Free Radical Oxidative Copolymerization of Indene with Vinyl Acetate and Isopropenyl Acetate: Synthesis and Characterization

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ABSTRACT: Copolyperoxides of different compositions of indene with vinyl acetate and isopropenyl acetate were synthesized by the free radical-initiated oxidative copolymerization. The compositions of copolyperoxides obtained from ^{1}H- and ^{13}C-NMR spectra have been used to determine the reactivity ratio of the monomers. The reactivity ratios reveal that the copolyperoxides contain a larger proportion of the indene units in random placement. The NMR studies further suggest irregularities in the copolyperoxide chain possibly due to the cleavage reactions of the propagating peroxide radical. The thermal analysis by differential scanning calorimetry (DSC) supports the alternating peroxide units in the copolymer chain. The activation energy for the thermal degradation suggests that the degradation is dependent on the dissociation of the peroxide (—O—O—) bonds in the copolyperoxide chain. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 639–646, 2002

Key words: indene copolyperoxides; reactivity ratios; exothermic thermal degradation

INTRODUCTION

Polymers having weak peroxy linkages in the backbone are of two types. They are (a) vinyl polyperoxides, obtained by oxidative polymerization of vinyl monomers[1,2] and (b) acid polyperoxides, obtained by the condensation of organic dibasic acids with sodium peroxide.[3] Compared to acid polyperoxides, vinyl polyperoxides have been much less studied. Vinyl polyperoxides, alternating copolymers of vinyl monomer and molecular oxygen, are of interest due to their potential applications as special fuels,[4] polymeric initiators,[5–7] and curatives in coating and molding.[8] They show interesting properties such as autopyrolyzability, autocombustibility,[9] and exhibit unusual autoaccelerating and autodecelerating kinetics.[10,11] Vinyl polyperoxides are relatively easier to handle compared to acid polyperoxides, which are hazardous. Therefore, vinyl polyperoxides are receiving renewed attention.

The term oxidative copolymerization is applied when two monomers (M_1 and M_2) reacting in the presence of high pressure of oxygen result in the formation of terpolymers of the type —[—(M_1—O—O—)$_X$—(M_2—O—O—)$_Y$—]—. The stability of these alternating copolymers depends upon the structure of the vinyl monomers in the polymer as well as the oxygen-absorbing capacity of the monomers.[12] Compared to simple vinyl polyperoxides obtained from a vinyl monomer and oxygen, those obtained from a mixture of vinyl monomers and oxygen have been less studied.[2] The earlier work on oxidative copolymerization was concerned with a study of the comparative rates of oxidation of different monomers and their relative reactivity towards peroxide radicals.[13,14] The oxidation of two monomers could be considered as a special case of terpolymerization, where the monomers (M) do not to homopolymerize. The uniqueness of this system is that it approximates to a binary copolymerization system in terms of —MO$_2^\bullet$ units. The rate of polymerization may then be described in terms of the copolymerization equation and reactivity ratios.[15,16]

Indene forms a stable solid polyperoxide.[17] However, polymeric peroxides from vinyl acetate and isopropenyl acetate are highly unstable, and they are difficult to isolate from the reaction mixture due to very low molecular weight.[18] In the present work, we have studied the oxidative copolymerization of indene–vinyl acetate and indene–isopropenyl acetate. The selection of indene is advantageous because it does not homopolymerize, even at low oxygen concentration,[19] unlike some other vinyl monomers. The determination of the reactivity ratios of the monomers by nuclear magnetic resonance spectroscopy (NMR) and the characterization of the copolyperoxides by other physical techniques such as FTIR, DSC, etc., are discussed.

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TABLE I
Experimental Results for the Oxidative Copolymerization of Indene with Vinyl Acetate
and Isopropenyl Acetate, Initiated by AIBN at 50°C

| Polymer | Reaction Time (h) | Yield (%) | Mol Fraction of Indene | | | Mol. wt. ($\bar{M}_n$) | PD-I |
| | | | Feed [I] | Copolyperoxide | | | |
				^{1}H-NMR	^{13}C-NMR		
			Indene/Vinyl Acetate				
PIP	10	8.7	1.0000	1.0000	1.0000	3240	1.15
COPO1	18	11.5	0.3306	0.8800	0.8970	2800	1.45
COPO2	24	10.0	0.2022	0.8034	0.8245	2880	1.25
COPO3	44	11.2	0.0807	0.6581	0.6273	2050	1.32
COPO4	68	7.8	0.0380	0.3812	0.4009	1900	1.56
PVAcP	84	8.3	0.0000	0.0000	0.0000	—	—
			Indene/Isopropenyl Acetate				
IIPA1	8	11.0	0.1189		0.7725	2600	1.40
IIPA2	14	12.8	0.0950		0.6964	2660	1.24
IIPA3	30	11.1	0.0711		0.5923	2120	1.33
IIPA4	65	7.7	0.0236		0.2078	1840	1.64
PIPAP	84	6.2	0.0000	0.0000	0.0000	—	—

