Macromolecules **1994,** *27,* 7109–7114

Vinyl Monomer Based Polyperoxides as Potential Initiators for Radical Polymerization: An Exploratory Investigation with Poly(α-methylstyrene peroxide)

K. Shanmugananda Murthy,[†,‡] **K. Kishore,***[,†] **and V. Krishna Mohan**[‡]

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India, and IDL—Nitro Nobel Basic Research Institute, Sankey Road, Malleswaram, Bangalore 560 003, India

Received January 27, 1994; Revised Manuscript Received May 6, 1994[®]

ABSTRACT: We describe the use of poly(α-methylstyrene peroxide) (PαMSP), an alternating copolymer of α-methylstyrene and oxygen, as initiator for the radical polymerization of vinyl monomers. Thermal decomposition of PαMSP in 1,4-dioxane follows first-order kinetics with an activation energy (E_a) of 34.6 kcal/mol. Polymerization of methyl methacrylate (MMA) and styrene using PαMSP as an initiator was carried out in the temperature range 60–90 °C. The kinetic order with respect to the initiator and the monomer was close to 0.5 and 1.0, respectively, for both monomers. The E_a for the polymerization was 20.6 and 22.9 kcal/mol for MMA and styrene, respectively. The efficiency of PαMSP was found to be in the range 0.02–0.04. The low efficiency of PαMSP was explained in terms of the unimolecular decomposition of the alkoxy radicals which competes with primary radical initiation. The presence of peroxy segments in the main chain of PMMA and polystyrene was confirmed from spectroscopic and DSC studies. $R_i'/2I$ values for PαMSP compared to that of BPO at 80 °C indicate that PαMSP can be used as an effective high-temperature initiator.

Introduction

Polymeric peroxides,[1–4] although long known, have not been studied extensively with regard to their initiating characteristics in vinyl polymerization unlike simple organic peroxides. Compared to conventional peroxides, the polyperoxides have been shown to produce comblike polymers[5] and interpenetrating networks.[6] Besides, the macromolecular nature of the initiator significantly influences both the molecular weight and the molecular weight distribution of the resulting polymer.[7] One of the main advantages of the polymeric initiators is that one can incorporate an initiator segment in the main polymer chain so that they could be converted into macroradicals under suitable conditions for further initiation of the polymerization to prepare block copolymers.[8,9]

Among the polymeric initiators[10,11] studied, most are obtained by condensation, e.g., polymeric acid peroxides obtained from dibasic organic acids.[12] Another class of polyperoxides is the alternating copolymers of vinyl monomers and oxygen, which are of interest due to special features such as the highly exothermic nature[13] of their primary degradation, the unusual phenomenon of autopyrolysis[14] and its implication in developing special fuel systems,[15] and their role in explaining the paradoxical effect of oxygen in vinyl polymerization.[16] In the present investigation we examine their role as initiators for radical polymerization. This problem has been little studied previously.[17–19]

Here we investigate the use of poly(α-methylstyrene peroxide) (PαMSP), an alternating copolymer of α-methylstyrene and oxygen,[20] as a free radical initiator for methyl methacrylate (MMA) and styrene polymerization, the main emphasis being on the kinetics of this process.

Experimental Section

Materials. α-Methylstyrene, styrene, and MMA were freed of inhibitor by washing with 5% NaOH solution and then with water several times. After drying over anhydrous Na_2SO_4, they were distilled under reduced pressure. Azobis(isobutyronitrile) was recrystallized twice from methanol. The solvents used were purified by standard procedures.[21]

Synthesis of PαMSP. Freshly distilled α-methylstyrene (40 mL) and AIBN (0.01 M) were placed in a 450 mL Parr reactor and pressurized to 50 psi with oxygen. The polymerization was carried out at 50 °C with stirring for 20 h and the polyperoxide was precipitated from the reaction mixture using methanol. PαMSP thus obtained was purified by repeated precipitation from benzene solution. The yield was 35%.

Characterization of PαMSP. The IR spectrum was recorded on a Bruker IFS-85 FT-IR spectrometer. ^1H spectra were recorded on a Bruker AC-F 200 MHz spectrometer in $CDCl_3$. The chemical shifts are reported in ppm with reference to tetramethylsilane. Thermal analysis was done on a Perkin-Elmer DSC-2C differential scanning calorimeter at heating rates of 2.5, 5, 10, and 20 °C/min. The temperature axis and the enthalpy were calibrated using indium. The molecular weight of PαMSP was obtained using a Waters ALC/GPC 244 instrument with THF as a mobile phase at 25 °C, using polystyrene standards.

