Oxidative Copolymerization: Microstructure Analysis of the Terpolymer of Styrene, Methyl Methacrylate, and Oxygen

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ABSTRACT: This paper reports the first study of the microstructure of a copolyperoxide by nuclear magnetic resonance spectroscopy. The copolyperoxides of styrene and methyl methacrylate (MMA) of various compositions have been synthesized. An analysis of the resonance signal of the backbone methylene protons gave the diad sequence probabilities which led to the calculation of the oxidative copolymerization reactivity ratios for styrene and MMA and the microstructural parameters like average chain length of the repeat unit sequences, run number, etc. The results point to the tendency of the SO_2 and MO_2 units to alternate in the chain. Compared to poly(styrene peroxide), the aromatic C1 seems to be stereosensitive in the terpolymers.

Introduction

The simultaneous occurrence of oxidation and polymerization of vinyl monomers has been the subject of many investigations. Regardless of the method of initiation, oxidative polymerization encompasses all instances of vinyl polymerization in the presence of oxygen. In spite of its technological importance in coatings and organic adhesives, in determining the thermal stability of commercial polymers and in synthesizing polymeric peroxides which are of interest as initiators and auto-combustible fuels, oxidative polymerization has yet to gain significance.[1-5]

In addition to the polyperoxide, oxidative polymerization of vinyl monomers yields low molecular weight carbonyl compounds due to the side reactions such as oxidation of the monomers, cleavage of the double bond, degradation of the peroxides formed, etc. The relative distribution of the products and the composition of the polymer obtained depends upon the partial pressure of oxygen. At a high partial pressure of oxygen, the formation of low molecular weight compounds is negligibly small, and the polymer formed will have peroxide units alternating with the vinyl monomer units.[6] The stability of these alternating copolymers depends upon the structure of the vinyl monomer unit in the polymer as well as the oxygen-absorbing capacity of the monomer.[3,7]

The term oxidative copolymerization is applied when two vinyl monomers (M_1 and M_2) along with oxygen, result in the formation of a terpolymer of the general formula $-[-(-M_1-O-O-)_x-(-M_2-O-O-)_y-]_n-$. The earlier work on oxidative copolymerization aimed at the comparative rates of oxidation of different monomers and their relative tendency for reaction with a peroxide radical.[8-10] The oxidative copolymerization kinetics of a number of systems has revealed that the organic part of the peroxide radical (M in $MO_2^\bullet$) has a small but significant effect on the propagation reactions of the peroxide radical. No attempt has been made so far to analyze the microstructure of the terpolymer formed, which conveys diagnostic information about the polymerization.

Nuclear magnetic resonance spectroscopy, a powerful tool in the quantitative examination of the microstructure and dynamic behavior of macromolecules, becomes quite simple in systems of this kind where the hydrocarbon entities are separated by a heteroatom unit. The transmission of the structural information through the heteroatom unit in relation to the hydrocarbon-backbone analogues is the principal feature of interest in these systems. There are a few studies on the ^1H and ^{13}C NMR spectra of synthetic polymers of the type $-[CH_2-CH(R)-X-]_n-$, which incorporate a heteroatom unit X (X = O, S, CO, etc.) and an asymmetric center in their backbone.[11-13] The only polyperoxide studied in this respect is poly(styrene peroxide). Cais and Bovey demonstrated the configurational sensitivity of the backbone carbons and the ideal Bernoullian nature of the chain propagation using NMR spectroscopy.[13] There are hardly any reports on the sequence analysis of the copolyperoxides, though there are a few studies on the kinetics and mechanism of their formation.[8]

In this paper, we report the synthesis of the terpolymer of styrene, methyl methacrylate, and oxygen and the monomer sequence distribution in the terpolymer by ^1H and ^{13}C NMR spectroscopy. On the basis of the unconditional diad probabilities, the reactivity ratios of the monomers and the run number of the copolymer are calculated.

Experimental Section

Reagents. Styrene and methyl methacrylate (MMA) were freed of inhibitor and distilled under reduced pressure prior to use. The oxygen used was of high purity. Azobis(isobutyronitrile) (AIBN) (Fluka, AG) was recrystallized three times from methanol.