EXPERIMENTAL

Materials

Vinyl acetate (VAc or A) (Rolex Laboratory Reagents, India) and isopropenyl acetate (IPA) (Aldrich) were freed from inhibitor by drying over $CaCl_2$ followed by fractional distillation. Indene (IN or I) (Aldrich) was first shaken with 6M HCl for 12 h, then refluxed with 40% NaOH for 2 h and then fractionally distilled. The distillate was passed through a column of activated silica gel. Finally, it was distilled under reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN) (Koch Light Laboratories, England) was recrystallized twice from methanol. High purity oxygen (Bhoruka gases, 99.9%) was used. Reagent grade solvents (Ranbaxy, India) such as petroleum ether, benzene, CH_2Cl_2, etc., were purified by standard procedures.

Synthesis

Homo- and copolymers were prepared using benzene solutions of the monomers and AIBN (0.01 mol L^{-1}) in a 300-mL Parr reactor (Parr Instruments Co., USA) equipped with a digital pressure transducer, temperature controller, and a mechanical stirrer. The polymerizations were carried out at 50 ± 0.5°C for 8–84 h under an oxygen pressure of 100 psi. Conversion was kept below 15%. The feed ratio was varied to get terpolymers of different compositions. The polymers were isolated from the reaction mixture using petroleum ether as a nonsolvent and purified by repeated precipitation from benzene solution followed by the removal of the solvent by vacuum drying. Details regarding the synthesis and identification of the copolyperoxides are given in Table I.

Measurements

The FTIR spectrum was recorded on a Bruker Equinox 55 FTIR spectrometer. The thermal analysis was carried out using a Perkin-Elmer DSC-2C differential scanning calorimeter (DSC) under nitrogen atmosphere at heating rates of 5, 10, 20, 40, and 80°C/min with a sample size of 1–5 mg. The molecular weight of the polymers was obtained using a Waters HPLC/GPC instrument (refractive index detector) with THF as a mobile phase at a flow rate of 1.0 mL min^{-1} at 30°C using polystyrene standards.

The ^{1}H- and ^{13}C-NMR spectra were recorded at room temperature on a Bruker ACF 200 MHz spectrometer in $CDCl_3$ and CH_2Cl_2 (D_2O external lock), respectively, using tetramethylsilane (TMS) as reference. The ^{13}C-NMR spectra were obtained under inverse gated decoupling with a 15-s delay between the pulses. A line broadening of 2 Hz was applied before Fourier transformation to enhance the signal-to-noise ratio.

RESULTS AND DISCUSSION

Copolymers obtained are either yellowish sticky or dry solid materials depending on the ratio of indene to vinyl monomer. The number-average molecular weight ($\bar{M}_n$) and polydispersity index (PD-I) of the polymers synthesized are presented in Table I. The polymers have low molecular weight because this category of polymers undergo facile degradation[20] during their polymerization itself, generating chain transfer agents such as aldehydes, which react with macrogrowing radicals resulting in low molecular weight. It is to be noted that the copolyperoxides should be
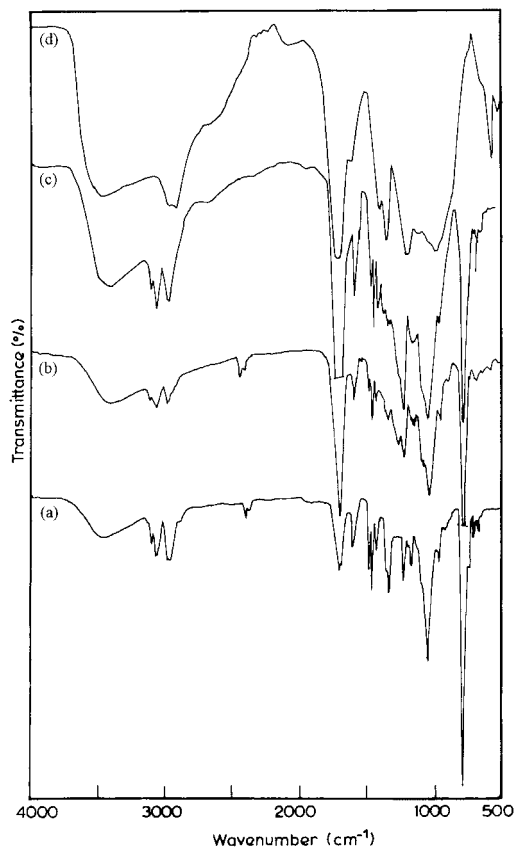
Figure 1 FTIR spectra of (a) PIP, (b) COPO2, (c) COPO3, and (d) PVAcP.

stored in dark and in a refrigerator to minimize degradation.

