

Reactivity Ratios for the Terpolymerization of Methyl Methacrylate, Vinyl Acetate, and Molecular Oxygen

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ABSTRACT: The copolymerization of methyl methacrylate (MMA) and vinyl acetate (VAc) under high oxygen pressure was investigated. Copolyperoxides of various compositions were synthesized by the free-radical-initiated oxidative copolymerization of MMA and VAc monomers. The copolyperoxide compositions obtained from ^1H and ^{13}C NMR spectra were used for determining the reactivity ratios of the monomers. The reactivity ratios indicated a larger proportion of MMA units statistically placed in the copolyperoxides. A theoretical analysis based on semiempirical AM1 calculations was performed to support the reactivity ratios. NMR studies showed irregularities in the copolyperoxide chain due to the cleavage reactions of the propagating peroxide radical. Thermal analyses of the copolyperoxides by differential scanning calorimetry gave evidence for the presence of alternating peroxide units in the copolyperoxide chain. The activation energies of thermal degradation suggested that degradation was controlled by the dissociation of the peroxide ($-\text{O}-\text{O}-$) bond in the backbone of the copolyperoxide chain. © 2002 John Wiley & Sons, Inc. *J Polym Sci Part A: Polym Chem* 40: 564–572, 2002; DOI 10.1002/pola.10115

Keywords: copolyperoxides; reactivity ratios; chain irregularities; low molecular weight; differential scanning calorimetry (DSC); exothermic degradation

INTRODUCTION

Studies on the role of oxygen in radical polymerization begun by Lebedev¹ and Staudinger² and subsequent research have established the principle features of the mechanism of polymerization of vinyl monomers with oxygen. Interestingly, oxygen has been found to exhibit two opposing roles, initiator and inhibitor, in vinyl polymerization, depending on the monomer and the reaction conditions. The role of oxygen in various polymerization reaction was reviewed by Kishore and Bhanu.³

Vinyl polyperoxides are alternating copolymers of vinyl monomers and molecular oxygen.⁴ They

are important as polymeric thermal initiators,^{5,6} photoinitiators,⁷ and base-catalyzed initiators⁸ for vinyl monomers in the syntheses of homopolymers and block and novel comb copolymers. The uniqueness of this class of polymers is that they pyrolyze highly exothermically,⁹ in contrast to other common polymers, which generally degrade endothermically. They are receiving renewed attention because of their autopyrolyzability and autocombustibility, which have made them candidates for specialized fuels of the future.¹⁰

With the goal of improving the quality of polymeric coatings and adhesives, the use of monomer mixtures and crosslinking agents has attracted much attention.¹¹ In this context, it is desirable to understand the mechanism of copolymerization of a mixture of monomers in the presence of oxygen. The term *oxidative copolymerization* is applied when two monomers (R_1 and R_2)

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Table I. Experimental Results for the Oxidative Copolymerization of MMA with VAc Initiated by AIBN at 50 °C

| Polymer | Reaction Time (h) | Yield (%) | [M] Feed | Molar Fraction of MMA | | | |
|---------|-------------------|-----------|----------|-----------------------|---------------------|-------|------|
| | | | | Copolyperoxide | | M_n | PDI |
| | | | | ¹ H NMR | ¹³ C NMR | | |
| PMMAP | 80 | 9.2 | 1.0000 | 1.0000 | 1.0000 | 2750 | 1.75 |
| VM1 | 60 | 7.5 | 0.7480 | 0.9035 | 0.9091 | 2800 | 1.27 |
| VM2 | 60 | 6.3 | 0.4750 | 0.7736 | 0.7846 | 2640 | 1.25 |
| VM3 | 60 | 5.5 | 0.3408 | 0.6906 | 0.7143 | 2148 | 1.39 |
| VM4 | 60 | 7.8 | 0.2022 | 0.5330 | 0.5556 | 1710 | 1.50 |
| PVAcP | 84 | 9.5 | 0.0000 | 0.0000 | 0.0000 | — | — |

reacting in the presence of high oxygen pressure result in the formation of terpolymers of the type $-\left[(R_1-O-O)_X(R_2-O-O)_Y\right]_n-$. The oxidation of two monomers can be considered a special case of terpolymerization when the monomers do not homopolymerize. The uniqueness of this system is that it approximates a binary copolymerization system in terms of $-RO_2^{\bullet}$ units. The rate of polymerization may then be described in terms of the copolymerization equation and reactivity ratios.¹² The relative rates of attack on the two monomers by each of the two peroxide radicals may be determined solely from the composition of the resulting copolyperoxide.¹³

Compared with simple vinyl polyperoxides obtained from a vinyl monomer and oxygen, those obtained by the oxygen copolymerization of a mixture of vinyl monomers have been less studied.⁴ Earlier work on oxidative copolymerization was aimed at studying the comparative rates of oxidation of different monomers and their reactivities toward peroxide radicals.^{14,15} In this work, we studied the oxidative copolymerizations of methyl methacrylate (MMA or M) and vinyl acetate (VAc or V). The objective was to study the reactivity ratios by NMR spectroscopy. Other physical techniques, such as Fourier transform infrared (FTIR) and differential scanning calorimetry (DSC), were also used for further characterization of the copolymers.

