A Novel (Main Chain)−(Side Chain) Polymeric Peroxide: Synthesis and Initiating Characteristics of Poly(α-(*tert*-butylperoxymethyl)styrene peroxide)

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ABSTRACT: A novel (main chain)−(side chain) vinyl polyperoxide, poly(α-(*tert*-butylperoxymethyl)styrene peroxide) (MCSCPP), an alternating copolymer of α-(*tert*-butylperoxymethyl)styrene (TPMS) and oxygen, has been synthesized by the oxidative polymerization of TPMS. The MCSCPP was characterized by ^{1}H NMR, ^{13}C NMR, IR, DSC, EI-MS, and GC-MS studies. The overall activation energy (E_a) for the degradation of MCSCPP was found to be 27 kcal/mol. Formaldehyde and α-(*tert*-butylperoxy)acetophenone (TPAP) were identified as the primary degradation products of MCSCPP; TPAP was found to undergo further degradation. The side chain peroxy groups were found to be thermally more stable than those in the main chain. Polymerization of styrene in the presence of MCSCPP as initiator, at 80 °C, follows classical kinetics. The presence of peroxy segments in the polystyrene chain was confirmed by both ^{1}H NMR and thermal decomposition studies. Interestingly, unlike other vinyl polyperoxides, the MCSCPP initiator shows an increase in molecular weight with conversion.

Introduction

Compared to conventional low molecular weight peroxides, the polymeric peroxide initiators have been found to significantly influence both the molecular weight and the molecular weight distribution of the resulting polymers. In addition, they can produce block copolymers, comblike polymers, interpenetrating polymer networks, etc.[1,2] Vinyl polyperoxides,[3,4] which are alternating copolymers of oxygen and vinyl monomers, are of current interest due to special features such as the highly exothermic nature of their degradation,[5] the unusual phenomenon of autopyrolysis,[6] their role in explaining the paradoxical effects of oxygen in vinyl polymerization,[7] and their use in developing special fuels.[8] They have also been investigated for their role as initiators.[9,10]

Ordinarily, the rate of polymerization increases with an increase in the concentration of the initiator, but the molecular weight decreases. This undesirable effect can be overcome by employing nontraditional initiators such as polyfunctional initiators.[1] Use of acid polyperoxides as initiators leads to not only an increase in the molecular weight with conversion but also a narrowing of the molecular weight distribution.[11] Among acid polyperoxides, those with peroxide groups of varying thermal stability were found to be more suitable for this purpose.[1,2] Vinyl polyperoxides, except for poly(butadiene peroxide),[12] being significantly less hazardous, are preferred over acid polyperoxides. Hence, vinyl polyperoxides, having peroxide groups of different thermal stabilities, could be more attractive as initiators than the corresponding acid polyperoxides; however, they do not show much difference in the stability of the peroxy linkages.[13] It was therefore decided to introduce the peroxy group in the monomer so that it would result in a polyperoxide having both main chain and side chain peroxide linkages differing substantially in thermal stability. Hitherto there is no report on the synthesis of such (main chain)−(side chain) vinyl polyperoxides.

We present here the first report on the synthesis and characterization of poly(α-(*tert*-butylperoxymethyl)styrene peroxide), an alternating copolymer of α-(*tert*-butylperoxymethyl)styrene and oxygen. Its use as radical initiator for styrene polymerization has also been examined.

Experimental Section

Materials. Styrene and α-methylstyrene were freed of inhibitor by washing with dilute NaOH solution and distilled under vacuum. Reagent grade solvents were used after distillation. The initiator, 2,2′-azobis(isobutyronitrile) (AIBN), was recrystallized twice from methanol. *N*-Bromosuccinimide (NBS) (Loba-Chemie, India) and *tert*-butyl hydroperoxide (70%) (Fluka) were used as received.

Synthesis of α-(*tert*-Butylperoxymethyl)styrene. α-(Bromomethyl)styrene was prepared according to the reported procedure,[14] but it contained 40% 1-bromo-2-phenylpropene. Since the removal of the desired monomer is generally difficult, the isomer mixture was used as such for synthesizing α-(*tert*-butylperoxymethyl)styrene (TPMS) as follows.

A mixture of *tert*-butyl hydroperoxide (70%) (5.00 g, 0.039 mol), NaOH (1.68 g, 0.042 mol), benzene (15 mL), and tetrabutylammonium bromide (0.4 g) was stirred for 15 min at room temperature. The α-(bromomethyl)styrene (60%) (10.0 g, 0.029 mol) was slowly added to the mixture over a period of 30 min and further stirred at room temperature for 4 h. The reaction was monitored by TLC; it was observed that the desired isomer reacted preferentially. The reaction mixture after solvent removal was chromatographed on a silica gel (60−120 mesh) column, initially eluting with petroleum ether/benzene (95:5) to remove the unreacted materials and later with petroleum ether/benzene (50:50) to obtain pure TPMS. The yield, based on α-(bromomethyl)styrene, was 57%.