FTIR spectra

The FTIR spectra of the neat films of poly(indene peroxide) (PIP), COPO2, COPO3, and poly(vinyl acetate peroxide) (PVAcP) are shown in Figure 1. The spectra are all similar except for the variations in the intensities of the different peaks. The strong band observed near 1010 cm^{-1} in the spectra is assigned to the peroxide (—O—O—) bond stretching mode. The very intense band appearing at 1715 cm^{-1} is assigned to the carbonyl groups of vinyl acetate. The intensity of this C═O stretching band is enhanced as the vinyl acetate content in the copolyperoxide is increased. The broad absorption between 3400 and 3500 cm^{-1} is due to the hydroxyl and hydroperoxide end groups. The formation of these end groups via various chain transfer mechanisms is known.[21,22] Similar observations were made for the IN-IPA series of copolyperoxides also.

Compositions of copolyperoxide

The ^{1}H- and ^{13}C-NMR spectra reveal that the monomers do not homopolymerize under high pressure of oxygen employed here. Figure 2 depicts typical ^{1}H-NMR spectra of COPO4 and homopolyperoxides, PIP and PVAcP. The observed downfield shift of the main chain CH_2 and CH protons is attributable to the two electronegative oxygen atoms to which they are directly bonded. The ^{1}H-NMR spectrum of PIP shows signals at 7.0–7.5, 5.5–5.8, and 4.6–5.2 ppm corresponding to the aromatic protons, methine protons, one bonded to the aromatic ring, and the other to the methylene group, respectively.[17] The two peaks at 2.8 and 3.2 ppm are attributed to the methylene group. In the ^{1}H-NMR spectrum of PVAcP, the signals at δ = 2.07, 4.11, and 6.45 ppm have been assigned to the methyl, methylene, and methine protons, respectively.[23] The methylene region is rather complex, which may be traced to the excess methylene groups present in the homo- or copolyperoxide chains as defects. This happens because, during the oxidation of vinyl acetate, the peroxy radical undergoes preferentially cleavage reactions rather than addition reaction to another VAc molecule. The compositions of the copolyperoxides given in Table I, were obtained from the ratio of the signal intensities of the CH_2 protons of the indene units to that of the CH_3 protons of VAc.

Similar NMR signals were obtained for indene units in indene–isopropenyl acetate copolyperoxides, as mentioned above. The IPA incorporated into the rigid PIP backbone shows signals at δ = 1.7, 2.09, and 4.5–5.5 ppm assigned to the α-methyl, acetate methyl, and methylene protons, respectively (Fig. 3). Due to the increased cleavage reactions of the peroxide radicals, the chain irregularities in this series of copolyperoxides are found to be higher compared to those of the other series. The copolyperoxide compositions could not be determined for this series from the ^{1}H-NMR spectra.

