Microstructure of Copolyperoxides of α-Methylstyrene with Styrene and Methyl Methacrylate

Saraswathyammal Jayanthi and Kaushal Kishore*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

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ABSTRACT: This paper reports a study on the microstructure of two series of copolyperoxides of α-methylstyrene, with styrene and with methyl methacrylate. The copolyperoxides were synthesized by the free radical-initiated oxidative copolymerization of the vinyl monomer pairs. The copolyperoxide compositions obtained from the ^{1}H and ^{13}C NMR spectra led to the determination of the reactivity ratios. The product of the reactivity ratios indicates that α-methylstyrene forms a block copolyperoxide with styrene and a random copolyperoxide with methyl methacrylate. Microstructural parameters like average sequence length, run number, etc. have been determined for the latter copolyperoxide from analysis of its ^{13}C NMR spectrum. The aromatic quaternary and carbonyl carbons were found to be sensitive to triad sequences. The end groups of the copolyperoxides have been identified by ^{1}H NMR as well as FTIR spectroscopic techniques. The thermal degradation of the copolyperoxides has been studied by differential scanning calorimetry, which confirms the alternating peroxide units in the copolyperoxide chain.

Introduction

Polymerization of vinyl monomers in the presence of oxygen, known as oxidative polymerization, is important from the viewpoint of technological applications.[1] The main products of oxidative polymerization, the polyperoxides, which are alternating copolymers of the vinyl monomer and oxygen, find importance as initiators[2,3] and autocombustible fuels[4] and in determining the thermal stability of commercial polymers. With the ever increasing progress in improving the quality of polymeric coatings and adhesives,[1] the use of monomer mixtures and cross-linking agents has attracted attention. In this context, it is desirable to understand how a mixture of monomers copolymerizes in the presence of oxygen. Hence, there is a need for detailed investigations to gain insight into the mechanism of oxidative copolymerization, particularly regarding the nature of the comonomers as reflected in the microstructure of the resulting copolymer.

Along with the polyperoxide, other low molecular weight carbonyl compounds are also formed during the oxidative polymerization of vinyl monomers.[5] The relative amounts of the various products and the microstructure of the polyperoxide obtained depend on the temperature and partial pressure of oxygen. At low temperatures (below 100 °C) and high partial pressure (above 760 mm) of oxygen, the formation of low molecular weight compounds is negligibly small, and the polyperoxide will have vinyl monomer units strictly alternating with peroxide groups. Oxidative copolymerization of two vinyl monomers in the presence of excess oxygen leads to the formation of a terpolymer, where the oxygen, as peroxide group, alternates with one or both of vinyl monomer units, having the general structure $-[-(M_1OO)_x-(M_2OO)_y-]_n$. The distribution of the two vinyl monomer units (M_1 and M_2) in the polyperoxide chain is dependent on the relative reactivities of the growing peroxide radicals toward the two monomers, which in turn is determined by the monomer unit (M in $MO_2^\bullet$) penultimate to the peroxide chain end.[6] The oxidative copolymerization of two vinyl monomers can be considered as a special case of terpolymerization, where the vinyl monomers are restrained not to homopolymerize. The uniqueness of this system is that it approximates a binary copolymerization system in terms of vinyl peroxide units. The rate of polymerization may then be described in terms of the copolymerization equation and reactivity ratios.[7] The relative rates of attack on two vinyl monomers by each of the two peroxide radicals may be determined from the composition of the resulting copolyperoxide alone.[5]

It may be noted that microstructural studies on copolyperoxides have not been carried out, except for our recent report on styrene−methyl methacrylate copolyperoxide.[8] In the present work, we have studied the oxidative copolymerizations of two more systems, α-methylstyrene/styrene and α-methylstyrene/methyl methacrylate (MMA). Inspite of high oxygen flux that is maintained in the polymerization process, the selection of α-methylstyrene is advantageous because, unlike other vinyl monomers, it does not homopolymerize, even in low oxygen concentration, due to the close proximity of the polymerization temperature to the ceiling temperature.[9] The second monomers, styrene and MMA, represent extreme behavior, styrene being the best electron donor and MMA being a good electron acceptor.[6] Therefore, the reactivity of the peroxide radical with a penultimate α-methylstyrene unit toward these monomers is expected to be different. Our main focus here is to study the microstructure of the copolyperoxides by nuclear magnetic resonance spectroscopy, although other physical techniques like FTIR, mass spectroscopy, and thermal analysis have also been used to supplement the structural assignments.

Experimental Section

α-Methylstyrene (A), styrene (S), and methyl methacrylate (MMA or M) were freed from inhibitor and distilled under reduced pressure prior to use. Oxygen used was of high purity. Azobis(isobutyronitrile) (AIBN, Fluka, AG) was recrystallized thrice from methanol.

