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Alternating Copolymers of Limonene with Methyl Methacrylate: Kinetics and Mechanism

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ABSTRACT

The radical copolymerization of limonene (optically active) with methyl methacrylate in xylene at 80 ± 0.1°C for 1 hr, initiated by benzoyl peroxide (BPO) yield alternating copolymer(s), under the inert atmosphere of nitrogen, as evidenced by reactivity ratios r_1 (MMA) = 0.07 and r_2 (limonene) = 0.012 using the Kelen–Tüdos method. The kinetic expression is $R\alpha[I]^{0.5}[MMA]^{1.0}[Lim.]^{-1.0}$. The decrease in the rate of polymerization with increase in concentration of limonene is due to penultimate unit effect. The overall energy of activation is calculated as 49 kJ/mole. FTIR of the copolymer(s) shows the characteristic frequencies at 1732.40 and 2951.40 cm^{-1} due to $-OCH_3$ of MMA and aromatic C—H stretching of limonene, respectively. ^1H NMR spectra shows peak at 3.8–4.1 δ and 5.3–5.6 δ due to $-OCH_3$ of MMA and trisubstituted olefinic protons [$-CH{=}CH-CH_2-$] of limonene, respectively.

Key Words: Limonene; Methyl methacrylate; Copolymerization; Kinetics and reactivity ratios.

INTRODUCTION

The latter part of the century witnessed a revolution in the field of synthetic polymers, which have been widely used in our daily life. This has been possible due to development

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of new polymerization techniques, initiators and monomers. In this series a new and extremely interesting field, allied to organic polymers is coming into being polymers from terpenes. The literature search reveals that notable progress has been achieved by the synthesis of versatile copolymers of terpenes and isopenes with vinyl monomers i.e., isoprene co-styrene/neodymium,[1] polystyrene-b-poly(1,2-isoprene-ran-3,4-isoprene)[2] poly(styrene-co-butadine-g-isobutylene and poly(styrene-co-isoprene-g-isobutylene),[3] α-pinene-co-styrene/$AlCl_3$/10°C,[4] β-pinene-co-styrene/CH_2Cl_2/30°C,[5] α-pinene-co-styrene/$AlCl_3$/$SbCl_3$,[6] β-pinene-co-maleic anhydride/BPO/60–90°C,[7] citronellol-co-styrene/BPO and As-ylide/80°C,[8] citronellol-co-1-vinyl-2-pyrolidinone/BPO/80°C,[9] citronellol-co-vinylacetate/BPO/80°C,[10] Gereniol-co-styrene/BPO/80°C[11] and linalool-co-acrylonitrile/BPO/80°C[12] mainly from this lab.

Limonene, on optically active, non-conjugated monocyclic terpenes, is susceptible to polymerization as it contains two double bonds. A search of the literature reveals that initially it was polymerized by Robert and Day[13] and Marvel[14] et al. using Freidal–Craft and Zeigler–Natter Catalyst, respectively. Later, it was copolymerized with maleic anhydride by Douchi et al.[15] However, to the best of our knowledge it has never been copolymerized with vinyl monomer. The present paper highlights the synthesis of the copolymer(s) of limonene with methyl methacrylate in xylene initiated by benzoyl peroxide at 80 ± 0.1°C for 1 hr under a nitrogen blanket.

EXPERIMENTAL

The methyl methacrylate (Merck-Schuchart) and solvents were purified by the usual methods.[16] Limonene (Fluka) ($M = 136\,\mathrm{gm/mole}$, b.p. = 176–177°C, $d = 0.8411$) was used after fractional distillation. Benzoyl peroxide (BPO) was recrystallized twice from chloroform.

Polymerization Procedure

The dilatometric technique has been used to follow the copolymerization runs in xylene for 1 hr under oxygen free conditions to limit the conversion up to 17% at 80 ± 0.1°C. The copolymer(s) were isolated with acidified methanol and dried to constant weight under vacuum. The copolymer(s) were refluxed with acetonitrile to remove polymethyl methacrylate. Finally, the copolymer(s) were dried to a constant weight. The rate of polymerization was calculated from the slope of graph between % conversion and time.