Synthesis of Poly(α-(*tert*-butylperoxymethyl)styrene peroxide). TPMS (28.0 mL), benzene (10.0 mL), and AIBN (0.013 M) were placed in a 450 mL Parr reactor and pressurized to 250 psi with oxygen. The polymerization was carried out at 50 °C with stirring for 15 h. After the solvent was removed, the reaction mixture was chromatographed on a silica gel (60−120 mesh) column using benzene/CHCl$_3$ (3:1) as the eluent initially, followed by diethyl ether to obtain poly(α-(*tert*-butylperoxymethyl)styrene peroxide) (MCSCPP). The conversion, based on TPMS, was 11%.

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Table 1. E_a, k_d, and DSC Peak Temperature Values for MCSCPP, TPMS, and PMSP

peroxide	E_a (kcal/mol)	DSC peak temp^a (K)	$k_d \times 10^6$ (s^{-1})	$t_{0.5}{}^b$ (h)	ref
MCSCPP	26.9	415			this work
TPMS	23.0	429	3.22	60	21
PMSP	35.0	393	21.37	9	9

[a] At a heating rate of 10 °C/min. [b] At 80 °C.

Techniques. ^1H and ^{13}C NMR spectra, in $CDCl_3$, were recorded on a Bruker ACF 200 MHz spectrometer using tetramethylsilane as internal standard. IR spectra were recorded on a Perkin-Elmer model 780 spectrometer. Thermal analysis was done on a Perkin-Elmer DSC-2C differential scanning calorimeter at heating rates of 5, 10, 20, and 40 °C/min. The temperature axis and the enthalpy were calibrated using indium. The purity of TPMS was estimated by iodimetry.

The molecular weight of MCSCPP was estimated by GPC (Waters, RI detector) using μ-Styragel columns at 42 °C. Toluene was used as a solvent at a flow rate of 1 mL/min. The GPC instrument was calibrated using standard polystyrene samples. Electron impact mass spectrometry (EI-MS) analysis (70 eV) was carried out on a Shimadzu QP 1100EX mass spectrometer at a heating rate of 20 °C/min. The GC-MS data were obtained on a Shimadzu QP-2000 instrument at 70 eV using an Ulbon HR1 fused silica capillary column (0.25 mm × 50 m). Helium was used as a carrier gas at a flow rate of 2 mL/min. The column was initially maintained at 100 °C for 6 min and then heated at a rate of 5 °C/min to 250 °C.

Low-Conversion Styrene Polymerization. Bulk and solution polymerizations (in toluene) of styrene in the presence of MCSCPP as initiator were carried out at 80 °C in evacuated and sealed ampules. The polymers were precipitated and purified from benzene solution using methanol as nonsolvent and finally dried under vacuum to constant weight. The rate of polymerization (R_p) and average degree of polymerization ($\overline{DP}_n$) were calculated from the conversion−time data and dilute solution viscosity measurements, respectively. $\overline{DP}_n$ values for polystyrene were obtained using the following empirical equation (in benzene at 30 °C):[15]

$$[\eta] = 4.61 \times 10^{-3}\, \overline{DP}_n{}^{0.73} \qquad (1)$$

Results and Discussion

Characterization of MCSCPP. MCSCPP, an alternating copolymer of TPMS and oxygen, was synthesized by copolymerizing TPMS with oxygen (250 psi) in the presence of AIBN initiator at 50 °C. The MCSCPP was separated from the reaction mixture by column chromatography as a yellow viscous liquid; $\bar{M}_w$ and $\bar{M}_n$ were found to be 1800 and 1200, respectively. The solubility in methanol and petroleum ether could be attributed to the very low molecular weight of the polymer. Generally, vinyl polyperoxides have low molecular weight[3,4] ($\bar{M}_n = 300-5000$) due to various chain transfer reactions occurring during the oxygen copolymerization; in the present case, the low molecular weight could also be due to the allylic nature of the monomer.