The terpolymers were synthesized by passing a copious flow of oxygen through the mixture of the vinyl monomers containing 0.01 M AIBN at 50 °C. The reaction was continued for up to 24−36 h. The reaction mixture was then concentrated and poured into petroleum ether. The copolyperoxides, precipi-

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Table 1. Experimental Data for the Oxidative Copolymerization of α-Methylstyrene with Styrene and Methyl Methacrylate, Initiated by AIBN at 50 °C

			mole fraction of α-methylstyrene		
				copolyperoxide (x)	
copolyperoxide	reaction time (h)	yield (wt %)	feed [A]	^{1}H NMR	^{13}C NMR
	α-Methylstyrene/Styrene				
COPMS 100/0	6	5.00	1.00	1.00	1.00
COPMS 90/10	8	4.22	0.90	0.97	0.90
COPMS 70/30	9	4.05	0.70	0.71	0.72
COPMS 50/50	10	4.50	0.50	0.54	0.54
COPMS 30/70	10	4.50	0.30	0.37	0.36
COPMS 10/90	12	3.50	0.10	0.15	0.15
COPMS 0/100	16	2.18	0.00	0.00	0.00
	α-Methylstyrene/Methyl Methacrylate				
COPMM 100/0	6	5.0	1.00	1.00	1.00
COPMM 75/25	24	3.0	0.17	0.77	0.74
COPMM 66/33	36	3.5	0.12	0.69	0.68
COPMM 50/50	36	2.8	0.05	0.51	0.51
COPMM 33/66	40	2.9	0.03	0.37	0.37
COPMM 25/75	48	3.0	0.02	0.30	0.29
COPMM 0/100	48	3.2	0.00	0.00	0.00

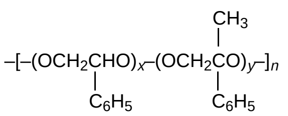
tated as gummy solids, were isolated and purified by reprecipitation from benzene solution. Details on initial monomer ratios, the identification numbers, and the compositions of the product copolyperoxides are presented in Table 1.

The compositions and microstructures of the homopolyperoxides and the copolyperoxides were analyzed on a Bruker AC-F 200 MHz NMR spectrometer using the standard pulse sequences. All the spectra of samples were recorded in $CDCl_3$ solutions. Chemical shifts are recorded in ppm from tetramethylsilane. All the ^{13}C NMR spectra were obtained under inverse gated decoupling conditions with 6 s delay between the pulses. A line broadening of 2 Hz was applied before Fourier transformation in order to enhance the signal-to-noise ratio. The spectral deconvolution of the Fourier transformed spectra was done using a separate computer program, assuming a Lorentzian line shape. The peak areas thus obtained were used to determine the monomer sequence fractions.

The FTIR spectra were recorded on a Bio-Rad FTS7 FTIR spectrometer. The FAB-MS of the copolyperoxides were recorded on a JEOL-SX-102 (FAB) spectrometer (CDRI, Lucknow, India). FTIR and FAB-MS spectra are used to confirm the major end groups. The thermal degradation of the polymers was studied using differential scanning calorimetry (DSC). The measurements were done on a DuPont 990 DSC equipped with a DuPont 9000 thermal analyzer.

Results and Discussion

Determination of Copolyperoxide Compositions. The copolyperoxide compositions were determined from their ^{1}H NMR and ^{13}C NMR spectra. Figure 1 depicts a typical ^{1}H NMR spectrum of COPMS 50/50 of this copolyperoxide series, along with the spectra of the homopolyperoxides poly(styrene peroxide) (PSP) and poly(α-methylstyrene peroxide) (PMSP). The resonance signals at 1.5, 4.02–4.2, 5.3, and 7.25–7.3 ppm are assigned to the α-methyl, methylene, methine, and aromatic protons, respectively.[3,10] Accordingly, the general structure of the copolyperoxide may be represented as



$$-[-(OCH_2\underset{C_6H_5}{C}HO)_x-(OCH_2\overset{CH_3}{\underset{C_6H_5}{C}}O)_y-]_n$$

The copolyperoxide compositions were obtained from the ratio of the integrated intensities of the CH and CH_3 resonance signals. The values obtained are given in Table 1.

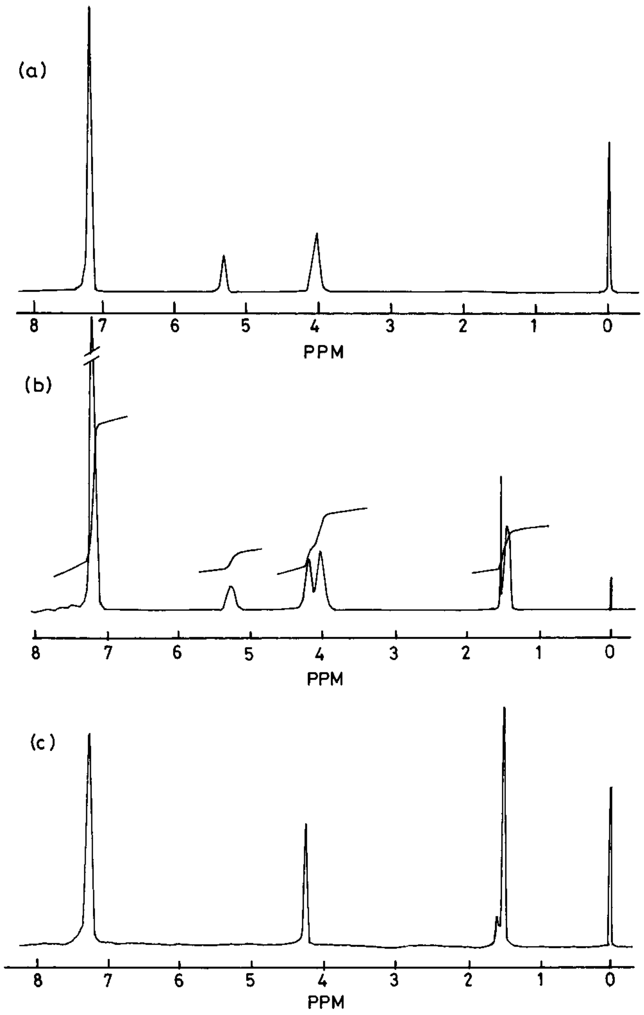
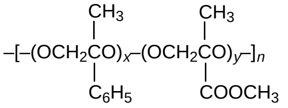


Figure 1. 200 MHz ^{1}H NMR spectra of the copolyperoxides of α-methylstyrene with styrene: (a) COPMS 0/100, (b) COPMS 50/50, and(c) COPMS 100/0.