Figure 4 shows the ^{13}C-NMR spectra of COPO2 and the homopolyperoxides. The downfield shift of the main chain carbons is observed here, too, which is due to the two highly electronegative oxygen atoms directly bonded to them. The ^{13}C-NMR spectrum of PIP exhibits signals at 125–129.6, 137.3, 142.8, 89.1, 86.0, and 35.5 ppm; they are assigned to the aromatic, two aromatic ipso, methine carbon attached to aromatic ring, methine carbon adjacent to the methylene group, and methylene carbon, respectively. The signals at δ = 20.7, 72.7, 95.0, and 169.6 ppm in the spectrum of PVAcP are assigned to the methyl, methylene, methine, and carbonyl carbons, respectively. The ratio of the signal intensity of the CH_2 carbons of IN units to the CH_3 carbons of VAc units gives directly the compositions of copolyperoxide. The evidence for the presence of IPA units in the copolymer has been obtained from the ^{13}C-NMR spectra of the corresponding copolyperoxides. The ^{13}C-NMR spectra of the two series of copolyperoxides are complicated due to chain irregularity. The ratio of the intensities of the methylene carbon to the α-methyl carbon gives a
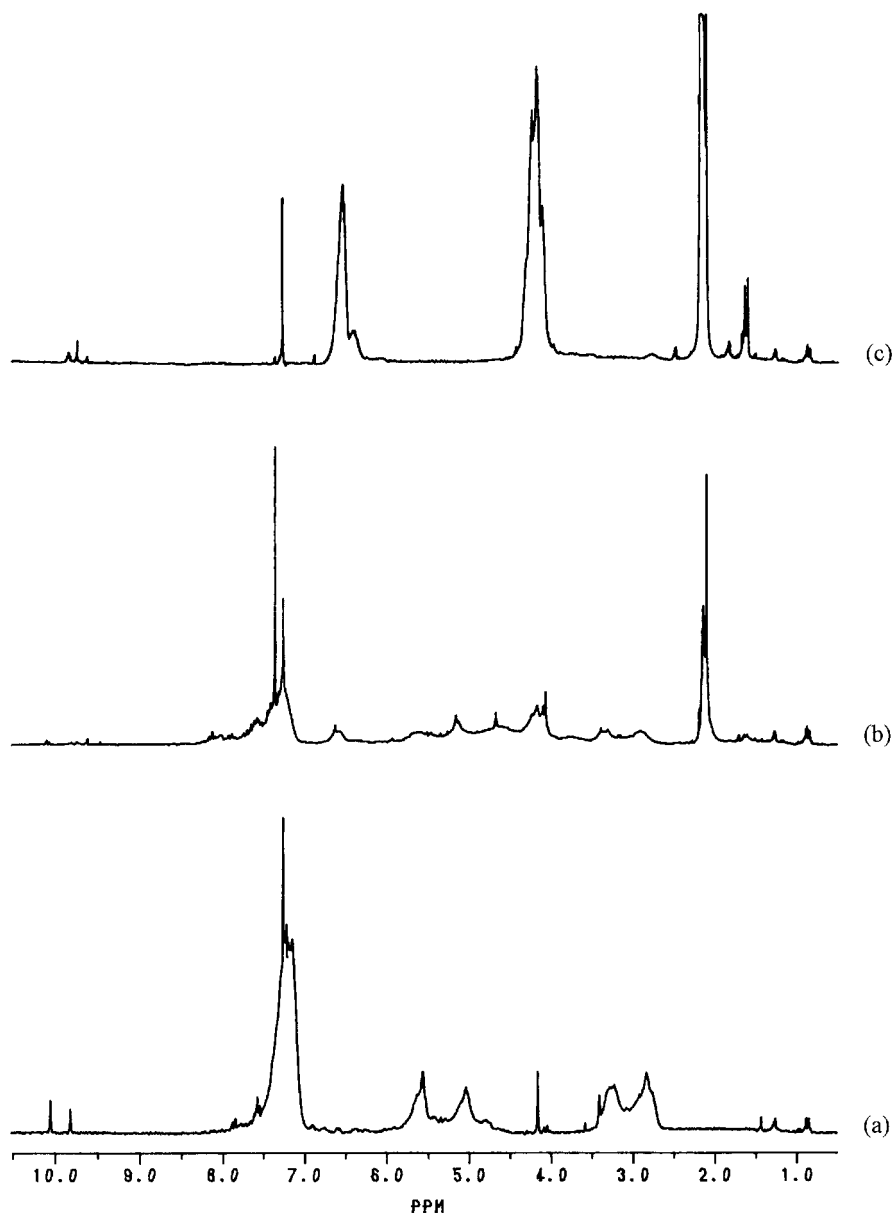
Figure 2 ^{1}H-NMR spectra of (a) PIP, (b) COPO4, and (c) PVAcP in CDCl$_3$.

direct measure of the copolyperoxide composition listed in Table I. The compositions of the copolyperoxides obtained from the ^{13}C-NMR spectra are in good agreement with those determined from the ^{1}H-NMR spectra. Based on the above discussion, the general formula of the copolyperoxide may be represented by
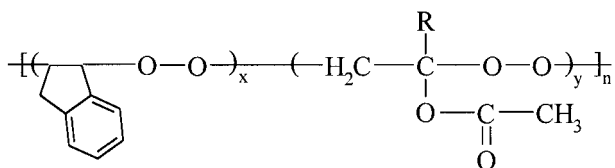
R = H or CH$_3$