The spectral analysis FTIR and ^1H NMR were recorded with Perkin Elmer 599 (with KBr pellets) and Varian 100HA Jeol 400 LA Spectrophotometer using $CDCl_3$ as a solvent and TMS as an internal reference, respectively.

RESULTS AND DISCUSSION

The kinetics of the copolymerization has been studied by the varying the concentration of initiator, MMA and limonene. The maximum conversion has been limited to 17% and the copolymerization runs were associated with a short induction period of 2–3 min.

Effect of Initiator [BPO]

Table 1 reveals the relationship between the rate polymerization (R_p) and initiator concentration for fixed monomer ratio [MMA] = 2.57 moll^{-1}, [limonene] = 0.84 moll^{-1}. It shows that the R_p is a direct function of [I] and the exponent value of the initiator, obtained from a linear graph of log R_p vs. log [I], is 0.5 ± 0.01 (Fig. 1) (Table 1).

Effect of Comonomer Concentration

The effect of [MMA] on the R_p has been studied by varying MMA concentration, while [limonene] and [BPO] were kept constant at 0.840 moll^{-1} and 1.17×10^{-2} moll^{-1}, respectively. It is observed the R_p is direct function of [MMA]. A plot of log R_p vs. log [MMA] is linear, the slope of which gives order unity. (Fig. 2) (Table 1).

The effect of [limonene] on the R_p has been studied by varying concentration of limonene, keeping [MMA] and [BPO] constant at 2.57 moll^{-1} and 1.17×10^{-2} moll^{-1}, respectively. On the contrary, the R_p is an inverse function of limonene concentration. A plot of log R_p vs. log [limonene] is linear and the order is unity. (Fig. 3) (Table 1). It might be due to a cross-termination or penultimate unit effect (PUE), which has been quantitatively discussed by Arlmen.[17]

Table 1. Effect of concentration of initiator and the comonomers on the rate of copolymerization.

Sample	[BPO] × 10^2 (moll^{-1})	[MMA] (moll^{-1})	[Lim.] (moll^{-1})	Conversion (%)	$R_p \times 10^6$ (moll^{-1} s^{-1})
1	0.59	2.57	0.840	4.8	6.82
2	1.18	2.57	0.840	7.9	9.33
3	1.17	2.57	0.840	13.0	11.40
4	2.36	2.57	0.840	15.01	13.07
5	2.95	2.57	0.840	17.7	17.07
6	1.17	1.542	0.840	8.4	6.90
7	1.17	2.052	0.840	10.5	8.61
3	1.17	2.57	0.840	13.0	11.46
8	1.17	3.08	0.840	14.9	13.72
9	1.17	3.60	0.840	17.01	19.2
10	1.17	2.57	0.504	15.1	14.1
3	1.17	2.57	0.84	13.0	11.46
11	1.17	2.57	1.17	10.2	10.2
12	1.17	1.57	1.51	7.03	9.6
13	1.17	2.57	1.85	5.2	6.6

Copolymerization time = 1 hr.
Copolymerization temp. = 80 ± 0.1°C.

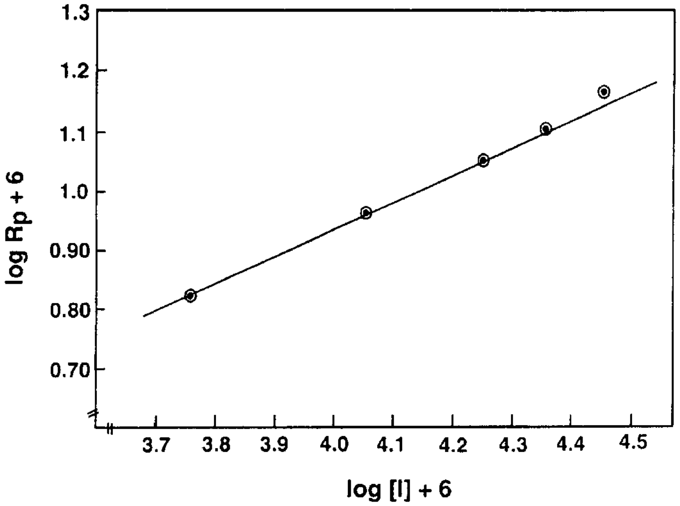


Figure 1. Relationship between the rate of copolymerization and [BPO], [limonene] = 0.840 moll^{-1}, [MMA] = 2.57 moll^{-1}, copolymerization time = 1 hr, copolymerization temperature = 80 ± 0.1°C.

