Photoinitiated copolymerization of citronellol and methylmethacrylate

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Received 2 November 2001; revised received 16 December 2002; accepted 28 December 2002

Free radical copolymerization of citronellol and methyl-methacrylate (MMA) in xylene at 30±0.2°C using benzyloperoxide (BPO) as the photoinitiator for 21 h has been carried out. The system follows non-ideal kinetics ($R_n = 0.62[BPO]^{0.62}[citronellol]^{0.87}[MMA]^{1.00}$) due to both primary radical termination and degradative chain transfer reaction. Analysis of the copolymer by IR and NMR shows the presence of alcoholic and acrylate group in the copolymer. The glass transition temperature of copolymer, calculated by differential scanning calorimetry (DSC) is 80°C. The nearly alternating nature of the copolymer is confirmed by the product of reactivity ratios $r_1 (MMA)=0.062$ and $r_2 (citronellol)=0.005$, calculated by Kelen-Tudos method. The Alfrey-Price, Q-e parameters for citronellol have been calculated as -1.09 and 1.47. The mechanism has also been explained.

Photopolymerization includes the utilization of electromagnetic radiation as the energy source for polymerization of functional monomer, which is the basis of important commercial process with broad applicability including photoimaging, UV curing of coatings and inks.

Availability of wide range of photoinitiators as well as monomers has increased devotion in the field of free radical photopolymerization. However, the application of photopolymerization of terpenoid class, the derivative of isoprene, is still scarce. In 1983, Tang et al. have carried out the photochemical polymerization of isoprene with the use of $H_2O_2$ as the photoinitiator.

Citronellol is susceptible to polymerization as it contains one double bond and one alcoholic group. Therefore, citronellol is selected to be photocopolymerised with methylmethacrylate as new novel functional monomer. The present paper highlights the synthesis, mechanism, kinetics and characterization of functional and optical active copolymers of citronellol and methylmethacrylate (MMA) in xylene at 30±0.2°C using benzyloperoxide as photoinitiator.

Experimental Procedure

Materials

Reagents grade methylmethacrylate (Merck-Schuchardt) and other solvents were purified by usual methods and distilled under vacuum before use.

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Polymers were precipitated twice from methanol followed by drying under vacuum.

Polymerization

Co-monomers were purified and charged to a quartz ampoule in xylene and photoinitiator (BPO) for 21 h at 30±0.2°C. This was covered with a blanket of nitrogen and irradiated using a Philips (125 W) high pressure mercury lamp (path length 10 cm, 440 nm interference filter) with a light intensity of $2.53\times10^4$ Lux. The polymer formed was precipitated with acidified methanol and then dried to a constant weight. It was then treated with acetonitrile to remove polymethyl methacrylate (PMMA). No detectable weight loss was observed. Finally the copolymer was dried to constant weight and percent conversion was calculated. The rate of polymerization ($R_p$) was calculated from the slope of the percentage versus time plots. The polymer was characterised by IR, NMR and DSC techniques. The monomer reactivity ratios were determined by Kelen-Tudos method.

Infrared spectrum

The infrared spectrum was recorded on a Perkin-Elmer Spectrophotometer (Model 599 B) using KBr pellets.

Nuclear magnetic resonance spectrum

The NMR spectrum was obtained from varian 100 HA Jeol 400 LA spectrophotometer.
Differential scanning calorimetry (DSC)

DSC was carried out on DuPont V4.1C Model 2000 at the heating rate of 10°C/min under nitrogen atmosphere.

Results and Discussion

It is well-established that few monomers like 1, 2-disubstituted olefins\(^1\), do not undergo homopolymerization due to steric hindrance\(^2\) and low stabilization energy. Citronellol too does not homopolymerise under experimental condition. No copolymer was obtained when monomer was alone exposed to light or when was left in dark with BPO. However, copolymerization of citronellol with MMA, proceeds with an induction period of about 8-9 h, as illustrated in Fig. 1.

The effect of [BPO] on the rate of copolymerization \(R_p\) has been studied by varying the concentration of BPO from 3.4\(\times\)10\(^{-3}\) to 20.6\(\times\)10\(^{-3}\) mol L\(^{-1}\) at a fixed intensity of light (Table 1). The \(R_p\) increases with increasing concentration of BPO. The initiator exponent, calculated from the slope of the plot of log \(R_p\) versus log [BPO] is 0.62. This value is greater than as expected for ideal radical kinetics.