The copolyperoxides show weak peaks between 9.7 and 10.2 ppm in the ^{1}H-NMR spectra due to the presence of two types of O=CH— groups at the chain ends. There is a peak at 92.5 ppm in the ^{13}C-NMR spectra. It may be attributed as due to the inclusion of methylene group with neighboring peroxy groups (—O—CH$_2$—O—) in the chain arising from cleavage reactions occurring to a considerable extent during the oxidative polymerization. Absence of this peak in the ^{13}C-NMR spectrum of PIP indicates that the 92.5-ppm peak appears only when the vinyl monomers are present in the copolyperoxides. Intensity of this peak increases with increase in the vinyl monomer content in the chain. The inclusion of (—O—CH$_2$—O—) moieties in the polyperoxide chain is reported during the
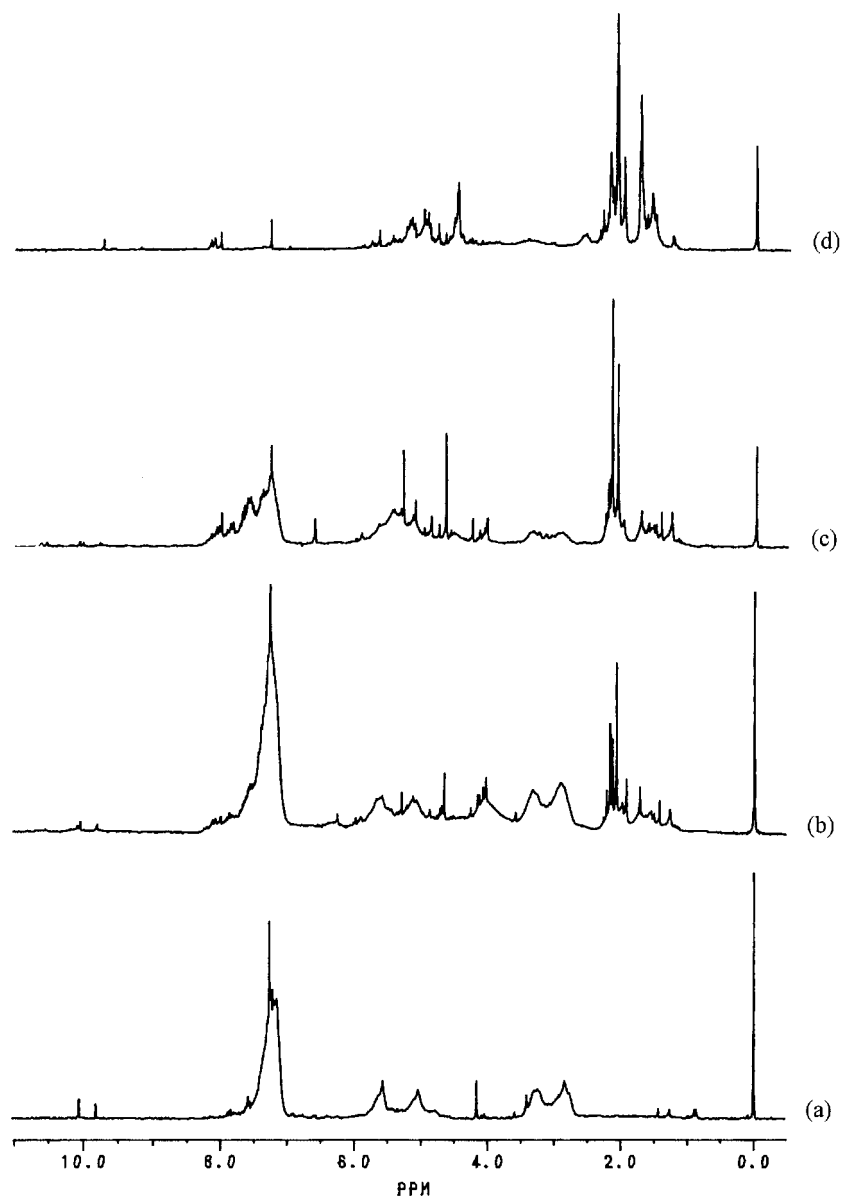
Figure 3 ^{1}H-NMR spectra of (a) PIP, (b) IIPA2, (c) IIPA4, and (d) PIPAP in CDCl$_3$.

oxidation of α-methylstyrene at very low pressures of oxygen.[24]

Reactivity ratios

In deriving the equation for the oxidation of two monomers, oxygen is considered as the third monomer. Under the conditions employed here such as high pressure of oxygen, the monomers do not homopolymerize.[2] Further, the propagation reactions involving the addition of one or the other monomer to a second monomer radical is assumed to be negligible. This assumption is supported by the absence of signals corresponding to IN-VAc or IN-IPA in the ^{1}H- and ^{13}C-NMR spectra of the copolyperoxides. In the oxidative polymerization, the reactivity of the mono-