EXPERIMENTAL

Materials

MMA (Rolex, India) was freed from the inhibitor by being washed first with 5% NaOH and then

with water several times. After drying over anhydrous Na_2SO_4 , it was distilled under reduced pressure. VAc (Rolex) was freed from the inhibitor by being dried over $CaCl_2$ and then being fractionally distilled. 2,2'-Azobisisobutyronitrile (AIBN; Koch Light, England) was recrystallized twice from methanol. High-purity oxygen (Bhruka gases, 99.9%) was used. Reagent-grade solvents (Ranbaxy, India), including petroleum ether and CH_2Cl_2 , were purified by standard procedures.

Synthesis of the Copolyperoxides

The required quantities of MMA, VAc, and AIBN (0.01 mol L^{-1}) as an initiator were placed in a 300-mL Parr reactor (Parr Instruments Co., United States) and pressurized to 100 psi with oxygen. The reactor was equipped with a digital pressure transducer, a temperature controller, and a mechanical stirrer. The polymerization was carried out at 50 °C with stirring for about 60–84 h, and the temperature was controlled within ± 0.5 °C. The conversion was kept below 10%. The feed ratio was varied to obtain terpolymers of different compositions. The polymers were isolated from the reaction mixture with petroleum ether as a nonsolvent and purified by repeated precipitation from a CH_2Cl_2 solution followed by removal of the solvent by vacuum drying. Details of the synthesis and the identification of the copolyperoxides are given in Table I.

Computational Methods

The well-documented commercial software package Insight II® and the semiempirical program

package Ampac/Mopac (version 6.0) from Biosym Technologies were used.¹⁶ The MSI Insight II® code assigns an empirical potential energy function to each atom from the central valence force field depending on the element type and the nature of the chemical bond. Furthermore, this code has been benchmarked for numerous other molecular systems, and its accuracy is documented in the literature. The geometries of all the compounds were fully optimized with AM1 Hamiltonian.^{17,18}

Techniques

¹H and ¹³C NMR spectra were recorded at room temperature on a Bruker ACF 200-MHz spectrometer in CDCl₃ and CH₂Cl₂ (D₂O external lock), respectively. The reference used was tetramethylsilane. The ¹³C NMR spectra were obtained under inverse-gated decoupling with 10-s delays between the pulses. A line broadening of 2 Hz was applied before Fourier transformation to enhance the signal-to-noise ratio.

The FTIR spectrum was recorded on a Bruker Equinox 55 FTIR spectrometer. Thermal analyses were performed with a PerkinElmer DSC-2C differential scanning calorimeter under a nitrogen atmosphere at heating rates of 5, 10, 20, 40, and 80 °C/min with sample sizes of 1–5 mg. The molecular weights of the polymers were obtained with a Waters high performance liquid chromatography (HPLC)/gel permeation chromatography (GPC) instrument (refractive-index detector) with tetrahydrofuran as a mobile phase at a flow rate of 1.0 mL min⁻¹ at 30 °C with polystyrene standards.

RESULTS AND DISCUSSION

The copolymers obtained were sticky materials. The number-average molecular weight (M_n) and polydispersity index (PDI) of the polymers are presented in Table I. The polymers had low molecular weights and underwent facile degradation during their polymerization, generating chain-transfer agents such as aldehydes, which reacted with growing macroradicals, resulting in the low molecular weights.¹⁹ The copolyperoxides needed to be stored in the dark and in a refrigerator to minimize degradation.

