

# Synthesis and Characterization of Polylimonene: Polymer of an Optically Active Terpene

Anamika Singh, Meet Kamal

Department of Chemistry, Christ Church P. G. College, Kanpur, India

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**ABSTRACT:** Radical polymerization of limonene (limonene) using benzoyl peroxide (BPO) as an initiator at  $85^{\circ}\text{C} \pm 1^{\circ}\text{C}$  under an inert atmosphere of nitrogen in xylene as solvent was carried out. The system follows nonideal kinetics:  $R_p \propto [I]^{0.3} [M]^{1.4}$ , due to both primary radical termination and degradative chain transfer reaction. The activation energy of the polymerization was estimated to be  $22.97 \text{ kJ mol}^{-1}$ .  $^1\text{H-NMR}$  spectrum of polymer shows the presence of a triplet between 2 and 2.5  $\delta$ , which reveals that  $\beta$ -carbon

of limonene is the active site in the polymerization of limonene. The FTIR spectrum of the polymer shows band at  $1645 \text{ cm}^{-1}$  due to gem disubstituted  $\text{C}=\text{C}$  stretching vibrations. The glass transition temperature ( $T_g$ ) of the polylimonene of the polylimonene is  $116^{\circ}\text{C}$ . © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1456–1459, 2012

**Key words:** limonene; radical polymerization; kinetics; mechanism

## INTRODUCTION

The enhanced interest displayed in recent years in chemistry of natural products made it desirable to study non benzenoid hydrocarbons termed as terpenes. They are generally regarded as derivatives of isoprene having general formula  $\text{C}_5\text{H}_8$ . Terpenes possess a wide scientific and technical interest. Although much has been published regarding the reactions of terpenes in synthetic organic chemistry,<sup>1</sup> yet their potential applications as a monomer in the domain of polymer science are still scarce. Yunxiang et al.<sup>2</sup> copolymerized  $\alpha$ -pinene with  $\infty$ -methyl styrene (Sty) in the presence of  $\text{AlCl}_3/\text{SbCl}_3$  as an initiator. They also copolymerized  $\infty$ -pinene with Sty cationically using same complex catalyst in which  $\text{SbCl}_3$  played an important role to reduce the difference in monomer reactivities and suppress the formation of homopolymers. Starkova et al.<sup>3</sup> copolymerized terpenes with methacrylic acid in the presence of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ . The preparation of polyterpenes by continuous polymerization of terpene hydrocarbons at  $80$ – $170^{\circ}\text{C}$  in the presence of acid catalyst was improved by Popov et al.<sup>4</sup> Several copolymers and terpolymers of vinyl monomers with terpenes were prepared in the presence of free radical initiator like azobisisobutyronitrile (AIBN)/benzoyl peroxide (BPO) such as [limonene-co-Sty]/AIBN/

$80^{\circ}\text{C}$ ,<sup>5</sup> [limonene-co-BMA]/BPO/ $80^{\circ}\text{C}$ ,<sup>6</sup> [limonene-co-MMA]/BPO/ $80^{\circ}\text{C}$ ,<sup>7</sup> and [limonene-Sty-MMA]/BPO/ $80^{\circ}\text{C}$ <sup>8</sup> by Srivastava et al.<sup>9–12</sup> Thus, a search of literature reveals that approach of polymer chemist to examine terpenes has been limited to mostly bicyclic monoterpenes like  $\alpha$ -pinene and  $\beta$ -pinene<sup>13–16</sup> and their copolymerization with vinyl monomers. In the present investigation, it is of great interest to investigate the limonene (limonene) having general formula  $\text{C}_{10}\text{H}_{16}$ , as new novel monomer as it exhibits monomeric activity due to the presence of  $\pi$  bonds and will have wide application in the synthesis of functional polymer in the near future. The present communication, therefore, highlights kinetics and mechanism of homopolymerization of optically active limonene.

## EXPERIMENTAL

### Materials

Solvents (Merck) and limonene (Merck) were used as such as received. BPO (M.P. =  $103^{\circ}\text{C}$ ) was recrystallized twice in chloroform.