Similar ^{1}H NMR spectra have been obtained for the α-methylstyrene–MMA copolyperoxide series. In Figure 2, the ^{1}H NMR spectrum of COPMM 50/50 is shown, along with those for the homopolyperoxides poly(methyl methacrylate peroxide) (PMMAP) and PMSP. The methyl resonance signals of the α-methylstyrene and MMA units appear at 1.4 and 1.5 ppm, respectively, as in the case of PMSP and PMMAP. The methoxy peak appears at 3.75 ppm as a singlet. There is a gradual downfield shift for this peak as the amount of MMA units in the chain is increased. This may be due to the methoxy groups going away from the proximity of the phenyl groups of the α-methylstyrene units as its concentration in the chain is reduced. This kind of a downfield shift for the methoxy peak is observed for the copolymers of styrene and MMA.[11] The methylene resonance signal (4.02–4.35 ppm) is rather complicated. The broad signal at 7.28 ppm due to the phenyl group also shows a gradual downfield shift as the MMA concentration in the chain is increased, in the same way as is reported for the copolyperoxides of styrene and MMA.[8] The general structure of the copolyperoxide could be represented as



$$-[-(OCH_2\overset{CH_3}{\underset{C_6H_5}{C}}O)_x-(OCH_2\overset{CH_3}{\underset{COOCH_3}{C}}O)_y-]_n$$

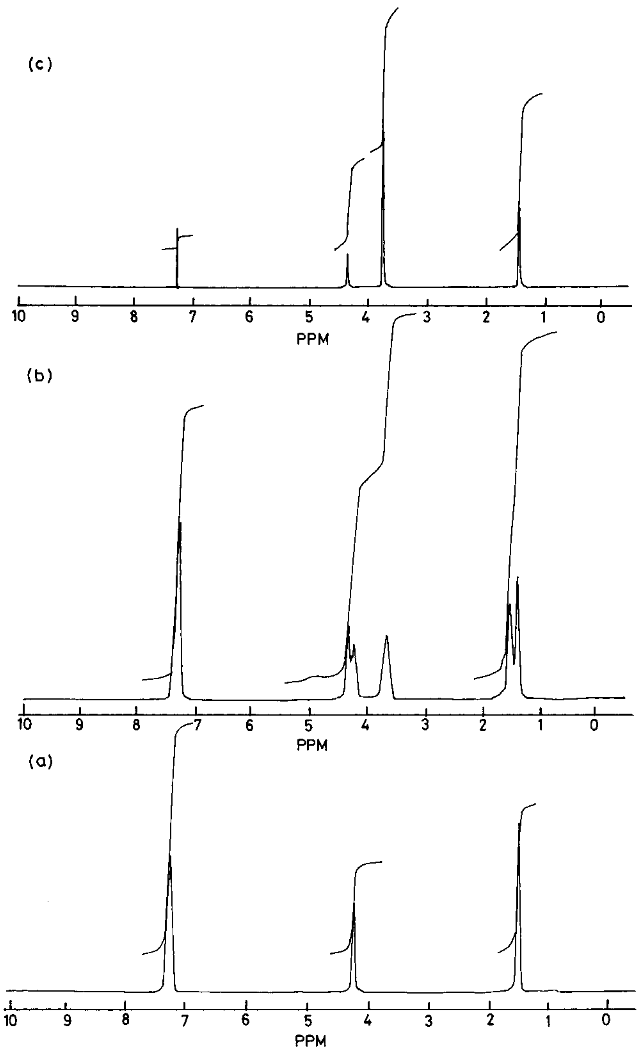


Figure 2. 200 MHz ^{1}H NMR spectra of the copolyperoxides of α-methylstyrene with methyl methacrylate: (a) COPMM 0/100, (b) COPMM 50/50, and (c) COPMM 100/0.

The copolyperoxide compositions can readily be obtained from the ratio of the integrated peak intensities of the aromatic and the aliphatic regions. The results are listed in Table 1.

The ^{13}C NMR spectra recorded under the conditions of inverse gated decoupling also allowed the determination of the copolyperoxide compositions from the integrated intensities of the different resonance signals. Figure 3 depicts the ^{13}C NMR spectrum of the copolyperoxide COPMS 7030, along with the spectra of the homopolyperoxides. The ratio of the intensities of the aromatic quaternary carbons and the methylene carbons gives directly the copolyperoxide composition. In Figure 4, the ^{13}C NMR spectrum of COPMM 50/50 is shown, along with those of PMSP and PMMAP. The ratio of the intensities of the methyl and methylene carbons gives a direct measure of the copolyperoxide compositions. The results are listed in Table 1.

Sequence Analysis. The ^{1}H and ^{13}C NMR spectra of the copolyperoxides of α-methylstyrene and styrene do not reveal any information about monomer sequence distributions. The absence of new signals which could throw light onto microstructural aspects points to the fact that, in the chain, the SO_2 and AO_2 units may exist as blocks, where S and A represent styrene and α-methylstyrene monomer units, respectively.

