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Synthesis and Characterization of Tetrapolymers of Styrene, Methyl Methacrylate, α-Methylstyrene, and Oxygen

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ABSTRACT: This paper presents the first report on a terpolyperoxide (TPPE) synthesized by the oxidative terpolymerization of styrene, methyl methacrylate, and α-methylstyrene. TPPEs of different compositions were synthesized by varying the vinyl monomers feed, and they were then characterized by spectroscopic and thermal studies. The conventional terpolymer equation has been used to predict the composition of TPPEs. The ^{1}H NMR chemical shift values of TPPEs were found to vary with the composition. The shape of the backbone methylene protons (4.00−4.50 ppm) was found to be sensitive to the sequence distribution of vinyl monomers in the polymer chain. Formaldehyde, benzaldehyde, acetophenone, and methyl pyruvate were identified as the primary degradation products. The overall thermal stability and the average enthalpy of degradation (ΔH_d), as obtained by thermogravimetric analysis and differential scanning calorimetry, respectively, do not vary much with the composition of TPPEs.

Introduction

Copolymerization and blending are commonly used to obtain polymers of desired properties. Due to adverse entropy effects, polymers are generally not miscible, and hence copolymerization offers a convenient way of incorporating different monomers in the polymer chain. It is possible to tailor-make polymers having wide variations in their properties by incorporating more monomers in the polymer chain. The problems associated with the synthesis of multicomponent polymers are the wide variations in the reactivity ratios of vinyl monomers and the difficulty in characterizing these polymers.

Here our interest is in the multicomponent polymers of vinyl monomers and oxygen, which fall under the broad area of vinyl polyperoxides[1,2] and which are attracting attention due to their technological potentials, including uses as special fuels,[3] initiators,[4,5] and curators in coatings and moulding applications.[6] Homopolyperoxides[7−9] and copolyperoxides[10,11] have been studied in some detail. Terpolyperoxides obtained by the simultaneous oxidative polymerization of three vinyl monomers and oxygen have not been reported. Terpolyperoxides can also be considered as tetrapolymers if oxygen is also considered as a monomer. There are few reports on the conventional tetrapolymer in the literature. Compared to that of conventional multicomponent polymers, characterization of multicomponent polymeric peroxides is relatively easier due to the long peroxide unit separating the vinyl monomers.[12] Another advantage is that the conventional terpolymer equation[13] can be used to predict the composition of the tetrapolymer of three vinyl monomers and oxygen. Formation of such polyperoxides is of interest in organic protective coatings applications,[14,15] where mixtures of monomers are commonly used, and in understanding the effect of oxygen in terpolymerization.

In this paper, we report the synthesis and characterization of the terpolyperoxides (TPPEs) of styrene, methyl methacrylate (MMA), and α-methylstyrene (AMS), which are strictly alternating polymers of vinyl monomers and oxygen.

Experimental Section

Materials. Styrene, MMA, and AMS were freed of inhibitor by washing with 5% NaOH and then with water several times. After being dried over anhydrous Na_2SO_4, they were distilled under reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol. The solvents used were purified by standard procedures.[16]

Synthesis of Terpolyperoxides. The required amounts of styrene, MMA, AMS, and AIBN(0.01 M) were placed in a 450 mL Parr reactor and pressurized to 400 psi with oxygen. The polymerization was carried out at 50 °C with stirring for about 20−30 h. The reaction mixture was concentrated by purging with nitrogen gas and finally precipitated in petroleum ether. The TPPE thus obtained was purified by repeated precipitation from benzene solution. Initial feed ratios of the vinyl monomers were varied to obtain TPPEs of different composition.

