

Azobisisobutyronitrile-Initiated Free-Radical Copolymerization of Limonene with Vinyl Acetate: Synthesis and Characterization

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Received 15 June 2005; accepted 13 January 2006

DOI 10.1002/app.24205

Published online 1 August 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The solution copolymerization of limonene (Lim) and vinyl acetate (VA) with azobisisobutyronitrile (AIBN) as an initiator in dioxane at $65 \pm 0.1^\circ\text{C}$ for 2 h under a nitrogen blanket has been carried out. The kinetic expression is $[\text{AIBN}]^{0.5}[\text{VA}]^{1.0}[\text{Lim}]^{-1.0}$. The overall energy of activation has been computed to be 30 kJ/mol. Fourier transform infrared spectroscopy has shown bands at 1731 cm^{-1} due to acetoxy protons of VA and at 1689 cm^{-1} due to trisubstituted olefinic protons ($-\text{CH}=\text{CH}-\text{CH}_2$) of Lim. $^1\text{H-NMR}$ spectroscopy of the copolymer has shown peaks at $\delta = 1.2\text{--}1.5$ and $\delta = 5.3\text{--}5.6$ due

to acetoxy and trisubstituted olefinic protons of VA and Lim, respectively. The reactivity ratios have been calculated to be 0.05 for VA and 0.011 for Lim with the Kelen-Tüdös method. The glass-transition temperature of the copolymer, determined by differential scanning calorimetry, is 32.4°C . The copolymer is likely biodegradable in nature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2689–2695, 2007

Key words: activation energy; FTIR; glass transition; kinetics (polym.); radical polymerization

INTRODUCTION

Today, the potential worldwide demand for biodegradable polymeric materials is quite significant from environmental and biomedical viewpoints. Poly(vinyl acetate) is a commercially important and environmentally friendly polymer because it is biodegradable in nature. Poly(vinyl acetate) and its copolymers are finding applications in more diverse areas such as contraction and adhesion to more difficult-to-bond surfaces because of the range of adhesion and the flexibility that can be built into the polymers.¹

A search of the literature reveals that vinyl acetate (VA) has been frequently copolymerized with many vinyl monomers, such as methyl methacrylate,² acrylonitrile,³ ethylene,⁴ vinylidene cyanide,⁵ and butyl acrylate.⁶ However, reports on copolymers of VA with terpenes are still scarce.⁷

Terpenes are among the most widespread and chemically interesting groups of natural products, having carbon skeletons of isoprene units.⁸ The applications of terpenes in organic chemistry are

well documented,⁹ yet their applications in the domain of polymer science are still scarce, except for isoprenes^{10,11} and a few terpenes such as α -pinene and β -pinene.^{12–14} Furthermore, the work has been emphasized by recent contributions of our laboratory, which has obtained optically active and functional polymers of cyclic/acyclic terpenes with different vinyl monomers, such as citronellol-*co*-styrene/tetraphenyl cyclopentadiene Arsoniumylide and citronellol-*co*-styrene/benzoyl peroxide (BPO) at 80°C ,¹⁵ citronellol-*co*-acrylonitrile/BPO at 75°C ,¹⁶ geraniol-*co*-styrene/BPO at 80°C ,¹⁷ linalool-*co*-acrylonitrile/BPO at 75°C ,¹⁸ α -terpineol-*co*-methyl methacrylate,¹⁹ α -terpineol-*co*-styrene/BPO at 80°C ,²⁰ limonene-*co*-acrylonitrile/BPO at 70°C ,²¹ limonene-*co*-methyl methacrylate/BPO at 80°C ,²² and limonene-*co*-styrene/azobisisobutyronitrile (AIBN) at 80°C .²³

Limonene (Lim), an optically active monocyclic terpene, is a constituent of citrus and orange fruits.⁸ The literature reveals that initially Lim was homopolymerized by Roberts and Day²⁴ and Marvel et al.²⁵ with Friedel–Crafts and Ziegler–Natta catalysts, respectively. Later, Doiuchi et al.²⁶ copolymerized it with maleic anhydride. To the best of our knowledge, no attention has been focused on the copolymerization of Lim with vinyl monomers, except by our group.^{21–23} Therefore, this article highlights the synthesis and characterization of a copolymer of VA with Lim in dioxane initiated by AIBN at $65 \pm 0.1^\circ\text{C}$ for 2 h. Furthermore, the polymer that is formed is significant because it is likely biodegradable in nature.