The IR spectrum of MCSCPP showed characteristic absorptions at 3050 and 2980 cm^{-1} corresponding to aromatic C−H and aliphatic C−H stretching, respectively; a 1600 cm^{-1} band was assigned to ring carbon stretching, and a doublet at 1385 and 1370 cm^{-1} was assigned to the *tert*-butyl group. A peak at 1190 cm^{-1} is due to C−C−O stretching. Bands at 3400 and 1680 cm^{-1} were assigned respectively to the stretching of hydroxy and aromatic carbonyl groups present at the chain ends. Similar end groups have been observed in poly(styrene peroxide)[16] and poly(α-methylstyrene peroxide) (PMSP).[17]

The ^1H NMR of MCSCPP showed signals at 7.2−7.5, 4.2−4.5, and 1.13 ppm corresponding to aromatic protons (5H), methylene protons (4H) attached to oxygen, and methyl protons (9H) of the *tert*-butyl group, respectively. The methyl protons of the *tert*-butyl group, which appeared at 1.23 ppm for TPMS,[18] appear upfield at 1.13 ppm for MCSCPP. Two further low-intensity peaks at 8.1 and 1.16 ppm were assigned to the ortho protons (benzoyl) and methyl protons of the *tert*-butyl group, respectively; they could be present in the end groups.

The ^{13}C NMR spectrum of MCSCPP showed signals at 125−129, 138.1, 85.9, 80.2, and 79.6, 75.1, and 26 ppm; they were assigned to aromatic, aromatic ipso, quaternary ($C_6H_5\mathit{C}(CH_2)_2(O)$), methylene, quaternary (-$\mathit{C}(CH_3)_3$), and methyl carbons of the *tert*-butyl group, respectively. These assignments were made on the basis of the ^{13}C NMR chemical shifts of PMSP[19] and TPMS.[20] Low-intensity peaks at 133.5, 130, and 171 ppm were also seen; they were assigned to the aromatic protons and carbonyl group, which could be present in the end groups. These additional peaks support the ^1H NMR and IR data discussed above for the presence of the terminal benzoyl group.

Thermal Decomposition of MCSCPP. As for other vinyl polyperoxides, the DSC thermogram of MCSCPP shows a highly exothermic degradation. The average enthalpy of decomposition (ΔH_d) of MCSCPP, at various heating rates (Φ), was found to be 256 cal/g, which is comparable to the ΔH_d of other vinyl polyperoxides.[9,13] Also, this exothermic enthalpy is much higher than that of the starting monomer (124 cal/g).[21] From the peak temperatures (T_m), using Kissinger's plot, the overall activation energy (E_a) for the decomposition was found to be 26.9 kcal/mol, corresponding to the peroxy bond dissociation. The overall thermal stability of MCSCPP can be judged by comparing the E_a values and the DSC peak temperatures of MCSCPP, PMSP, and TPMS (Table 1); both values for MCSCPP fall between those for TPMS and PMSP. Table 1 also provides the rate constant for the decomposition (k_d) and

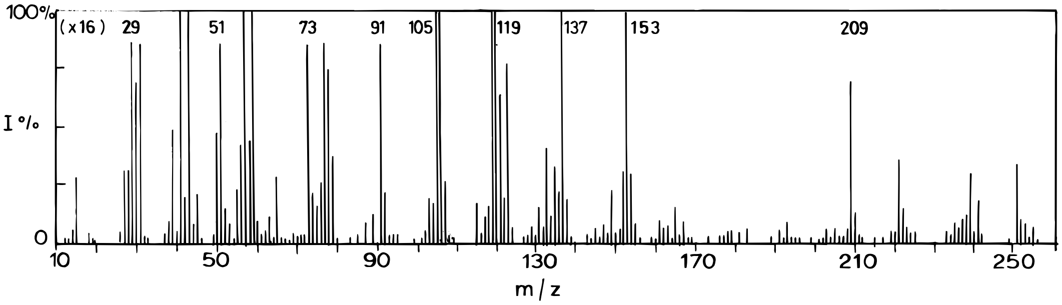
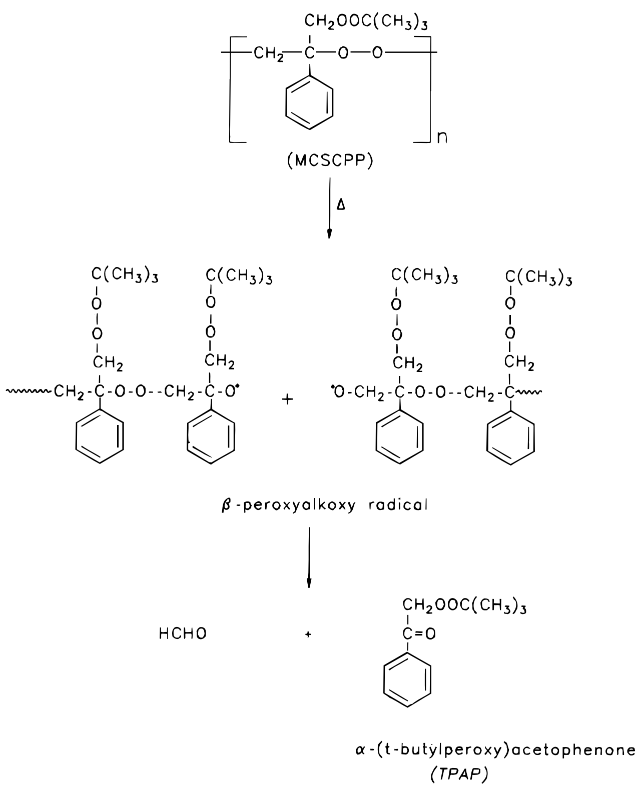


Figure 1. EI mass spectrum of MCSCPP.