### Polymerization technique

The solution polymerization of limonene in xylene, using BPO as an initiator at  $85^{\circ}\text{C} \pm 1^{\circ}\text{C}$  was carried out for 4 h under an inert atmosphere of nitrogen in polymerization tubes. Polymers formed at low conversion were precipitated with excess of methanol and then dried to constant weight. The rate of polymerization ( $R_p$ ) was calculated from the slope of

Correspondence to: M. Kamal (meetk\_dwi@yahoo.co.in).

**TABLE I**  
Effect of [BPO] on Polymerization

| S. No. | [BPO] × 10 <sup>-2</sup><br>(mol/L) | Conversion<br>(%) | R <sub>p</sub> × 10 <sup>6</sup><br>(mol/L s) |
|--------|-------------------------------------|-------------------|---|
| 1      | 0.83                                | 2.3               | 0.69  |
| 2      | 1.37                                | 6.8               | 0.92  |
| 3      | 2.06                                | 7.7               | 1.86  |
| 4      | 2.75                                | 11.5              | 2.02  |

[Limonene] = 1.96 mol/L, temperature = 85°C ± 1°C, and time = 4 h.

percentage conversion versus time plots. The polymer was characterized by using FTIR, <sup>1</sup>H-NMR, DSC, and GPC techniques.

Fourier transform infrared spectrum

The FTIR spectrum was recorded on a Perkin Elmer spectrophotometer (Model 377) using KBr pellets.

Nuclear magnetic resonance

The <sup>1</sup>H-NMR spectrum was recorded by Varian 100HA spectrometer using CDCl<sub>3</sub> as a solvent and TMS as an internal standard.

Differential scanning calorimeter

Measurements of glass transition temperature (*T<sub>g</sub>*) were carried out with a differential scanning calorimeter (General V 2.2 Dupont Model 9900). DSC curves were recorded under nitrogenous atmosphere at a flow rate of 10°C/min. The sample weight was 4.5 ± 0.1 mg.

Gel permeation chromatography

The gel permeation chromatographic (GPC) study was done with E. Merck RI-L-7490. The elution solvent was THF at 25°C.

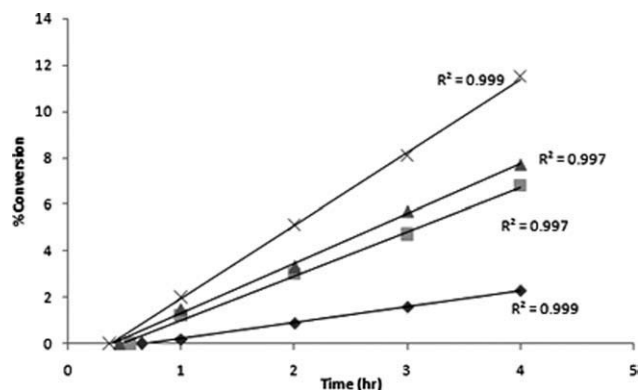
## RESULTS AND DISCUSSION

The polymerization of limonene proceeds with an induction period of about 30 min.

**TABLE II**  
Effect of [Limonene] on Polymerization

| S. No. | Limonene<br>(mol/L) | Conversion<br>(%) | R <sub>p</sub> × 10 <sup>6</sup><br>(mol/L s) |
|--------|---------------------|-------------------|---|
| 5      | 0.98                | 5.5               | 0.34  |
| 2      | 1.96                | 6.8               | 0.92  |
| 6      | 2.96                | 7.0               | 1.00  |
| 7      | 3.96                | 9.8               | 1.23  |

[BPO] = 1.37 × 10<sup>-2</sup> mol/L, temperature = 85°C ± 1°C, and time = 4 h.