Decomposition Kinetics of PαMSP. The thermal decomposition of PαMSP was studied in 1,4-dioxane (1×10^{-3} mol-equiv/L) in sealed glass ampules at 70, 80, 86, and 90 °C. The reaction mixture was directly analyzed on a Hitachi 557 double-beam UV spectrophotometer for absorption at 272 nm, corresponding to the $\pi \rightarrow \pi^*$ transition in acetophenone.

Low-Conversion Polymerization. Bulk polymerization and solution polymerization (in toluene) of MMA and styrene were carried out in evacuated and sealed ampules. The polymers were precipitated using methanol as nonsolvent, and further purified by repeated precipitation from chloroform solution, and dried under vacuum at ambient temperature. Conversions were generally kept below 15% for reliable kinetic analysis. Rate (R_p) and average degree of polymerization ($\bar{P}_n$) were calculated from the conversion–time data and dilute solution viscosity measurements, respectively. $\bar{P}_n$ values were obtained using the following empirical equations (in benzene at 30 °C):[22,23]

$$\text{PMMA:} \quad [\eta] = 5.2 \times 10^{-3} \bar{P}_n^{\,0.76} \tag{1}$$

$$\text{polystyrene:} \quad [\eta] = 4.61 \times 10^{-3} \bar{P}_n^{\,0.73} \tag{2}$$

Results and Discussion

Characterization of PαMSP. The $\bar{M}_n$ and $\bar{M}_w$ of PαMSP were found to be 5300 and 8700, respectively.

[†] Indian Institute of Science.

[‡] IDL—Nitro Nobel Basic Research Institute.

[®] Abstract published in *Advance ACS Abstracts,* October 1, 1994.

0024-9297/94/2227-7109$04.50/0

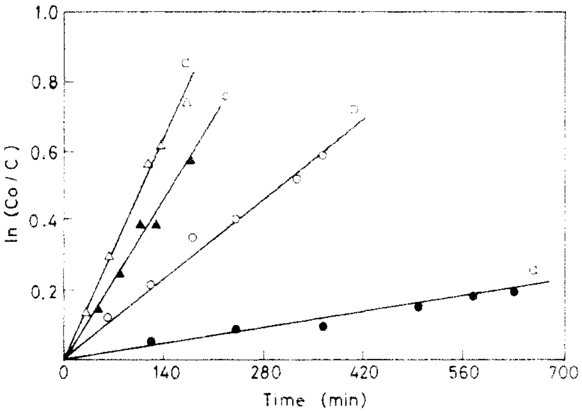

Figure 1. First-order plot for the thermal decomposition of PαMSP in 1,4-dioxane: (a) 70, (b) 80, (c) 86, and (d) 90 °C.

The ^{1}H NMR spectrum of PαMSP in CDCl$_3$ showed resonance signals at 7.2, 4.16, and 1.46 ppm, which were assigned to the aromatic, methylene, and methyl protons, respectively. The IR spectrum showed all the characteristic absorptions of the repeat unit.[20] These results confirm the 1:1 alternating copolymeric structure of PαMSP.

Thermal Decomposition of PαMSP. DSC thermograms reveal a highly exothermic degradation for PαMSP; the average enthalpy of decomposition, ΔH_d, at various heating rates (ϕ) was found to be 254 cal/g. From the peak temperatures (T_m), using Kissinger's plot, the E_a value for the decomposition was found to be 35 kcal/mol, which compares well with the dissociation energy of the O–O bond in dialkyl peroxides.[24]

The decomposition of PαMSP in 1,4-dioxane was followed by measuring the UV absorption of acetophenone, which is one of the two major products of its primary degradation.[20] The decomposition followed first-order kinetics. The plot of $\ln(C_0/C)$ versus time is given in Figure 1; the rate constant (k_d) was determined from the slope. From an Arrhenius plot, the activation energy (E_a) was found to be 34.6 kcal/mol, which matches with the value reported by Mayo et al.[20] Thus, it may be seen that the decomposition of PαMSP in its neat form as well as in solution follows the same activation process, which is consistent with literature reports.[18,25]

Kinetics of Low-Conversion Polymerization. PαMSP was utilized as a free radical initiator for the polymerization of MMA and styrene. Conversions were generally kept below 15% for the reliable analysis of the kinetic results. R_p values were calculated by subtracting the purely thermal rates of polymerization.