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Contract grant sponsor: CSIR (New Delhi, India); contract grant number: 9/75 (5) 2004 EMR-1.

TABLE I
Effects of the Initiator and Comonomers on R_p

Sample	[AIBN] $\times 10^3$ (mol/L)	[VA] (mol/L)	[Lim] (mol/L)	Conversion (%)	$R_p \times 10^6$ (mol L ⁻¹ s ⁻¹)	$[\alpha]_D$
1	1.52	1.83	0.441	6.3	2.15	—
2	2.28	1.83	0.441	7.01	2.52	—
3	3.04	1.83	0.441	8.04	2.84	34.2
4	3.81	1.83	0.441	9.7	3.15	—
5	4.57	1.83	0.441	11.5	3.48	—
6	3.04	0.784	0.441	7.1	1.50	—
7	3.04	1.30	0.441	7.6	2.17	36.4
8	3.04	2.35	0.441	8.4	3.47	33.3
9	3.04	2.87	0.441	9.2	4.37	—
10	3.04	1.83	0.147	11.01	4.9	—
11	3.04	1.83	0.294	9.4	3.2	32.5
12	3.04	1.83	0.588	6.7	2.01	35.6
13	3.04	1.83	0.735	5.9	1.66	—

The copolymerization time was 2 h, and the copolymerization temperature was $65 \pm 0.1^\circ\text{C}$.

EXPERIMENTAL

Materials

Reagent-grade VA (Merck-Schuchardt) and solvents were purified with the usual method,²⁷ stored over anhydrous silica gel, and dried under a vacuum.

Lim (Fluka; molecular weight = 136 g/mol, bp = $176\text{--}177^\circ\text{C}$, $[\alpha]^{20} = +113 \pm 2$, $d = 0.8411$) was used after fractional distillation. AIBN was recrystallized twice from methanol.

Copolymerization procedure

The copolymerization of Lim and VA with AIBN in dioxane was carried out at $65 \pm 0.1^\circ\text{C}$ for 2 h with dilatometric techniques under oxygen-free conditions. The polymer, isolated with acidified methanol and dried *in vacuo*, was refluxed with toluene for the removal of poly(vinyl acetate) when no detectable weight loss was observed. Finally, the copolymer was dried to a constant weight, and the conversion percentage was calculated. The rate of polymerization (R_p) was calculated from the slope of the graph between the conversion percentage and time (min).

The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer 599 B (with KBr pellets), and $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded with Varian 100 HA and JEOL LA 40 spectrometers with CDCl_3 as a solvent and tetramethylsilane as an internal reference, respectively. Differential scanning calorimetry (DSC) was carried out on a PerkinElmer thermal analyzer at $10^\circ\text{C}/\text{min}$ heating rate under a nitrogen blanket. The optical rotations of the copolymer were determined on an Autopol III automatic polarimeter.

RESULTS AND DISCUSSION

The solution copolymerization of VA and Lim was carried out to a maximum conversion of 11.5%

through the variation of the AIBN, Lim, and VA concentrations. All the reactions were associated with short induction periods of 1–3 min. The results of the kinetic investigation are presented in Table I.

The effect of the AIBN concentration was studied through the variation of the initiator concentration from 1.52×10^{-3} to 4.57×10^{-3} mol/L, with the $[\text{VA}]/[\text{Lim}]$ monomer ratio kept constant at 4.15 mol/L. The initiator exponent value, calculated from the slope of $\log R_p$ against $\log [\text{AIBN}]$, is 0.5 ± 0.1 (Fig. 1).

The effect of the monomer concentration on R_p is summarized in Table I. R_p is a direct function of the VA concentration and an inverse function of the Lim concentration. The plots of $\log R_p$ versus $\log [\text{VA}]$ and $\log [\text{Lim}]$ give an order of unity (Figs. 2 and 3).