Synthesis of the Terpolymers. The terpolymers were synthesized by passing a copious flow of oxygen through the mixture of styrene and methyl methacrylate containing 0.01 M AIBN for 20–36 h. The feed ratio was varied to get terpolymers of different composition. The amount of MMA in the feed was always kept greater since its oxygen absorption is 10 times less than that of styrene.[8] The polymer was separated from the reaction mixture by precipitation into petroleum ether and was further purified by repeated precipitation from benzene solution.

NMR Spectra. All ^1H and ^{13}C NMR spectra were recorded at room temperature, on a Bruker AC-F 200-MHz spectrometer. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ (10 mg/mL) and DMSO-d_6 (150 mg/mL), respectively. The chemical shifts are reported in ppm from tetramethylsilane. The ^1H NMR signals were deconvoluted and peak areas determined by a separate computer program, assuming a Lorentzian line shape. The inverse gated decoupling experiments were carried out with an initial delay of 25 s and a spectral width of 12 500 Hz. A total of 16K data points were used for acquisition. A line broadening of 2 Hz was applied before Fourier transformation in order to increase the signal-to-noise ratio in the ^{13}C NMR spectra.

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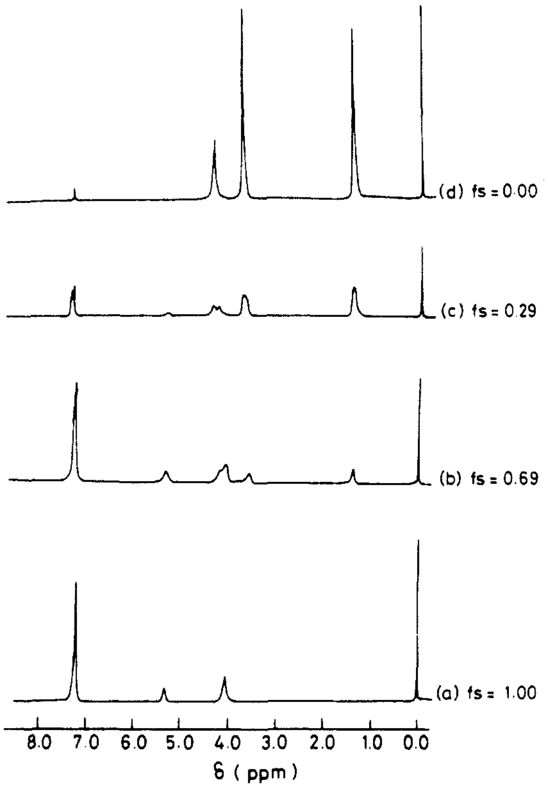
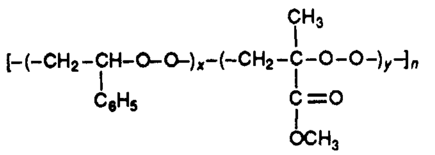


Figure 1. 200-MHz ^{1}H NMR spectra of the terpolymers of styrene, oxygen, and methyl methacrylate in $CDCl_3$ at 298 K.

Results and Discussion

Proton Spectra. Composition of the Terpolymer. The ^{1}H NMR spectra of the terpolymers of different composition are shown in Figure 1. The peaks were assigned to the respective protons in comparison with the ^{1}H spectra of the homopolyperoxides, viz. poly(styrene peroxide) (PSP) and poly (methyl methacrylate peroxide) (PMMAP). The shielding of the $-CH_3$ of the MMA unit due to the phenyl group is not visible in this case, as observed in the hydrocarbon-backbone analogue, the styrene–MMA copolymer, owing to the long peroxide group separating the monomer units.[14] As the concentration of styrene in the chain is decreased, the aromatic protons shift downfield. On the basis of this the general structure of the copolymer was derived as



$$[-(-CH_2-\underset{C_6H_5}{CH}-O-O-)_x-(-CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}-O-O-)_y-]_n$$

The overall chain composition was determined from the integrated intensity ratio of the different peaks of styrene and MMA units. For example, the intensities of phenyl (I_{Ph}) and methyl (I_{Me}) resonances at $\delta = 7.3-7.2$ ppm and $\delta = 1.4-1.3$ ppm, respectively, give the mole fraction of styrene (f_S) in the copolymer as

$$f_S = 3I_{Ph}/(3I_{Ph} + 5I_{Me})$$

The f_S values so obtained for the copolymers of different composition are given in Table I.