FTIR Spectra

The FTIR spectra of neat films of poly(methyl methacrylate peroxide) (PMMAp), VM3, and

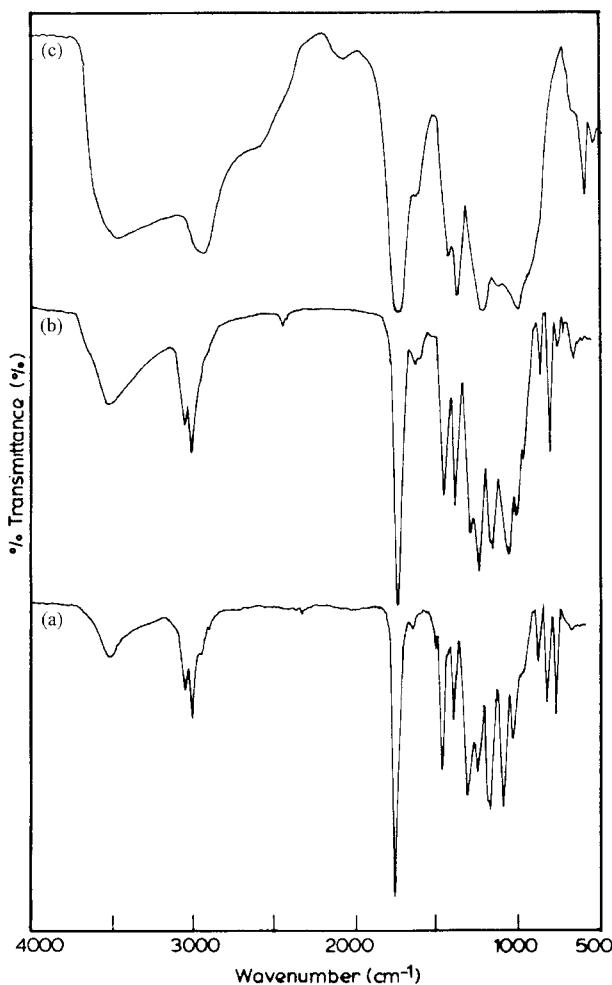


Figure 1. FTIR spectra of (a) PMMAP, (b) VM3, and (c) PVAcP.

poly(vinyl acetate peroxide) (PVAcP) are shown in Figure 1. The spectra are all similar, except for the variation in the intensities of the different peaks. The strong band seen near 1020 cm⁻¹ in the spectra was assigned to the peroxide (—O—O—) bond stretch. The very intense band appearing at 1750 cm⁻¹ was assigned to the carbonyl groups. Other carbonyl groups present at different end groups also showed infrared absorption in this region and so were not distinguishable. The C—H absorption can be observed at 2890–3020 cm⁻¹. The broad absorption between 3400–3500 cm⁻¹ was due to the hydroxyl and hydroperoxide end groups. The formation of these end groups via various chain-transfer mechanisms is known.^{20–22} The bands at 1625 cm⁻¹ in the copolyperoxides were due to the stretching of C=C groups present as chain ends. There is evidence for the presence of the carbonyl and C=C

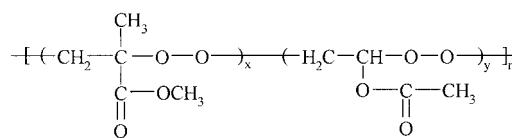
end groups in vinyl polyperoxides.²¹ The intensity of the peroxide stretching band at 1020 cm⁻¹ of VM3 slowly decreased at room temperature when the sample was kept for a longer time and finally disappeared. Also, the hydroxyl band became broad, demonstrating the instability of the copolyperoxides.

Compositions of the Copolyperoxides

Both the ¹H and ¹³C NMR spectra reveal that the monomers did not homopolymerize under the high oxygen pressure employed. For all the polymers, the downfield shift in the main-chain CH₂ and CH protons was due to two additional electronegative oxygen atoms directly attached to them. Figure 2 shows typical ¹H NMR spectra of VM2, VM4, and the homopolyperoxides PMMAP and PVAcP. The ¹H NMR spectrum of PMMAP shows signals at δ = 1.45, 3.76, and 4.34 ppm, which were assigned to the α -methyl, —OCH₃, and —CH₂— protons, respectively.²³ In the ¹H NMR spectrum of PVAcP, the signals at δ = 2.07, 4.1, and 6.45 ppm were assigned to the methyl, methylene, and methine protons, respectively.²⁴ The copolyperoxide compositions were obtained from the ratio of the intensities of the peak corresponding to the methyl group at δ = 1.45 ppm to that at δ = 2.07 ppm. The results are given in Table I. The methylene region of the spectrum is complex because of the excess methylene groups present in the homopolyperoxide and copolyperoxide chains as defects. This happened because, during the oxidation of VAc, the peroxy radical preferentially underwent cleavage reactions rather than addition reactions with another VAc molecule.²⁴ This kind of excess methylene group has reported for poly(α -methylstyrene peroxide).²⁵