mer radical (M$^\bullet$) with oxygen is very high compared to that of —MO$_2^\bullet$ with the monomer (M). In the oxidation of monomers, because the copolymer composition is not proportional to the feed composition, a penultimate effect could be expected.[25] Thus, assuming a penultimate effect, the important rate determining propagation steps involved in the oxidative copolymerization of indene (I) with vinyl acetate (A) may be written as follows:[26]
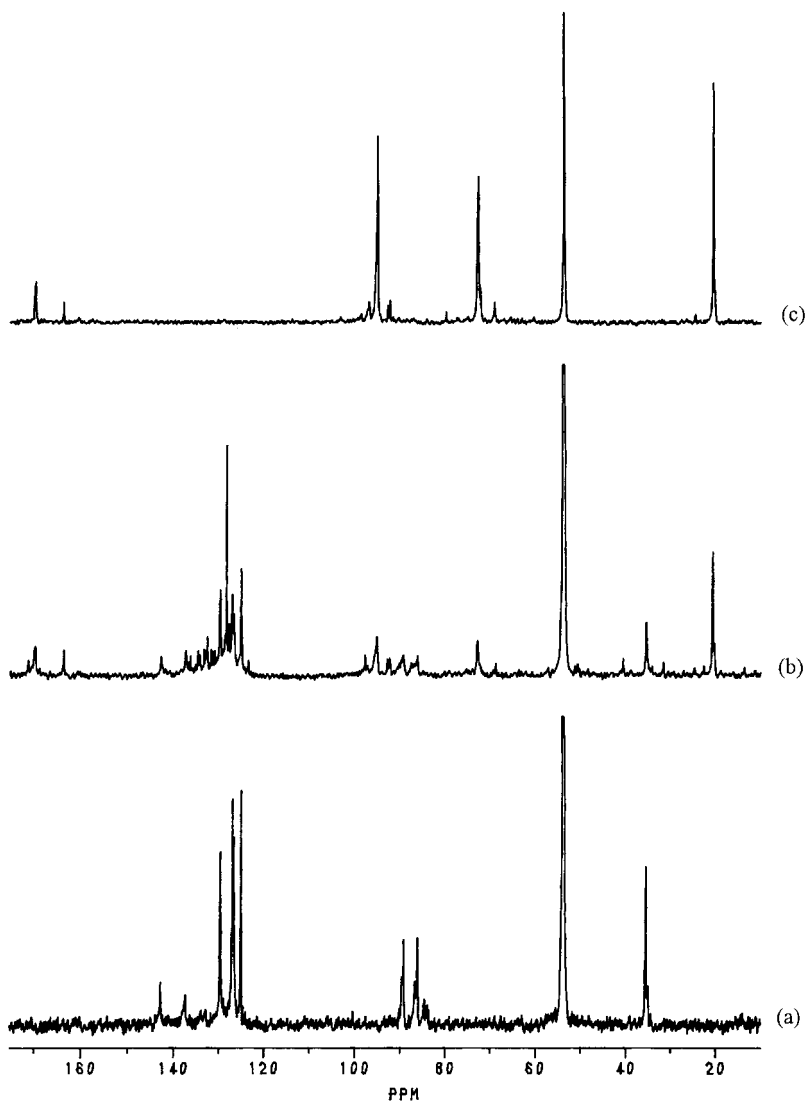
$$IO_2^\bullet + I \rightarrow IO_2I^\bullet \quad k_{IOI} \qquad (1)$$

$$IO_2^\bullet + A \rightarrow IO_2A^\bullet \quad k_{IOA} \qquad (2)$$

$$AO_2^\bullet + I \rightarrow AO_2I^\bullet \quad k_{AOI} \qquad (3)$$

$$AO_2^\bullet + A \rightarrow AO_2A^\bullet \quad k_{AOA} \qquad (4)$$

Figure 4 ^{13}C-NMR spectra (a) PIP, (b) COPO4, and (c) PVAcP in CH_2Cl_2.

Applying the steady-state approximation separately for the reactive species, $—IO_2^{\bullet}$ and $—AO_2^{\bullet}$, the copolymerization composition could be expressed in terms of the feed composition and the reactivity ratios

$$\frac{d[I]}{d[A]} = \frac{[I]}{[A]}\frac{(r_I[I] + [A])}{([I] + r_A[A])} \quad (5)$$

where $d[I]/d[A]$ denotes the ratio of indene to vinyl acetate in the copolyperoxide, $[I]/[A]$ is the corresponding feed ratios, and r_I and r_A are respectively the reactivity ratios for the monomers indene and VAc, defined as[16]

$$r_I = \frac{\text{rate constant for the reaction of} —IO_2^{\bullet} + I}{\text{rate constant for the reaction of} —IO_2^{\bullet} + A} = \frac{k_{IOI}}{k_{IOA}}$$

$$r_A = \frac{\text{rate constant for the reaction of} —AO_2^{\bullet} + A}{\text{rate constant for the reaction of} —AO_2^{\bullet} + I} = \frac{k_{AOA}}{k_{AOI}}$$

The eq. (5) for the oxidative copolymerization of two vinyl monomers resembles the Mayo-Lewis copolymerization equation[26] for a two-monomer system, except in the definition of the reactivity ratio. The reactivity ratios give the relative tendencies of the peroxide radicals ($—IO_2^{\bullet}$ or $—AO_2^{\bullet}$) to add on to a monomer of the same kind or the other. In the same way, the rate equations can be written for the oxidative copolymerization of indene–isopropenyl acetate.