The above mentioned structure and composition are further confirmed by the study of the thermal degradation of the copolyperoxide. The degradation products of the copolyperoxide have been identified by GC–MS as benzaldehyde, methyl pyruvate, and formaldehyde (the major products), which must be the result of the random scission followed by the unzipping of a pure alternating peroxide chain, according to the mechanism proposed for the degradation of poly(styrene peroxide).[15] The detailed thermochemical studies of the thermal degradation of PSP and PMMAP are reported in the literature.[15,16] From GC–MS data of the degradation products for the copolyperoxide, the ratio of styrene to methyl methacrylate in the chain can be determined as the ratio of the intensity of the peaks, at $m/e = 106$ and $m/e = 43$, which are the base peaks for benzaldehyde and methyl pyruvate, respectively. The compositions thus obtained are in good agreement with those determined from ^{1}H NMR.[17]

Table I
Experimental Data for the Oxidative Copolymerization of Styrene and Methyl Methacrylate, Initiated by AIBN at 50 °C

copolymer no.	mole fraction of styrene		reaction time (h)	conversion (wt %)
	feed	copolymer		
1	1.00	1.00	12	10.0
2	0.50	0.94	20	5.3
3	0.20	0.69	24	5.0
4	0.10	0.54	28	6.3
5	0.05	0.35	32	4.0
6	0.03	0.29	36	2.8
7	0.01	0.15	40	2.7
8	0.00	0.00	48	3.2

Sequence Distribution. Styrene (S), methyl methacrylate (M), and oxygen (O_2) do not homopolymerize under the terpolymerization conditions of high oxygen pressure, as employed here. The radical polymerizations of S with O_2 and M with O_2 always give alternating copolymers, indicating that SS, SM, MS, and MM sequences in the copolymer are negligibly small.[8] Hence, the distribution of the four possible "diad" sequences, SO_2SO_2, SO_2MO_2, MO_2SO_2, and MO_2MO_2, was determined from the ^{1}H NMR spectra (Figure 2). The CH_2 resonance signal at $\delta = 4.02$ ppm was assigned to the SO_2SO_2 diad and the one at $\delta = 4.37$ ppm, to the MO_2MO_2 diad in comparison with the respective homopolyperoxides, PSP and PMMAP (Figure 1a,d). The signal at $\delta = 4.2$ ppm was assigned to the $SO_2MO_2 + MO_2SO_2$ diad on the basis of its intensity variation, which is in accordance with the overall chain composition. These kinds of diads are reported in alkene–alkyne–sulfur dioxide terpolymers where sulfur dioxide units strictly alternate with the hydrocarbon units.[18]

The unconditional probabilities of the four possible diads were derived from the peak areas of the respective ^{1}H NMR signals (Figure 2). The principle of "equivalence of sequence reversibility" was applied to the SO_2MO_2 sequence.[19]

$$P_2[SO_2SO_2] + P_2[SO_2MO_2] + P_2[MO_2SO_2] + P_2[MO_2MO_2] = 1$$

$$P_2[SO_2MO_2] = P_2[MO_2SO_2]$$

$$P_2[SO_2SO_2] + P_2[SO_2MO_2] = P_1[SO_2]$$

$$P_2[MO_2SO_2] + P_2[MO_2MO_2] = P_1[MO_2]$$

where $P_n[A_n]$ is the unconditional probability of the "n"-ad sequence, $[A_n]$. The unconditional probabilities of these diads calculated from the peak areas are given in Table II.

