Free radical copolymerization of limonene with butyl methacrylate: Synthesis and characterization

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The radical copolymerization of monocyclic terpene namely limonene with butyl methacrylate in xylene at 80±0.1°C for 50 min, using benzoylperoxide (BPO) as an initiator has been carried out under the inert atmosphere of nitrogen. The system follows ideal kinetics i.e., \( R_p \alpha [BPO]^{0.5}[BMA]^{1.0}[Lim.]^{-1.0} \). The rate of polymerization \( (R_p) \) decreases as [limonene] increases, which might be due to penultimate unit effect. The overall energy of activation has been calculated as 34 kJ/mol. The formation of the copolymer is confirmed by the presence of bands at 1727 and 2956 cm–1 due to ester carbonyl of butyl methacrylate and olefinic C–H stretching of limonene, respectively. Further, the peaks at 3.8–4.2 and 5.0–5.6 \( \delta \), were observed in \(^1\)H NMR spectra due to methylene proton adjacent to ester linkage of butyl methacrylate and trisubstituted olefinic protons of limonene, respectively. The value of reactivity ratios \( r_1(BMA) = 0.125 \) and \( r_2(Lim.)= 0.026 \) has been calculated by using Kelen-Tüdos method. Alfrey-Price Q–e parameter for limonene has been calculated as 0.30 and –0.46. The glass transition temperature of the copolymer is determined as 35 °C.

Keywords: Limonene, butyl methacrylate, copolymers, reactivity ratios.

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The chemistry of natural products holds a prominent place as green chemistry in most advanced organic chemistry. Amongst the various classes of natural products, the terpenes have occupied a special position because of their biological and commercial applications. Yet their applications in the domain of polymer science is still scarce. Polymer chemists have examined isoprenes and few terpenes such as \( \alpha,\beta \)-pinene and limonene for the homo 3-6, and copolymerization 7-10. Recently, the terpene polymerization has been extended by the synthesis of new versatile optically active and functional polymers of cyclic/acyclic terpenes with vinyl monomers i.e. citronellol-co-styrene11, citronellol-co-vinyl acetate12, linalool-co-acrylamide13, gereniol-co-styrene14, linalool-co-acrylonitrile15, \( \alpha \)-terpeniol-co-methyl methacrylate16, \( \alpha \)-terpeniol-co-buty1 methacrylate17, limonene-co-acrylonitrile18, limonene-co-methyl methacrylate19 and limonene-co-styrene20.

Limonene, an optically active monocyclic terpene, is the constituent of citrus and orange fruits. The literature reveals that initially limonene was homopolymerized by Roberts and Day5 and Marvel et al.6 using Friedel-Crafts catalyst and Ziegler-Natta catalyst, respectively. Later, it was first time copolymerized by Doiuchi et al.21 with maleic anhydride using radical initiator. Recently, the copolymers of limonene with vinyl monomers i.e. AN18, MMA19 and styrene20 have been synthesized. Here, the synthesis and characterization of copolymer(s) of limonene with vinyl monomer i.e. butyl methacrylate in xylene initiated by benzoyl peroxide (BPO) at 80 ± 0.1°C for 50 min under nitrogen blanket has been undertaken and the results are presented in this communication.

Experimental Procedure
Butyl methacrylate (Lancaster) and solvents were purified by usual methods22. Limonene (Fluka) (b.p. = 176-177°C, d= 0.8411) was used after fractional distillation. Benzoyl peroxide (BPO) was recrystallized twice from chloroform and then dried in vacuo.

Polymerization method
The dilatometric technique (dilatometer cap.= 3 mL, cap. length = 9.5 cm, capillary diameter = 2 mm) has been used to follow the copolymerization runs in xylene for 50 min under oxygen free condition to limit the conversion up to 17.9% at 80±0.1°C. The

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copolymer(s), isolated with acidified methanol and dried in vacuo, were refluxed with acetonitrile to remove polybutyl methacrylate. No detectable weight loss was observed. Finally, the copolymer(s) were dried to constant weight. The rate of polymerization was calculated from the slope of graph between the percentage conversion and time (min) (Fig. 1).

FTIR and 1H-NMR spectral analyses were recorded with Perkin-Elmer 599 B (with KBr pellets) and Varian 100 HA JEOL 400 LA spectrophotometer using CDCl3 as a solvent and TMS as an internal reference, respectively. Differential scanning calorimetry (DSC) was carried out on Perkin-Elmer thermal analyser at a heating rate 10°C/min under the nitrogen atmosphere.

Results and Discussion

Limonene did not homopolymerize under the experimental conditions. The kinetics of the copolymerization has been studied by the variations in the BPO concentration (1.74×10⁻³ – 15.67×10⁻³ mol L⁻¹), keeping the monomer ratio [BMA/lim] constant at 2.06. The reaction proceeds with a short induction period of about 2-3 min (Fig. 1). The R_p is a direct function of the [initiator] and the exponent value, determined from a linear graph of log R_p versus log[BPO], 0.5 ± 0.01 (Fig. 2).