The rates of initiation (R_i) and polymerization (R_p) in a free radical polymerization are given by[26-28]

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

$$R_p = k_p[\mathrm{M}](fk_d[\mathrm{I}]/k_t)^{0.5} \tag{4}$$

where [M] and [I] are the monomer and initiator concentrations; k_d, k_p, and k_t are the rate constants, respectively, for the decomposition of peroxy groups, chain propagation, and termination; and f is the initiator efficiency. Conversion versus time curves for the bulk polymerization of MMA and styrene using PαMSP as initiator are given in Figures 2 and 3, respectively. For comparison, the conversion–time plot for the bulk polymerization of MMA at 60 °C using benzoyl peroxide (BPO) as initiator is provided in Figure 2. From the Arrhenius plot of R_p, obtained from the time–conversion data, the overall E_a for the polymerization process using PαMSP as initiator was 20.6 and 22.9 kcal/mol for MMA and styrene, respectively. The rates of polymerization of MMA and styrene are nearly proportional to the first power of the monomer concentration and the square root of the initiator concentration, indicating the usual bimolecular termination. Figure 4 shows the effect of PαMSP concentration on R_p at 80 °C. The overall polymerization rate constants (k) for the bulk polymerization of MMA and styrene are given in Table 1. The k values indicate that PαMSP is ~6 times less efficient than BPO at 60 °C for both monomers.

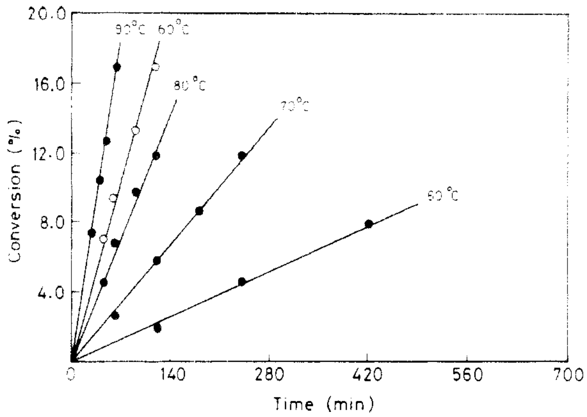

Figure 2. Conversion vs time plots for the bulk polymerization of MMA with PαMSP as initiator: (●) [PαMSP] = 0.02 mol-equiv/L; (○) [BPO] = 0.02 mol/L.

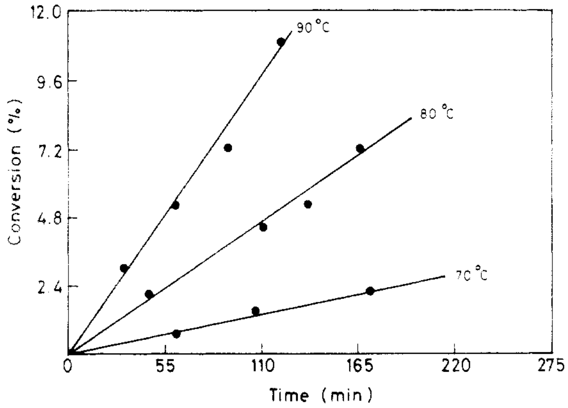

Figure 3. Conversion vs time plots for the bulk polymerization of styrene with PαMSP as initiator: [PαMSP] = 0.02 mol-equiv/L.

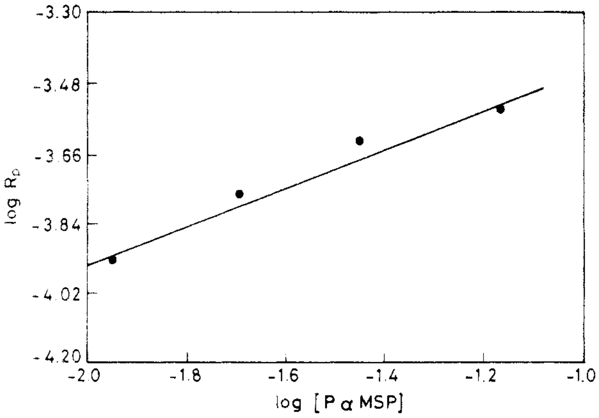

Figure 4. Dependence of R_p on PαMSP concentration for MMA polymerization at 80 °C.

The term $k_p^2(fk_d/k_t)$ is denoted as K^2 and is a measure of the initiator reactivity.[28] The values of K^2 can be obtained from the slope of the plot of R_p^2 versus $[\mathrm{M}]^2[\mathrm{I}]$ (Figures 5 and 6). For our system the K^2 were estimated

Table 1. Kinetic Parameters for the Bulk Polymerization of MMA Initiated by PαMSP

initiator	[I] (mol-equiv[a] L^{-1})	T (°C)	$R_p \times 10^5$ (mol L^{-1} s^{-1})	$k \times 10^5$ [b] (L$^{0.5}$ mol$^{-0.5}$ s^{-1})	E_a (kcal/mol)
			PMMA		
PαMSP	0.02	60	3.525	2.65	
	0.02	70	8.616	6.44	20.6
	0.02	80	17.468	13.14	
	0.02	90	48.020	36.12	
BPO	0.02	60	21.760	16.37	
			Polystyrene		
PαMSP	0.02	60	0.720	0.59	
	0.02	70	1.967	1.59	
	0.02	80	6.000	4.86	22.9
	0.02	90	12.510	10.11	
BPO[c]	0.026	60	5.750	4.07	

[a] 1 mol-equiv of peroxide is the equivalent weight of the repeat unit expressed in grams. [b] k is the overall rate constant. [c] From ref 27.

