

Synthesis and Characterization of Functional Copolymer of Linalool and Vinyl Acetate: A Kinetic Study

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ABSTRACT: Linalool (LIN) and vinyl acetate (VA) were copolymerized by benzoyl peroxide (BPO) in *p*-xylene at 60°C for 90 min. The system follows nonideal kinetics: $R_p \propto [I]^{0.6}[\text{LIN}]^{1.2}[\text{VA}]^{1.1}$. It results in the formation of alternating copolymer as evidenced from reactivity ratios as r_1 (VA) = 0.01, r_2 (LIN) = 0.0015, which have been calculated by Kelen–Tudos method. The overall activation energy is 82 kJ/mol. The FTIR spectrum of the copolymer shows the presence of the band at 3425 cm^{-1} due to alcoholic group of LIN and at 1641 cm^{-1} due to $>\text{C}=\text{O}$ group of VA. The $^1\text{H-NMR}$ spectrum shows peaks at 7.0–7.7 δ due to hydroxy proton of LIN and at 1.0–1.4 δ due to acetoxy protons of VA. $^{13}\text{C-NMR}$ spectrum of copolymer shows peaks at 167 ppm due to acetoxy group and at 75–77 ppm due to C–OH

group. The Alfrey–Price $Q-e$ parameters for LIN has been calculated as $Q_2 = 1.24$ and $e_2 = 3.11$. The copolymer is highly thermally stable and has a glass transition temperature (T_g) of 85°C, evaluated from DSC studies. The mechanism of copolymerization has been elucidated. This article also reports measurement of Mark–Houwink constants in THF at 25°C by means of GPC as $\alpha = 0.8$ and $K = 3.0 \times 10^{-4}$ dl/g. The thermal decompositions of copolymer are established with the help of TGA technique. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1134–1143, 2004

Key words: Linalool; Mark–Houwink's constants; nonideal kinetics; reactivity ratio; vinyl acetate

INTRODUCTION

Polymers with unsaturated functional groups are applicable as reactive polymers, which can be functionalized by polymer reactions. Polymerization of monomers with a higher degree of unsaturation is an attractive method used to produce polymers bearing unsaturated moieties. These polymerizations often include problems such as instability of monomers and side reactions, giving unregulated polymer structures. To construct well-defined polymers bearing unsaturated moieties, many others have been made in the polymerization of dienes,^{1,2} acetylenes,³ cyclic olefins,⁴ heterocumulenes,⁵ and so on. In this aspect, we have developed the copolymerization of monomers to give unsaturated bonds.

The free-radical polymerization of vinyl acetate (VA) has attracted much attention^{6–8} because of its unusual kinetic features. VA copolymerizes easily with a few monomers such as ethylene, and vinyl chloride, which has a reactivity ratio close to its own. Diblock copolymers of vinyl acetate with methyl methacrylate,⁹ acrylonitrile, and vinyl pyrrolidinone have been prepared by copolymerization in viscous and poor solvents, whereas ethylene¹⁰ and butyl acrylate have been prepared by semibatch emulsion.¹¹

Many polymer chemists have examined isoprene for homo-¹² and copolymerization,^{13,14} and a few used terpenoids such as α - and β -pinene^{15,16}; however, linalool (acyclic monoterpene) is still far from being considered by researchers. Acyclic monoterpene do not undergo homopolymerization because of steric hindrance,^{17,18} low stabilization energy between monomer and free radicals in transition state,¹⁹ excessive chain transfer,²⁰ and termination by cyclization, as in the case of 1,2-disubstituted ethylenes.²¹

Linalool (LAL) is an acyclic monoterpene which is an unsaturated tertiary alcohol and is optically active. It has two double bonds, and therefore, is susceptible to copolymerization with vinyl monomers. It is of great interest of investigation because it yields an optically active and functional copolymer.^{22–25} In this article, an attempt has been made to study the details of the kinetics, mechanism, and characterization of copolymerization of LAL with VA in *p*-xylene initiated by benzoyl peroxide (BPO) at 60°C.

EXPERIMENTAL

VA (Merck–Schuchardt) was purified by passing it through alkali to remove inhibitor, followed by vacuum distillation before polymerization. Other solvents were purified by the usual methods.^{26,27} LAL (Merck–Schuchardt) [boiling point (b.p.) = 196°C; $d_{15}^0 = 0.8621$; $[\alpha] = (-)20.7^\circ$] was used after fractional distillation. BPO was recrystallized twice from methanol, followed by drying under vacuum.

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TABLE I
Effect of [BPO] on the Rate of Copolymerization of LIN and VA

Sample no.	[BPO] × 10 ³ (mol/l)	% Conversion	R _p × 10 ⁶ (mol/l/s)
1	6.88	10.4	5.75
2	13.77	11.8	6.16
3	20.66	13.4	7.41
4	27.54	16.6	8.31
5	34.43	20.2	9.10

[LIN] = 0.93 mol/l; [VA] = 1.8 mol/l; copolymerization time = 90 min; copolymerization temp. = 60°C.