Table I reveals that an increase in the concentration of Lim markedly reduces R_p , and this may be

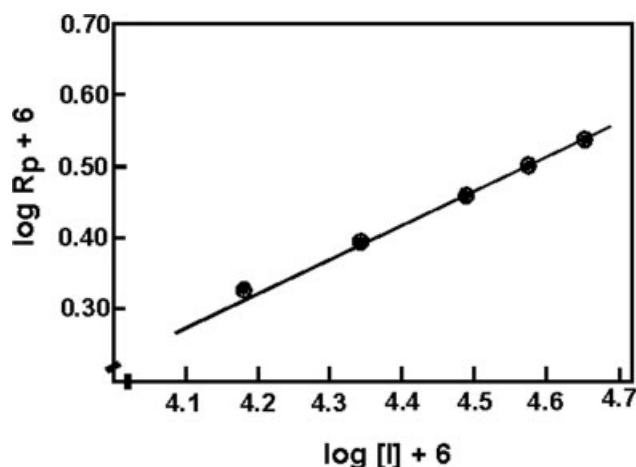


Figure 1 Relationship between R_p and the AIBN concentration with a constant VA concentration of 1.83 mol/L, a Lim concentration of 0.441 mol/L, a copolymerization time of 2 h, and a copolymerization temperature of $65 \pm 0.1^\circ\text{C}$.

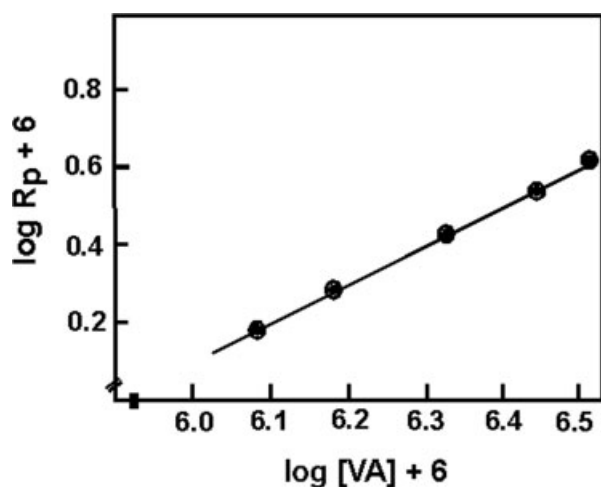


Figure 2 Relationship between R_p and the vinyl acetate concentration with a constant Lim concentration of 0.441 mol/L, an AIBN concentration of 3.04×10^{-3} mol/L, a copolymerization time of 2 h, and a copolymerization temperature of $65 \pm 0.1^\circ\text{C}$.

due to a penultimate unit effect (cross-termination), which was quantitatively discussed by Arlman.²⁸

In this system, four cross-termination reactions are possible:

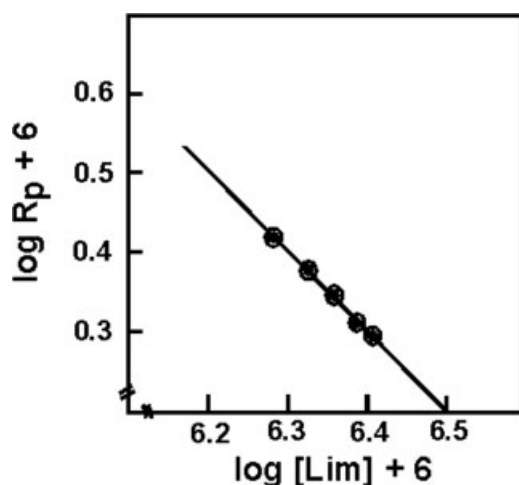


Figure 3 Relationship between R_p and the Lim concentration with a constant VA concentration of 1.83 mol/L, an AIBN concentration of 3.04×10^{-3} mol/L, a copolymerization time of 2 h, and a copolymerization temperature of $65 \pm 0.1^\circ\text{C}$.

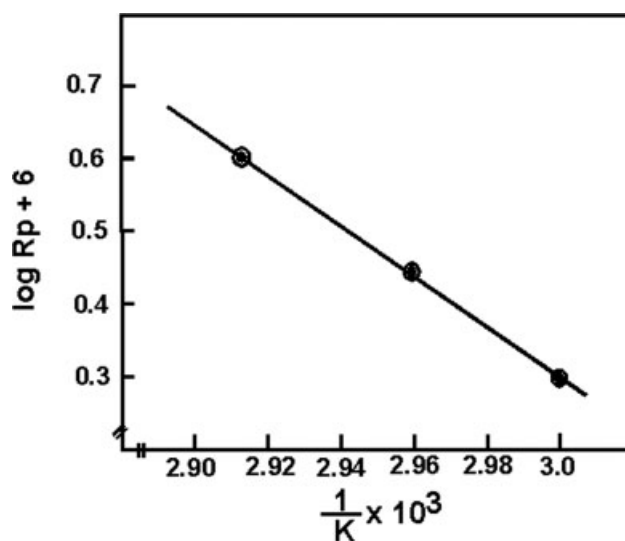


Figure 4 Arrhenius plot of R_p versus the polymerization temperature with an AIBN concentration of 3.04×10^{-3} mol/L, a VA concentration of 1.83 mol/L, an Lim concentration of 0.441 mol/L, and a copolymerization time = 2 h.



where M_1 is VA, M_2 is Lim and k is the rate constant for the propagation reaction.