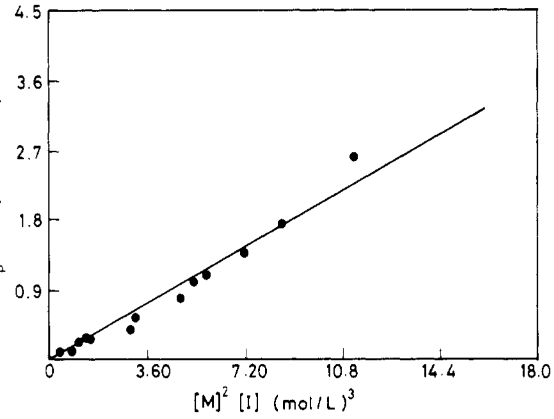

Figure 5. Plot of R_p^2 vs [M]^2[I] according to eq 4 for MMA polymerization in bulk at 80 °C initiated by PαMSP.

to be 2.41 × 10^{-8} and 3.6 × 10^{-9} L mol^{-1} s^{-2} for the bulk polymerization of MMA and styrene, respectively, at 80 °C (Tables 2 and 3).

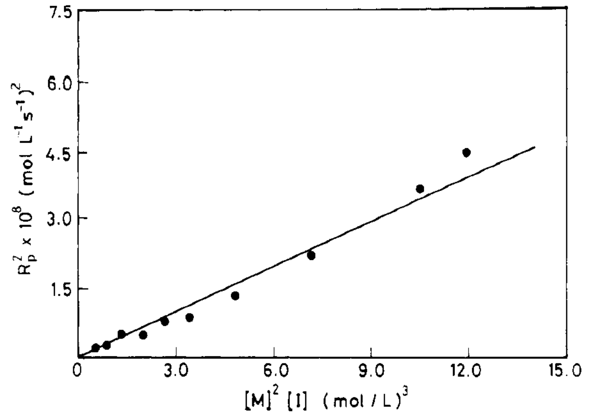

Figure 6. Plot of R_p^2 vs [M]^2[I] according to eq 4 for styrene polymerization in bulk at 80 °C initiated by PαMSP.

Table 2. Bulk Polymerization of MMA Initiated by PαMSP at 80 °C

run	[I] × 10^3 (mol-equiv L^{-1})	time (min)	conv (%)	$R_p \times 10^5$ (mol L^{-1} s^{-1})	$1/\bar{P}_n \times 10^4$
1	4.53	35	2.21	9.91	1.42
2	11.10	61	4.46	11.47	2.07
3	14.27	35	2.75	14.52	2.11
4	18.27	35	3.85	17.22	2.28
5	20.00	61	6.70	17.23	2.10
6	41.73	52	6.82	20.19	3.17
7	44.40	61	9.20	23.62	3.81
8	68.00	61	10.95	28.14	4.34
9	75.26	48	10.43	31.63	4.36
10	81.93	39	8.32	33.42	4.37
11	102.60	45	10.70	37.26	5.79
12	122.00	39	10.40	41.88	5.65
13	161.00	34	11.10	51.18	6.55
14	197.00	28	10.53	58.93	8.22

Table 3. Bulk Polymerization of Styrene Initiated by PαMSP at 80 °C

run	[I] × 10^3 (mol-equiv L^{-1})	time (min)	conv (%)	$R_p \times 10^5$ (mol L^{-1} s^{-1})	$1/\bar{P}_n \times 10^4$
1	7.00	97	2.97	4.46	2.88
2	12.00	77	2.73	5.16	3.32
3	19.10	90	4.44	7.19	3.39
4	28.40	50	2.52	7.34	4.72
5	38.50	80	4.84	8.81	5.06
6	50.00	62	4.00	9.41	5.64
7	71.00	50	3.94	11.47	7.10
8	106.00	47	4.75	14.73	6.64
9	155.60	35	4.55	18.96	11.33
10	177.30	38	5.52	21.17	13.61