Polymerization procedure

A solution containing a requisite concentration of LAL with VA in the presence of BPO was polymerized in a dilatometric apparatus (capillary diameter = 4 mm; capillary length = 9.1 cm; lower bulb capacity = 5 ml). The copolymerization runs were performed for 90 min at 60°C in *p*-xylene under an inert atmosphere of N₂. The copolymer, precipitated with acidified methanol, was dried to constant weight. It was then treated with toluene to remove homopolymer. Finally, the copolymer was dried to constant weight and the percentage conversion was calculated. The rate of copolymerization (R_p) was calculated from the slope of linear plot of percent conversion versus time.²⁸

Characterization

¹H-NMR and ¹³C-NMR spectra were recorded with a Varian 100HA Jeol LA 400 spectrometer by using CDCl₃ as solvent and tetramethylsilane as internal reference. The FTIR spectra were recorded with Perkin-Elmer, 599B, with KBr pellets. The GPC studies were made with Merck RI-L-7490. The elution solvent was tetrahydrofuran at a temperature of 25°C. The TGA runs were carried out by using V5.1A DuPont 2100 analyzer, sample weight ~ 10 mg, at a heating rate 10°C per minute. The DSC runs were carried out by using V4.0B DuPont 2100 analyzer, sample weight ~ 10 mg, heating rate 10°C per minute.

RESULTS AND DISCUSSION

The kinetics of copolymerization have been studied by varying [BPO] from 6.80 × 10⁻³ to 34.4 × 10⁻³ mol/l, keeping [LIN] and [VA] constant at 0.93 and 1.8 mol/l, respectively. The effect of [BPO] on R_p is shown in Table I. The R_p increases with increasing concentration of BPO as expected for free-radical copolymerization. The order of reaction with respect to [BPO], calculated from the slope of the plot of log R_p versus log[BPO] (Fig. 1), is 0.6.

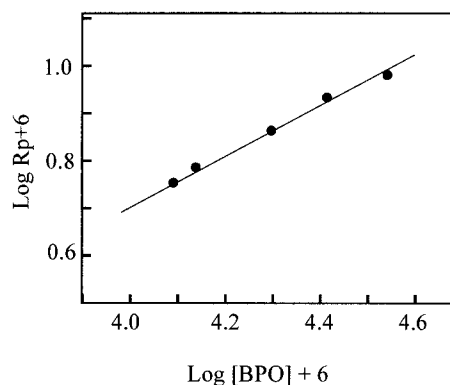


Figure 1 Relationship between rate of copolymerization and [BPO]. [LIN] = 0.93 mol l⁻¹; [VA] = 1.8 mol l⁻¹; copolymerization time = 90 min; copolymerization temp. = 60°C.

The effect of [LIN] on R_p has been studied by varying [LIN] from 0.18 to 1.67 mol/l, keeping [VA] and [BPO] constant at 1.80 and 20.66 × 10⁻³ mol/l, respectively (Table II). A plot between log R_p and log[LIN] (Fig. 2) is linear, the slope of which gives the relationship:

$$R_p \propto [\text{LIN}]^{1.2}$$

The effect of [VA] on R_p has been studied by varying [VA] from 0.36 to 3.13 mol/l, keeping [LIN] and [BPO] constant at 0.93 and 20.66 × 10⁻³ mol/l, respectively (Table II). A plot between log R_p and log[VA] (Fig. 2) is linear, the slope of which gives relationship:

$$R_p \propto [\text{VA}]^{1.1}$$

The deviation on the values of initiator, LAL, and VA exponents suggests that the present system follows nonideal kinetics, which can be explained on the

TABLE II
Effect of [Comonomer(s)] on the Rate of Copolymerization of LIN and VA Initiated by BPO

Sample no.	[LIN] (mol/l)	[VA] (mol/l)	% Conversion	R _p × 10 ⁶ (mol/l)
06	0.93	0.36	10.8	2.58
07	0.93	1.08	11.2	4.69
03	0.93	1.80	13.4	7.41
08	0.93	2.73	16.7	10.98
09	0.93	3.13	19.2	12.04
10	0.18	1.80	07.8	3.30
11	0.55	1.80	11.8	5.48
03	0.93	1.80	13.4	7.41
12	1.30	1.80	16.2	10.33
13	1.67	1.80	18.8	12.49

[BPO] = 20.66 × 10⁻³ mol/l; copolymerization time = 90 min; copolymerization temp. = 60°C.

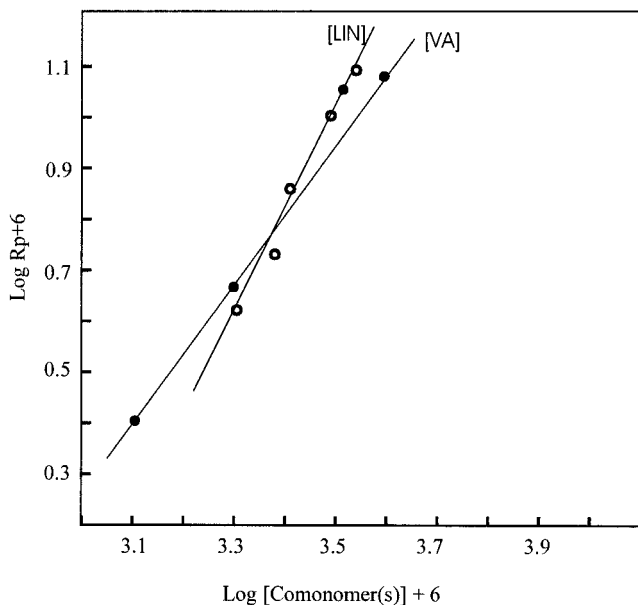


Figure 2 Relationship between rate of copolymerization and [comonomer(s)]. [BPO] = $20.66 \times 10^{-3} \text{ mol l}^{-1}$; copolymerization time = 90 min; copolymerization temp. = 60°C .

basis of primary radical termination and degradative chain transfer.