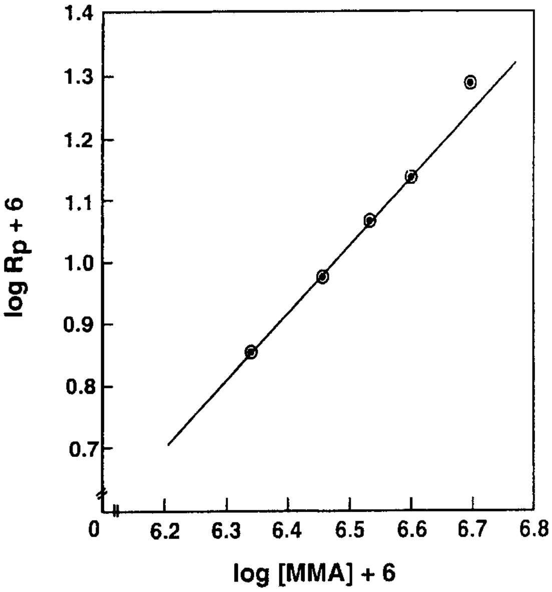


Figure 2. Relationship between the rate of copolymerization and [MMA] with constant [limonene] = 0.840 moll^{-1}, [BPO] = 1.17 × 10^{-4} moll^{-1}, copolymerization time = 1 hr, copolymerization temperature = 80 ± 0.1°C.

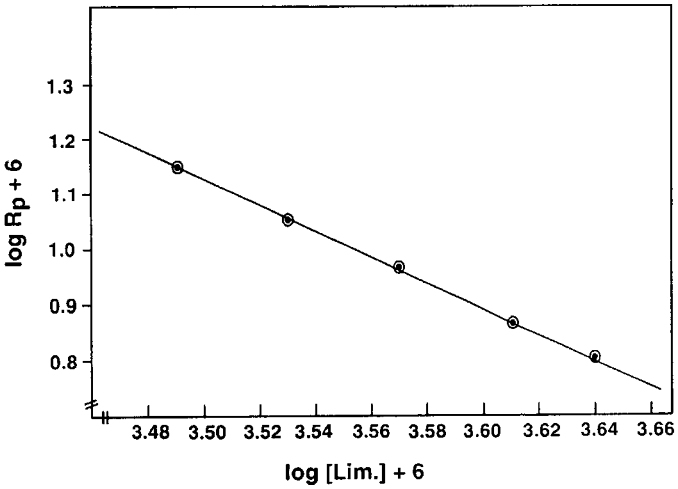


Figure 3. Relationship between the rate of copolymerization and [limonene] with constant $[\mathrm{MMA}] = 2.57\,\mathrm{moll}^{-1}$, $[\mathrm{BPO}] = 1.17 \times 10^{-4}\,\mathrm{moll}^{-1}$, copolymerization time = 1 hr, copolymerization temperature = 80 ± 0.1°C.

In the present system the four cross-termination reactions are possible:

$$M_1 + M_2 \quad k_{11} \quad M_1M_1. \tag{1}$$

$$M_1 + M_2 \quad k_{12} \quad M_2M_1. \tag{2}$$

$$M_2 + M_2 \quad k_{21} \quad M_1M_2. \tag{3}$$

$$M_2 + M_2 \quad k_{22} \quad M_2M_2. \tag{4}$$

M_1 = Methyl methyacrylate

M_2 = Limonene

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

$$R_p = \frac{-d[M_1] + d[M_2]}{Dt}$$
$$= k_{11}[M_1][M_1] + k_{12}[M_1][M_2] + k_{22}[M_2][M_2] + k_{21}[M_2][M_1] \tag{5}$$