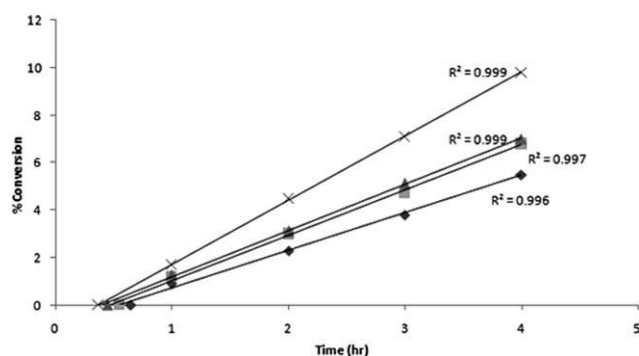
**Figure 1** Time conversion plot for polymerization of limonene by varying the initiator concentration.

The effect of [BPO] on the rate of polymerization (*R<sub>p</sub>*) was studied by varying the concentration of BPO from 0.826 to 2.75 mol L<sup>-1</sup> (Table I) Figure 1. The data reveals that the *R<sub>p</sub>* increases with the increase in the concentration of BPO. The initiator exponent, calculated from the slope of log *R<sub>p</sub>* versus log BPO, is 0.3. The value is less than as expected for ideal radical kinetics. The *R<sub>p</sub>* also increases with increasing concentration of limonene from 0.98 to 3.96 mol L<sup>-1</sup> (Table II) Figure 2, and the monomer exponent, calculated from the slope of log *R<sub>p</sub>* versus log [limonene], is 1.4.

The low value of initiator exponent and higher value of monomer exponent suggest that the system follows nonideal kinetics. The kinetic nonideality can be explained by analyzing the role of BPO as primary radical terminator and degradative chain transfer agent. To analyze the effect of primary radical termination, a suitable expression, given by Deb and Meyerhoff<sup>17</sup> in the following form, was used.

$$\log \frac{R_p^2}{[I][M]^2} = \log \frac{2f_k k_d k_p^2}{k_t} - 0.8684 \frac{k_{prt}}{k_i k_p} \frac{R_p}{[M]} \quad (1)$$

where *f<sub>k</sub>* is the fraction of free radicals to initiate chain growth, *k<sub>d</sub>* the initiator decomposition rate



**Figure 2** Time conversion plot for polymerization of limonene by varying the monomer concentration.

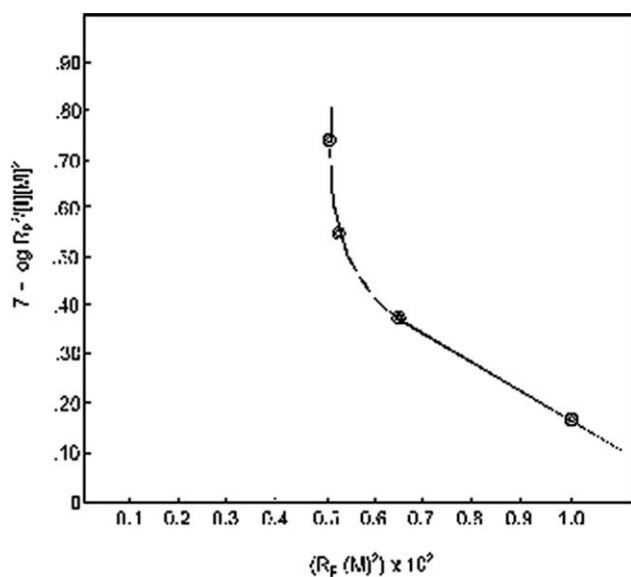


Figure 3 Plot of  $7 + \log R_p^2/[I][M]^2$  versus  $R_p/[M]^2 \times 10^2$ .

constant,  $k_p$  the propagation rate constant, and  $k_{prt}$  the primary radical termination constant.

A plot of the left hand side of the above equation versus  $R_p/[M]^2$  gave a negative slope (Fig. 3), indicating significant primary radical termination in the present system.

The following equation derived by Deb<sup>18</sup> and simplified by Ghosh and Mitra was used to examine the degradative chain transfer as follows:

$$\log \frac{R_p^2}{[I][M]^2} = \log \frac{2f_k k_d k_p^2}{k_t} - 0.434 \frac{k_p^2 k_{rti}}{k_t k_{ij} k_p} C_I \frac{[I]}{[M]} \quad (2)$$

where  $C_I$  is the initiator transfer constant,  $K_{rti}$  the rate constant for degradative chain transfer to initiator, and  $K_{il}$  the initiator rate constant.