Reactivity Ratios. The polymer and feed composition data show that the relative rates of styrene and methyl methacrylate uptake are dependent on the structure of the growing radical. Consequently, the ratio of styrene to

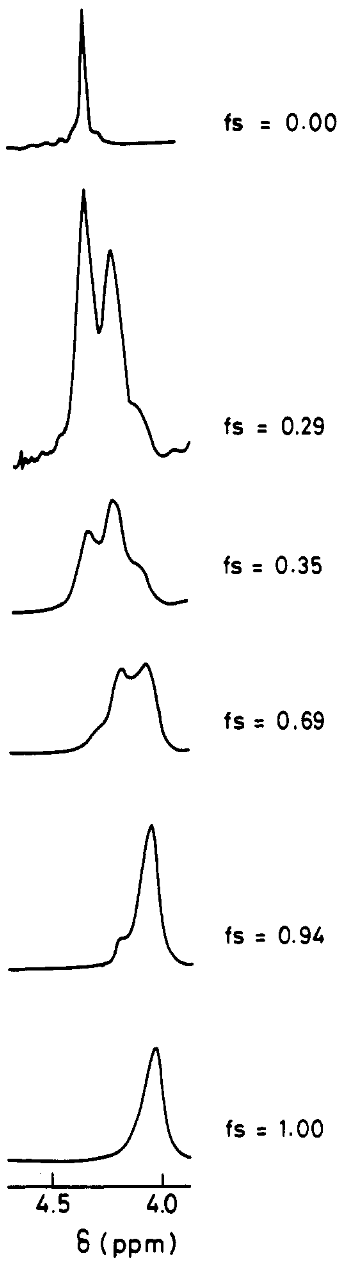


Figure 2. Expanded ^1H signals of the methylene protons of the styrene and methyl methacrylate units in the terpolymers.

Table II
Distribution of the Diad Sequences along the Copolymer Chains, for Styrene–Methyl Methacrylate–Oxygen Terpolymers Prepared by the Oxidative Copolymerization of Styrene and Methyl Methacrylate

copolymer no.	f_S (copolymer)	diad sequence	diad probabilities exptl	diad probabilities calcd
3	0.69	SO_2SO_2	0.424	0.461
		SO_2MO_2 (MO_2SO_2)	0.273	0.233
		MO_2MO_2	0.030	0.073
4	0.54	SO_2SO_2	0.194	0.216
		SO_2MO_2 (MO_2SO_2)	0.308	0.279
		MO_2MO_2	0.190	0.225
5	0.35	SO_2SO_2	0.044	0.107
		SO_2MO_2 (MO_2SO_2)	0.294	0.257
		MO_2MO_2	0.367	0.372
6	0.29	SO_2SO_2	0.030	0.051
		SO_2MO_2 (MO_2SO_2)	0.244	0.210
		MO_2MO_2	0.484	0.529

MMA units in the copolyperoxide (R_p) is not simply proportional to the ratio of styrene to MMA in the feed. This indicates a penultimate effect in this polymerization system. It is clear from Table I that the $SO_2^{\bullet}$ radical reacts with styrene at a faster rate than MMA. In the application of the copolymerization equation, as applied to a terpolymerization system with penultimate effect, where all three monomers are not homopolymerizable, the styrene and methyl methacrylate radicals ($S^{\bullet}$ and $M^{\bullet}$) are assumed to react only with oxygen. This assumption is justified by the absence of resonance signals corresponding to the sequences SS, MM, SM, and MS in the ^1H and ^{13}C NMR spectra (Figures 1 and 3). The relevant propagation steps which control the terpolymer composition are

$$SO_2^{\bullet} + S \xrightarrow{k_{ss}} SO_2S^{\bullet}$$

$$SO_2^{\bullet} + M \xrightarrow{k_{sm}} SO_2M^{\bullet}$$

$$MO_2^{\bullet} + S \xrightarrow{k_{ms}} MO_2S^{\bullet}$$

$$MO_2^{\bullet} + M \xrightarrow{k_{mm}} MO_2M^{\bullet}$$

The monomer reactivity ratios may be defined as[8,20]

$$r_s = \frac{\text{rate constant for the reaction of } SO_2^{\bullet} \text{ and S}}{\text{rate constant for the reaction of } SO_2^{\bullet} \text{ and M}} = \frac{k_{ss}}{k_{sm}}$$

$$r_m = \frac{\text{rate constant for the reaction of } MO_2^{\bullet} \text{ and M}}{\text{rate constant for the reaction of } MO_2^{\bullet} \text{ and S}} = \frac{k_{mm}}{k_{ms}}$$

Since the monomer conversion is less than 10% (Table I) in all cases, the diad probabilities from NMR data are sufficient to solve for the reactivity ratios.