Techniques. The IR spectrum was recorded on a Perkin-Elmer Model 780 spectrometer. ^{1}H and ^{13}C NMR spectra (150 mg/mL) in $CDCl_3$ were recorded on a Bruker AC-F 200 MHz spectrometer. The inverse gated decoupling experiments were carried out with an initial delay of 3.5 s, and the number of scans accumulated was 2000. Thermal analysis was done on a Perkin-Elmer DSC-2C differential scanning calorimeter. The temperature axis and enthalpy were calibrated using indium. Thermogravimetric (TG) analysis was carried out on a Perkin-Elmer TGS-2 instrument under nitrogen atmosphere. A JEOL JMX DX-300 mass spectrometer was used for obtaining DI-MS (70eV) mass spectra. The molecular weights of TPPEs were estimated by GPC (Waters, RI detector) using toluene as eluent at a flow rate of 1.0 mL/min.

Results and Discussion

The term “oxidative terpolymerization” is applied when three vinyl monomers along with oxygen results in the formation of a terpolyperoxide of the general formula

$$[-(M_1OO)_x-(M_2OO)_y-(M_3OO)_z-]_n \qquad (1)$$

where M_1, M_2, and M_3 represent three different vinyl monomers. In the present study, styrene, MMA, and AMS were chosen as monomers, as their corresponding

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Table 1. Oxidative Terpolymerization of Styrene, MMA, and AMS Using AIBN as Initiator at 50 °C[a]

	mol % in the feed			reaction		
TPPE	St	MMA	AMS	time (h)	yield (g)	$\bar{M}_n$
TPPE-1	1.1	98.0	0.9	30	1.6	2360
TPPE-2	2.9	94.2	2.9	27	2.5	
TPPE-3	7.8	86.2	6.0	30	3.8	
TPPE-4	19.3	72.2	8.5	24	4.0	1760
TPPE-5	29.0	66.1	4.9	24	4.3	2730
TPPE-6	6.6	64.2	29.2	23	5.0	

[a] Total volume of monomer mixture, 50 mL; oxygen pressure, 400 psi.

Table 2. ^{1}H NMR Chemical Shift Values (in ppm) for TPPEs of Different Compositions[a]

peroxide	aromatic protons	CH (St)	CH_2 (St, MMA, AMS)	OCH_3	CH_3 (MMA)	CH_3 (AMS)
TPPE-1	7.32	5.30	4.00−4.50	3.75	1.44	1.60
TPPE-2	7.31	5.29	4.00−4.50	3.67	1.41	1.54
TPPE-3	7.30	5.29	4.00−4.50	3.63	1.40	1.52
TPPE-4	7.25	5.30	4.00−4.50	3.58	1.40	1.51
TPPE-5	7.23	5.29	4.00−4.50	3.56	1.39	1.51
TPPE-6	7.20	5.28	4.00−4.50	3.56	1.37	1.50
PSP	7.20	5.30	4.02			
PMSP	7.20		4.20			1.46
PMMAP			4.36	3.76	1.46	

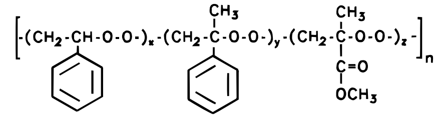
[a] For TPPE compositions, see Table 3.

homopolyperoxides, poly(styrene peroxide) (PSP),[7] poly(α-methylstyrene peroxide) (PMSP),[8] and poly(methyl methacrylate peroxide) (PMMAP)[9] have been studied previously. Initial feed ratios were varied to obtain TPPEs of different compositions.

Characterization of TPPEs. TPPEs obtained are sticky material, and their number-average molecular weights ($\bar{M}_n$) are in the range 1500−3000. They are soluble in aromatic solvents, chloroform, etc. and insoluble in methanol and petroleum ether. It may be noted that PMMAP is soluble in methanol. Like other vinyl polyperoxides, the TPPEs also burn with a “puff” sound and explode only when heated above 100 °C. They can be stored as solution in benzene at 5−10 °C without appreciable decomposition for a long period. Details of the oxidative terpolymerization of styrene, MMA, and AMS are given in Table 1.

