strengths drop with increasing soft component (PnBMA) in the copolymers whereas ultimate elongations increase as expected.

As a concluding point, it may be stated that this method of copolymer synthesis is effective in producing block polymers with high yields and within reasonable polymerization times.

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