The overall rate of copolymerization is given by the sum of the four propagation rates:

$$R_p = \frac{-d[M_1] + d[M_2]}{dt} = k_{11}[M_1^\bullet][M_1] + k_{12}[M_1^\bullet][M_2] + k_{22}[M_2^\bullet][M_2] + k_{21}[M_2^\bullet][M_1] \quad (5)$$

To eliminate the radical concentration from eq. (5), two steady-state assumptions are made:

$$k_{21}[M_2^\bullet][M_1] = k_{12}[M_1^\bullet][M_2] \quad (6)$$

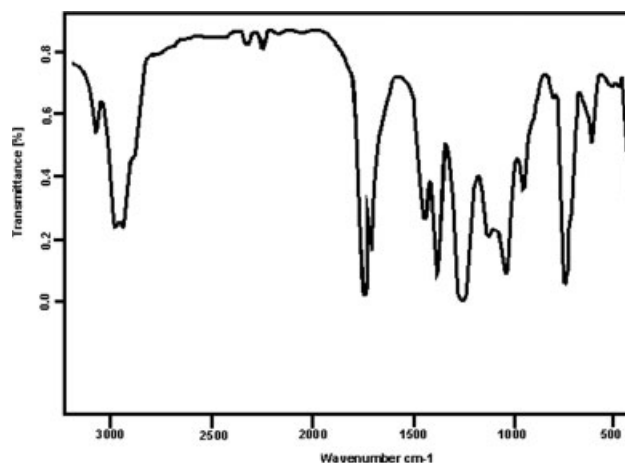


Figure 5 FTIR spectrum of the copolymer (sample 3).

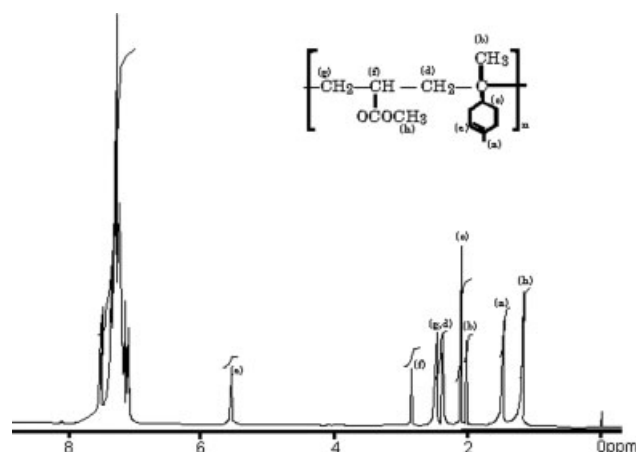


Figure 6 ^1H -NMR spectrum of the copolymer (sample 3).

The steady state is also assumed for the total concentration of the radical:

$$R_i = 2k_{t11}[\text{M}_1^\bullet]^2 + 2k_{t12}[\text{M}_1^\bullet][\text{M}_2^\bullet] + 2k_{t22}[\text{M}_2^\bullet]^2 \quad (7)$$

where k_t is the rate constant for termination.

From eqs. (5)–(7), R_p is obtained:

$$R_p = \frac{(r_1[\text{M}_1]^2 + 2[\text{M}_1][\text{M}_2] + r_2[\text{M}_2]^2)R_i^{1/2}}{\left\{ r_1^2\delta_1^2[\text{M}_1]^2 + 2\phi r_1 r_2\delta_2\delta_1[\text{M}_1][\text{M}_2] + r_2^2\delta_2^2[\text{M}_2]^2 \right\}^{1/2}}$$