In free radical polymerization, the average degree of polymerization ($\bar{P}_n$) is related to R_p by[26-28]

$$\frac{1}{\bar{P}_n} = C_M + C_S\frac{[S]}{[M]} + \frac{A'R_p}{[M]^2} + C_I\frac{R_p^{\ 2}}{K^2[M]^3} \qquad (5)$$

and

$$A' = \frac{2k_{td} + k_{tc}}{k_p^{\ 2}} \qquad (6)$$

where C_M, C_I, and C_S represent the chain transfer constants to monomer, initiator, and solvent, respectively. The quantity A' is a function of the monomer and the temperature of the reaction. For bulk polymerization $C_S = 0$, and if $C_I = 0$, a plot of $1/\bar{P}_n$ versus $R_p/[M]^2$ should coincide with the monoradical line. These plots are shown for MMA and styrene in Figures 7 and 8. The monoradical lines computed from literature values[28,29] are also included in these figures. In Figure 7 it is seen that the $1/\bar{P}_n$ versus $R_p/[M]^2$ curve for MMA deviates from the monoradical line, indicating chain transfer to the initiator. However, in the case of styrene (Figure 8), a similar plot roughly coincides with the monoradical line. The slope of this straight line was found to be 426, which compares well with the reported value[28] of 417, indicating thus the absence of chain transfer to the initiator. The intercept of these curves with the $1/\bar{P}_n$ axis gives C_M. For MMA and styrene, C_M values were found to be 3 × 10^{-5} and 6 × 10^{-5}, respectively which are in good agreement with reported values.[21]

The importance of A' lies in its role in relating the rate of initiation of polymer chains, R_i, to the rate of polymerization, R_p:

$$R_i(1 + x) = \frac{2A'R_p^{\ 2}}{[M]^2} \qquad (7)$$

$$\frac{R_i(1 + x)}{2I} = \frac{R_i'}{2I} = A'K^2 \qquad (8)$$

where x is the ratio of disproportionation to the overall termination and can vary between 0 and 1. Table 4 lists the values of K^2 and $R'_i/2I$ for PαMSP initiator for MMA and styrene polymerization. The values for di-*tert*-butyl peroxide (DTBP), 2,5-dimethyl-2,5-dihydroperoxyhexane (Luperox-2,5-2,5), and benzoyl peroxide (BPO) are also included in this table for comparison. It may be noted

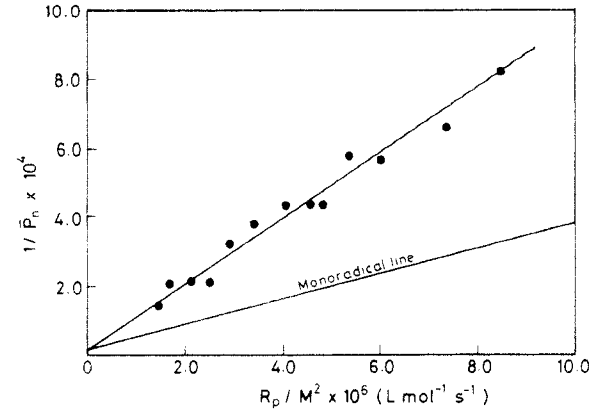

Figure 7. Plot of $1/\bar{P}_n$ vs $R_p/[M]^2$ according to eq 5 for MMA polymerization in bulk at 80 °C initiated by PαMSP.

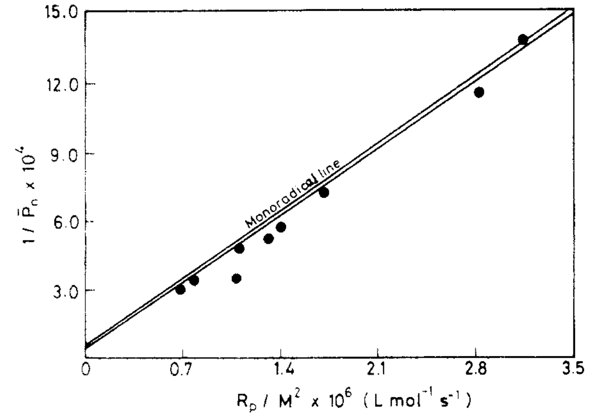

Figure 8. Plot of $1/\bar{R}_n$ vs $R_p/[M]^2$ according to eq 5 for styrene polymerization at 80 °C initiated by PαMSP.

Table 4. Polymerization of MMA and Styrene with Various Initiators at 80 °C

monomer	initiator	K^2 (L mol^{-1} s^{-2})	$R_i'/2I$ (s^{-1})	ref
MMA	PαMSP	2.40×10^{-8}	8.91×10^{-7}	this work
	BPO	1.34×10^{-6}	4.96×10^{-5}	28, 33
	Luperox 2,5-2,5[a]	1.77×10^{-8}	6.55×10^{-7}	34
	DTBP[b]	4.71×10^{-10}	1.74×10^{-8}	35
styrene	PαMSP	3.60×10^{-9}	1.50×10^{-6}	this work
	BPO	1.10×10^{-7}	4.59×10^{-5}	28, 33
	Luperox 2,5-2,5[a]	6.00×10^{-9}	2.50×10^{-6}	34
	DTBP[b]	1.93×10^{-10}	8.06×10^{-8}	35

[a] 2,5-Dimethyl-2,5-dihydroperoxyhexane. [b] Di-*tert*-butyl peroxide, at 70 °C.

that Luperox-2,5-2,5 has two peroxy bonds per molecule; therefore, the $R_i'/2I$ value must be divided by 2 for comparison. In the case of PαMSP, 1 mol-equiv of peroxide is the equivalent weight of the repeat unit expressed in grams. Such a comparison indicates that PαMSP could be used as an effective high-temperature initiator for radical polymerization.