The ^{1}H NMR spectra of the copolyperoxides of α-methylstyrene and MMA display complicated methylene resonance signals which could not be assigned unambigously. On the other hand, the ^{13}C NMR spectra give more information regarding the monomer sequences in the polyperoxide chain. A cursory examination of the ^{13}C NMR spectra of the copolyperoxides (COPMM) shows that the carbonyl and aromatic quaternary carbon resonance regions are more suitable for the analysis of comonomer sequences in the chain.

At first we consider the ^{13}C NMR signal of the carbonyl carbon of the MMA unit in the chain. There is no resonance from α-methylstyrene units in this region. As the MMA concentration is increased, new peaks appear at 171.31, 171.18, and 171.01 ppm. The peak at 171.01 ppm reaches maximum intensity at the highest composition of MMA in the copolyperoxide, which matches with the carbonyl signal of the homopolyperoxide, PMMAP. Therefore, it is assigned to the $MO_2MO_2MO_2$ "triad" sequence. The peak at 171.18 ppm is assigned to the $MO_2MO_2AO_2$ + $AO_2MO_2MO_2$ sequence, according to its intensity variation with respect to the overall copolyperoxide composition. The peak at 171.31 ppm is assigned to the $AO_2MO_2AO_2$ "triad", as its intensity reaches a maximum only at a very low concentration of MMA units in the chain. The expanded region of the spectra, showing the MO_2 centered "triads", is depicted in Figure 5. The results of the calculated and experimental "triad" sequence distributions are presented in Table 2. The results show good agreement between the deconvoluted and calculated data.

In a similar way, the three peaks observed in the ipso carbon region can be assigned to AO_2-centered triads. The $AO_2AO_2AO_2$, $AO_2AO_2MO_2$ + $MO_2AO_2AO_2$, and $MO_2AO_2MO_2$ triads are assigned in the order of increasing shielding, as shown in Figure 6. The triad fractions obtained by the deconvolution of the peaks and the calculated values according to the Markov model (Table 3) show a good agreement, confirming the peak assignments.

The "triad" fractions thus obtained can be used for the calculation of microstructural parameters like average sequence length, run number, etc. The experimental quantities, namely, triad fractions, are related to the conditional probabilities of the different "diads" as

$$F_{AO_2AO_2AO_2} = (1 - P(MO_2/AO_2))^2$$

$$F_{MO_2AO_2MO_2} = P(MO_2/AO_2)^2$$

$$\begin{aligned} F_{MO_2AO_2AO_2} &= F_{AO_2AO_2MO_2} \\ &= P(MO_2/AO_2)[1 - P(MO_2/AO_2)] \end{aligned}$$

The conditional probabilities, in turn, lead to the average sequence length and run number:[12]

$$l_{AO_2} = [P(AO_2/MO_2)]^{-1}$$

$$l_{MO_2} = [P(MO_2/AO_2)]^{-1}$$

The run number is defined as the average number of monomer sequences or runs per hundred units occurring in the copolymer chain.[13] In the case of the copolyperoxides, since oxygen (peroxide group) strictly alternates with both α-methylstyrene and methyl methacrylate