The diad probabilities led to the calculation of r_s and r_m as follows.[21]

$$r_s = (l_s - 1)/\mathbf{x}$$

$$r_m = (l_m - 1)\mathbf{x}$$

where l_s and l_m are the average sequence lengths of the SO_2 and MO_2 sequences in the copolymer and $\mathbf{x}$ is the feed ratio (S/M). l_s and l_m are given by the unconditional diad probabilities,

$$l_s = P_1[SO_2]/P_2[SO_2MO_2]$$

$$l_m = P_1[MO_2]/P_2[MO_2SO_2]$$

The oxidative copolymerization reactivity ratios for styrene and MMA thus obtained are $r_s = 5.95$ and $r_m = 0.065$. These values are comparable with that reported by Mayo et al.[8] where the reactivity ratios have been calculated from the rates of oxidation and polymerization. The product of the reactivity ratios, $r_s r_m = 0.39$ shows the tendency for the SO_2 and MO_2 units to alternate in the copolymer. The ratio of the reactivity ratios $r_s/r_m \simeq 10$ indicates that styrene is 10 times more reactive to the peroxide radical than MMA. This value is equal to the relative oxygen absorption rate for styrene compared to that for MMA.[8]

Though the calculation of reactivity ratios from NMR data is straightforward, the basic assumption about the absence of the cleavage products introduces a little error in the calculations.

Run Number. The microstructure of a copolymer is generally expressed in terms of the run number, which is

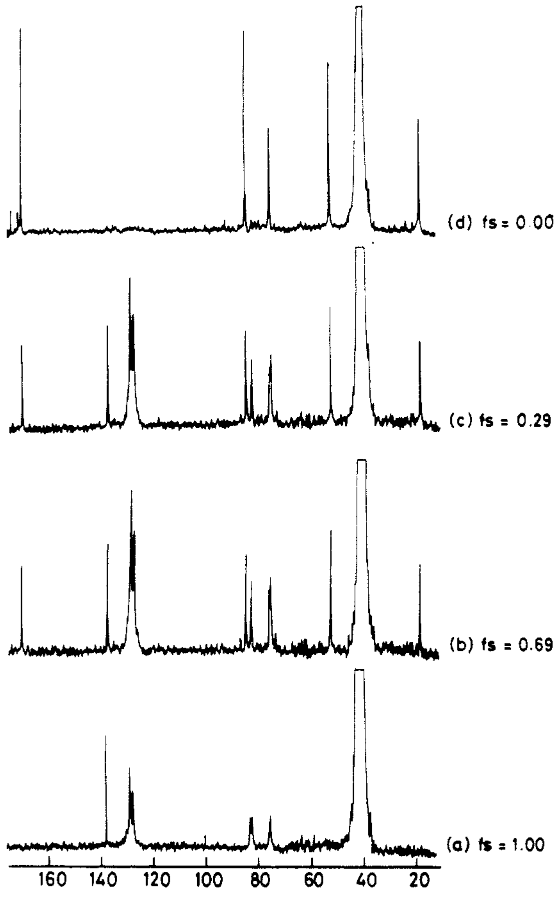


Figure 3. 50.12-MHz ^{13}C NMR spectra of the terpolymers in DMSO-d_6.

Table III
Average Sequence Length and Run Number of the Copolymers Calculated from the Diad Fractions

		av sequence length		run no.	
copolymer no.	f_s (copolymer)	l_{SO_2}	l_{MO_2}	R	R_{random}
3	0.69	2.55	1.11	55	43
4	0.54	1.63	1.62	62	50
5	0.35	1.15	2.25	59	46
6	0.29	1.12	2.98	49	41

the average number of monomer sequences (runs) per hundred units occurring in the copolymer chain. Here, since oxygen (the peroxide group) strictly alternates with both styrene and methyl methacrylate units in the chain, the run number can be expressed in terms of the runs of SO_2 and MO_2 units. The diad probabilities are related to the run number as follows.