Initiator Efficiency. The f values have been calculated from the k_d values using eq 4. The f values (Table 5) obtained are very low and are in the range 0.02–0.04. Such a low efficiency has been reported for styrene polymerization using poly(styrene peroxide) as initiator.[18] The reason for the very low efficiency in the case of PαMSP can be explained as follows.

The β-peroxyalkoxy radicals formed by the homolytic cleavage of the peroxy bonds in PαMSP can undergo facile unzipping forming acetophenone and formaldehyde[20] or combine with a monomer for polymerization. A quantum yield of 21 for the photolysis of PαMSP both in benzene and in α-methylstyrene (a good radical scavenger) indicates that the unzipping of alkoxy radicals will be rapid even in the presence of a monomer.[20] The gas chromatogram of the methanol filtrate confirmed the presence of acetophenone, indicating the simultaneous occurrence of primary radical initiation and unzipping of the alkoxy radicals. The latter process is energetically more favorable (85 kcal/mol) than the former (20 kcal/mol). Kinetically, too, the alkoxy radicals require a higher activation energy for addition to a double bond than to undergo unzipping.[30] The random scission of PαMSP and subsequent unzipping will significantly curtail the initiator efficiency.

Table 5. f Values at 80 °C for the Polymerization of MMA and Styrene Using PαMSP as Initiator[a]

monomer	[M] (mol/L)	[I] × 10^2 (mol-equiv L^{-1})	R_p × 10^5 (mol L^{-1} s^{-1})	f
MMA	7.26	2.00	13.23	0.029
	6.42	2.00	11.71	0.029
	5.57	2.00	11.01	0.034
	4.69	2.00	8.32	0.027
	8.35	1.11	11.47	0.029
	8.35	4.44	23.62	0.032
	8.35	6.80	28.14	0.029
	8.35	10.26	37.26	0.034
styrene	7.38	2.00	3.78	0.025
	5.74	2.00	2.56	0.020
	4.92	2.00	2.27	0.021
	8.20	1.73	4.08	0.029
	8.20	2.37	4.92	0.030
	8.20	3.44	6.87	0.040
	8.20	4.82	8.25	0.041

[a] k_d calculated from the Arrhenius equation: $k_d = 5.84 \times 10^{16} \exp(-17424/T)$.

The possibility of the local viscosity in reducing the initiator efficiency is considered now. The monomers (styrene and MMA) are good solvents for PαMSP. Moreover, the concentration of the initiator in the monomer is very low (<3 wt %). Thus, initiator chains being very short and somewhat extended in dilute solution, there is no reason for the radical chain end to experience a relatively different local environment from the average bulk. Further, the low initiator concentration also suggests that local viscosity and bulk viscosity are comparable.[31] Chains of more than 100 bonds are necessary to obtain a compact structure.[32] Only in such a situation will the chain end environment differ from the bulk. In the absence of such a compact structure, the trapping of the initiator radical chain end is ruled out, lest the observed initiator exponent should have been more than 0.5.[31] The experimental data summarized in Table 5 clearly show f to be independent of the initiator as well as the monomer concentrations. Hence, the low efficiency of PαMSP is most probably due to the unzipping of alkoxy radicals to nonradical products. Interestingly, the polymeric acid peroxides of comparable molecular weight and k_d values have much higher efficiencies (0.3 and above),[12] since the unzipping does not occur in this case.

The values of the rate constant for initiation $k_i(fk_d)$ for the bulk polymerization of MMA at different temperatures are given in Table 6. The activation energy (33.0 kcal/mol) calculated from the determined values of k_i corresponds to the activation energy required for O–O bond dissociation. Table 6 shows the temperature dependence of k_i for a given concentration of PαMSP. At lower temperatures, k_i exhibits the usual relationship with initiator concentration but at higher temperatures, k_i decreases with an increasing PαMSP concentration. The most plausible reason for this unusual behavior at higher temperatures could be attributed to the increased propor-