IR spectra of TPPEs showed characteristic absorption bands of the repeat unit present in the polymer chain: aromatic CH stretching, 3050 cm^{-1}; carbonyl, 1743 cm^{-1}; C−C−O stretching, 1281 and 1026 cm^{-1}. A representative IR spectrum of TPPE-6 is given in Figure 1; in addition to the bands corresponding to the repeat units, it shows bands at 3466 and 1680 cm^{-1} assigned to hydroxyl and carbonyl (benzoyl) groups which are present as end groups in TPPEs. Such end groups are reported in PSP[12] and PMSP.[8]

^{1}H NMR Spectra. The ^{1}H NMR spectrum of TPPE-3 (Figure 2) showed signals at 1.40, 1.52, 3.63, 4.00−4.50, 5.3, and 7.2−7.3 ppm which are assigned to α-methyl (MMA), α-methyl (AMS), methoxy, methylene (styrene, MMA, and AMS), methine, and aromatic protons, respectively. These assignments are based on the ^{1}H NMR spectra of the corresponding homopolyperoxides.[4,12,17] Based on the information gathered from ^{1}H NMR and IR, the structure of TPPE can be given as



(TPPE)

The overall chain compositions of TPPEs were determined from the integrated intensities of methine (I_{CH}(St)), methyl (I_{Me}(MMA)), and methyl (I_{Me}(AMS)) protons (Table 3). For example the mole fraction of styrene (f_s) and the mole fraction of MMA (f_m) in the TPPE were calculated from the following equations:

$$f_s = \frac{3I_{CH}(St)}{3I_{CH}(St) + I_{Me}(MMA) + I_{Me}(AMS)} \tag{2}$$

$$f_m = \frac{I_{Me}(MMA)}{I_{Me}(MMA) + I_{Me}(AMS) + 3I_{CH}(St)} \tag{3}$$

The ^{1}H NMR chemical shift values were found to be sensitive to the compositions of the TPPEs. The effects of compositions of TPPEs on the ^{1}H NMR chemical shift values are given in Table 2; it can be seen that the methoxy protons, which appear at 3.76 ppm in PMMAP,

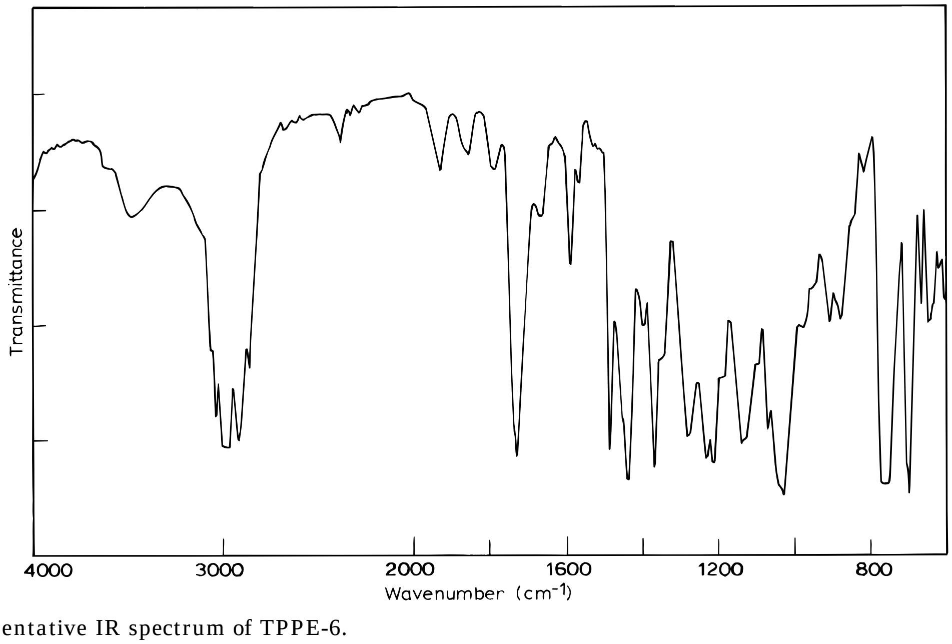


Figure 1. Representative IR spectrum of TPPE-6.