The ¹³C NMR spectra also show considerable downfield shifts of the main-chain carbons due to the two highly electronegative oxygen atoms to which they were directly bonded. Figure 3 depicts the ¹³C NMR spectra of the copolyperoxides VM2 and VM4 and the homopolyperoxides. In the ¹³C NMR spectrum of PMMAP, the signals at δ = 18.4, 52.2, 75.7, 84.9, and 170.9 ppm were assigned to the α -methyl, —OCH₃, —OCH₂—C=O, and C=O carbons, respectively. Similarly, for PVAcP, the peaks at δ = 20.7, 72.7, 95.0, and 169.6 ppm were assigned to the methyl, methylene, methine, and carbonyl carbons, respectively. The compositions of the copolyperoxides were obtained from the ratio of the inte-

grated intensities of the two methylene group signals. The results are listed in Table I. The compositions of the copolyperoxides obtained from ¹³C NMR spectra were in good agreement with those determined from the ¹H NMR spectra. On the basis of this discussion, the general formula of the copolyperoxide could be represented as follows:



The methylene carbon signal is also complex because of the stereochemistry of this backbone carbon and the excess methylene groups present in the polyperoxide chain. There is a peak at 92.5 ppm in the ¹³C NMR spectrum, which may be attributed to the inclusion of the methylene group with neighboring peroxy (—O—CH₂—O—) groups in the chain. It indicates that cleavage reactions occurred to a considerable extent during oxidative polymerization. The presence of the —O—CH₂—O— group in the polyperoxide chain has also been reported for the oxidation of α -methylstyrene at very low oxygen pressures.²⁵ The copolyperoxides showed a very small peak near 9.75 ppm in ¹H NMR spectra due to the O=CH— group present at the chain ends.

Reactivity Ratios

In the derivation of the equation for the cooxidation of two monomers, oxygen was considered a third monomer. Under the conditions employed here, such as high partial oxygen pressure, both monomers did not homopolymerize.⁴ Furthermore, the propagation reactions involving the addition of one or the other monomer to a second monomer radical were assumed to be negligible. This assumption was supported by the absence of signals corresponding to —MMA—VAc— in the ¹H and ¹³C NMR spectra of the copolyperoxides. In the oxidative polymerization, the reactivity of the monomer radicals (R[•]) with oxygen was very high compared with that of —RO₂[•] with the monomer (R). Because the copolymer composition was not proportional to the feed composition, a penultimate effect could be expected.²⁶ Therefore, with a penultimate effect assumed, the important rate-determining propagation steps in the oxidative copolymerization of MMA with VAc may be writ-