$$P[SO_2/SO_2] = (\%\ [SO_2] - R/2)/\%\ [SO_2]$$

$$P[SO_2/MO_2] = R/2 \times \%\ [SO_2]$$

where $P[A/B]$ represents the conditional probability that a unit A succeeds the unit B and R is the run number. In terms of the unconditional probabilities,

$$R = 2 \times 100 \times P_2[SO_2MO_2]$$

The run numbers calculated for different copolymers are given in Table III. For a strictly random copolymer the run number is given as

$$R_{random} = \%\ SO_2 \times \%\ MO_2/50$$

The run numbers obtained for these copolymers are higher than R_{random}, which again points to the tendency of the SO_2 and MO_2 units to alternate in the chain.[22]

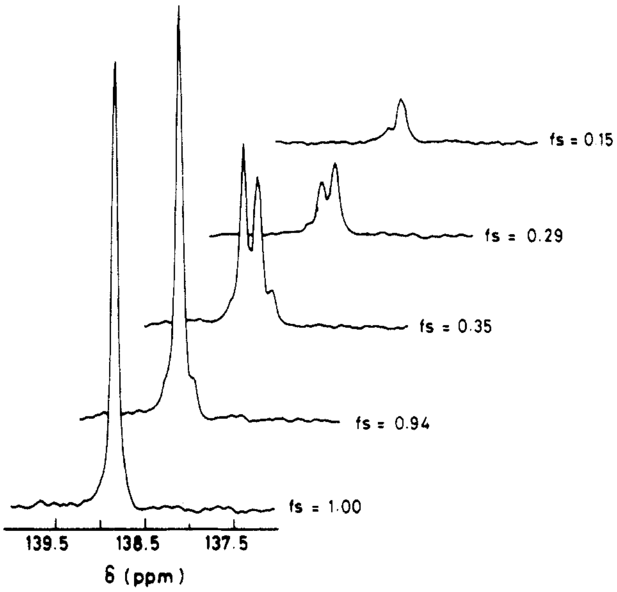


Figure 4. Expanded ^{13}C signals of the aromatic C1 of the styrene units in the terpolymers.

Carbon-13 Spectra. Figure 3 shows the 50.12-MHz $^{13}C\{^1H\}$ spectra of the different terpolymers. The assignment of the different carbons was made from the spectra of the homopolyperoxides. The terpolymer compositions were determined from the integrated intensity of the peaks after inverse gated decoupling. The chemical shift and $J_{^{13}C-^1H}$ observed (J values obtained from the off-resonance spectra) for the terpolymers do not differ substantially from the respective values for the homopolyperoxides. The configurational sensitivity of the backbone carbons of the SO_2 unit is found to be less in the terpolymers than in PSP. As the concentration of the $SO_2SO_2SO_2$ triads in the chain is reduced, the methine and methylene carbons of the SO_2 unit tend to give single peaks. The three signals observed for the aromatic C1 carbon of the terpolymers (Figure 4) may be due to the SO_2-centered configurational triads. The sensitivity of the aromatic C1 to the chain configuration has been reported in the case of alternating copolymers of styrene with carbon monoxide,[23] sulfur,[11] and methyl methacrylate.[24] However, due to the lack of suitable model compounds, an assignment of these signals and determination of the prevailing stereochemical mode of enchainment were not possible. Since these signals differ by only 0.15 ppm and their intensities drastically vary with the copolymer composition in a way similar to the intensity variation of stereochemical triads as predicted by Bernoulli statistics, we believe that these signals could be due to different SO_2-centered configurational triads, though we do not find any factor responsible for a biased configurational arrangement. The signals due to other carbons like C=O, OCH_3, and CH_3 did not show any resolvable peaks which could shed light on the microstructure of the polymer.

Conclusion

The ^1H and ^{13}C NMR spectra of the terpolymers of styrene, oxygen, and MMA enable us to draw a number of conclusions regarding the intramolecular chain structure. It is shown that in the ^1H NMR spectra, the peak grouping in the region of the methylene protons is sensitive to diad sequences. The new peaks seen for the aromatic C1 may give information on the stereochemistry of the chain. Finally, we wish to say that, unlike those of conventional terpolymers, the NMR spectra of copolyperoxides are simple but intriguing owing to the long-range interactions which are transmitted through the heteroatom units in the backbone.

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