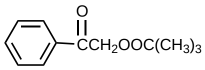
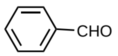
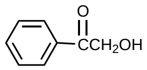
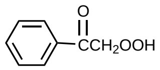
Scheme 1



half-life ($t_{0.5}$) for PMSP[9] and TPMS[21] at 80 °C, which suggest that the side chain peroxide group has a relatively higher thermal stability than the main chain peroxide in MCSCPP.

EI-MS Analysis of MCSCPP. EI-MS of MCSCPP, recorded at 70 eV, is shown in Figure 1. Formaldehyde (m/z 29, M − 1) and α-(*tert*-butylperoxy)acetophenone (TPAP) (m/z 209, M + 1) were identified as the major primary degradation products which are obtained as a result of random scission of the main chain peroxy bonds, followed by unimolecular decomposition of the β-peroxyalkoxy radicals[16] (Scheme 1). The formation of TPAP indicates that the side chain peroxy group is thermally more stable than that in the main chain. The peroxy ketone (TPAP), being thermally unstable, undergoes secondary degradation, giving many nonradical products.

Table 2. Structural Assignments in the EI Mass Spectrum of MCSCPP

m/z	product	structure
29[a]	formaldehyde	HCHO
209[b]	α-(*tert*-butylperoxy)acetophenone	
106	benzaldehyde	
137[b]	α-hydroxyacetophenone	
153[b]	phenacyl hydroperoxide	

[a] (M − 1) peak. [b] (M + 1) peak.

The secondary degradation products identified are benzaldehyde (m/z 106), α-hydroxyacetophenone (m/z 137, M + 1), and phenacyl hydroperoxide (m/z 153, M + 1)[22] (Table 2). Because of the secondary degradation, the mass spectrum is complex due to the mixing up of the molecular ions with the fragment ions. It may be noted here that many of the molecular ions are not detected in the EI-MS; instead, the protonated molecular ions (M + 1) are seen. The presence of such (M + 1) ions instead of the usual molecular ions has been observed in the EI-MS of poly(trimethylene carbonate).[23] The mechanism of formation of the secondary degradation products is given in Scheme 2. The formation of benzaldehyde and α-hydroxyacetophenone as the secondary degradation products was further confirmed by GC-MS analysis.

GC-MS Analysis of MCSCPP. The total ion chromatogram of the on-line GC-MS analysis of MCSCPP is given in Figure 2; the major peaks accounting for more than 80% of the degradation products are labeled. Mass spectra of the GC peaks 1−5 are given in Figure 3. The most intense GC peaks (Figure 2) are due to benzaldehyde (1), α-hydroxyacetophenone (2), *tert*-butyl benzoate (3), phenacyl *tert*-butyl ether (4), and α-benzoylacetophenone (5). The assignments for the first three of these compounds were confirmed by comparing with the published mass spectra of the authentic samples;[22] the remainder were identified by analyzing the fragmentation patterns.