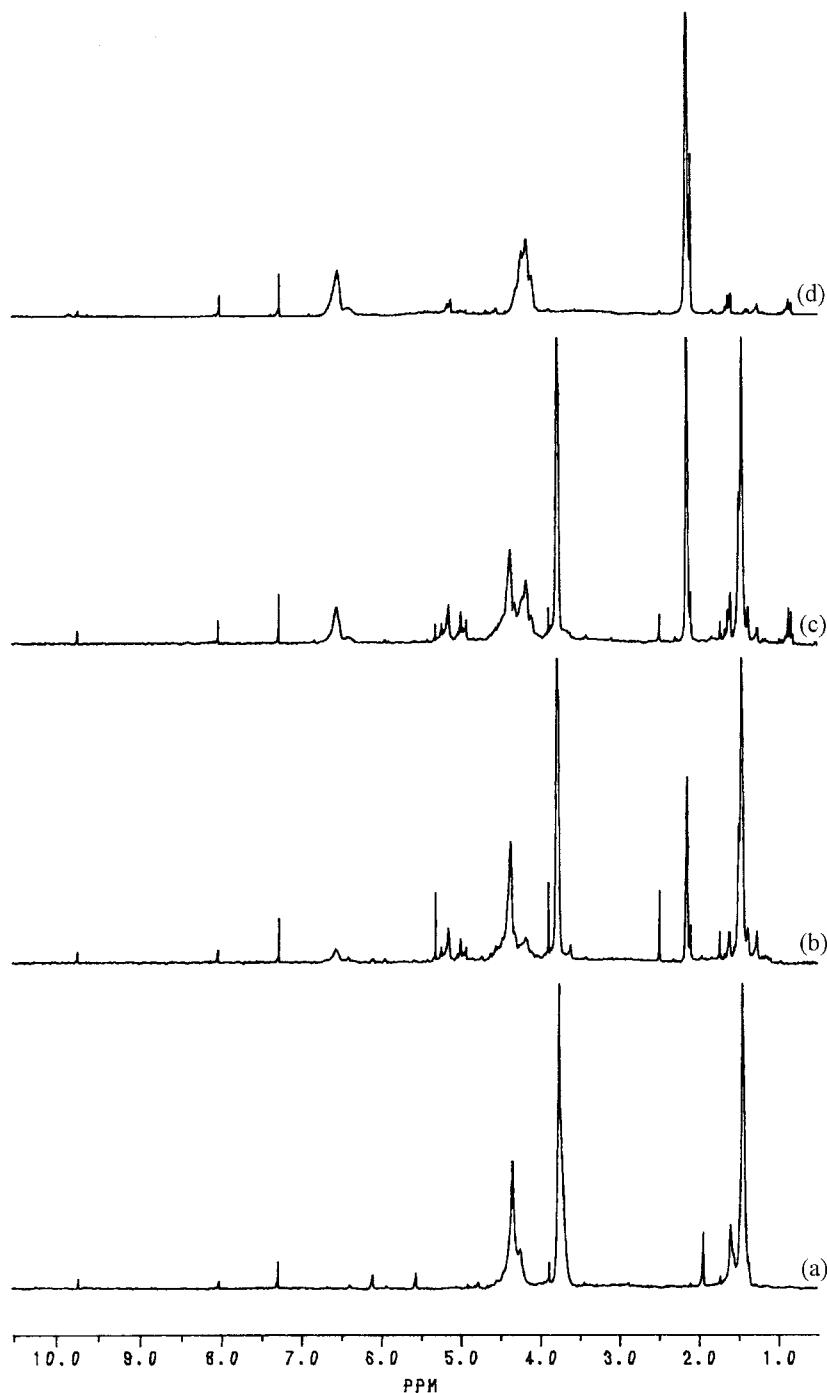


Figure 2. ^1H NMR spectra of (a) PMMAP, (b) VM2, (c) VM4, and (d) PVAcP in CDCl_3 .

ten as follows (the rate constants are also shown):²⁷



If we apply the steady-state approximation separately for the reactive species —MO_2^\bullet and —VO_2^\bullet ,