The \(R_p\) also increases with increasing [citronellol] from 0.42 to 1.72 mol L\(^{-1}\) keeping [MMA] and [BPO] constant at 1.5 mol L\(^{-1}\) and 13.77\(\times\)10\(^{-3}\) mol L\(^{-1}\) respectively (Table 2). The monomer exponent value, calculated from the slope of the linear plot of log \(R_p\) versus log [citronellol] is 0.87.

The value of \(R_p\) also increases with increasing [MMA] from 0.75 to 3.0 mol L\(^{-1}\), keeping [citronellol] and [BPO] constant at 1.28 mol L\(^{-1}\) and 13.77\(\times\)10\(^{-3}\) mol L\(^{-1}\) respectively (Table 2). The monomer exponent value, calculated from the slope of the linear plot of log \(R_p\) versus log [MMA] is 0.90.

The deviated values of initiator and monomer exponents suggest that the system follows non-ideal kinetics, which can be explained on the basis of primary radical termination.

Table 1—Effect of initiator concentration on the rate of photnocopolymerization of citronellol and MMA

<table>
<thead>
<tr>
<th>Sample</th>
<th>[BPO](\times)10(^{-3}) mol L(^{-1})</th>
<th>Conversion (%)</th>
<th>(R_p)(\times)10(^6) mol L(^{-1})s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.4</td>
<td>4.8</td>
<td>2.61</td>
</tr>
<tr>
<td>2</td>
<td>6.8</td>
<td>5.2</td>
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<tr>
<td>3</td>
<td>10.3</td>
<td>6.6</td>
<td>3.26</td>
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<tr>
<td>4</td>
<td>13.7</td>
<td>7.0</td>
<td>4.30</td>
</tr>
<tr>
<td>5</td>
<td>17.2</td>
<td>7.9</td>
<td>4.89</td>
</tr>
<tr>
<td>6</td>
<td>20.6</td>
<td>8.6</td>
<td>5.74</td>
</tr>
</tbody>
</table>

Table 2—Effect of concentration of comonomer on the rate of photocopolymerization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Citronellol] (mol L(^{-1}))</th>
<th>[MMA] (mol L(^{-1}))</th>
<th>Conversion (%)</th>
<th>(R_p)(\times)10(^6) mol L(^{-1})s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.42</td>
<td>1.5</td>
<td>5.7</td>
<td>3.54</td>
</tr>
<tr>
<td>8</td>
<td>0.854</td>
<td>1.5</td>
<td>7.0</td>
<td>4.30</td>
</tr>
<tr>
<td>9</td>
<td>1.28</td>
<td>1.5</td>
<td>8.1</td>
<td>5.0</td>
</tr>
<tr>
<td>10</td>
<td>1.70</td>
<td>1.5</td>
<td>8.4</td>
<td>5.24</td>
</tr>
<tr>
<td>11</td>
<td>0.854</td>
<td>0.75</td>
<td>4.9</td>
<td>3.0</td>
</tr>
<tr>
<td>12</td>
<td>0.854</td>
<td>1.5</td>
<td>7.0</td>
<td>4.30</td>
</tr>
<tr>
<td>13</td>
<td>0.854</td>
<td>2.25</td>
<td>8.3</td>
<td>5.0</td>
</tr>
<tr>
<td>14</td>
<td>0.854</td>
<td>3.0</td>
<td>10.1</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Fig. 1—Time conversion plot for the photocopolymerization of citronellol and MMA. [Citronellol]=0.854 mol L\(^{-1}\); [MMA]=1.5 mol L\(^{-1}\); copolymerization time=21 h; copolymerization temperature=30±0.2°C; [BPO]: 3.4\(\times\)10\(^{-3}\) mol L\(^{-1}\); 6.8\(\times\)10\(^{-3}\) mol L\(^{-1}\); 10.3\(\times\)10\(^{-3}\) mol L\(^{-1}\); 13.77\(\times\)10\(^{-3}\) mol L\(^{-1}\); 17.2\(\times\)10\(^{-3}\) mol L\(^{-1}\); 20.6\(\times\)10\(^{-3}\) mol L\(^{-1}\)
To analyse the effect of primary radical termination, the following expression given by Deb and Meyerhoff\textsuperscript{12,13} have been used.

\[
\log \frac{R_p^2}{[I][M]^2} = \log \frac{2f_i k_d k_p^2}{k_i k_p} - 0.8684 \frac{R_p}{k_i k_p [M]^2}
\]

where \( f_i \) 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 and \( k_p \) is the primary radical termination constant. \([M]\) is the monomer concentration.