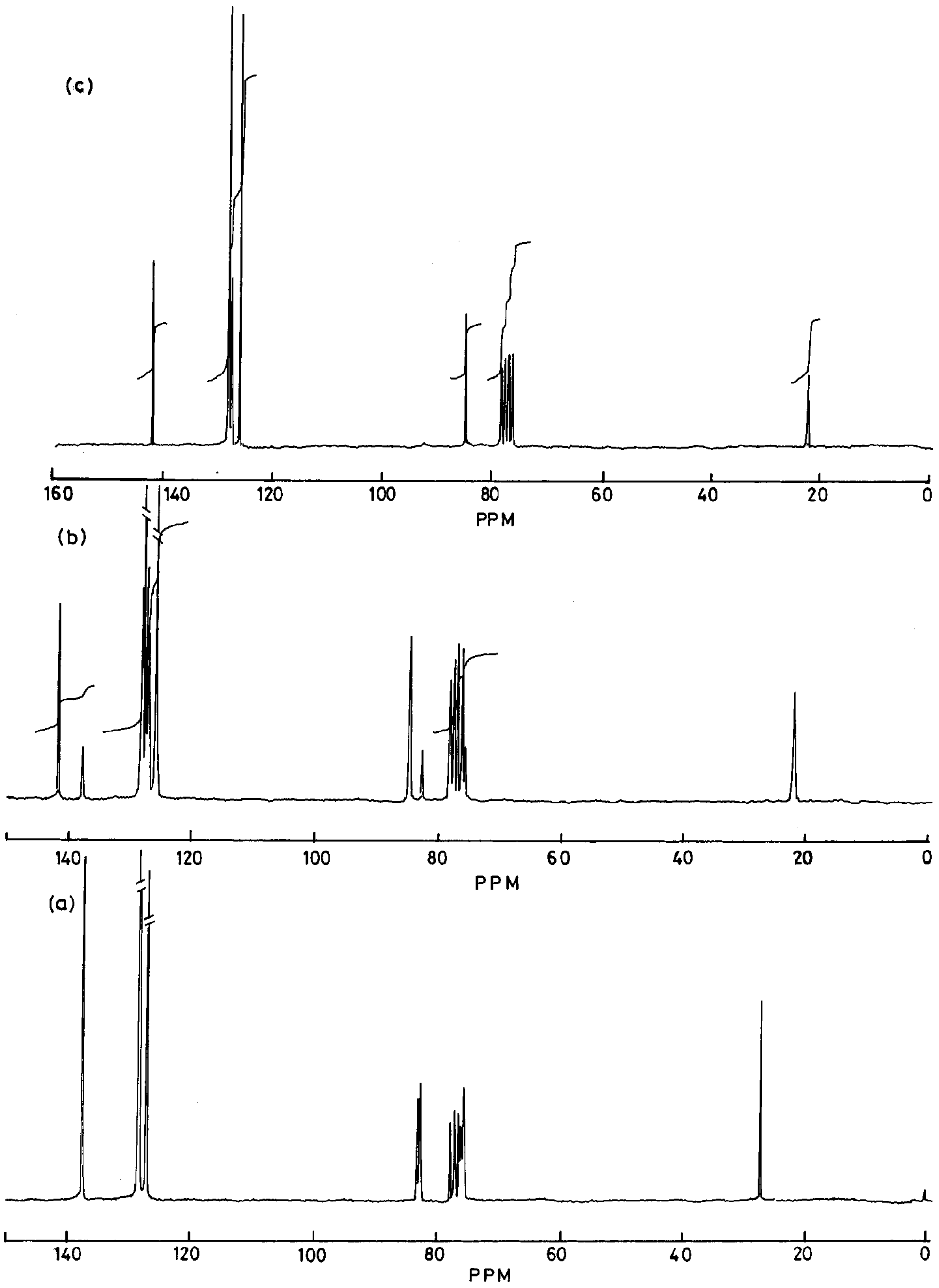


Figure 3. 50.32 MHz broadband decoupled ^{13}C NMR spectra of the copolyperoxides of α-methylstyrene with styrene: (a) COPMS 0/100, (b) COPMS 50/50, and (c) COPMS 100/0.

units in the chain, the run number can be expressed in terms of the runs of AO_2 and MO_2 units. The diad probabilities are related to the run number (R) as follows:

$$P(AO_2/AO_2) = (\%[AO_2] - R/2)/\%[AO_2]$$

$$P(AO_2/MO_2) = R/(2\%[AO_2])$$

where $P[A/B]$ represents the conditional probability that a unit A succeeds the unit B, and R is the run number. The average sequence lengths and run numbers for copolyperoxides of different composition are given in Table 4.

End Group Analysis. As in the case of homopolyperoxides, in copolyperoxides also the molecular weight and the end groups are controlled by some chain transfer reactions.[14] Mayo has reported that, in PMSP, made at 1 atm of oxygen, the chains begin with $HO_2CH_2C(CH_3)(ph)-$ and $O{=}CHC(CH_3)(ph)-$ groups and end with $-CH{=}C(CH_3)(ph)$ groups.[15] Thus, the major terminating group in PMSP is the unsaturated chain end.[16] This is clearly seen in the ^1H NMR spectrum of PMSP. The peak at 4.9 ppm corresponds to the $O_2CH{=}C(CH_3)(ph)$ proton. In ^{13}C NMR spectrum, the signal corresponding to such an unsaturated carbon falls in the region of aromatic carbon signals and hence is not detectable. In the FTIR spectrum, the C=C stretch is clearly seen as a shoulder at 1603 cm^{-1}. In the FAB-MS, the peaks at m/z 149 and 133 could be assigned to the end groups, $-OOCH{=}C(CH_3)(C_6H_5)$ and $-OCH{=}C(CH_3)(C_6H_5)$, respectively. The benzoyl group, which is

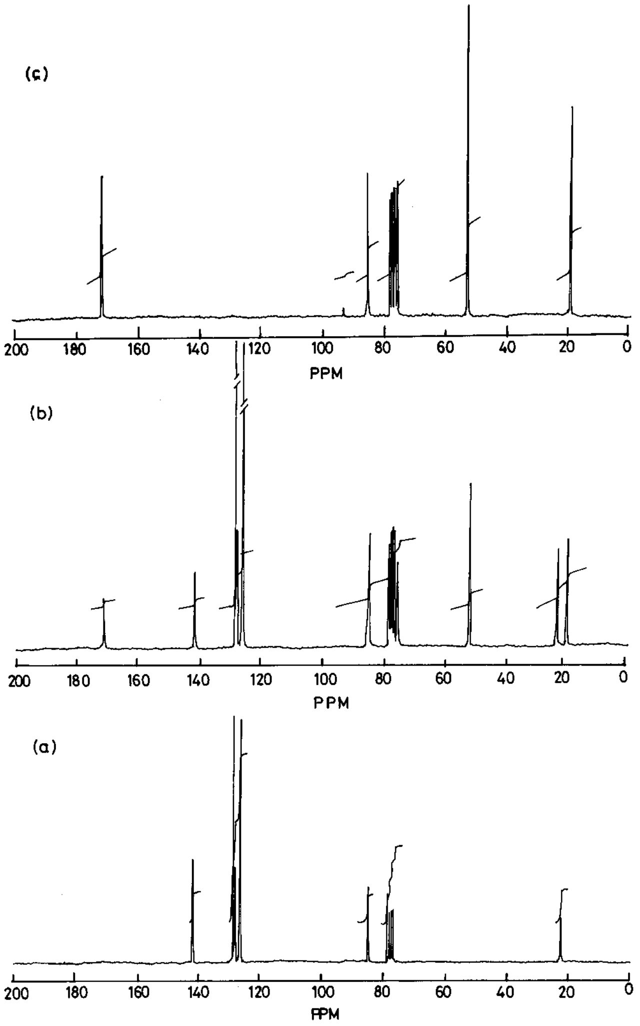


Figure 4. 50.32 MHz broadband decoupled ^{13}C NMR spectra of the copolyperoxides of α-methylstyrene with methyl methacrylate: (a) COPMM 0/100, (b) COPMM 50/50, and (c) COPMM 100/0.