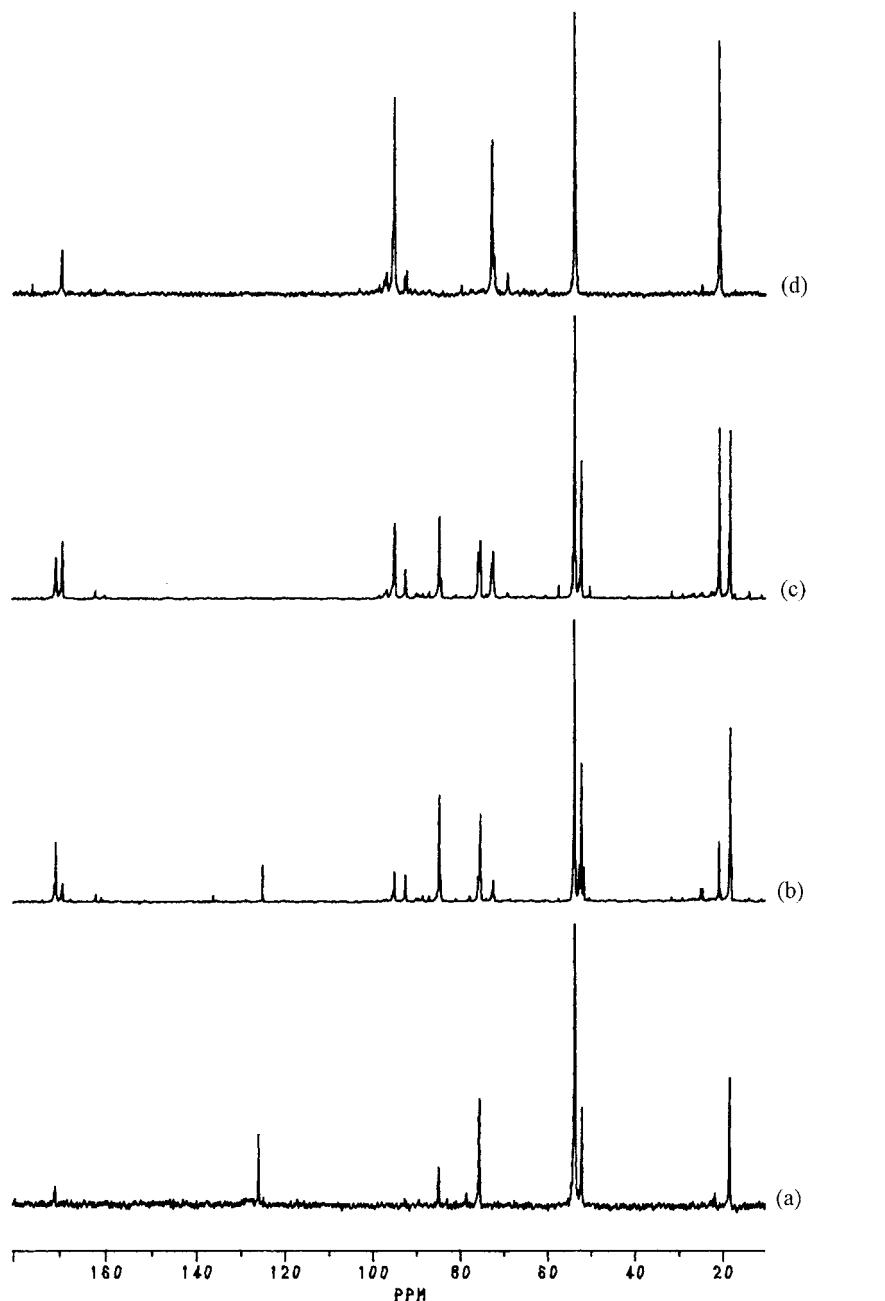


Figure 3. ^{13}C NMR spectra of (a) PMMAP, (b) VM2, (c) VM4, and (d) PVAcP in CH_2Cl_2 (D_2O external lock).

the composition of the copolymer can be expressed in terms of the feed composition and the reactivity ratios:

$$\frac{d[\text{M}]}{d[\text{V}]} = \frac{[\text{M}](r_{\text{M}}[\text{M}] + [\text{V}])}{[\text{V}]([\text{M}] + r_{\text{V}}[\text{V}])} \quad (5)$$

where $d[\text{M}]/d[\text{V}]$ denotes the ratio of MMA to VAc in the copolyperoxide; $[\text{M}]$ and $[\text{V}]$ are the corre-

sponding feed ratios; and r_{M} and r_{V} are the reactivity ratios for MMA and VAc, respectively.¹⁴

$$r_{\text{M}}$$

$$= \frac{\text{rate constant for the reaction of } -\text{MO}_2^\bullet + \text{M}}{\text{rate constant for the reaction of } -\text{MO}_2^\bullet + \text{V}}$$

$$= \frac{k_{\text{MOM}}}{k_{\text{MOV}}}$$

r_V

$$= \frac{\text{rate constant for the reaction of } -\text{VO}_2^\bullet + \text{V}}{\text{rate constant for the reaction of } -\text{VO}_2^\bullet + \text{M}}$$

$$= \frac{k_{\text{VOV}}}{k_{\text{VOM}}}$$

Equation 5 for the oxidative copolymerization of two vinyl monomers resembles the Mayo–Lewis copolymerization equation²⁷ for a two-monomer system, except in the definition of the reactivity ratio. Therefore, the reactivity ratios give the relative tendency of the peroxide radical ($-\text{MO}_2^\bullet$ or $-\text{VO}_2^\bullet$) to add to a monomer of the same kind or another.

The reactivity ratios, determined from Fineman–Ross²⁸ and Kelen–Tudos²⁹ plots and the Joshi–Joshi³⁰ method, were $r_M = 2.919 \pm 0.016$ and $r_V = 0.088 \pm 0.030$, $r_M = 3.001 \pm 0.017$ and $r_V = 0.108 \pm 0.025$, and $r_M = 2.927 \pm 0.071$ and $r_V = 0.090 \pm 0.040$, respectively. The product of the Fineman–Ross reactivity ratios, $r_M r_V = 0.257$, shows that the two monomers were statistically placed along the copolymer chain with an increasing tendency toward alternation. Copolymers containing appreciable amounts of the acetate monomers were not expected because $r_M \gg r_V$.³¹ The reactivity ratio of r_M to r_V ($\equiv 33$) indicates that MMA was 33 times more reactive toward a peroxide radical than VAc. In the MMA–VAc system, copolymerization was not efficient because the MMA radical was too unreactive to add onto the VAc monomer. In the absence of oxygen, the reactivity ratio of MMA was nearly 10^3 times higher than that of VAc.³¹ However, during oxidative copolymerization, the reactivity ratio of MMA to VAc was greatly reduced and was only about 30 times higher than that of VAc.