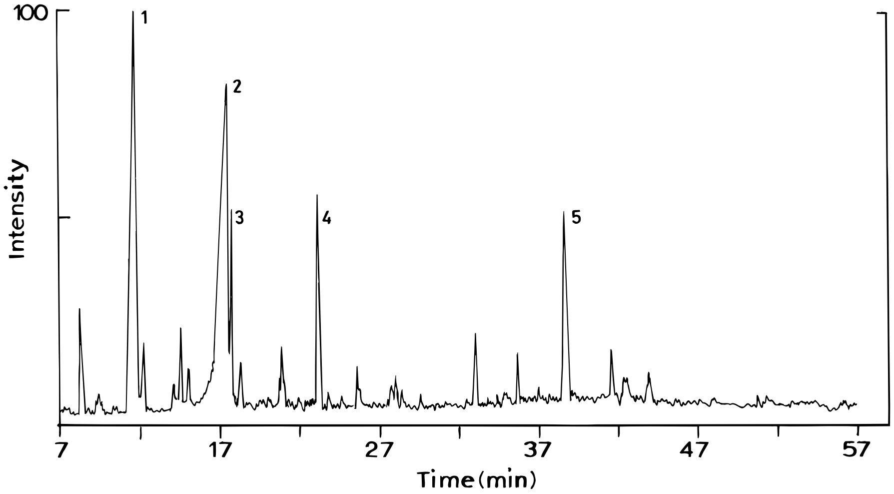
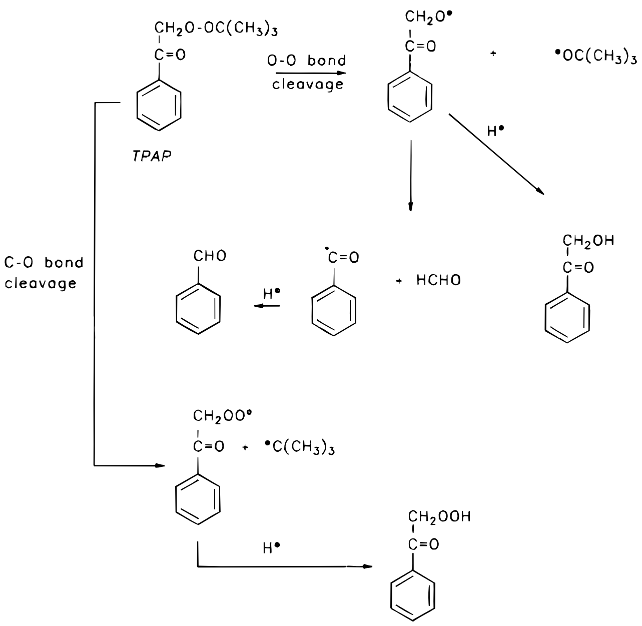


Figure 2. Total ion chromatogram of the on-line GC-MS analysis of the MCSCPP. The most intense peaks have been numbered; the corresponding mass spectra are given in Figure 3.

Scheme 2



The primary decomposition product, TPAP, which was observed in EI-MS, is not seen in the GC-MS chromatogram. This may be due to the relatively long residence time of the primary degradation products in the column (50 m) at relatively higher temperatures, resulting in secondary degradation. Also, the phenacyl hydroperoxide, which is one of the secondary degradation products, is not seen in the chromatogram due to its thermal instability. The GC-MS products of MCSCPP are primarily due to the secondary degradation of the TPAP as a result of cleavage of the peroxy bond, followed by further fragmentation through hydrogen transfer and recombination reactions.

The proposed mechanism for the formation of the products (labeled 3, 4, and 5 in Figure 2) as obtained by the GC-MS analysis is given in Scheme 3. The mechanism of formation of benzaldehyde and α-hydroxyacetophenone is already suggested in Scheme 2. The source of hydrogen is probably formaldehyde or benzaldehyde, which have been reported as good chain transfer agents.[24] The formation of α-benzoylacetophenone (Scheme 3) is explained through the breakage of the side chain C—O bond of TPAP followed by coupling with the benzoyl radical. The breakage of the side chain C—O bond is further supported by the formation of phenacyl hydroperoxide in the EI-MS of MCSCPP (Scheme 2).

Kinetics of Radical Polymerization of Styrene Using MCSCPP as Initiator. To study MCSCPP as an initiator, bulk and solution polymerizations of styrene were carried out in its presence at 80 °C. Polymerization proceeded without any induction time. Conversion was kept below 15% for reliable kinetic analysis. The rate of polymerization (R_p) calculated from the slope was 8.601×10^{-5} mol L^{-1} s^{-1}. The results of styrene polymerization at different initiator and monomer concentrations show that the rate of polymerization of styrene is nearly proportional to $[\text{monomer}]^1$ and $[\text{MCSCPP}]^{0.5}$

$$R_p = k[M]^{1.1}[I]^{0.51} \qquad (2)$$

where k, [M], and [I] respectively are the overall rate constant and the monomer and initiator concentrations.