where

$$\delta_1 = \left(\frac{2k_{t11}}{k_{11}} \right)^{1/2}$$

$$\delta_2 = \left(\frac{2k_{t22}}{k_{22}^2} \right)^{1/2}$$

$$\phi = \frac{k_{t12}}{2(k_{t11} \times k_{t22})^{1/2}}$$

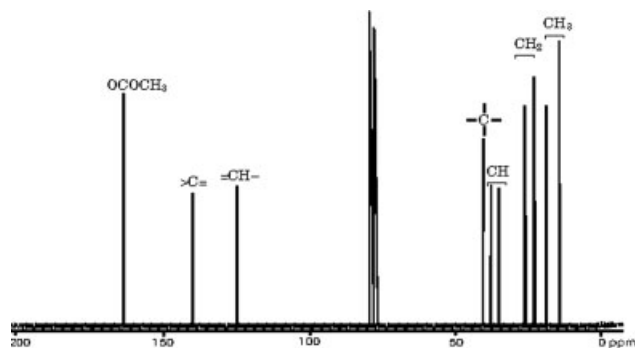


Figure 7 ^{13}C -NMR spectrum of the copolymer (sample 3).

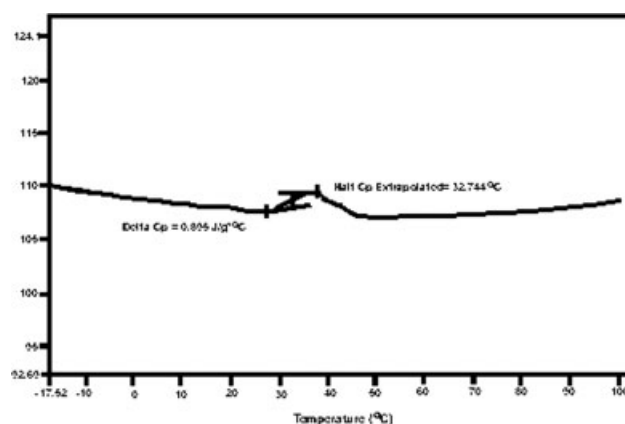


Figure 8 DSC curve of the copolymer (sample 3).

The value of ϕ has been computed to be 4.5. Because it is more than unity, a penultimate unit effect^{29,30} is favored in this system. The specific optical rotation of the copolymer decreases with the VA concentration and increases with the Lim concentration (Table I).

R_p increases with increasing temperature. The overall energy of activation has been calculated to be 30 kJ/mol from the slope of an Arrhenius plot of $\log R_p$ versus 1/Kelvin (K) (Fig. 4).

Characterization of the copolymers

FTIR spectroscopy

The following bands have been assigned for the FTIR spectra of the copolymer (Fig. 5):

- 3062 cm^{-1} : C–H stretching vibration due to CH_3 .
- 2933–2970 cm^{-1} : C–H stretching due to olefinic protons of Lim.
- 1731 cm^{-1} : acetoxy group of VA.
- 1689 cm^{-1} : C=C stretching of trisubstituted olefinic protons of Lim.
- 1436 cm^{-1} : C–H bending vibration due to CH_3 .

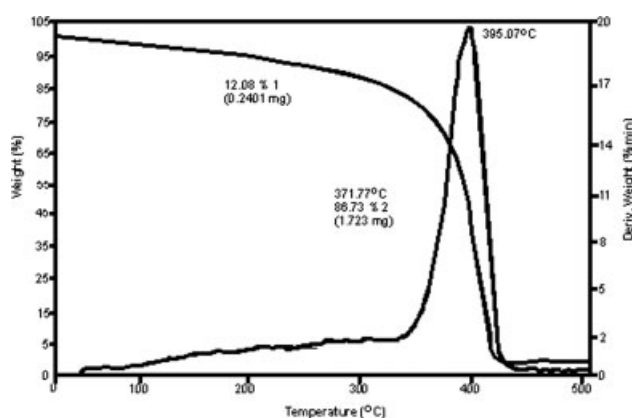


Figure 9 TGA curves of the copolymer (sample 3).