The AM1 calculations for the heat of formation (ΔH_f^0) for model compounds showed that for the radicals $(\text{CH}_3)(\text{CH}_3)(\text{CO}—\text{OCH}_3)\text{C}^\bullet$ and $(\text{CH}_3)(\text{H})(\text{O}—\text{COCH}_3)\text{C}^\bullet$, ΔH_f^0 was -77.8 and -67.5 kcal mol⁻¹, respectively. This indicates that VAc was more reactive than MMA for homopolymerization. However, under high oxygen pressure, the reactivity ratio was determined by the radicals, $(\text{CH}_3)(\text{CH}_3)(\text{CO}—\text{OCH}_3)\text{C}—\text{O}—\text{O}^\bullet$ and $(\text{CH}_3)(\text{H})(\text{O}—\text{COCH}_3)\text{C}—\text{O}—\text{O}^\bullet$, and the calculated values of ΔH_f^0 for these two radicals were -94.9 and -99.2 kcal mol⁻¹, respectively. This shows that the peroxy radical ($-\text{MO}_2^\bullet$) derived from MMA was more reactive than the peroxy radical derived from VAc ($-\text{VO}_2^\bullet$) for the addition reaction. Inter-

estingly, the monomer that was more reactive to oxygen copolymerization was less reactive to homopolymerization. Because of the presence of the peroxide unit, the difference in ΔH_f^0 from $-\text{MMA}^\bullet$ to $-\text{VAc}^\bullet$ and from $-\text{MMAO}_2^\bullet$ to $-\text{VAcO}_2^\bullet$ changed from -10.3 to 4.3 kcal mol⁻¹. The chief interest in this system is, therefore, the effect of the heteroatom unit on the transmission of reactivity information, particularly in relation to the hydrocarbon backbone analogues. The calculation of the reactivity ratios from the NMR spectral data was straightforward. However, the assumption about the absence of the cleavage products introduced some error into the calculations.

Thermal Degradation

According to the Mayo mechanism,³² vinyl polyperoxides generally undergo random thermal scission at the peroxy bond followed by unzipping of the β -peroxyalkoxy radicals, giving carbonyl compounds. For example, PMMAP on thermal degradation yields methyl pyruvate and formaldehyde in equimolar quantities.²³ However, PVAcP undergoes degradation into formaldehyde, acetic acid, carbon monoxide, and an unidentified reddish-black, noncrystalline substance.²⁴ The DSC thermograms of the copolyperoxides indicated highly exothermic degradation. A representative DSC thermogram of VM3 is given in Figure 4. The enthalpy changes (ΔH_d^0) during the thermal degradation obtained from the DSC thermogram are given in Table II.

The activation energy (E_a) for the process of thermal degradation was determined by Kissinger's method.³³ A plot of $\ln(\phi/T_m^2)$ against $1/T_m$, where ϕ is the heating rate and T_m (K) is the peak temperature obtained from the DSC data, is given for VM3 in Figure 5. The slope of this plot gives the values of E_a tabulated in Table II, and they compare well with the dissociation energy of the peroxide ($—\text{O}—\text{O}—$) bond in dialkyl peroxides,³⁴ homopolyperoxides, and, for example, VM3. The thermal stability, noted from the E_a values,³⁵ reveals PMMAP to be more stable than PVAcP. The E_a values of the copolyperoxides lie between the two homopolyperoxides. The results show that the thermal degradation of the copolyperoxides followed a radical chain scission followed by a chain unzipping mechanism similar to that reported for other polyperoxides.⁹

The copolyperoxides underwent facile thermal decomposition on heating. The products of the

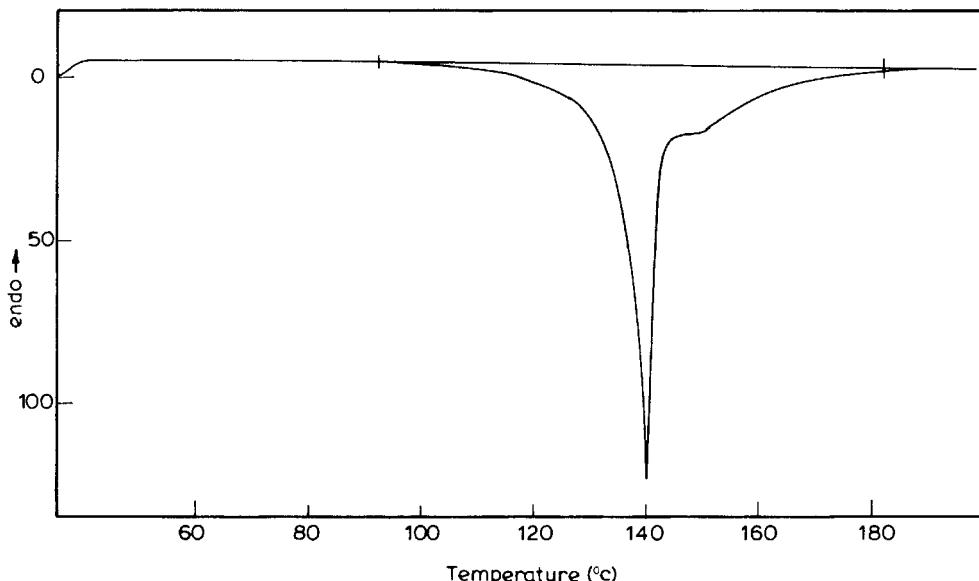


Figure 4. DSC thermogram of VM3.