To analyze the effect of primary radical termination, the following expression given by Deb and Meyerhoff^{29,30} has been frequently used^{31,32} for homo- as well as copolymerization

$$\log R_p^2/[I][M]^2 = \log 2f_k k_d k_p^2 / k_t - 0.8684 k_{prt} R_p / k_t k_p [M]^2$$

where f_k represents the fraction of free radical to initiate chain growth; k_d is the initiator decomposition rate constant; k_p is the propagation rate constant; k_{prt} is the primary radical termination constant; and $[I]$ and $[M]$ are initiator and monomer concentrations, respectively. In the present study, a plot on the left-hand side of the above equation versus $R_p/[M]^2$ gave a negative slope (Fig. 3), indicating significant primary radical termination.

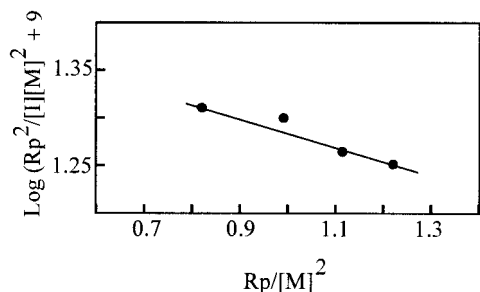


Figure 3 Plot of $R_p^2/[I][M]^2$ versus $R_p/[M]^2$. [LIN] = 0.93 mol l^{-1} ; [VA] = 1.8 mol l^{-1} ; copolymerization time = 90 min; copolymerization temp. = 60°C .

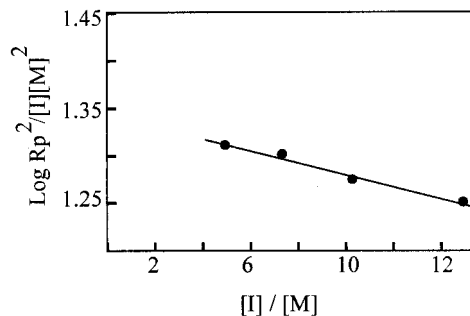


Figure 4 Plot of $R_p^2/[I][M]^2$ versus $[I]/[M]$. [LIN] = 0.93 mol l^{-1} ; [VA] = 1.8 mol l^{-1} ; copolymerization time = 90 min; copolymerization temp. = 60°C .

The equation by Ghosh and Mitra³³ has frequently been used^{31,32} to examine degradative chain transfer as

$$\log R_p^2/[I][M]^2 = \log 2f_k k_d k_p / k_t - 0.434 k_{prt}^2 C_i [I] / k_t k_{it} k_p [M]$$

where C_i is the initiator transfer constant; k_{it} is the rate constant for degradative chain transfer to initiator; and k_{it} is the initiator rate constant. A plot on the left-hand side of the above equation versus $[I]/[M]$ gave a linear negative slope (Fig. 4), suggesting measurable degradative initiator transfer with the observed exponent values of [BPO], [LIN], and [VA]. The nonideality in the present system appears to be due to both primary radical termination and degradative chain transfer.

The R_p increases with increasing temperature. The overall energy of activation was computed to be 82 kJ/mol from the slope of Arrhenius plot³⁴ of $\log R_p$ versus $1/T$ (Fig. 5).

Gel permeation chromatography

The Mark-Houwink equation $[\eta] = K[M]^\alpha$ relates the intrinsic viscosity $[\eta]$ of a polymer to its molecular weight $[M]$ through empirical constants K and α . The

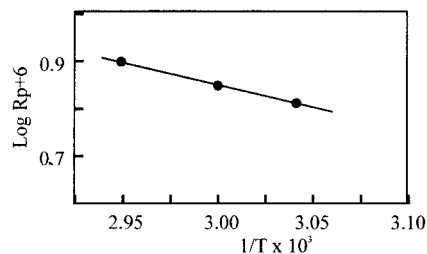


Figure 5 Arrhenius plot of the rate of copolymerization and copolymerization temperature. [LIN] = 0.93 mol/l ; [VA] = 1.8 mol/l ; [BPO] = $20.66 \times 10^{-3} \text{ mol/l}$; copolymerization time = 90 min.

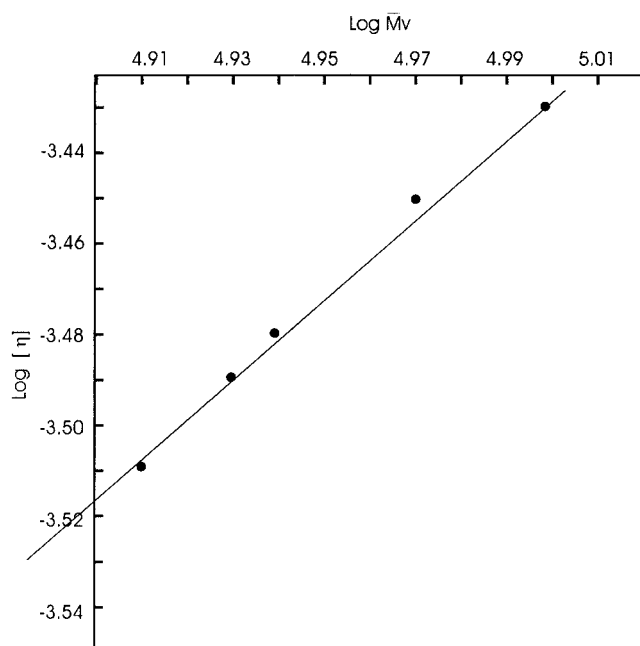


Figure 6 Plot of $\log[\eta]$ versus $\log \bar{M}_v$ (Mark-Houwink curve). $[\text{BPO}] = 4.13 \times 10^{-3} \text{ mol l}^{-1}$; copolymerization time = 90 min; copolymerization temp. = 60°C .