proved to be the major chain initiating end in the oxidative polymerization of styrenes, is detected in ^{13}C NMR spectra, as the para carbon of the benzoyl group appears at 131 ppm.[10] In a similar way, the major terminating group in PMMAP is reported to be the hydroperoxide group.[17] This appears at 5.2 ppm in the ^{1}H NMR spectra. In FTIR spectra, the broad absorption at 3500 cm^{-1} is due to the hydroperoxide end groups.[10] In the copolyperoxides, both of the terminal groups are observed. As the α-methylstyrene concentration in the chain is increased, the terminal groups of PMSP are found to predominate. In the proton NMR spectra the variation of intensity of the peaks at 5.2–4.9 ppm (Figure 7) confirms these terminal groups.

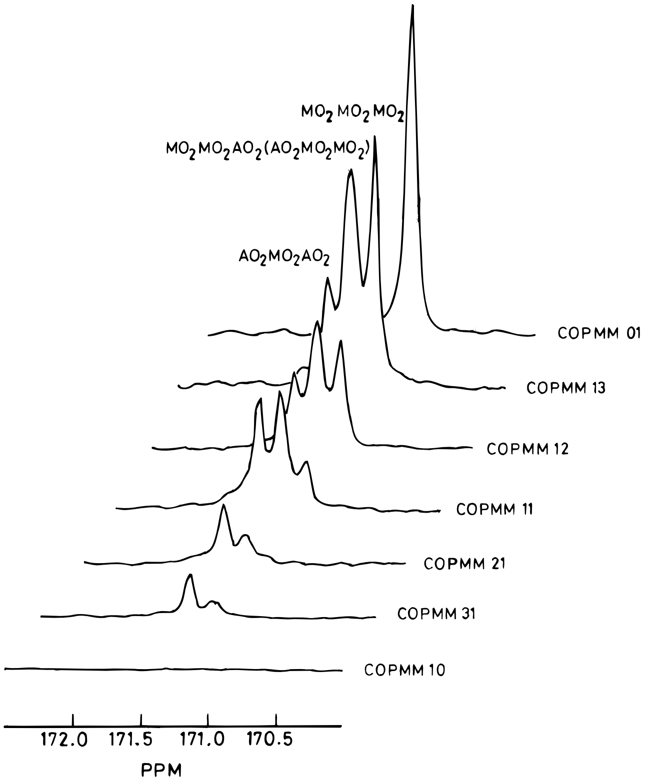


Figure 5. Expanded region of the carbonyl carbon of the copolyperoxides, showing the MO_2-centered triads.

Table 2. AO_2-Centered Triad Fractions for α-Methylstyrene–Methyl Methacrylate Copolyperoxides Prepared by the Oxidative Copolymerization of α-Methylstyrene and Methyl Methacrylate

		triad fractions	
copolyperoxide	triad	exptl	calcd[a]
COPMM 75/25	$AO_2AO_2AO_2$	0.52	0.55
	$AO_2AO_2MO_2$ ($MO_2AO_2AO_2$)	0.21	0.16
	$MO_2AO_2MO_2$	0.05	0.07
COPMM 66/33	$AO_2AO_2AO_2$	0.47	0.44
	$AO_2AO_2MO_2$ ($MO_2AO_2AO_2$)	0.24	0.22
	$MO_2AO_2MO_2$	0.05	0.11
COPMM 50/50	$AO_2AO_2AO_2$	0.22	0.20
	$AO_2AO_2MO_2$ ($MO_2AO_2AO_2$)	0.26	0.25
	$MO_2AO_2MO_2$	0.26	0.30
COPMM 33/66	$AO_2AO_2AO_2$	0.07	0.11
	$AO_2AO_2MO_2$ ($MO_2AO_2AO_2$)	0.21	0.22
	$MO_2AO_2MO_2$	0.50	0.45
COPMM 25/75	$AO_2AO_2AO_2$	0.04	0.06
	$AO_2AO_2MO_2$ ($MO_2AO_2AO_2$)	0.16	0.19
	$MO_2AO_2MO_2$	0.64	0.56

[a] Calculated using the reactivity ratios reported in the literature.[6]