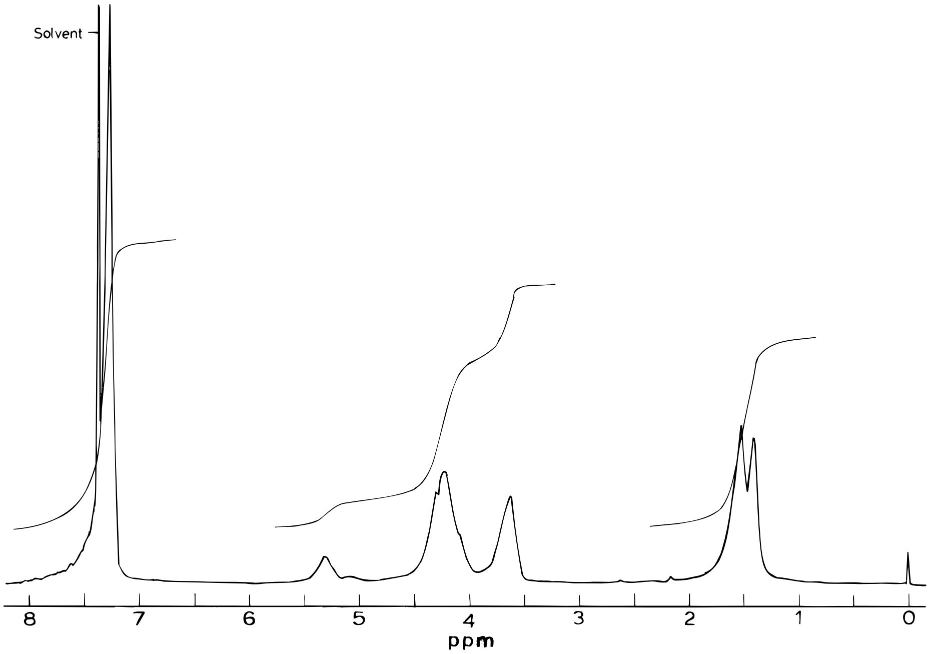


Figure 2. Representative ^{1}H NMR (200 MHz) spectrum of TPPE-3 in $CDCl_3$.

show an upfield shift with an increase in the aromatic monomer concentration. This could be due to the shielding of methoxy protons by phenyl rings.[10] The α-methyl groups of both MMA and AMS units are shifted from the corresponding positions in their homopolyperoxides. Also, the phenyl protons (styrene and AMS) showed a downfield shift with an increase in the concentration of MMA in the chain. Such variations in chemical shifts have been reported in the copolyperoxide systems of styrene−MMA−O_2 and AMS−MMA−O_2.[10,11]

The backbone methylene protons appear as a broad triplet between 4.00 and 4.50 ppm (Figure 3); the appearance of this signal is sensitive to the monomer sequence distribution in the chain and could be assigned to the diad sequences. The diad sequences are SO_2SO_2, MO_2MO_2, AO_2AO_2, SO_2MO_2 (MO_2SO_2), AO_2MO_2 (MO_2AO_2), and AO_2SO_2 (SO_2AO_2), where S, M, and A represent styrene, MMA, and AMS respectively. The methylene proton signal of the copolyperoxide of styrene and α-methylstyrene did not show any overlap of peaks corresponding to homopolyperoxides and hence the assignment for the AO_2SO_2 (SO_2AO_2) diad could not be made.[11] Therefore, at the most, five out of the total six diads could be assigned. But it should be pointed out here that the CH_2 signal of the copolyperoxides of MMA and α-methylstyrene is rather complicated and the chemical shift assignment for the AO_2MO_2 (MO_2AO_2) diad could not be made unambiguously earlier.[11] Hence, we present here the most plausible assignments for these diads in comparison with the ^{1}H NMR spectra of homo- and copolyperoxides and from the intensity variation of the peaks. When the MMA content in the TPPE is high, the three peaks appear at 4.46, 4.30, and 4.23 ppm; on the other hand, when the styrene content is high, the three peaks appear at 4.30, 4.23 and 4.08 ppm. The extreme signals at 4.08 and 4.46 ppm have been assigned to SO_2SO_2 and MO_2MO_2 diads respectively, in comparison with the spectra of the corresponding homopolyperoxides.[12,17] The signal at 4.23 ppm is assigned to SO_2MO_2 (MO_2SO_2) + AO_2AO_2 diads.[4,10] The signal at 4.30 ppm is assigned to the AO_2MO_2 (MO_2AO_2) diad on the basis of the intensity variation of the CH_2 signal. The composition of the TPPE and the deconvoluted peak areas (assuming a Lorentzian line shape) further support the above assignments.