standard procedure for measuring these constants requires \bar{M}_v and $[\eta]$ of polymer samples, which are measured by gel permeation chromatography (GPC). The two constants α and K of the empirical Mark-Houwink expression were evaluated from the slope

and intercept of the plot of $\log[\eta]$ versus $\log \bar{M}_v$ (Fig. 6) for copolymer samples. The following relationship is established

$$[\eta] \text{dl/g} = 3.0 \times 10^{-4} \bar{M}_v^{0.8} \quad \text{in THF at } 25^\circ\text{C}$$

The value $\alpha = 0.8$ is in between the most expected values 0.5–1.0.³⁵

Characterization of copolymers

¹³C-NMR spectroscopy

The ¹³C-NMR spectrum of copolymer (Fig. 7) shows the two following distinct signals: (1) Due to $-\text{C}-\text{OH}$ group of LAL at $\delta = 75\text{--}77 \text{ ppm}$.³⁶ (2) Due to $-\text{COOCH}_3$ group of VA resonates at $\delta = 167.1 \text{ ppm}$. This confirms the incorporation of both the monomers in the copolymer.

¹H-NMR spectroscopy

In the ¹H-NMR spectrum, the chemical shifts of protons attached to elements other than carbon-like $-\text{OH}$, $-\text{NH}$, and $-\text{SH}$, to a greater or lesser extent, are influenced by a related phenomenon of intermolecular exchange and hydrogen bonding. Appearance of signals in the ¹H-NMR, due to $-\text{OH}$ protons with the species of small molecular weight, where intermolecular association is not hindered, generally resonates in the region of 3.0–5.5 δ (hydroxyl proton of CH_3OH

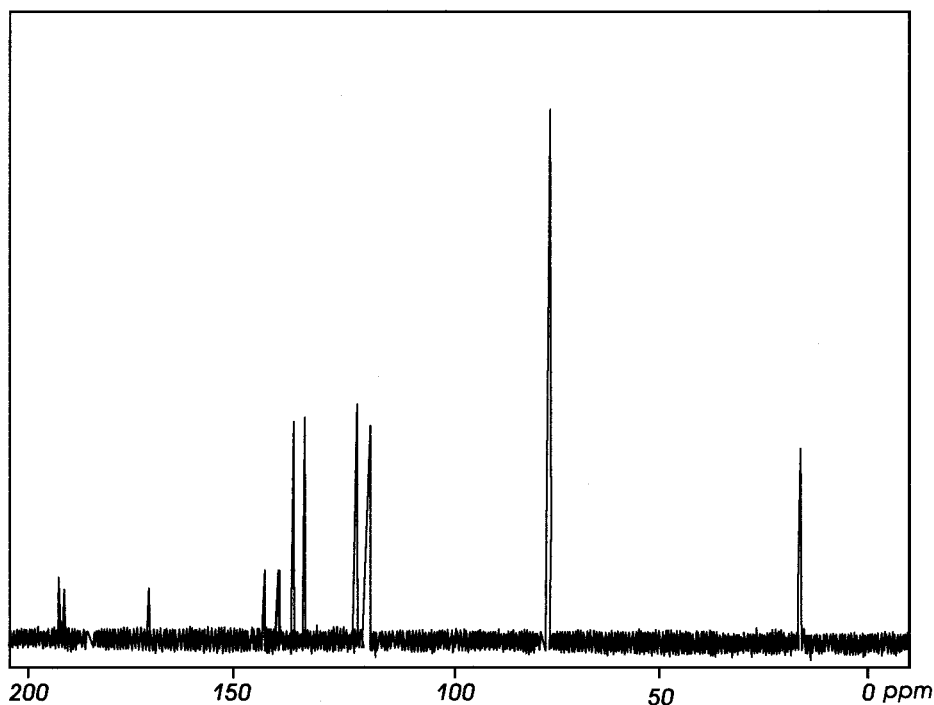


Figure 7 ¹³C-NMR spectrum of copolymer.

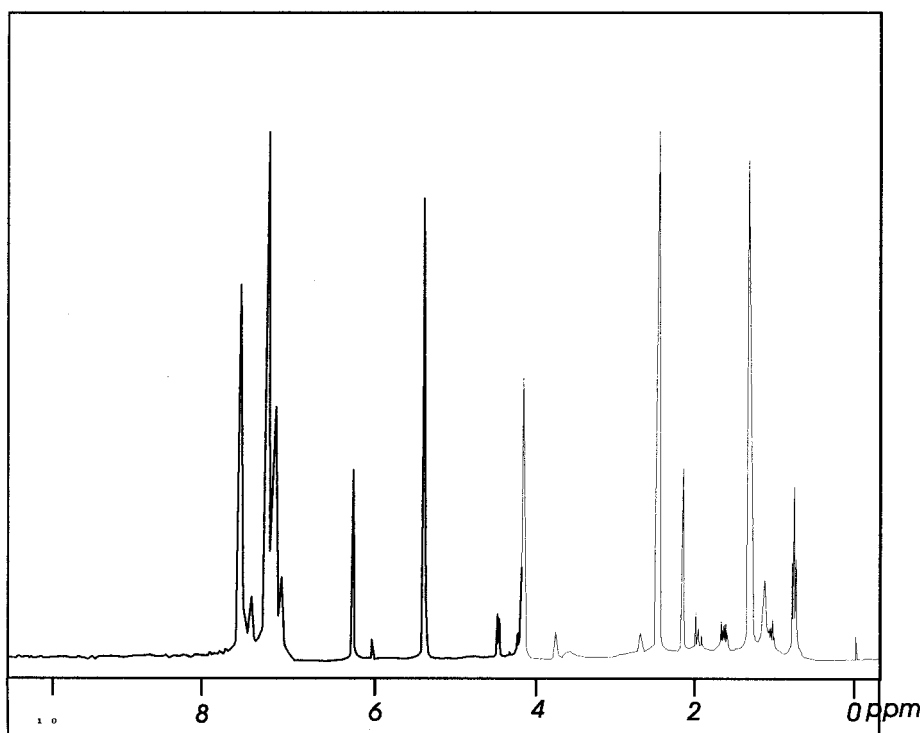


Figure 8 $^1\text{H-NMR}$ spectrum of copolymer.