Reactivity Ratios. In deriving the copolymerization equation for the cooxidation of two vinyl monomers, oxygen is considered as a third monomer. Under the copolymerization conditions employed here, such as a high partial pressure of oxygen, etc., all three monomers are not homopolymerizable.[8] Besides, the propagation reactions involving the addition of one or the other vinyl monomer to the second vinyl monomer radical are assumed to be negligible. This assumption is supported by the absence of signals corresponding to the AS or SA units in the ^{1}H or ^{13}C NMR spectra of the copolyperoxides. The only reaction in which vinyl monomers are consumed is the reaction of the peroxide radicals with styrene or α-methylstyrene. Hence, the rate-determining steps are[18]

$$AO_2^{\bullet} + A \xrightarrow{k_{AA}} AO_2A^{\bullet} \tag{i}$$

$$AO_2^{\bullet} + S \xrightarrow{k_{AS}} AO_2S^{\bullet} \tag{ii}$$

$$SO_2^{\bullet} + A \xrightarrow{k_{SA}} SO_2A^{\bullet} \tag{iii}$$

$$SO_2^{\bullet} + S \xrightarrow{k_{SS}} SO_2S^{\bullet} \tag{iv}$$

From steady state approximation, the copolymerization

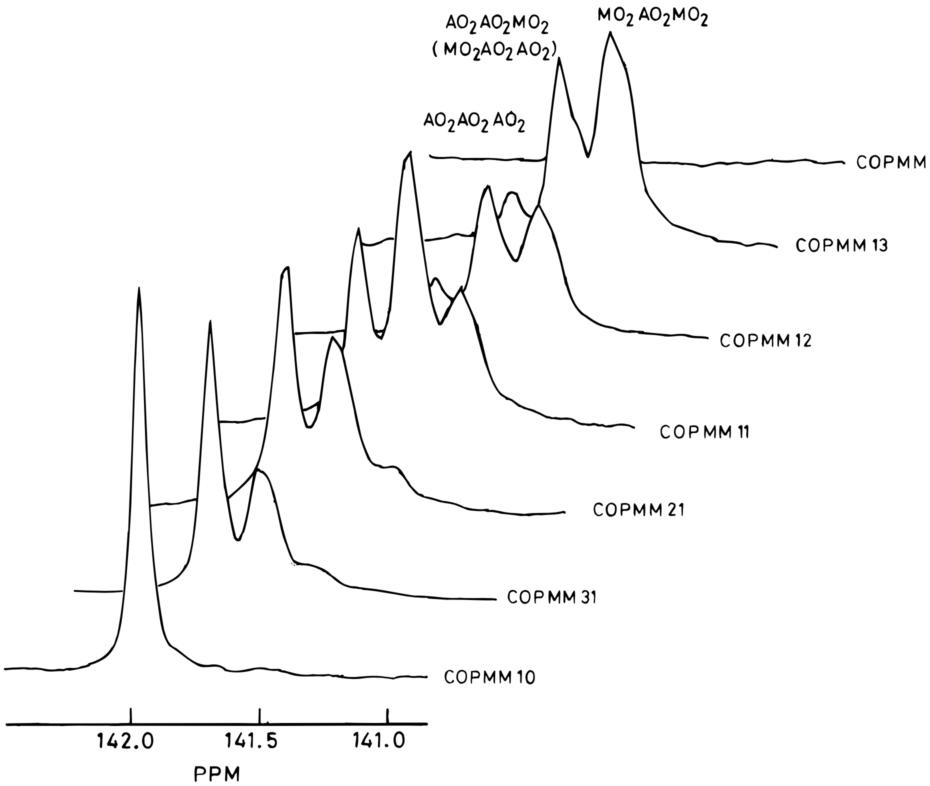


Figure 6. Expanded region of the aromatic quaternary carbon of the copolyperoxides, showing the AO_2-centered triads.

Table 3. MO_2-Centered Triad Fractions for α-Methylstyrene–Methyl Methacrylate Copolyperoxides Prepared by the Oxidative Copolymerization of α-Methylstyrene and Methyl Methacrylate

		triad fraction	
copolyperoxide	triad	exptl	calcd[a]
COPMM 66/33	$MO_2MO_2MO_2$	0.06	0.01
	$MO_2MO_2AO_2$ ($AO_2MO_2MO_2$)	0.18	0.16
	$AO_2MO_2AO_2$	0.59	0.67
COPMM 50/50	$MO_2MO_2MO_2$	0.18	0.10
	$MO_2MO_2AO_2$ ($AO_2MO_2MO_2$)	0.24	0.24
	$AO_2MO_2AO_2$	0.33	0.40
COPMM 33/66	$MO_2MO_2MO_2$	0.31	0.27
	$MO_2MO_2AO_2$ ($AO_2MO_2MO_2$)	0.25	0.28
	$AO_2MO_2AO_2$	0.20	0.18
COPMM 25/75	$MO_2MO_2MO_2$	0.42	0.35
	$MO_2MO_2AO_2$ ($AO_2MO_2MO_2$)	0.23	0.26
	$AO_2MO_2AO_2$	0.13	0.13

[a] Calculated from the reactivity ratios reported in the literature.[6]

Table 4. Average Sequence Length and Run Number of the Copolyperoxides Calculated from the Diad Probabilities

	average sequence length		
copolyperoxide	l_{AO_2}	l_{MO_2}	run number, R
COPMM 25/75	1.29	2.73	50
COPMM 33/66	1.41	2.38	57
COPMM 50/50	1.95	1.56	53
COPMM 66/33	4.60	1.23	30

equation can be derived as

$$\frac{d[A]}{d[S]} = \frac{[A]}{[S]}\,\frac{r_A[A] + [S]}{[A] + r_S[S]}$$

where d[A]/d[S] represents the ratio of α-methylstyrene to styrene in the copolyperoxide, [A]/[S] is the corresponding feed ratio, and r_A and r_S are the reactivity ratios, defined as[6]

$$r_A = \frac{\text{rate constant for the reaction of } AO_2^{\bullet} \text{ and A}}{\text{rate constant for the reaction of } AO_2^{\bullet} \text{ and S}} = \frac{k_{AA}}{k_{AS}}$$

$$r_S = \frac{\text{rate constant for the reaction of } SO_2^{\bullet} \text{ and S}}{\text{rate constant for the reaction of } SO_2^{\bullet} \text{ and A}} = \frac{k_{SS}}{k_{SA}}$$