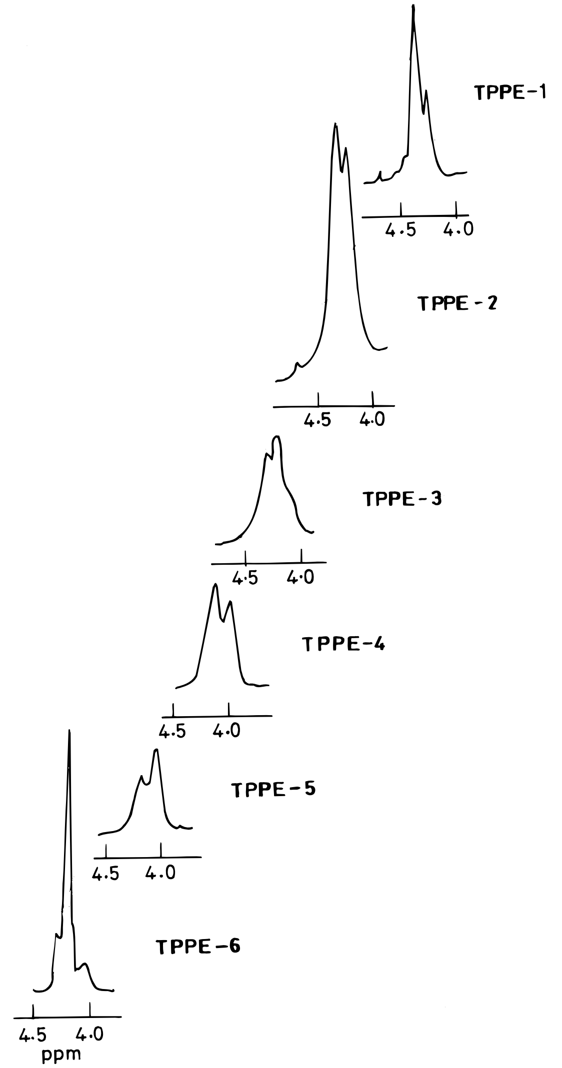


Figure 3. ^{1}H NMR (200 MHz) signals of the methylene protons of styrene, MMA, and AMS units in TPPEs.