The effect of [BMA] on the R_p has also been studied by varying the BMA concentration (0.721 to 2.88 mol L⁻¹), while limonene and BPO concentration was kept constant at 0.840 and 8.71×10⁻³ mol L⁻¹ respectively. The R_p is directly proportional to the [BMA]. A plot of log R_p versus log [BMA] is linear, the slope of which gives order unity (Fig. 3).

The effect of [limonene] on the R_p has been studied by varying the concentration of limonene from 0.168 to 1.58 mol L⁻¹, keeping [BMA] and [BPO] constant at 1.73 and 8.71 × 10⁻³ mol L⁻¹, respectively. The R_p is inverse function of [limonene]. A plot of log R_p versus log [limonene] is linear and the order is unity (Fig. 4). It might be due to penultimate unit effect (PUE), which has been quantitatively discussed by Arlman²³,

\[
\begin{align*}
M' + M_1 & \rightarrow M_1M' \quad \text{(PR type 11)} \\
M_1 + M_2 & \rightarrow M_1M_2 \quad \text{(PR type 12)} \\
M_2 + M' & \rightarrow M_2M' \quad \text{(PR type 21)} \\
M_1 + M_2 & \rightarrow M_1M_2 \quad \text{(PR type 22)} \\
M_1 = & \text{BMA} \\
M_2 = & \text{Limonene}
\end{align*}
\]

Fig. 1—Relationship between the percentage conversion and polymerization time, [BPO] =1.74×10⁻³ mol L⁻¹, 5.22×10⁻³ mol L⁻¹, 8.71×10⁻³ mol L⁻¹, 12.19×10⁻³ mol L⁻¹, 15.67×10⁻³ mol L⁻¹, with constant [BMA]=1.73 mol L⁻¹, [Lim] 0.840 mol L⁻¹ copolymerization time = 50 min, copolymerization temperature = 80 ± 0.1°C.

Fig. 2—Relationship between the rate of polymerization and [BPO] with constant [BMA] = 1.73 mol L⁻¹, [Lim] = 0.840 mol L⁻¹, copolymerization time = 50 min, copolymerization temperature = 80 ± 0.1°C.
The overall rate of copolymerization is given by the sum of the four propagation rates,

\[
R_p = \frac{d[M_1]}{dt} + \frac{d[M_2]}{dt} = k_{11} [M_1]^2 [M_1] + k_{12} [M_1^2] [M_2] + k_{21} [M_2^2] [M_1] + k_{22} [M_2^2] [M_2]
\]

\[\ldots \text{(5)}\]

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

\[
k_{21} [M_2^2] [M_1] = k_{12} [M_1^2] [M_2]
\]

\[\ldots \text{(6)}\]

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

\[
R_i = 2k_{111} [M_1] + 2k_{112} [M_1^2] [M_2] + 2k_{122} [M_2^2]
\]

\[\ldots \text{(7)}\]

From Eqs (5), (6) and (7) the rate of polymerization is obtained.

\[
R_p = \frac{(r_1 [M_1]^2 + 2[M_1^2] + r_2 [M_2^2]) R_i^{1/2}}{[r_1^2 \delta_1^2 [M_1] + 2\phi r_1 \delta_1 [M_1^2] + r_2^2 \delta [M_2^2]^{1/2}}
\]

where,

\[
\delta_1 = \left( \frac{2k_{111}}{k_{11}} \right)^{1/2}
\]

\[
\delta_2 = \left( \frac{2k_{112}}{k_{12}} \right)^{1/2}
\]

\[
\phi = \frac{k_{122}}{2(k_{111} \times k_{122})^{1/2}}
\]

The value of \(\phi\) is 8.77, which is more than unity, indicating the penultimate unit effect (PUE) is favoured in the present system\textsuperscript{24,25}.

**Effect of temperature**

The polymerization runs were also carried out at 75 and 85°C to evaluate the activation energy using Arrhenius equation. The overall energy of activation is computed as 34 kJ mol\textsuperscript{-1} (Fig. 5).