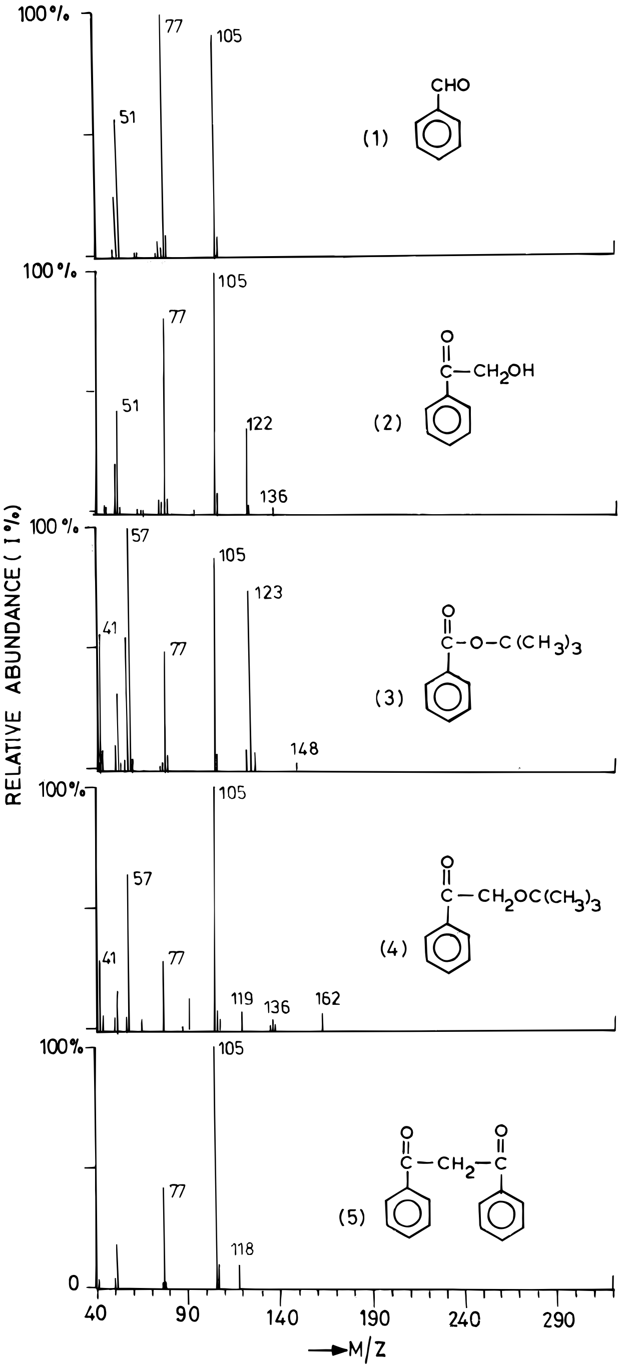


Figure 3. Mass spectra corresponding to the peaks labeled 1—5 in Figure 2.

The term $k_p^2(fk_d/k_t)$ is denoted as K^2 and is a measure of the initiator reactivity;[25] the terms have their usual meanings. K^2 was evaluated from the slope of the plot of R_p^2 versus $[M]^2[I]$ (Figure 4). For styrene polymerization using MCSCPP as initiator, the value of K^2 was estimated as 6.178×10^{-9} L mol^{-1} s^{-2}. In the case of MCSCPP, 1 mol equiv is the equivalent weight of the repeat unit, expressed in grams. MCSCPP has two peroxy bonds per repeat unit, and hence this value of K^2 has to be divided by 2 in order to get the average value of K^2 per mol of peroxy unit. The value thus obtained (3.089×10^{-9} L mol^{-1} s^{-2}) is comparable to those for PMSP (3.6×10^{-9} L $mol^{-1}s^{-2}$) and 2,5-dimethyl-2,5-dihydroperoxyhexane (6.00×10^{-9} L $mol^{-1}s^{-2}$).[9] The 2,5-dimethyl-2,5-dihydroperoxyhexane also has two peroxy bonds per molecule, and

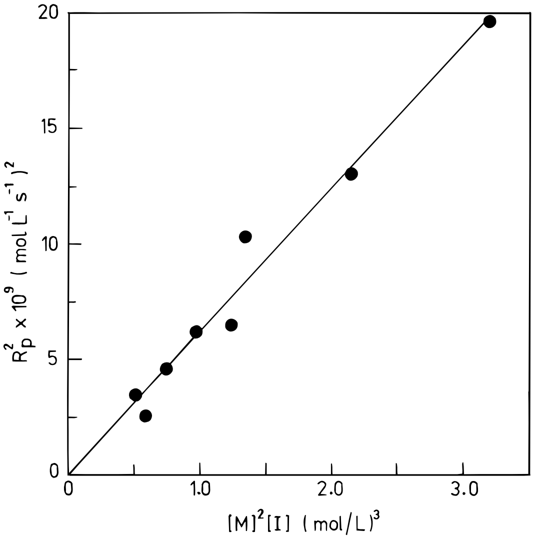
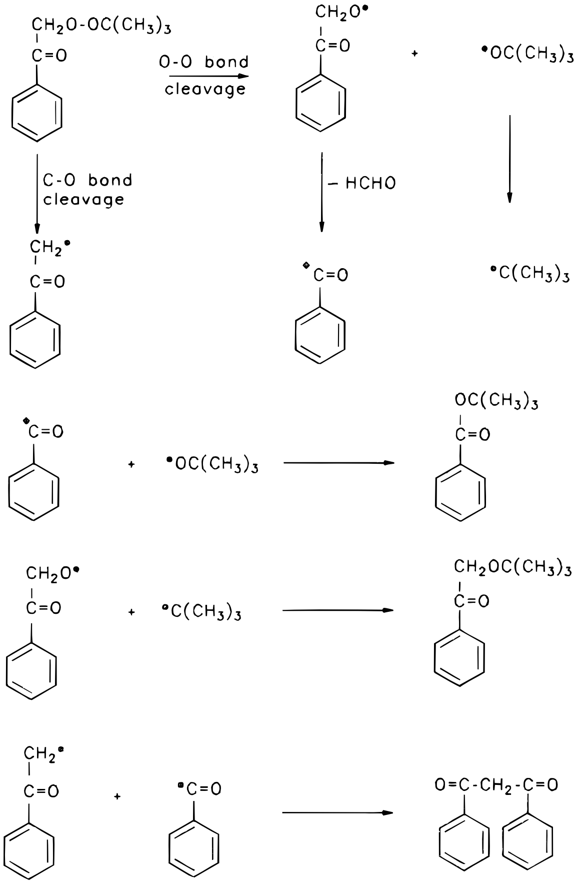