In order to eliminate radical concentration from Eq. (5), two steady state assumptions are made:

$$k_{21}[M_2][M_1] = k_{12}[M_1][M_2] \tag{6}$$

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

$$R_i = 2k_{t^{11}}[M_1]_2 + 2k_{12}[M_1][M_2] + 2k_{t^{22}}[M_2]^2 \tag{7}$$

From Eqs. (5–7), the rate of polymerization obtained:

$$R_p = \frac{(r_1[M_1]_2 + 2[M_1][M_2] + r_2[M_2])^2 Ri^{1/2}}{\{r_1^2\delta_1^2[M_1]^2 + 2\Phi r_1 r_2 \delta_2 \delta_1 [M_1][M_2] + r_2^2\delta_2^2[M_2]^2\}^{1/2}}$$

Where,

From the experimental data, the value of Φ is 5.45. It is more than unity, indicating the penultimate unit effect (PUE) is favored in the present system.[18,19]

Effect of Temperature

The polymerization runs were also carried out at 75°C and 85°C to evaluate the activation energy using the Arrhenius equation. The overall energy of activation is computed as 49 kJ mol^{-1} (Fig. 4).

Characterization of Copolymerization(s)

Fourier Transform Infrared Spectroscopy

The FTIR spectra of the copolymer(s) shows the characteristic frequencies at 2951.40 cm^{-1} due to C—H stretching band of aromatic ring of liomonene and at 1732.40 cm^{-1} due to —OCH$_3$ group of MMA, respectively (Fig. 5).

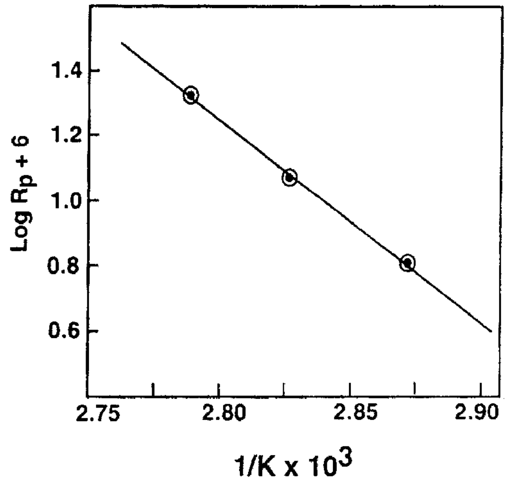


Figure 4. Arrhenius plot of rate of polymerization versus polymerization temperature with constant [BPO] = 1.17×10^{-4} moll^{-1}, [MMA] = 2.57 moll^{-1}, [limonene] = 0.840 moll^{-1}, copolymerization time = 1 hr.

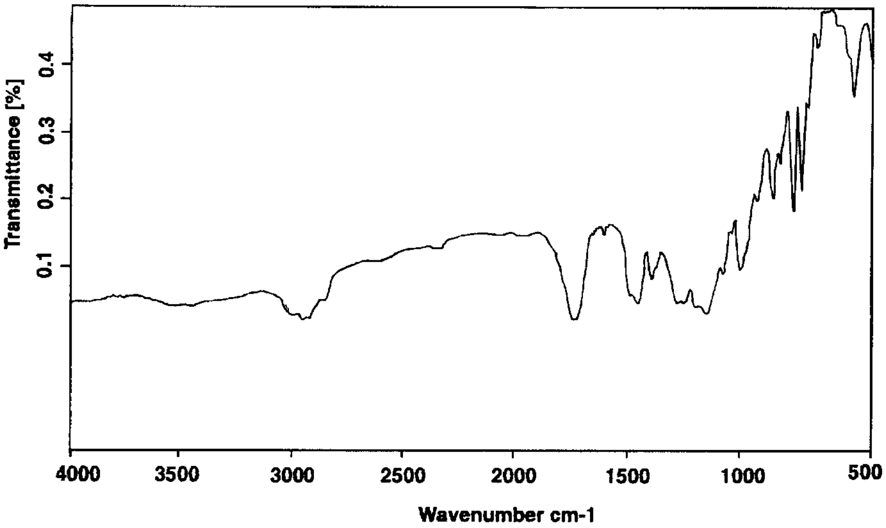
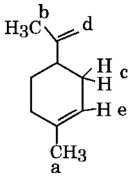


Figure 5. FTIR spectrum of the copolymer (sample-3).