Table 6. k_i Values for the Bulk Polymerization of MMA Using PαMSP as Initiator

temp (°C)	polyperoxide ((mol-equiv $L^{-1})^{0.5}$)	$R_p \times 10^5$ (mol L^{-1} s^{-1})	$k_i \times 10^8$ (s^{-1})	
			calcd[a]	calcd[b]
60	0.10324	1.496	2.00	
	0.14140	2.214	1.53	2.43
	0.20298	3.019	2.11	
	0.21168	3.340	2.37	
70	0.10000	5.167	18.66	
	0.14140	7.333	18.80	20.43
	0.20000	10.023	17.55	
	0.24495	13.200	20.30	
80	0.10535	11.470	61.70	
	0.14140	17.213	77.00	56.70
	0.20980	23.620	65.97	
	0.26076	28.142	60.62	
90	0.08561	18.588	188.96	
	0.14140	32.908	217.00	161.54
	0.18760	45.040	231.04	
	0.26076	53.455	168.00	

[a] Calculated from eq 4. [b] Calculated from the plot of R_p vs $[M][I]^{0.5}k_p/k_t^{0.5}$.

tion of the decomposition of PαMSP leading to nonradical products. If it were due to a retarding effect of the decomposition products, i.e., acetophenone and formaldehyde, one would have seen the retardation at all temperatures. To further eliminate the possibility of retardation due to these products, separate experiments were carried out on the bulk polymerization of MMA initiated by PαMSP in the presence of acetophenone and formaldehyde at 80 °C. We did not observe any significant effect of these products.

Characterization of PMMA and Polystyrene Polymers. When a polyperoxide is used as an initiator, $\bar{M}_n$ of the polymer increases with conversion. This could be due to the polymerization–recombination mechanism,[8] and such a process will introduce peroxy segments at random positions in the main chain of the resulting polymer. Since β-peroxyalkoxy radicals in the case of PαMSP undergo facile unzipping forming nonradical products, a fairly high concentration of the initiator is required for introducing a perceptible amount of peroxy segments in the chain. In the present case we do not see any noticeable increase in $\bar{M}_n$ with conversion for both monomers at a low concentration of PαMSP (0.02 mol-equiv/L). This may be the reason for the coincidence of the monoradical line with the experimental data points in the case of styrene polymerization (Figure 8) at a PαMSP concentration below 0.2 mol-equiv/L.

To introduce sufficient peroxy segments in the chain, we have prepared polystyrene and PMMA using a PαMSP concentration of 0.2 mol-equiv/L and the "active" polymers thus obtained were freed of unreacted PαMSP by precipitating the polymers twice in petroleum ether/ethyl acetate (1:1) followed by methanol. The presence of peroxy segments in PMMA and polystyrene chains was confirmed by DSC and ^{1}H NMR studies. The former showed an exothermic peak between 90 and 150 °C, characteristic of PαMSP decomposition. Decomposition of these "active" polymers was carried out in chlorobenzene at 120 °C, and $\bar{M}_n$ values for the polymers before and after decomposition are given in Table 7. The relatively larger decrease of $\bar{M}_n$ in polystyrene compared to PMMA on decomposition may be due to the presence of more peroxy linkages in polystyrene. For a given concentration of PαMSP, more peroxy linkages are introduced in the chain when the termination occurs by combination.[8] In the case of styrene polymerization, termination by combination occurs to a larger extent in contrast to MMA, where it is predominantly by disproportionation. Hence, the decrease in $\bar{M}_n$ on account of O–O bond scission is more pronounced in polystyrene.

Table 7. Decomposition of PMMA and Polystyrene in Chlorobenzene at 120 °C[a]

polymer	[I] (mol-equiv L^{-1})	$\bar{M}_n$[b]	
		initial	after decomp
PMMA	0.2	247 000	229 000
polystyrene	0.2	167 300	113 500

[a] Reaction time 10 h. [b] $\bar{M}_n$ obtained from viscosity measurements.

Conclusions

The unique feature of PαMSP, like other similar polyperoxides obtained by the oxidative polymerization of a vinyl monomer and oxygen, is unimolecular decomposition of the alkoxy radicals formed by the thermal breakdown of the O–O bond. It is likely that this process is competing with primary radical initiation thereby decreasing the efficiency of PαMSP. In this investigation PαMSP shows a slower initiation at 80 °C compared to the conventional initiator BPO, suggesting that PαMSP could be used as a high-temperature initiator. Vinyl polymers containing "active" segments of peroxy groups in the main chain are attractive for preparing block copolymers by radical polymerization. The formation of PMMA and polystyrene containing active peroxy segments has been demonstrated here, and these materials may be useful for making block copolymers.

Acknowledgment. K.S.M. thanks the Management of IDL Chemicals Ltd. and Dr. G. D. Prasad, Chief Executive, INBRI Division, for sponsorship to the Ph.D. program.