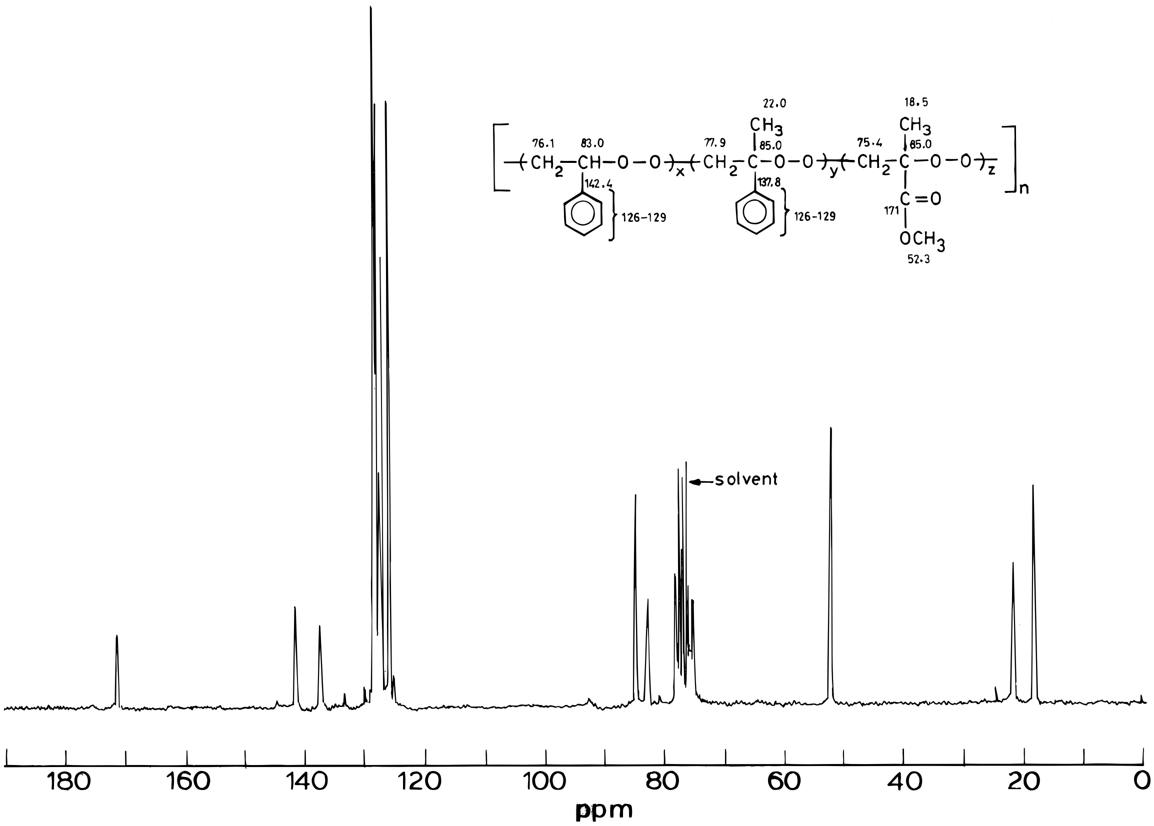


Figure 4. 50.12 MHz ^{13}C NMR spectrum of TPPE-3 in CDCl$_3$.

^{13}C NMR Spectra of TPPEs. The 50.12 MHz broadband ^{13}C NMR spectrum of TPPE-3 is given in Figure 4. As in the case of ^{1}H NMR, the assignments have been made with respect to the spectra of the corresponding homopolyperoxides. ^{13}C NMR chemical shift values of TPPEs of different compositions do not differ from those of the corresponding homopolyperoxides.[12,17,18] In PSP, unlike in PMSP and PMMAP, the backbone carbons appear as doublets, indicating their sensitivity to the stereochemistry.[12] When one more monomer is introduced in the chain along with styrene, this sensitivity is reduced.[10] Likewise, the stereosensitivity of the backbone carbons of styrene units in TPPE is also reduced, which is reflected in the appearance of a single signal for these carbons.

Thermal Degradation of TPPEs. The structure of TPPE was further confirmed by thermal degradation studies. In general, according to Mayo mechanism,[7] vinyl polyperoxides undergo random thermal scission at the peroxy bond, followed by unzipping of the β-peroxyalkoxy radicals, giving carbonyl compounds. For example, PSP on thermal degradation gives benzaldehyde and formaldehyde in equimolar amounts.[7] In the case of TPPE, the expected thermal degradation products are benzaldehyde, acetophenone, methyl pyruvate, and formaldehyde. The DI-MS mass spectrum (Figure 5) of TPPEs indicated the presence of primary degradation products, namely benzaldehyde (*m*/*z* 106), acetophenone (*m*/*z* 120) and methyl pyruvate (*m*/*z* 102). The formation of the above products was confirmed by comparison with the mass spectra of pure compounds.[19]

The DSC thermogram of TPPE indicated a highly exothermic degradation. A representative DSC thermogram of TPPE-4 is given in Figure 6. The average enthalpy of degradation, ΔH_d, at various heating rates was around 250 cal/g, which is close to the values reported for homo- and copolyperoxides.[4,11] From the DSC peak temperatures (T_m), using Kissinger's plot, the activation energy (E_a) values were found to be close to 35 kcal/mol for all TPPEs, which compares well with the dissociation energy of the O−O bond in dialkyl peroxides.[20] This further confirms the initiation of degradation through O−O bond cleavage, followed by unzipping of the alkoxy radicals. The DSC peak temperatures of TPPEs (Table 3), measured at a constant heating rate of 10 °C/min, increase with an increase in the concentration of MMA units in the chain. Among the homopolyperoxides, PMMAP has a higher peak temperature. For comparison, DSC peak temperatures of PSP, PMMAP, and PMSP are also given in the Table 3.