Nuclear Magnetic Resonance

The ^{1}H NMR spectra of pure limonene[20,21] shows the following peaks:

a—1.64 δ (3H, CH_3) (Singlet)
b—1.72 δ (3H, CH_3) (Singlet)
c—1.92 δ (2H, CH_2) (Doublet)
d—4.66 δ (2H,CH_2) (Doublet)
e—5.35 δ (1H, CH) (Singlet)



The ^{1}H NMR spectra of the copolymer shows the singlet at 5.3–5.6 δ and 3.8–4.1 δ due to trisubstituted olefinic protons (double bond between C-1, C-2) of limonene and —OCH_3 of MMA, respectively. The disappearance of peak at 4.6 δ indicates that external double bond involve in the bond formation with methyl methacrylate (Fig. 6).

Copolymer Composition and Value of Reactivity Ratios

The relative peak areas of methoxy and trisubstituted olefinic protons of MMA and limonene at 3.8–4.1 δ and 5.3–5.6 δ, respectively in the copolymers have been used to calculate the copolymer composition. The Kelen–Tüdos[22] approach is used for the evaluation of reactivity ratios r_1 and r_2 for the monomer pair according to the following

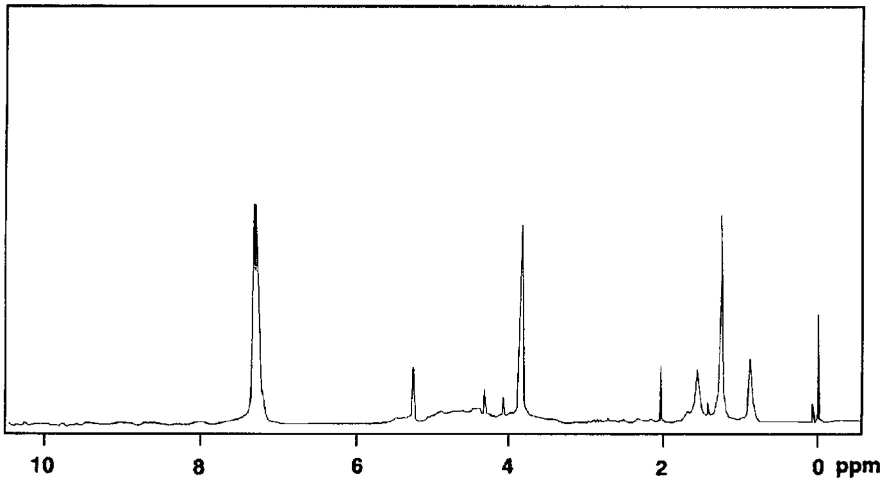


Figure 6. ^{1}H NMR spectrum of copolymer (sample-3).

equation:

$$\eta = r_1\xi - \frac{r_1}{\alpha}(1-\xi)$$

$$\text{where } \eta = \frac{G}{\alpha + H}G \quad \text{and} \quad \xi = \frac{H}{\alpha + H}$$

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 highest value of H for copolymerization series. Graphical evaluation for MMA and limonene yields values of $r_1 = 0.07$ and $r_2 = 0.012$, respectively (Fig. 7) (Table 2) .

MECHANISM

The mechanism of copolymerization of limonene may be discussed as below.

The copolymer(s), formed is an unsaturated polymer since it decolorizes Baeyers reagent.