The reactivity ratios have been determined from Fineman-Ross[27] and Kelen-Tudos[28] plots, and they are presented in Table II. The reactivity ratios reveal that the placement of the two monomers along the copol-

TABLE II
Reactivity Ratios for the Oxidative Copolymerization of Indene with Vinyl Acetate and Isopropenyl Acetate

Method	r_I	r_A	$r_I r_A$
	Indene/Vinyl Acetate		
Fineman-Ross	17.567 ± 0.007	0.050 ± 0.003	0.878
Kelen-Tudos	18.128 ± 0.011	0.056 ± 0.018	1.015
	Indene/Isopropenyl Acetate		
Fineman-Ross	51.402 ± 0.181	0.184 ± 0.040	9.460
Kelen-Tudos	51.194 ± 0.094	0.183 ± 0.007	9.369

TABLE III
DSC Data for the Copolyperoxides

Polymer	ΔH_d° (cal g^{-1})	E_a (kcal mol^{-1})	T_g (°C)
	Indene/Vinyl Acetate		
PIP	−292.7	47.2 ± 1.1	39.3
COPO1	−232.8		5.9
COPO2	−183.8		1.0
COPO3	−247.8	41.3 ± 0.8	−6.2
COPO4	−204.7		−26.4
PVAcP	−213.6	24.5 ± 2.1	−37.12
	Indene/Isopropenyl Acetate		
IIPA1	−223.6		
IIPA2	−239.9		
IIPA3	−225.6	34.2 ± 1.5	
IIPA4	−198.3		
PIPAP	−187.3	20.7 ± 0.6	

ymer chain is random and that copolymers containing appreciable amounts of the acetate monomers cannot be obtained because $r_I >> r_A$.[29] The ratio of reactivity ratios shows that IPA is more reactive than VAc towards the propagating peroxy radicals. It is in the order of increasing π-electron density at the vinyl double bond of the monomers and the electron accepting property of the corresponding peroxy radicals. The calculation of reactivity ratios from NMR data is rather straightforward. However, the assumption about the absence of the cleavage products may introduce some error in the calculations.

Thermal analysis

The structure of copolyperoxides was further supported by thermal analysis studies. In general, according to Mayo mechanism,[30] vinyl polyperoxides undergo random thermal scission at the peroxy bond, followed by unzipping of the β-peroxyalkoxy radicals giving carbonyl compounds. For example, PVAcP undergoes degradation exothermally to yield formaldehyde, acetic acid, carbon monoxide, and an unidentified reddish black noncrystalline substance.[23] The PIPAP also undergoes degradation exothermally giving
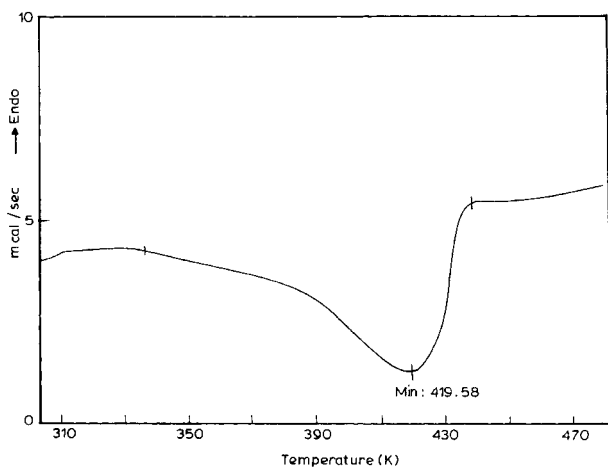
formaldehyde, acetic anhydride, acetic acid, and carbon monoxide. The DSC thermogram of the copolyperoxides indicates a highly exothermic degradation. A representative DSC thermogram of COPO3 is given in Figure 5. The enthalpy of degradation, ΔH_d, obtained from the DSC thermogram, is 200–300 cal g^{-1} as shown in Table III.