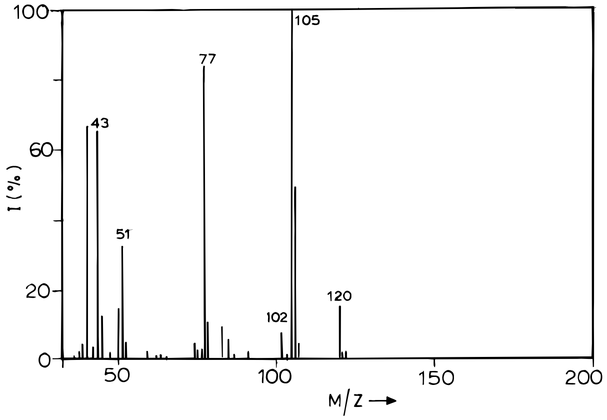


Figure 5. DI mass spectrum of TPPE-5.

The thermogravimetric analysis of TPPEs was done at a heating rate of 20 °C/min. The TG trace of TPPE-3 is given in Figure 7. The weight loss was found to occur in a single step, starting at 105 °C and ending at 145 °C. The maximum weight loss occurred at 125 °C. We did not see any significant change in the shape of TG

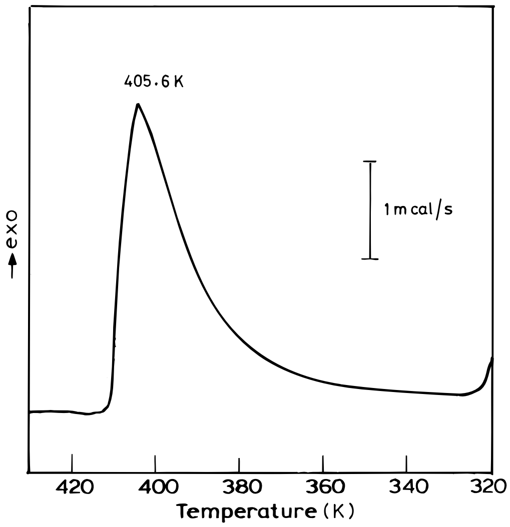


Figure 6. DSC thermogram of TPPE-4 at a heating rate of 10 °C/min.

Table 3. Experimental and Calculated Values of TPPE Compositions (mol %)

peroxide	DSC peak temp[a] (K)	exptl[b] St	exptl[b] MMA	exptl[b] AMS	calcd[c] St	calcd[c] MMA	calcd[c] AMS
TPPE-1	410.5	9.4	79.2	11.4	9.3	75.1	15.6
TPPE-2	410.0	18.2	56.5	25.4	10.0	70.1	19.9
TPPE-3	407.0	29.0	29.4	41.6	29.1	25.5	45.4
TPPE-4	405.6	46.8	15.6	37.6	42.3	19.2	38.5
TPPE-5	nd	62.9	14.0	23.1	61.5	16.9	21.5
TPPE-6	403.5	8.3	11.3	80.4	8.8	11.1	80.1
PMSP	402.0						
PSP	407.0						
PMMAP	418.4						

[a] At a heating rate of 10 °C/min. nd, not determined. [b] From proton NMR data. [c] From terpolymer equation (ref 13).