**Characterization of copolymer(s)**

**FTIR Spectrum**

From Fig.6 the assignments are,

<table>
<thead>
<tr>
<th>Band width (cm\textsuperscript{-1})</th>
<th>Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>2875–2956</td>
<td>C–H stretching due to CH\textsubscript{2} and CH\textsubscript{3}</td>
</tr>
<tr>
<td>1727</td>
<td>(–OCH\textsubscript{2}–) group of butyl methacrylate ester carbonyl</td>
</tr>
<tr>
<td>1660</td>
<td>C=C stretching of tri-substituted olefinic group of limonene</td>
</tr>
<tr>
<td>1384–1463</td>
<td>C–H bending vibration due to CH\textsubscript{2} and CH\textsubscript{3}</td>
</tr>
</tbody>
</table>
The 1H NMR spectrum of pure limonene shows the following peaks,

- a – 1.64 δ (3H, CH₃)
- b – 1.72 δ (3H, CH₃)
- c – 1.92 δ (2H, CH₂)
- d – 4.66 δ (2H, CH₂)
- e – 5.35 δ (1H, CH)

The 1H NMR spectra of the copolymer (Fig. 7) show the singlet at 5.3-5.5 δ and triplet at 3.8-4.2 δ due to tri-substituted olefinic protons [>C=CH—CH₂—] of limonene and methylene proton adjacent to ester linkage group of butyl methacrylate, respectively.

Differential scanning calorimetry

The DSC curve of the copolymer shows the glass transition temperatures (Tᵣ) as 35°C (Fig. 8). The value is in agreement with those reported in literature for other terpene copolymers with vinyl monomers. The Tᵣ is the temperature at which the curve deviates from the base line. It is a measure of the initiation of the reaction.

Copolymer composition and value of reactivity ratios

The relative peak areas of (–OCH₂–) and [>C=CH—CH₂—] of butyl methacrylate and limonene at 3.8-4.2 and 5.3-5.5 δ, respectively in the copolymers have been used to calculate the copolymer composition (Table 1). The Kelen-Tüdos approach is used for evaluation of reactivity ratios r₁ and r₂ for the monomer pair as follows,
\[ \eta = \xi - \xi \alpha \]

where

\[ H = G(\alpha + H) \]

and

\[ \xi = \frac{H}{(\alpha + H)} \]

The transformed variables \( G \) and \( H \) are given by,

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

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

The parameter \( \alpha \) is calculated by taking the square root of the product of the lowest and highest value of \( H \) for copolymerization series. Graphical evaluation for BMA and limonene (least square method), yields values of \( r_1 = 0.125 \) and \( r_2 = 0.026 \), respectively (Fig. 9, Table 2).

**Mechanism**

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

(i) The copolymer(s), formed is an unsaturated polymer since it decolourises Baeyer's reagent.

(ii) The acid catalysed hydration of limonene proceeds on the vinyl bond, giving \( \alpha \)-terpeniol, though on dehydration it gives back limonene\(^{29}\).

(iii) It has been already reported that cationic polymerization of limonene involved the opening of bicyclic bridge structure to give a repeating unit through the terminal methylene group\(^{30}\).

**Table 1—Copolymer(s) composition**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Monomer feed [BMA/Lim]</th>
<th>Mole fraction of BMA in copolymer</th>
<th>Copolymer feed [BMA/Lim]</th>
<th>( \eta )</th>
<th>( \xi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.06</td>
<td>0.540</td>
<td>1.17</td>
<td>0.0408</td>
<td>0.495</td>
</tr>
<tr>
<td>7</td>
<td>1.50</td>
<td>0.526</td>
<td>1.109</td>
<td>0.0257</td>
<td>0.354</td>
</tr>
<tr>
<td>8</td>
<td>2.79</td>
<td>0.544</td>
<td>1.22</td>
<td>0.0499</td>
<td>0.633</td>
</tr>
<tr>
<td>11</td>
<td>2.91</td>
<td>0.550</td>
<td>1.25</td>
<td>0.0555</td>
<td>0.646</td>
</tr>
<tr>
<td>12</td>
<td>1.47</td>
<td>0.510</td>
<td>1.04</td>
<td>0.00978</td>
<td>0.359</td>
</tr>
</tbody>
</table>

**Table 2—Reactivity parameters**

<table>
<thead>
<tr>
<th>( r_1 )</th>
<th>( r_2 )</th>
<th>( r_1r_2 )</th>
<th>( Q_2 )</th>
<th>( e_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>0.026</td>
<td>0.00325</td>
<td>0.302</td>
<td>-0.46</td>
</tr>
</tbody>
</table>

\[ Q_1 = 0.78 \]
\[ e_1 = 0.51 \]

\[ \eta = r_1^* - \frac{r_1^*}{\alpha}(1-\xi) \]

Fig. 9—Kelen-Tüdos plot for the determination of reactivity ratios.

Limonene

\( \alpha \)-terpeniol
Based on the above facts, it is clear that the double bond (π bond) between C–8 and C–10 is more susceptible to take part in polymerization.

Conclusion
The copolymer of limonene with BMA has been synthesized via free radical route. The penultimate unit effect is favoured in the present system as the rate of polymerization decreases as [limonene] increases and the value of φ is more than unity.

Acknowledgement
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References
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