The activation energy for the thermal degradation process was determined by Kissinger's method.[31] A plot of ln (ϕ/T_m^2) against $1/T_m$, where ϕ is the heating rate and T_m (K), the peak temperature obtained from the DSC data are given in Figure 6 for COPO3 and IIPA3. The slope of this plot yields the activation energy (E_a) for the process of thermal degradation. The E_a values tabulated in Table III compare well with the dissociation energy of the O—O bond in dialkyl peroxides,[32] homopolyperoxides and COPO3 and IIPA3. The thermal stability as noted from their E_a values[33] shows PIP to be more stable compared to
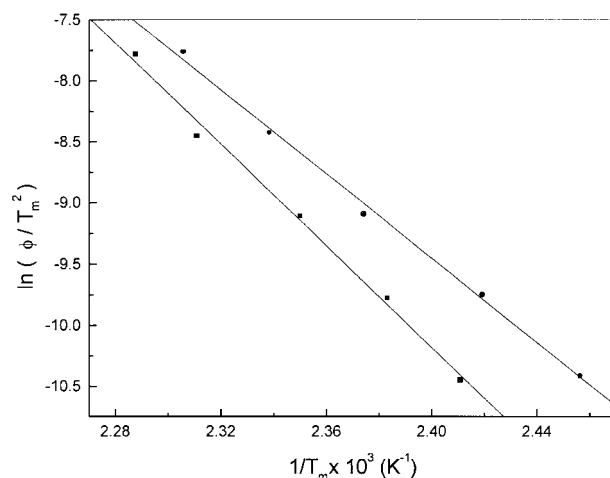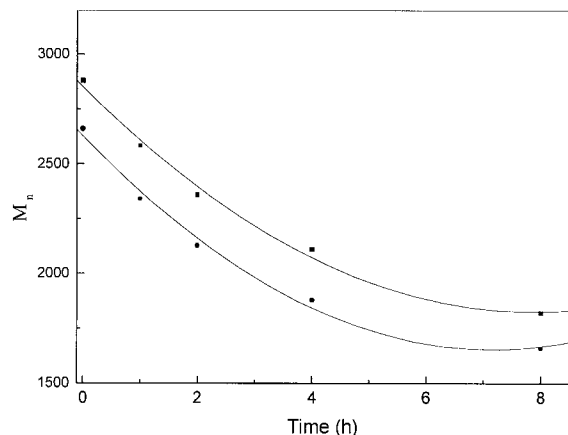

Figure 5 DSC thermogram of COPO3.

Figure 6 Kissinger's plot of ln ϕ/T_m^2 against $1/T_m$ for COPO3 (■) and IIPA3 (●).

Figure 7 Changes in the molecular weight of COPO2 (■) and IIPA2 (●) during thermal degradation at 75°C in toluene.

other polyperoxides, and the E_a values of copolyperoxides fall in between the two respective homopolyperoxides. It can be concluded from thermal studies that copolyperoxides undergo a radical chain scission followed by chain unzipping mechanism, which has been proposed for other polyperoxides.[20]

The copolymers undergo facile thermal decomposition on heating. The products of decomposition of the copolyperoxide heated in a glass tube at 120°C for 2 h under nitrogen atmosphere were monitored by GPC. It indicates that copolyperoxide degrades to small molecular weight products.[34] However, the products of decomposition were not isolated. The thermal degradation in toluene solution at 75°C of the copolymers COPO2 and IIPA2 proceed slowly. The changes in $\bar{M}_n$ value of the copolymers COPO2 and IIPA2 are shown in Figure 7. The thermal degradation of polyperoxides was found to depend on the dissociation of the peroxide (—O—O—) bond.

Glass transition temperatures (T_g) for the homo- and copolyperoxides of indene–vinyl acetate are listed in Table III. The glass transition arises from the onset of backbone motions. The order of mobility can be deduced from the T_g data of the bulk polymers.[35] The higher the T_g value, the lower the flexibility of the polymer. From the T_g data we infer that PIP is the most rigid polyperoxide. The T_g values of the copolyperoxides fall in between the two respective homopolyperoxides.

CONCLUSIONS

Two series of copolyperoxides of indene with vinyl acetate and isopropenyl acetate have been synthesized. The composition of copolyperoxides and reactivity ratios were determined from the ^{1}H- and ^{13}C-NMR spectra. The reactivity ratios suggest that the two monomers are randomly placed along the copolymer chain and copolymers containing appreciable

amounts of the acetate monomers cannot be obtained. The NMR studies have shown irregularities in the copolyperoxide chain possibly due to the cleavage reactions of the propagating peroxide radical.

The copolyperoxides undergo highly exothermic degradation and the degradation studies have indicated the presence of alternating peroxide units in the copolyperoxide chain. The activation energy for the thermal degradation suggests that degradation is controlled by the dissociation of the peroxide (—O—O—) bonds in the backbone of the copolyperoxide chain. The thermal stability and flexibility both decrease with increase in the indene content in the copolyperoxide chain.

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