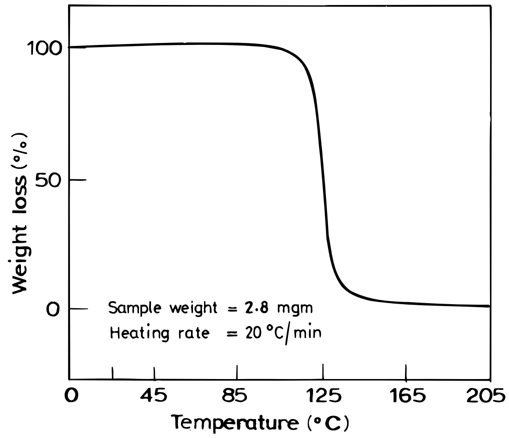


Figure 7. TG trace of TPPE-3 at a heating rate of 20 °C/min, under nitrogen atmosphere.

traces of TPPEs compared to those of their respective homopolyperoxides.

Both DSC and TG studies indicate that, although the peroxy bonds in the TPPE chains are flanked by different monomer units, the thermal stabilities of these peroxy bonds do not vary much.

Kinetics of Oxidative Terpolymerization. In oxidative polymerization, the reactivity of $M^{\bullet}$ with oxygen is very high compared to that of $MO_2^{\bullet}$ with M. Thus, assuming a penultimate effect, the important propagation steps involved in the oxidative terpolymerization of styrene (1), MMA (2), and α-methylstyrene (3) may be written as follows:[15]

$$-M_1O_2^{\bullet} + M_1 \xrightarrow{k_{11}} -M_1^{\bullet} \tag{4a}$$

$$-M_1O_2^{\bullet} + M_2 \xrightarrow{k_{12}} -M_2^{\bullet} \tag{4b}$$

$$-M_1O_2^{\bullet} + M_3 \xrightarrow{k_{13}} -M_3^{\bullet} \tag{4c}$$

$$-M_2O_2^{\bullet} + M_1 \xrightarrow{k_{21}} -M_1^{\bullet} \tag{4d}$$

$$-M_2O_2^{\bullet} + M_2 \xrightarrow{k_{22}} -M_2^{\bullet} \tag{4e}$$

$$-M_2O_2^{\bullet} + M_3 \xrightarrow{k_{23}} -M_3^{\bullet} \tag{4f}$$

$$-M_3O_2^{\bullet} + M_1 \xrightarrow{k_{31}} -M_1^{\bullet} \tag{4g}$$

$$-M_3O_2^{\bullet} + M_2 \xrightarrow{k_{32}} -M_2^{\bullet} \tag{4h}$$

$$-M_3O_2^{\bullet} + M_3 \xrightarrow{k_{33}} -M_3^{\bullet} \tag{4i}$$

The six reactivity ratios are[21]

$$r_{12} = k_{11}/k_{12} = 7.90 \qquad r_{13} = k_{11}/k_{13} = 0.48$$

$$r_{21} = k_{22}/k_{21} = 0.08 \qquad r_{23} = k_{22}/k_{23} = 0.04$$

$$r_{31} = k_{33}/k_{31} = 2.10 \qquad r_{32} = k_{33}/k_{32} = 15.00$$

The value of r_{12} expresses the relative tendency of the $M_1O_2^{\bullet}$ radicals to react with M_1 in comparison with M_2. In the present study, an attempt was made to use these values of the kinetic characteristics of the oxidative copolymerization of the binary systems of monomers to calculate the compositions of the TPPEs. Using the conventional terpolymer equation for the polymerization of three vinyl monomers,[13] in the absence of oxygen, the compositions of TPPEs were calculated and were found to match with the experimentally observed values (Table 3). It may be pointed out here that the basic assumptions about the absence of the cleavage products during oxidative copolymerization and the low molecular weights of TPPEs do not introduce any perceptible error in the calculations.

Conclusion

Terpolyperoxides of styrene, MMA, and α-methylstyrene were synthesized by polymerizing these monomers under excess oxygen pressure by varying the initial feed. The TPPEs have been characterized, and it has been shown that all these monomers are present in the polymer chain. As shown by TG and DSC studies, the presence of vinyl monomers of different structures in the polymer backbone does not seem to have any significant effect on the thermal stabilities of the peroxide units, even though they may be present in different environments. Formaldehyde, benzaldehyde, acetophenone, and methyl pyruvate were identified as the primary degradation products of TPPE. It has been demonstrated that the conventional terpolymer equation can be used to predict the compositions of TPPEs.

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