decomposition of the copolyperoxide heated in a glass tube at 120 °C for 2 h under a nitrogen atmosphere were monitored by GPC. The copolyperoxide degraded into small molecular weight products.³⁶ However, the products of decomposition were not isolated. The thermal degradation in a toluene solution of the copolymer VM2 proceeded slowly at 75 °C. The variation in the M_n value of VM2 is displayed in Figure 6. The thermal degradation of the polyperoxides depended on the dissociation of the peroxide (—O—O—) bond.

CONCLUSION

Copolyperoxides of MMA and VAc were synthesized. The compositions of the copolyperoxides were determined from ^1H and ^{13}C NMR spectra. The calculated reactivity ratios for the monomers

showed that the two monomers were statistically placed along the copolymer chain, and copolymers containing appreciable quantities of the acetate monomers could not be obtained. The NMR studies showed irregularities in the copolyperoxide chain due to the cleavage reactions of the propagating peroxide radical.

The copolyperoxides underwent highly exothermic degradation. The thermal degradation of the copolyperoxides gave evidence in support of alternating peroxide units in the copolyperoxide chain. Thermal stability increased with the in-

Table II. DSC Data for the Polymers Investigated

| Polymer | ΔH_d^0 (cal g $^{-1}$) | E_a (kcal mol $^{-1}$) |
|---------|---------------------------------|---------------------------|
| PMMAP | -169.6 | 38.0 ± 1.2 |
| VM1 | -188.0 | |
| VM2 | -186.2 | |
| VM3 | -198.6 | 32.1 ± 0.9 |
| VM4 | -210.0 | |
| PVAcP | 213.6 | 24.5 ± 1.0 |

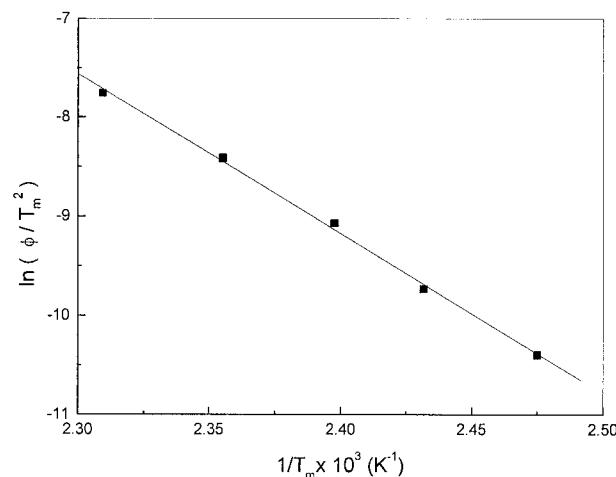


Figure 5. Kissinger's plot of $\ln(\phi/T_m^2)$ against $1/T_m$ for VM3.

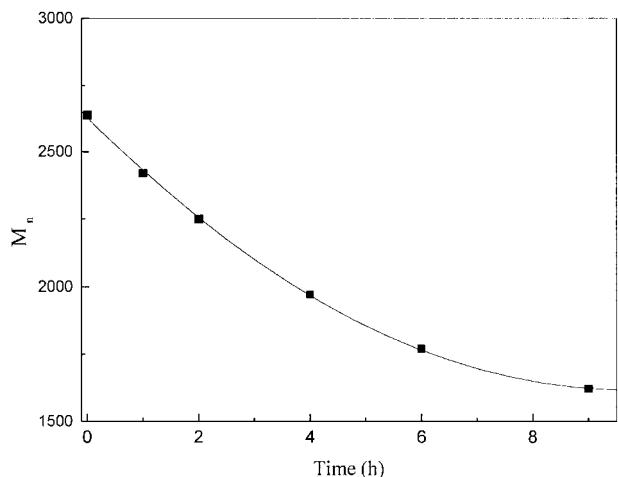


Figure 6. Change in the molecular weight of VM2 during thermal degradation at 75 °C in toluene.

crease in the content of MMA units in the copolyperoxide. E_a values for the thermal degradation suggested that the degradation was controlled by the dissociation of the peroxide (O—O) bonds in the backbone of the copolyperoxide chain.

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