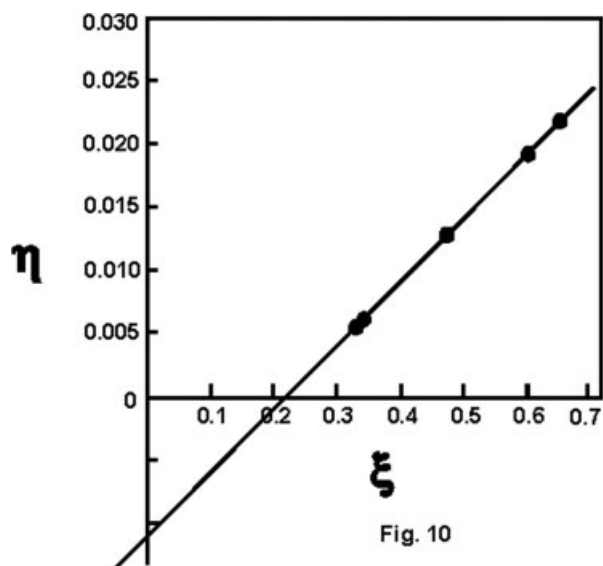


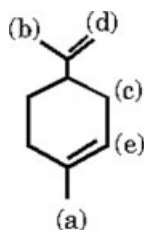
Figure 10 Kelen-Tüdös plot for the determination of the reactivity ratios.

1372 cm^{-1} : C—H bending vibration of olefinic protons of Lim.

^1H -NMR spectroscopy

The ^1H -NMR spectrum of pure Lim^{31,32} shows the following peaks:

- Peak a: $\delta = 1.64$ (3H, CH_3).
- Peak b: $\delta = 1.72$ (3H, CH_3).
- Peak c: $\delta = 1.92$ (2H, CH_2).
- Peak d: $\delta = 4.66$ (2H, CH_2).
- Peak e: $\delta = 5.35$ (1H, CH).



A comparison of the ^1H -NMR spectra of the copolymer (Fig. 6) and Lim shows that the peak at $\delta = 4.6$ ppm, due to an exo olefinic bond of Lim, has disappeared, whereas the peak at 5.3 δ ppm, due to an endo bond, remains in the copolymer. This indicates that an external double bond is involved in bond formation with VA.

Thus, the ^1H -NMR spectra of the copolymer show peaks at $\delta = 1.2$ – 1.5 due to acetoxy protons of VA and at $\delta = 5.3$ – 5.6 due to trisubstituted olefinic protons of Lim, and this indicates the formation of the

TABLE II
Copolymer Composition

Sample	Monomer feed (VA/Lim)	Molar ratio in the polymer (VA/Lim)	Molar fraction of VA in the copolymer	η	ξ
7	2.96	1.05	0.510	0.0052	0.337
8	5.32	1.15	0.534	0.0619	0.600
3	4.15	1.12	0.530	0.0140	0.484
11	6.22	1.20	0.540	0.0209	0.663
12	3.11	1.09	0.520	0.0101	0.351

η and ξ are the numeric values of Kelen-Tüdös method used for calculating the reactivity ratios.

copolymer. The peak at $\delta = 7.0$ – 8.0 ppm is due to the presence of the solvent CDCl_3 .

^{13}C -NMR spectroscopy

The ^{13}C -NMR spectrum of the copolymer (Fig. 7) shows the following distinct signals:

- Signal a: Due to the carbon ($=\text{CH}-$) of Lim (C-2) at $\delta = 125$ ppm.
- Signal b: Due to the carbon ($>\text{C}=\text{}$) of Lim (C-1) at $\delta = 140$ ppm.
- Signal c: Due to the group ($-\text{OCOCH}_3-$) of VA at $\delta = 166$ ppm.

DSC

The DSC curve indicates that the glass-transition temperature of the copolymer is 32.4°C (Fig. 8).

Thermogravimetric analysis (TGA)

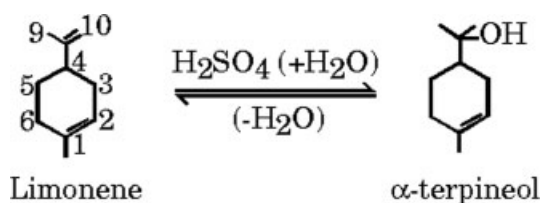
The TGA curve of the copolymer (Fig. 9) exhibits a weight loss with the temperature. The copolymer behavior is as follows:

- The onset of major weight loss occurs at 333°C, and the completion of major weight loss occurs at 430°C.
- The total weight loss in the range of 30–430°C is 98%.
- The weight losses at different temperatures are as follows: 4% at 100–200°C, 8% at 200–300°C, and 55% at 300–400°C.
- The total decomposition of the polymer occurs at 395°C.

