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

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ABSTRACT: Radical polymerization of limonene (limonene) using benzoyl peroxide (BPO) as an initiator at 85°C \pm 1°C under an inert atmosphere of nitrogen in xylene as solvent was carried out. The system follows nonideal kinetics: $R_p \alpha$ [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 kJ mol⁻¹. ¹H-NMR spectrum of polymer shows the presence of a triplet between 2 and 2.5 δ , which reveals that β -carbon

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 C5H8. Terpenes possess a wide scientific and technical interest. Although much has been published regarding the reactions of terpenes in synthetic organic chemistry,¹ yet their potential applications as a monomer in the domain of polymer science are still scarce. Yunxiang et al.² copolymerized α-pinene with ∞ -methyl styrene (Sty) in the presence of AlCl₃/SbCl₃ as an initiator. They also copolymerized ∞ -pinene with Sty cationically using same complex catalyst in which SbCl₃ played an important role to reduce the difference in monomer reactivities and suppress the formation of homopolymers. Starkova et al.³ copolymerized terpenes with methacrylic acid in the presence of H_2SO_4 and H_2O . The preparation of polyterpenes by continuous polymerization of terpene hydrocarbons at 80-170°C in the presence of acid catalyst was improved by Popov et al.⁴ 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/

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

Key words: limonene; radical polymerization; kinetics; mechanism

80°C,⁵ [limonene-*co*-BMA]/BPO/80°C,⁶ [limonene*co*-MMA]/BPO/80°C,⁷ and [limonene-Sty-MMA]/ BPO/80°C⁸ by Srivastava et al.^{9–12} Thus, a search of literature reveals that approach of polymer chemist to examine terpenes has been limited to mostly bicyclic monoterpenes like α-pinene and β-pinene^{13–16} and their copolymerization with vinyl monomers. In the present investigation, it is of great interest to investigate the limonene (limonene) having general formula $C_{10}H_{16}$, as new novel monomer as it exhibits monomeric activity due to the presence of π 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° C) was recrystallized twice in chloroform.

Polymerization technique

The solution polymerization of limonene in xylene, using BPO as an initiator at 85°C \pm 1°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

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TABLE I Effect of [BPO] on Polymerization				
S. No.	[BPO] × 10 ⁻² (mol/L)	Conversion (%)	$\frac{R_p \times 10^6}{(\text{mol/L s})}$	
1 2 3 4	0.83 1.37 2.06 2.75	2.3 6.8 7.7 11.5	0.69 0.92 1.86 2.02	

[Limonene] = 1.96 mol/L, temperature = $85^{\circ}C \pm 1^{\circ}C$, and time = 4 h.

percentage conversion versus time plots. The polymer was characterized by using FTIR, ¹H-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 ¹H-NMR spectrum was recorded by Varian 100HA spectrometer using CDCl₃ as a solvent and TMS as an internal standard.

Differential scanning calorimeter

Measurements of glass transition temperature (T_g) 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 (mol/L)	Conversion (%)	$\frac{R_p \times 10^6}{(\text{mol/L s})}$	
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^{-2} mol/L, temperature = $85^{\circ}C \pm 1^{\circ}C$, 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_p) was studied by varying the concentration of BPO from 0.826 to 2.75 mol L⁻¹ (Table I) Figure 1. The data reveals that the R_p increases with the increase in the concentration of BPO. The initiator exponent, calculated from the slope of log R_p versus log BPO, is 0.3. The value is less than as expected for ideal radical kinetics. The R_p also increases with increasing concentration of limonene from 0.98 to 3.96 mol L⁻¹ (Table II) Figure 2, and the monomer exponent, calculated from the slope of log R_p 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 Meyerhoff¹⁷ in the following form, was used.

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

where f_k is the fraction of free radicals to initiate chain growth, k_d the initiator decomposition rate



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

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

0.5 0.6 0.7

(R_c (M)²) x 10²

0.8 0.9 1.0

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 Deb¹⁸ and simplified by Ghosh and Mitra was used to examine the degradative chain transfer as follows:

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

where C_I is the initiator transfer constant, K_{rtI} the rate constant for degradative chain transfer to initiator, and K_{iI} the initiator rate constant.

1.55

1.50 1.45

1.40

1.25 1.20 1.15

> 1.10 1.05

> > 0

WIIII/₂¹ 1.35 1.30 1.25



7.01 7.02 7.03 7.04 7.05 7.06

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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 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 cm⁻¹ due to gem disubstituted C=C stretching vibrations. Absorptions of limonene at 889 cm⁻¹ are caused due to C-H bending vibration of gem disubstituted olefenic group. The band at 2922



Figure 6 FTIR spectrum of polylimonene.

.90

.80

.70

.60

.40

.30

.20

.10

0

0.1

0.2 0.3 0.4

7 - 00 R₆4(II)[HI]²



Figure 7 ¹H-NMR spectrum of polylimonene.

cm⁻¹ is due to —CH bending of —CH₂ group. The presence of triplet at 2.25 δ that reveals in the ¹H-NMR spectrum (Fig. 7) reveals that the β -carbon atom is the active site for polymerization and the α -carbon remains ineffective. The glass transition temperature (T_g) recorded from the DSC curve is 116°C (Fig. 8). The weight–average molecular weight of polylimonene is 42,728, and viscosity average molecular weight is 137,961, as obtained by the GPC analysis.

Mechanism

The polymer decolorizes bromine water and alkaline $KMnO_4$ that shows that one of the two double bond is retained, and it does not take part in the polymerization. Based on the above data, following mechanism is proposed (Scheme 1).

CONCLUSION

On the basis of above evidences, it is concluded that polylimonene is synthesized via free radical polymerization of limonene (an optically active terpene) using BPO as an initiator. The system follows noni-



Figure 8 DSC curve of polylimonene.

Initiation



Termination



Scheme 1 Mechanism of synthesis of polylimonene.

deal kinetics due to primary radical termination as well as degradative chain transfer reaction.

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