Figure 4. Plot of R_p^2 versus $[M]^2[I]$ for styrene polymerization at 80 °C, initiated by MCSCPP.

Scheme 3



hence the corresponding K^2 value has to be divided by 2 for comparison. Such a comparison indicates that MCSCPP may be used as a high-temperature initiator.

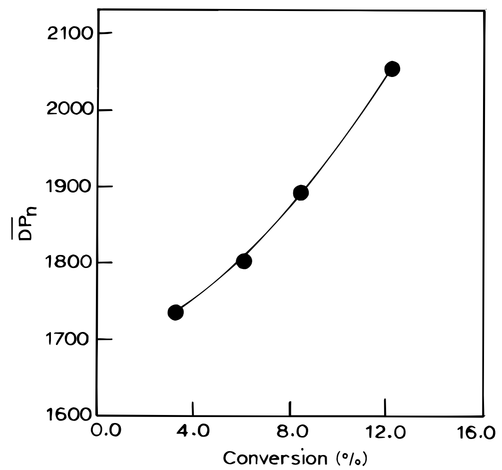


Figure 5. Plot of $\overline{DP}_n$ of polystyrene, prepared in the presence of MCSCPP (0.02 mol equiv/L) as initiator at 80 °C, versus conversion.

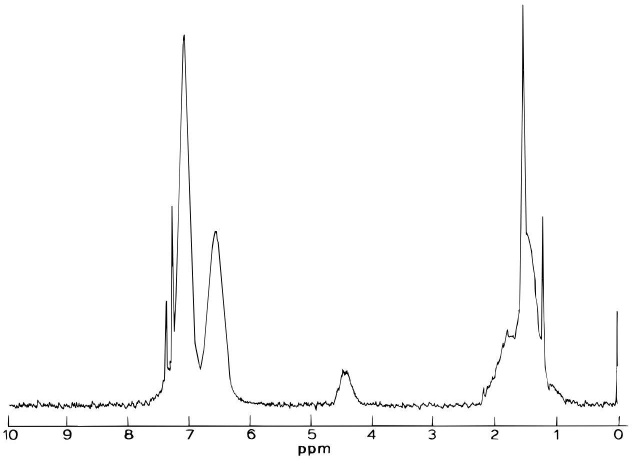


Figure 6. ^{1}H NMR spectrum (90 MHz) of polystyrene prepared using 0.24 mol equiv/L of MCSCPP.

Effect of Molecular Weight of Polystyrene on the Conversion. A common feature of radical polymerization in the presence of polyfunctinal initiators is the increase in the molecular weight with conversion due to the polymerization−recombination mechanism.[1] Vinyl polyperoxides, having peroxy groups of differing thermal stabilities, are also expected to show an increase in the molecular weight with conversion. Indeed, the plot of $\overline{DP}_n$ of PS, prepared using MCSCPP as initiator (0.02 mol equiv/L), versus conversion (Figure 5) showed an increase in $\overline{DP}_n$ with conversion. Such a process is also reported to bring about narrowing of polydispersity.[1]

Characterization of Polystyrene (PS). ^{1}H NMR of PS prepared using 0.02 mol equiv/L of MCSCPP did not clearly reveal the signals corresponding to the MCSCPP segments. To introduce sufficient peroxy segments in the chain, we have prepared PS using a MCSCPP concentration of 0.24 mol equiv/L. The final polymer was purified by repeated precipitation in methanol. The presence of peroxy segments in the resultant polymer chain was confirmed by both ^{1}H NMR and thermal decomposition studies. The ^{1}H NMR (Figure 6) of PS showed signals corresponding to MCSCPP segments. Decomposition of this "active" PS was carried out in chlorobenzene at 120 °C for 20 h, and $\overline{M}_n$ values before and after decomposition were found to be 45 400 and 34 600, respectively, confirming the incorporation of peroxy segments in the chain.