appears at 3.3 δ , whereas that of $\text{C}_2\text{H}_5\text{OH}$ appears at 5.4 δ).³⁷ However, with many large molecules, the hydroxyl protons often resonate near 8.0 δ even at relatively high concentrations, partially because the molar concentration is low and partially because of the steric effect.³⁸ In the present article, the $-\text{OH}$ peaks are assigned in the range of 7.0–7.7 δ in the $^1\text{H-NMR}$ spectra of LAL as well as copolymer. The $^1\text{H-NMR}$ spectrum of copolymer of LIN and VA (Fig. 8) shows peaks at 7.0–7.7 δ because of the hydroxy proton of LIN and at 1.0–1.4 δ because of the acetoxy protons of VA, confirming the incorporation of both comonomers in the copolymer chain.

FTIR spectroscopy

The FTIR spectrum of copolymer (Fig. 9) shows bands at 3425 cm^{-1} of the alcoholic group of LAL and at 1641 cm^{-1} for $>\text{C}=\text{O}$ group of VA. This confirms the incorporation of both the monomers in the copolymer.

Thermal analysis

Differential scanning calorimetry

The DSC scans of copolymer samples (Fig. 10) showed a well-pronounced endothermic transition in the temperature range of 50–300°C. The values of glass transition temperature (T_g), onset temperature (T_o), and peak temperature (T_p) of the copolymer are as follows:

$$T_g = 85^\circ\text{C}, \quad T_o = 198^\circ\text{C}, \quad T_p = 203.2^\circ\text{C}, \quad T_p - T_o = 5.2^\circ\text{C}$$

The initial temperature (T_i) is the temperature at which the curve deviates from the baseline. It is a measure of initiation of the reaction. The onset temperature (T_o) is obtained at the intercept of the tangents to the baseline at the lower temperature side of the endotherm peak. The difference between T_p and T_o ($T_p - T_o$) is the measure of the overall rate of reaction. The smaller the difference, the greater is the rate of reaction.

Thermogravimetric analysis (TGA)

The TGA curve for copolymer (Fig. 11) exhibits weight loss with temperature.^{39,40} The copolymer was stable up to a temperature of 187°C and starts to decompose at 187°C. The thermal behavior data are as follows:

- Onset of major weight loss 388°C; completion of major weight loss occurs at 470°C;
- The total weight loss in the range 40 to 470°C = 95%;
- Weight losses at different stages of temperature are as follows:
 - 0–200°C = 7.2%;
 - 200–300°C = 25.5%;

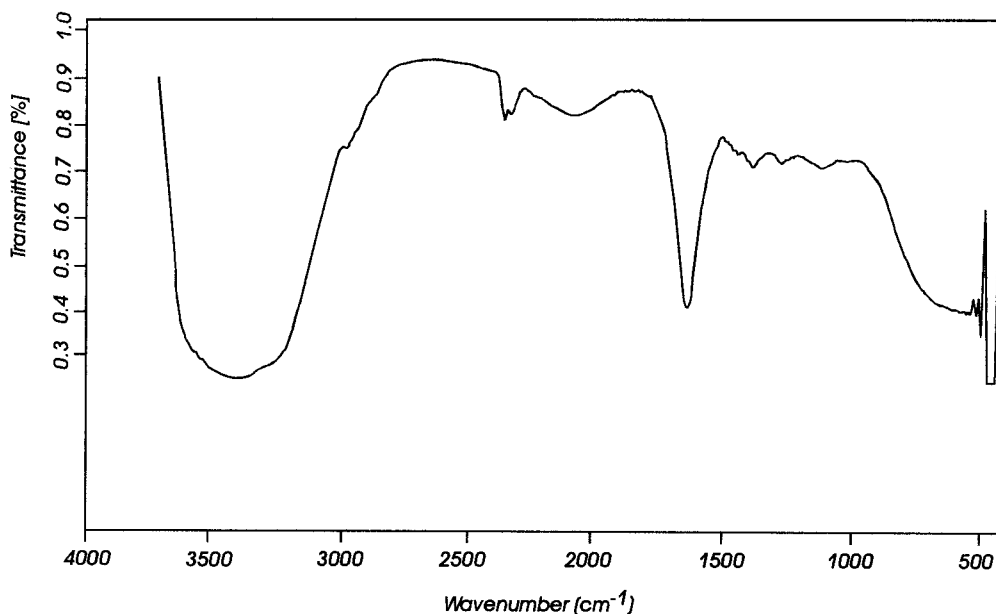


Figure 9 FTIR spectrum of copolymer.

- (iii) 300–400°C = 46.0%;
- (iv) 400–480°C = 15.5%;

(d) Almost total volatilization of copolymer occurred at 388°C.