TABLE III
Reactivity Ratios

r_1	r_2	$r_1 r_2$	Q_2	e_2
0.05	0.011	0.00055	0.012	+0.925

$$Q_1 = 0.026; e_1 = -0.88.$$

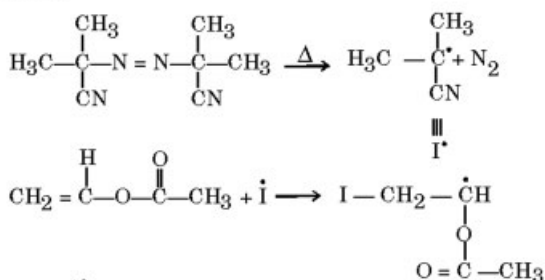


Scheme 1

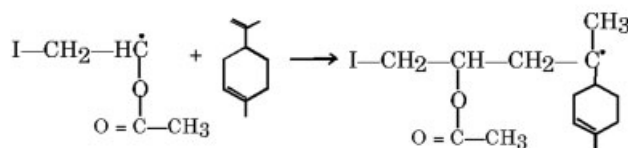
Copolymer Compositions and Values of the Reactivity Ratios

The composition of copolymers has been evaluated from high-resolution $^1\text{H-NMR}$ spectra. The relative peaks at $\delta = 1.2\text{--}1.5$ due to acetoxy protons of vinyl acetate (VA) and at $\delta = 5.3\text{--}5.6$ due to trisubstituted olefinic protons of Lim have been used to calculate the copolymer compositions (Table II) (Fig. 10). The values of r_1 (VA) and r_2 (Lim) have been computed to be 0.05 and 0.011, respectively, by the use of the Kelen-Tüdös method³³ with the help of the least-square method.

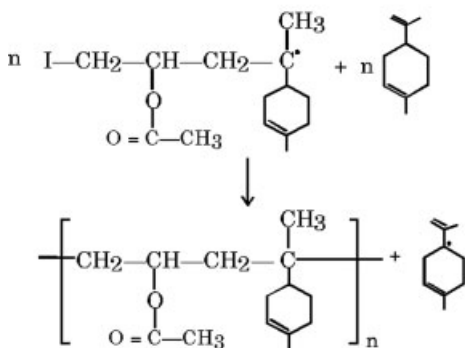
Initiation:



Propagation:



Termination:



Scheme 2

The e_2 and Q_2 values for Lim have been calculated with $e_1 = -0.88$ and $Q_1 = 0.026$ for VA with the following equation (Table III):

$$e_2 = e_1 \pm \log(r_1 r_2)^{0.5}$$

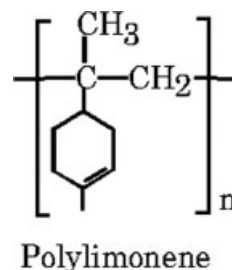
$$Q_2 = Q_1 / r_1 \exp[-e_1(e_1 - e_2)]$$

where e_1 and e_2 are the polarization characteristics, Q_1 and Q_2 indicates the resonance ability of the monomers VA (M_1) and Lim (M_2), respectively.

Mechanism

The mechanism of the copolymerization can be discussed as follows:

1. The acid-catalyzed hydration of Lim proceeds on the double bond, giving α -terpineol, although upon dehydration, it gives back Lim (Scheme 1).³⁴
2. The copolymer decolourises Baeyer's reagent because it is an unsaturated copolymer.
3. The following structure for polylimonene was reported by Roberts and Day²⁴ and Marvel et al.:²⁵



This shows that an exo double bond has been used for homopolymerization. We have also reported the same during its copolymerization with acrylonitrile,²¹ methyl methacrylate,²² and styrene.²³ These are the copolymers of limonens with different vinyl monomers synthesized using radical initiators in our laboratory.

4. A comparison of $^1\text{H-NMR}$ spectra of the copolymer and Lim shows that the peak at $\delta = 4.6$ ppm due to an exo olefinic bond of Lim has disappeared, whereas the peak at $\delta = 5.5$ ppm remains in the copolymer. This indicates that external double bonds are involved in bond formation with VA.

On the basis of this evidence, it is concluded that a double bond (π bond) between C-8 and C-10 is more likely to take part in polymerization. The proposed steps of this mechanism are shown in Scheme 2.

CONCLUSIONS

Poly(limonene-*co*-vinyl acetate) has been synthesized via free-radical solution polymerization with AIBN as an initiator. A penultimate unit effect is favored in this system. The synthesized polymer is optically active, functional, and biodegradable in nature.

The authors thank R. P. Singh, Director of the H. B. Technological Institute (Kanpur, India), for providing the necessary facilities. They also thank Council of Scientific and Industrial Research (New Delhi, India) for sanctioning this project.

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