References and Notes

(1) Hendry, D. G. *Encycl. Polym. Sci. Technol.* **1968**, *9*, 807.
(2) Bovey, F. A.; Kolthoff, I. M. *J. Am. Chem. Soc.* **1947**, *69*, 2143.
(3) Baysal, B. *Commun. Fac. Sci. Univ. Ankara* **1952**, *4B*, 57 (*Chem. Abstr.* **1954**, *48*, 9155i).
(4) Mukundan, T.; Kishore, K. *Prog. Polym. Sci.* **1990**, *15*, 475.
(5) Budtov, V. P.; Ivanchev, S. S.; Balyaev, V. M.; Romanova, O. S.; Otradina, G. A. *Vysokomol. Soedin., Ser. A.* **1976**, *18*, 2328 (*Chem. Abstr.* **1977**, *86*, 30114h).
(6) Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum Press: New York, 1981.
(7) Ivanchev, S. S.; Uvarova, L. R.; Matveyentseva, M. S.; Zyatkov, I. P. *Vysokomol. Soedin.* **1983**, *A25*, 1838 (*Chem. Abstr.* **1984**, *100*, 7269m).
(8) Kuchanov, S. I. *Usp. Khim.* **1991**, *60*, 1346 (*Chem. Abstr.* **1991**, *115*, 208631g).
(9) Hazer, B.; Baysal, B. M. *Polymer* **1986**, *27*, 961.
(10) Simonescu, C. I.; Comanita, E.; Pastravanu, M.; Dumitriu, S. *Prog. Polym. Sci.* **1986**, *12*, 1.
(11) Nyuken, O.; Weidner, R. *Adv. Polym. Sci.* **1986**, *73*, 145.
(12) Tsvetkov, N. S.; Zhukovskii, V. Ya.; Markovskaya, R. F.; Prieto, E. F. *Vysokomol. Soedin.* **1983**, *A25*, 1478 (*Chem. Abstr.* **1983**, *99*, 122983n).
(13) Kishore, K.; Ravindran, K. *Macromolecules* **1982**, *15*, 1638.
(14) Kishore, K.; Mukundan, T. *Nature* **1986**, *324*, 130.
(15) Mukundan, T.; Annakutty, K. S.; Kishore, K. *Fuel*, in press.
(16) Bhanu, V. A.; Kishore, K. *Chem. Rev.* **1991**, *91*, 99.
(17) Mukundan, T.; Bhanu, V. A.; Kishore, K. *J. Chem. Soc., Chem. Commun.* **1989**, *12*, 780.
(18) Zikmund, L. *Collect. Czech. Chem. Commun.* **1972**, *37*, 2911.
(19) Razuvaev, G. A.; Boguslavskaya, L. S.; Barabashina, R. A. *Zh. Org. Khim.* **1972**, *8*, 1601 (*Chem. Abstr.* **1973**, *78*, 4579d).
(20) Mayo, F. R.; Miller, A. A. *J. Am. Chem. Soc.* **1958**, *80*, 2480.
(21) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1988.
(22) Brandrup, J.; Immergut, E. H., Eds. *Polymer Handbook*, 1st

ed.; Interscience: New York, 1967; Chapter IV, p 26.
(23) Mayo, F. R.; Gregg, R. A.; Matheson, M. S. *J. Am. Chem. Soc.* **1951**, *73*, 1651.
(24) Scott, G. *Atmospheric Oxidations and Antioxidants*; Elsevier: London, 1965; p 37.
(25) Sawada, H. *Thermodynamics of Polymerization*; Dekker: New York, 1976; p 321.
(26) Mayo, F. R.; Gregg, R. A.; Matheson, M. S. *J. Am. Chem. Soc.* **1951**, *73*, 1651.
(27) Baysal, B. M.; Tobolsky, A. V. *J. Polym. Sci.* **1952**, *8*, 529.
(28) Tobolsky, A. V.; Baysal, B. M. *J. Polym. Sci.* **1953**, *11*, 471.
(29) Ferington, T. E.; Tobolsky, A. V. *J. Polym. Sci.* **1955**, *16*, 536.
(30) Mayo, F. R. *J. Am. Chem. Soc.* **1958**, *80*, 2465.
(31) (a) North, A. M.; Reed, G. A. *Trans. Faraday Soc.* **1961**, *57*, 859. (b) North, A. M. In *Progress in High Polymers*; Robb, J. C.,Peaker, F. W., Eds.; CRC Press: Cleveland, OH, 1968; Vol. 2, p 95.
(32) (a) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience Publishers: New York, 1969; p 2. (b) Flory P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; pp 605–611.
(33) Tobolsky, A. V.; Mesrobian, R. B. *Organic Peroxides*; Interscience: New York, 1954; p 147.
(34) Baysal, B. M.; Bayramli, E.; Yuruk, H.; Hazer, B. *Makromol. Chem.* **1985**, *186*, 1269.
(35) Offenbach, J. A.; Tobolsky, A. V. *J. Am. Chem. Soc.* **1957**, *79*, 258.