In present study a plot of the left hand side of the above equation versus \( R_p/[M]^2 \) gave a negative slope (Fig. 2) indicating significant primary radical termination.

The IR spectrum of copolymer(s) (Fig. 3) consists of following groups of bands (i) The range of C—H stretching vibrations of methyl and methylene group at 2953.82 and 2929.72 cm\(^{-1}\), respectively; (ii) The >C=O stretching range shows ester carbonyl band at 1731.77 cm\(^{-1}\) for MMA; (iii) The C—H deformation range shows bands in the region of 1383.90 to 1451.44 cm\(^{-1}\); (iv) The ester stretching band (C—O—C) appears in the region of 1149.57 to 1273.83 cm\(^{-1}\); (v) The alcoholic group of citronellol shows bands at 3414.27 cm\(^{-1}\).

The chemical shifts of protons, attached to elements other than carbon like —OH, —NH and —SH, are generally very sensitive to concentration which affects intermolecular hydrogen bonding. In case where small association is not hindered, the hydroxy protons generally resonate in the region of 3 \( \delta \) to 5.5 \( \delta \) ppm eq. The signals of —OH group of methanol and ethanol appear at 3.3 and 5.4 \( \delta \) respectively in the NMR spectra\textsuperscript{14}. However, with large molecules, the hydroxyl protons often resonate near \( \delta = 8 \) ppm even at relatively “high” concentrations, partially because the molar concentration is low and partially due to steric effect.

Therefore, the peaks of —OH group have been assigned in the range of 7 to 7.7 \( \delta \) as appeared in the NMR spectra of citronellol as well as copolymer of citronellol and MMA.
The NMR spectrum of pure citronellol (I) and those of copolymers (II) (Fig. 4) shows the peaks of (1H, OH) at 7-7.7 in triplet; (3H, CH3) at 0.9 δ in triplet; (2H, CH2) at 1.2-2.2 δ in triplet and extra peak at 3.4-4.0 δ in singlet appears in copolymer. The comparison of NMR of monomer (citronellol) and that of copolymer confirms the formation of copolymer.

The DSC curve (Fig. 5) indicates the glass transition temperature (Tg) of citronellol-co-MMA as 80°C.

**Copolymer composition and values of reactivity ratios**

Determination of copolymer microstructure from a high resolution NMR study has become a matter of increasing concern in these days. However, an attempt for a quantitative estimate of microstructure from these peaks has been made satisfactorily. The relative peak area of resonance peaks at 7-7.7 δ due to hydroxyl proton of citronellol and at 3.4-4 δ due to methoxy protons of MMA unit are used to calculate the mole fraction of monomers as well as copolymer composition.

The monomer reactivity ratios of citronellol and MMA have been estimated by Kelen-Tiadas method (Table 3). The values of \( r_1 \) (MMA) and \( r_2 \) (citronellol), calculated from Kelen-Tiados plot of \( \eta \) vs \( \xi \) (Fig. 6) are 0.062 and 0.005 respectively. The product of \( r_1 r_2 \) is nearly zero which is a sign of alternating copolymerization.

The \( e_2 \) and \( Q_2 \) values for citronellol were calculated using \( e_1 = 0.40 \) and \( Q_r = 0.74 \) for MMA by following equation:\ref{eq:reactivity}

\[
e_2 = e_1 \pm \log r_1 r_2^{0.5} \\
Q_2 = Q_1/d_1 \exp [-e_1(e_1-e_2)]
\]
Mechanism

It has been reported\(^1\), that >C=C< is more susceptible than alcoholic O—H bond and, therefore, \(\pi\) bond takes part in polymerization. Therefore, the following reaction mechanism is suggested:

Initiation

\[
\begin{align*}
\text{Initiation} & \\
\text{Propagati on} & \\
\text{Termination} &
\end{align*}
\]

Conclusion

From the above discussions, it is concluded that citronellol can be successfully photocopolymerized with MMA, resulting in the formation of an alternating and functional copolymer. The rate equation of photocopolymerization in the citronellol-alt-MMA system can be simply expressed by:

\[ R_p \propto [\text{BPO}]^{0.02}[\text{citronellol}]^{0.87}[\text{MMA}]^{0.68} \]

Acknowledgements

Authors are thankful to the Director, Harcourt Butler Technological Institute, Kanpur for providing necessary facilities. One of the authors thank DST, New Delhi for the sanction of the research project “synthesis and characterization of copolymers of terpenes with vinyl monomers”.

References