The TGA data show a weight loss of 7.2% as the temperature increases to 200°C, which is attributed to

the loss of absorbed water.^{41,42} The weight loss in the range of temperature 200–400°C are the regions of major weight loss and appear to be due to dehydration and to the extensive degradation of the copolymer backbone chain. Grant and Grassie⁴³ suggested the anhydride formation in the case of polymethacrylic acid by the dehydration reaction. Likewise, in LIN-VA copolymer, there is the possibility of dehy-

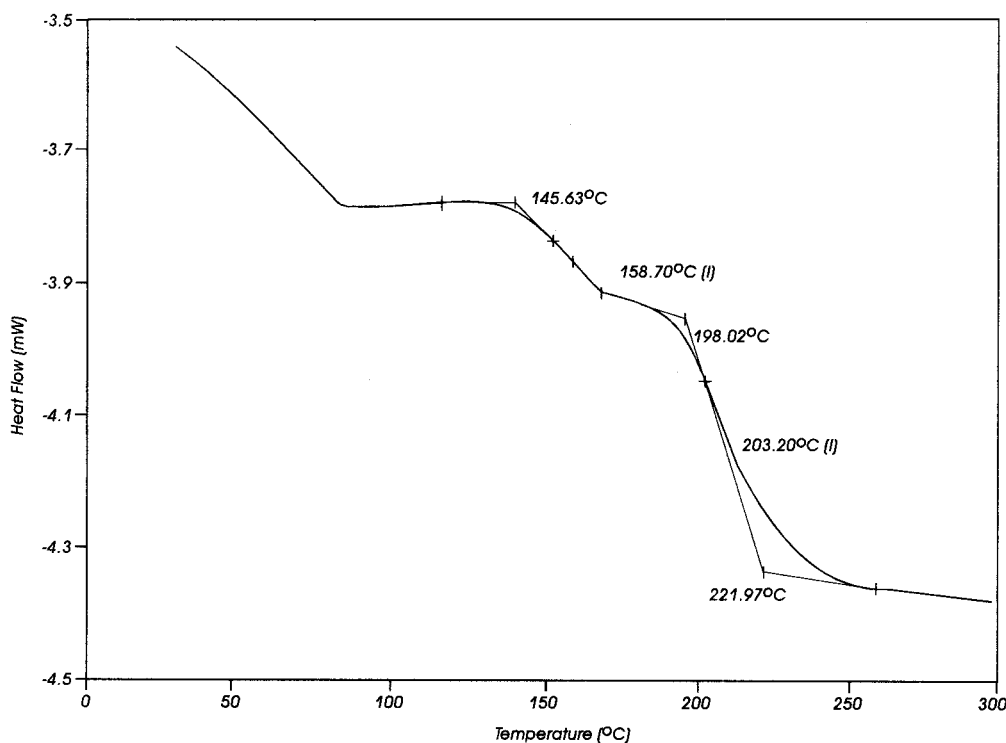


Figure 10 DSC curve of copolymer (sample 2).

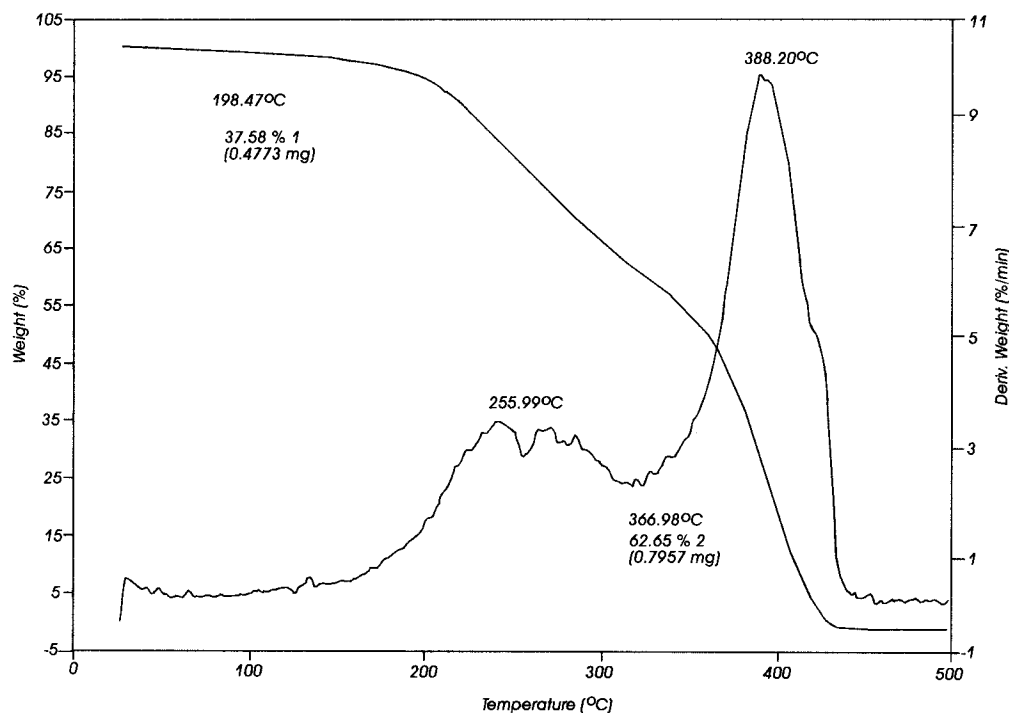


Figure 11 TGA curve of copolymer (sample 2).

dration reaction (i.e., elimination of —H and —OH groups present to adjacent C-atoms in the copolymer at this temperature range).