In the present study, we have carried out the polymerization of styrene at 80 °C, and we expect the resulting PS to have linear structure; a few branching PS segments may be present due to the initiation through the side chain peroxide groups, but such branched structures are more likely to form at higher temperatures.

Conclusions

MCSCPP having peroxy groups of different thermal stability in both the main chain and side chain has been synthesized by the oxidative polymerization of a peroxy group containing monomer (TPMS). Formaldehyde and α-(*tert*-butylperoxy)acetophenone have been identified as the primary degradation products of MCSCPP. The MCSCPP-initiated styrene polymerization followed classical kinetics, and an increase in the molecular weight of PS with conversion was also observed. The (main chain)−(side chain) vinyl polyperoxides, having labile groups of different thermal stability, appear to be more attractive than relatively hazardous acid polyperoxides for this purpose. Besides, by controlling the polymerization temperature, it is possible to retain a major proportion of side chain peroxy groups, which may be used subsequently at higher temperatures for making graft polymers.

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References and Notes

(1) Kuchanov, S. I. *Usp. Khim.* **1991**, *60*, 1346; *Chem. Abstr.* **1991**, *115*, 208631g.

(2) Simonescu, C. I.; Comanita, E.; Pastravanu, M.; Dimitriu, S. *Prog. Polym. Sci.* **1986**, *12*, 1.

(3) Kishore, K.; Shanmugananda Murthy, K. Vinyl polyperoxides (Oxygen copolymerization). In *The Polymeric Materials Encyclopedia: Synthesis, Properties and Applications*; Salamone, J. C., Ed.; CRC Press: New York (in press).

(4) Mukundan, T.; Kishore, K. *Prog. Polym. Sci.* **1990**, *15*, 475.

(5) Kishore, K.; Ravindran, K. *Macromolecules* **1982**, *15*, 1638.

(6) Kishore, K.; Mukundan, T. *Nature* **1986**, *324*, 130.

(7) Bhanu, V. A.; Kishore, K. *Chem. Rev.* **1991**, *91*, 99.

(8) Mukundan, T.; Annakutty, K. S.; Kishore, K. *Fuel* **1993**, *72*, 688.

(9) Shanmugananda Murthy, K.; Kishore, K.; Krishna Mohan, V. *Macromolecules* **1994**, *27*, 7109.

(10) Mukundan, T.; Bhanu,V. A.; Kishore, K. *J. Chem. Soc., Chem. Commun.* **1989**, *12*, 780.

(11) Ivanchev, S. S.; Uvarova, L. R.; Matveyentseva, M. S.; Zyatkov, I. P. *Vysokomol. Soedin.* **1983**, *A25*, 1838; *Chem. Abstr.* **1984**, *100*, 7269m.

(12) Alexander, D. S. *Ind. Eng. Chem.* **1959**, *51*, 733.

(13) Jayanthi, S. Ph.D Thesis, Indian Institute of Science, Bangalore, India, 1995.

(14) Pines, H.; Alul, H.; Kolobielsky, M. *J. Org. Chem.* **1957**, *22*, 1113.

(15) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*, 1st ed.; Interscience: New York, 1967; Chapter IV.

(16) Miller, A. A.; Mayo, F. R. *J. Am. Chem. Soc.* **1956**, *78*, 1017.

(17) Mayo, F. R.; Miller, A. A. *J. Am. Chem. Soc.* **1958**, *80*, 2480.

(18) Rizzardo, E.; Meijs, G. F.; Thang, S. H. *Polym. Prepr.* **1992**, *33*, 893.

(19) Shanmugananda Murthy, K.; Kishore, K.; Krishna Mohan, V. In *Macromolecules: Current Trends*;Venkatachalam, S., Joseph, V. C., Ramaswamy, R., Krishnamurthy, V. N., Eds.; Allied Publishers: New Delhi, India, 1995; Vol. 1, p 251.

(20) Shanmugananda Murthy, K.; Kishore, K. Unpublished results.

(21) Shanmugananda Murthy, K.; Kishore, K. *J. Polym. Sci., Polym. Chem.* (in press).

(22) Stenhagen, E., Abrahamson, S., McLafferty, F. W., Eds. *Registry of Mass Spectral Data*; John Wiley & Sons: New York, 1974.

(23) Montaudo, G.; Pugilisi, C.; Rapisardi, R.; Samperi, F. *Polym. Degr. Stab.* **1991**, *31*, 229.

(24) Cais, R. E.; Bovey, F. A. *Macromolecules* **1977**, *10*, 169.

(25) Tobolsky, A. V.; Baysal, B. M. *J. Polym. Sci.* **1953**, *11*, 471.

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