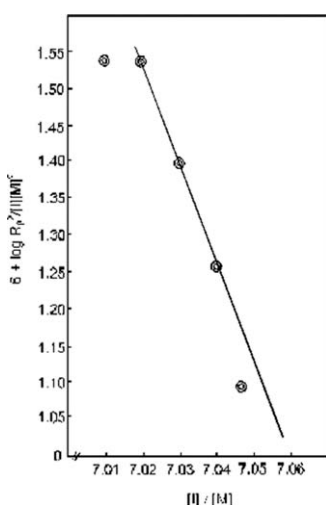


Figure 4 Plot of  $6 + \log R_p^2/[I][M]^2$  versus  $[I]/[M]$ .

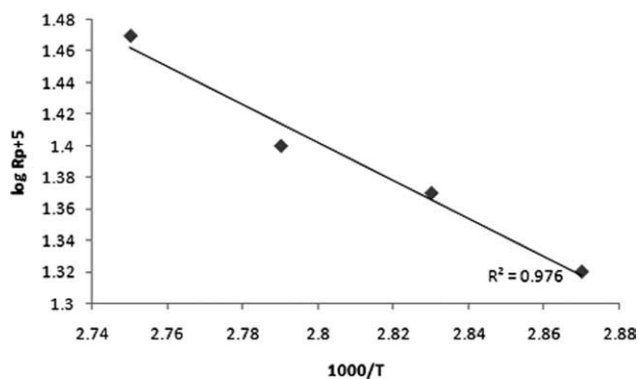


Figure 5 Plot of  $\log R_p$  versus  $1/T$ .

A plot of the left hand side of the above equation versus  $[I]/[M]$  gave a linear negative slope (Fig. 4) suggesting measurable degradative chain transfer reaction due to BPO. Thus, the nonideality, in the present system, appears to be due to both factors, which are primary radical termination and degradative chain transfer reaction.

#### Effect of temperature

The polymerization reactions were also carried out at different temperatures for 4 h at 75–90°C at fixed concentrations of BPO and limonene. The rate of polymerization increases with an increase in the temperature. The energy of activation is calculated as  $22.97 \text{ kJ mol}^{-1}$  by the linear plot of  $\log R_p$  versus  $1/T$  (Fig. 5).

#### Characterization

The FTIR spectrum (Fig. 6) of polylimonene shows band at  $1645 \text{ cm}^{-1}$  due to gem disubstituted  $\text{C}=\text{C}$  stretching vibrations. Absorptions of limonene at  $889 \text{ cm}^{-1}$  are caused due to  $\text{C}-\text{H}$  bending vibration of gem disubstituted olefinic group. The band at  $2922$

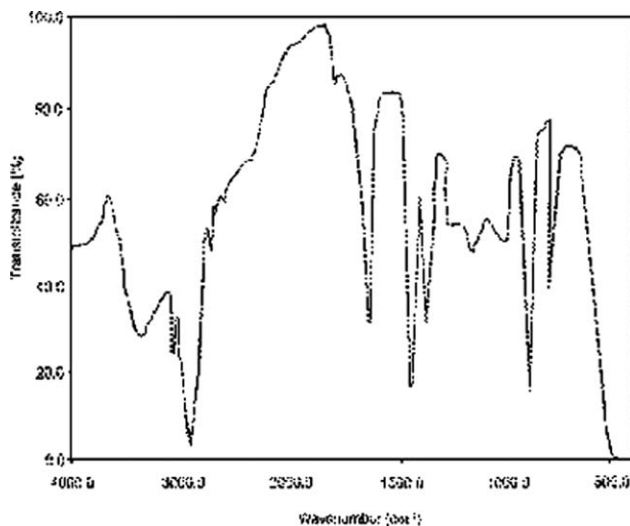


Figure 6 FTIR spectrum of polylimonene.