Copolymer composition and reactivity ratios

To calculate the reactivity ratios, the composition of LAL content (Table III) has been calculated from the peak area of hydroxy protons and VA content from the peak area of acetoxy protons of $^1\text{H-NMR}$ spectra of copolymers. The Kelen-Tudos⁴⁴ approach is used for evaluation of reactivity ratios, r_1 (VA) and r_2 (LIN), for the monomer according to

$$\eta = r_1\xi - r_2(1 - \xi)/\alpha$$

TABLE III
Composition of LIN-VA Polymer

Sample no.	Molar ratio in monomer feed (F) [VA]/[LIN]	% Conversion	Molar ratio in copolymer composition (f) [VA]/[LIN]
03	1.93	13.4	1.030
07	1.16	11.2	1.021
08	2.93	16.7	1.036
11	3.27	11.8	1.050
12	1.38	16.2	1.023

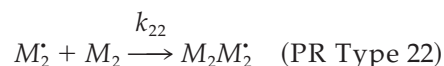
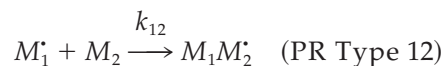
where $\eta = G/(\alpha + H)$ and $\xi = H/(\alpha + H)$. The transformed variables G and H are given by

$$G = \frac{[M_1]/[M_2][(d[M_1]/d[M_2]) - 1]}{d[M_1]/d[M_2]}$$

$$H = \frac{([M_1]/[M_2])^2}{d[M_1]/d[M_2]}$$

The parameter α is calculated by taking the square root of the product of the lowest and the highest values of H for the copolymerization series. The graphical evaluation for VA/LIN yields values of $r_1 = 0.01$ and $r_2 = 0.0015$ (Fig. 12). The product of r_1r_2 is nearly 0, which is the sign of nearly alternating copolymerization.

According to the Alfery-Price $Q-e$ scheme, the alternating tendency of the copolymer is given by a product of monomer reactivity ratios r_1 and r_2 with respect to monomers M_1 (VA) and M_2 (LIN) in the four growing propagating reactions (PR):



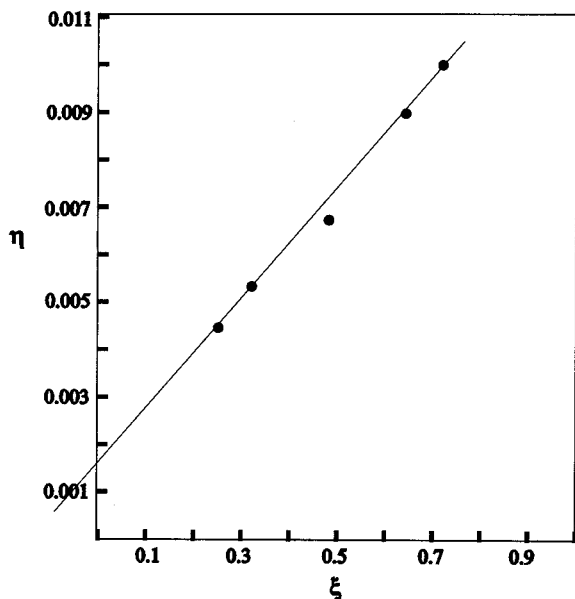


Figure 12 Kelen-Tudos plot of copolymer for determination of reactivity ratio.



where r_1 and r_2 are given by the ratio among the rate constants k_{11} , k_{12} , k_{21} , and k_{22} as

$$r_1 = k_{11}/k_{12}$$

and

$$r_2 = k_{22}/k_{21}$$

By the values of r_1 and r_2 , it is clear that r_1 and r_2 are less than 1 (i.e., the propagation reaction type 12 and 21 are preferred to type 11 and 22). The value of r_2 is nearly zero, which shows that the probability of propagation reaction 22 is very less or somewhat impossible because of the fact that no homopolymerization of M_2 takes place, and hence, a chain ending with M_2 will add only an M_1 .

The $e_2 = 3.11$ and $Q_2 = 1.24$ values for LAL were calculated by using $e_1 = -0.22$ and $Q_1 = 0.026$ for VA with the help of the following Alfrey-Price equation^{45,46}

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

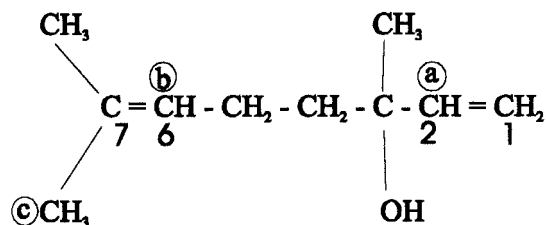
$$Q_2 = Q_1 / r_1 \exp[-e_1(e_1 - e_2)]$$

These equations express r_1 and r_2 in terms of constants Q and e and are assumed to be characteristic of each monomer. Q is related to the extent of resonance stabilization in the monomer (i.e., its reactivity) and e is

related to the polarity of double bond. It has been found that strong alternating copolymers are formed when comonomers with widely differing polarities are reacted together. The high polarization characteristic of LAL in comparison to that of VA is evidenced from its high value of e . An alternating copolymerization is suggested from high difference of e values of both comonomers.

Mechanism

The ¹H-NMR facilitates the interpretation of the mechanism of copolymerization. The structure of LAL is



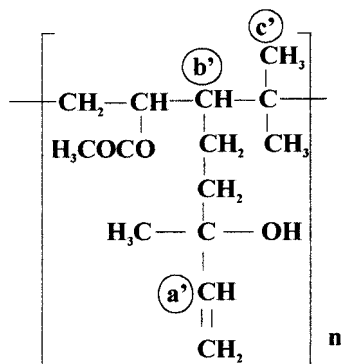
There are two possible sites in LAL structure for involvement in polymerization; the participation of $>\text{C}=\text{C}<$ bond is present between C-1 and C-2 and between C-6 and C-7. The ¹H-NMR spectrum of LAL shows the peaks of

- a. $-\text{CH}=\text{CH}_2$ at 4.1–4.6 δ
- b. $-\text{CH}=\text{C}<$ at 5.1–5.3 δ
- c. $\text{CH}_3-\text{C}=\text{C}<$ at 1.6 δ