It has already been reported that the acid catalyzed hydration of limonene proceeds on the vinyl double bond, giving α-terpeniol, though on dehydration it gives back

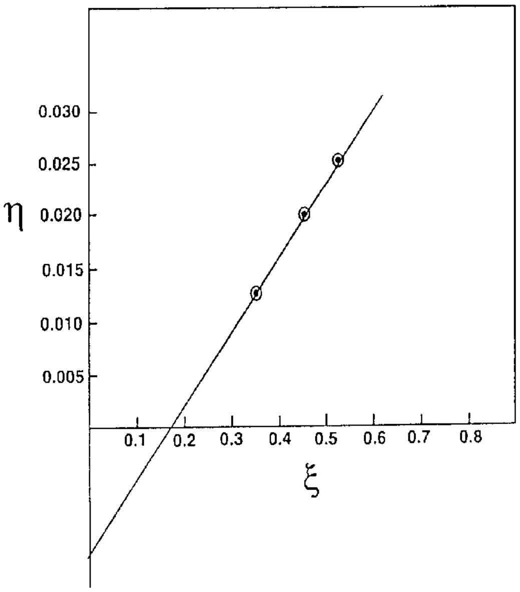
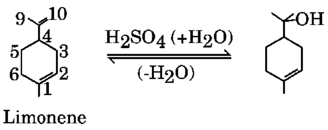


Figure 7. Kelen–Tüdos plot of limonene and MMA for determination of reactivity ratios.

limonene.[23]



Limonene on cationic polymerization yields polylimonene which involved the opening of bicyclic bridge structure to give a repeating unit through the terminal methylene group.[24]

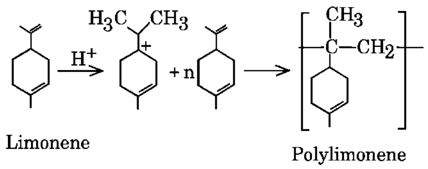
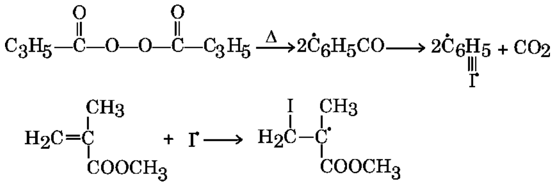


Table 2. Copolymer(s) composition.

Sample no.	Monomer feed [MMA/lim] (F)	Mole fraction of MMA in copolymer	Copolymer feed [MMA/lim] (f)	η	ξ
3	3.059	0.533	1.14	0.0206	0.451
8	3.66	0.54	1.17	0.0248	0.534
10	5.099	0.548	1.21	0.0281	0.682

Based on the above facts, it is clear that the C=C bond between C-8 and C-10 is more respectable to take part in polymerization. Therefore, the following mechanism can be proposed.

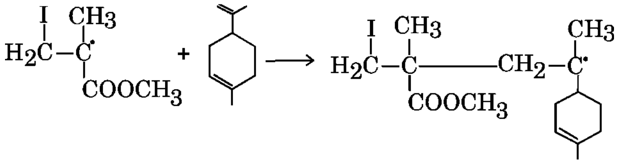
Initiation



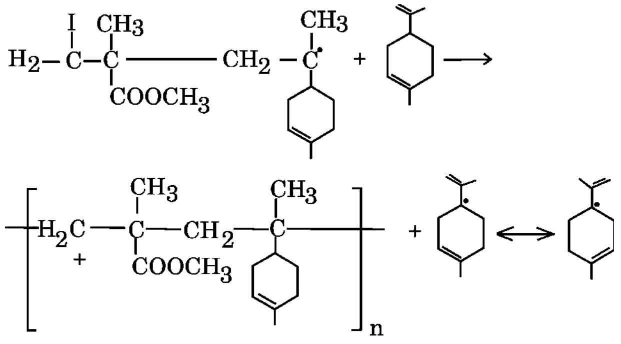
$$C_3H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_3H_5 \xrightarrow{\Delta} 2\dot{C}_6H_5CO \longrightarrow 2\dot{C}_6H_5 + CO_2 \qquad 2\dot{C}_6H_5 \equiv I^{\bullet}$$

$$H_2C=\underset{COOCH_3}{\overset{CH_3}{C}} + I^{\bullet} \longrightarrow H_2\overset{I}{C}-\underset{COOCH_3}{\overset{CH_3}{\dot{C}}}$$

Propagation



Termination



CONCLUSION

For the first time, the present paper aims to report the kinetics and mechanism of free radical copolymerization of limonene with methyl methacrylate. In the present system the penultimate unit is favored as the value of Φ is greater than unity. The copolymer, being unsaturated, is a functional polymer.

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