Thus, the reactivity ratios give the relative tendency of the peroxide radicals ($AO_2^{\bullet}$ or $SO_2^{\bullet}$) to add the monomer of the same kind or the other. In the same way, the rate equations can be written for α-methylstyrene and MMA oxidative copolymerization also. The reactivity ratios are defined as

$$r_A = \frac{\text{rate constant for the reaction of } AO_2^{\bullet} \text{ and A}}{\text{rate constant for the reaction of } AO_2^{\bullet} \text{ and M}} = \frac{k_{AA}}{k_{AM}}$$

$$r_M = \frac{\text{rate constant for the reaction of } MO_2^{\bullet} \text{ and M}}{\text{rate constant for the reaction of } MO_2^{\bullet} \text{ and A}} = \frac{k_{MM}}{k_{MA}}$$

The reactivity ratios have been determined from Finemann–Ross plots[9] and Kelen–Tüdos[20] plot. In the case of the COPMM series, the reactivity ratios can be

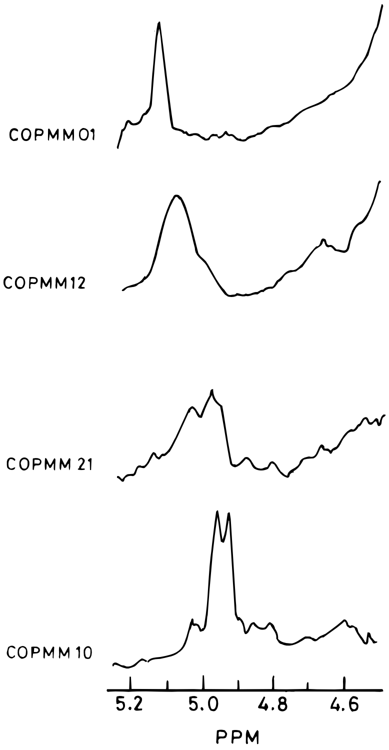


Figure 7. Expanded region of the ^{1}H NMR spectra, showing the end groups.

Table 5. Reactivity Ratios for the Oxidative Copolymerization of α-Methylstyrene with Styrene and Methyl Methacrylate, Initiated by AIBN at 50 °C

method	r_A	r_S	$r_A r_S$	ref
α-Methylstyrene/Styrene				
literature	1.60	0.71	1.10	19
Finemann−Ross	0.96	0.65	0.62	this work
Kelen−Tüdos	0.98	0.67	0.66	this work
α-Methylstyrene/MMA				
literature	15.00	0.04	0.62	6
Finemann−Ross	13.98	0.04	0.62	this work
Kelen−Tüdos	14.51	0.05	0.66	this work
triad fractions (from ^{13}C NMR spectra)	14.31	0.04	0.54	this work

calculated from the "triad" fractions also. The reactivity ratios were calculated from "diad" probabilities as follows:

$$r_A = \frac{[P(AO_2/MO_2)]^{-1} - 1}{x}$$

$$r_M = ([P(MO_2/AO_2)]^{-1} - 1)x$$

where x is the feed ratio [A]/[M]. The "diad" probabilities, as discussed earlier, were obtained from "triad" fractions.[12] The reactivity ratios for the two series of copolyperoxides calculated using different methods are given in Table 5.

Thermal Degradation. All the copolyperoxides undergo exothermic degradation. The major products of degradation have been found to be acetophenone, benzaldehyde, and formaldehyde in the case of the copolyperoxides of styrene and α-methylstyrene. In the case of the copolyperoxides with MMA, methyl pyruvate is obtained instead of benzaldehyde. The energetics of the thermal degradation of these copolyperoxides have been studied by DSC. The value of the exothermicity of degradation was found to be $\Delta H_d = 788 \pm 20$ kJ/mol, for all the copolyperoxides. The activation energy for degradation obtained from the Kissinger plot[21] gave a value of ~152 kJ mol^{-1}, which is roughly the O−O bond dissociation energy. These results confirm that the copolyperoxides pyrolyze according to a random scission of the peroxide group, followed by a chain unzipping mechanism, similar to the one reported for the homopolyperoxides.[22]

Conclusions

Two series of copolyperoxides of α-methylstyrene have been synthesized, and their microstructures have been analyzed. The results obtained from the solution NMR indicate that, in the case of the copolyperoxide of α-methylstyrene and styrene, the AO_2 and SO_2 units tend to be more random, whereas in the case of the copolyperoxide of α-methylstyrene and MMA, the AO_2 and MO_2 units tend to alternate. This is consistent with our earlier studies on the copolyperoxide of styrene and methyl methacrylate. From the ^{13}C NMR spectra, it is clear that the carbonyl and ipso carbons are sensitive to a "triad" sequence. The experimental data from ^{13}C NMR spectra match with the calculated sequence distributions, confirming the assignment of the resonance signals. The peroxide radical, being an electron acceptor, is more reactive toward monomers having more electron-donating ability. Hence, MO_2 radicals will always have a preference for α-methylstyrene rather than methyl methacrylate.

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