The ¹H-NMR spectrum of copolymer (Fig. 8) shows the peaks of

- a'. $-\text{CH}=\text{CH}_2$ at 4.1–4.6 δ
- b'. $>\text{CH}-\overset{|}{\text{C}}-\text{CH}_3$ at 1.3–1.5 δ
- c'. $\text{CH}_3-\overset{|}{\text{C}}-\overset{|}{\text{C}}-$ at 0.9–1.2 δ

The ¹H-NMR spectrum of copolymer (LIN-VA) shows that $-\text{CH}=\text{C}<$ does not resonate at 5.1–5.3 δ , indicating the participation of $>\text{C}=\text{C}<$ bond present between C-6 and C-7 in the copolymerization. Further, the presence of peaks due to $-\text{CH}=\text{CH}_2$ at 4.5 δ indicates that $>\text{C}=\text{C}<$ bond present between C-1 and C-2 does not participate in copolymerization. This also indicates that it is an unsaturated copolymer. It is further confirmed by the fact that it gives a positive unsaturation test (decolorizes Br_2 water). Thus, the structure of copolymer may be assigned as



The participation of double bond in the copolymerization present between C-6 and C-7 is more likely because its homolysis forms more stable tertiary free radical than the free radical formed by the homolysis of double bond present between C-1 and C-2.

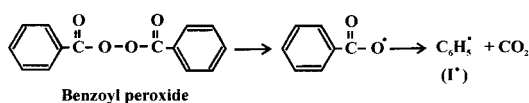
The FTIR spectrum of LAL shows

- (A) Bands of $\text{CH}_3 - \overset{\text{CH}_3}{\text{C}} = \text{CH} -$ group
 $=\text{C}-\text{H}$ stretching at 2971 cm^{-1}
 $>\text{C}=\text{C}-\text{H}$ stretching at 1668 cm^{-1}
 $\text{C}-\text{H}$ bending at 835 cm^{-1}
- (B) Bands of $-\text{CH}=\text{CH}_2$ group
 $\text{C}-\text{H}$ stretching at 3086 cm^{-1}
 $>\text{C}=\text{C}<$ stretching at $1641-1647 \text{ cm}^{-1}$
 $\text{C}-\text{H}$ bending at $1000-1150 \text{ cm}^{-1}$

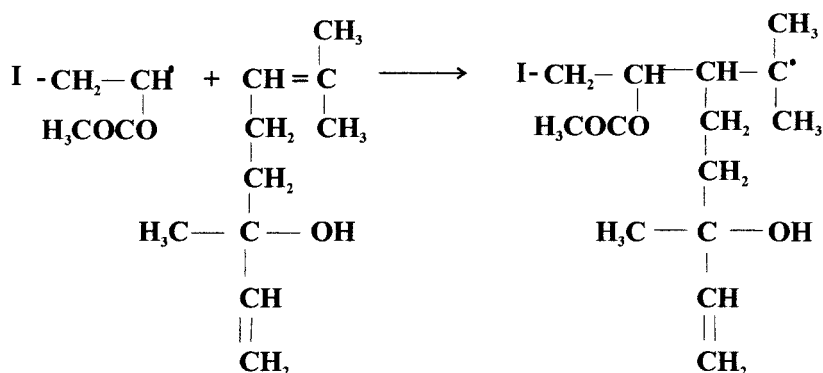
The FTIR spectrum of copolymer (Fig. 9) shows the bands of $-\text{CH}=\text{CH}_2$ group, which confirms the formation of unsaturated copolymer.

The proposed mechanism of copolymerization initiated by BPO is as follows:

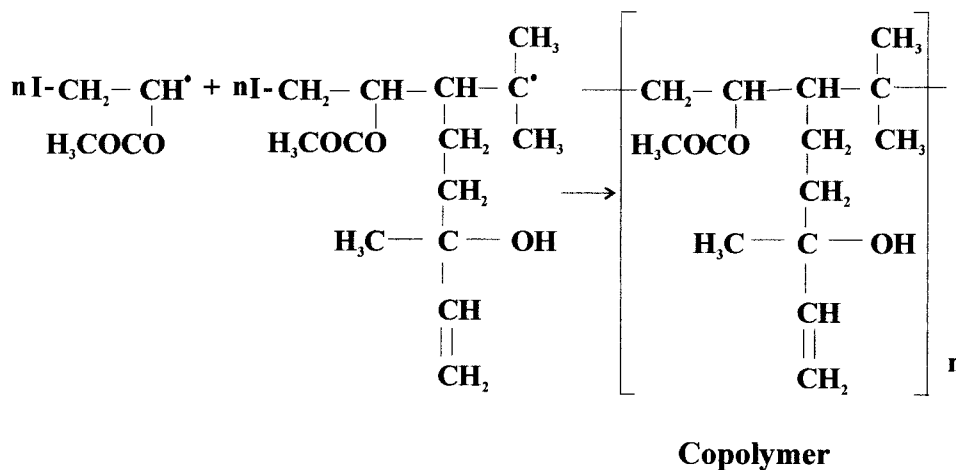
Initiation



Propagation



Termination



CONCLUSIONS

Poly(LIN-*alt*-VA) has been synthesized via free-radical solution polymerization by using BPO as initiator, which has $T_g = 85^\circ\text{C}$ and Mark-Houwink constants $K = 3.0 \times 10^{-4} \text{ dl/g}$ and $\alpha = 0.80$. The copolymer is thermally stable. The system follows nonideal kinetics because of primary radical termination as well as degradative chain transfer. The energy of activation is evaluated as 82 kJ/mol.

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