Synthesis and Characterization of a Terpolymer of Limonene, Styrene, and Methyl Methacrylate via a Free-Radical Route

Saroj Sharma, A. K. Srivastava

H. B. Technological Institute, Kanpur 200 002, India

ABSTRACT: The free-radical terpolymerization of a monocyclic terpene, namely, limonene (Lim), with styrene (Sty) and methyl methacrylate (MMA) in xylene at $80 \pm 0.1°C$ for 2 h, with benzoyl peroxide (BPO) as an initiator under an inert atmosphere of nitrogen was extensively studied. The kinetic expression was $R_p \alpha [BPO]^{0.5}[Sty]^{1.0}[MMA]^{1.0}[Lim]^{-1.0}$, where R_p is the rate of polymerization. The overall energy of activation was calculated as 26 kJ/mol. R_p decreased as [Lim] increased. This was due to a penultimate unit effect. The Fourier transform infrared spectra of the terpolymer showed bands at 3025–3082, 1728, and 2851–2984 cm^{-1} due to C—H stretching of phenyl (—C_6H_5) protons of Sty, —OCH_3 of MMA, and trisubstituted olefinic protons of Lim, respectively. The ^1H-NMR spectra showed peaks at 7.3–8.1, 3.9–4.4, and 5.0–5.5 δ due to the phenyl, methoxy, and trisubstituted olefinic protons of Sty, MMA and Lim, respectively. The values of the reactivity ratios r_1 (MMA; 0.33) and r_2 (Sty + Lim; 0.06) were calculated with the Kelen–Tudos method. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2343–2347, 2004

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INTRODUCTION

The terpolymerization technique provides a convenient method for the synthesis of new polymeric materials with a wide range of properties; therefore, it has continued to evoke the interest of both academics and industrialists. The problem of terpolymerization is readily approached through the application of a concept and techniques already developed for a two-component system. Multicomponent polymerization, especially terpolymerization, allows for the development of information for a certain class of monomer not otherwise available. Although voluminous literature is available for homopolymerization and copolymerization, very little kinetic information is available for terpolymerization. This is due to a wide variation in monomer reactivity with radicals and difficulties in the simultaneous polymerization of three monomers together.

A search of literature revealed that most of the work has been devoted to the terpolymerization of three vinyl monomers, such as poly(ethylene glycol) ethylether methacrylate-*co*-methacrylic acid-*co*-sodium styrene sulfonate,[1] methyl methacrylate (MMA)-*co*-acrylonitrile-*co*-4-vinylpyridine and styrene (Sty),[2] maleic anhydride–(*n*-butyl methacrylate)–Sty–acrylonitrile,[3] acrylamide–acrylic acid–acrylonitrile,[4] Sty–vinylpyrrolidone–acrylonitrile,[5] Sty–acrylonitrile–copperacrylate,[6] and Sty–acrylonitrile–chromium acrylate.[7] However, reports regarding the synthesis of terpolymers containing a terpene as one of the monomers are scarce, except for a few recent contributions from our laboratory, such as for the syntheses of citronellol–Sty–MMA/benzoyl peroxide (BPO)/80°C[8] and linalool–Sty–MMA/BPO/80°C.[9] The probable reason is that the terpenes generally do not undergo homopolymerization due to steric hindrance, low stabilization energy between monomers, and free radicals in the transition state. Therefore, we extended our studies to synthesize a functional terpolymer of limonene (Lim), Sty, and MMA.

Lim, an optically active monocyclic terpene was long ago homopolymerized by Roberts and Day[10] and Marvel et al.[11] with Friedel–Crafts and Ziegler–Natta catalysts, respectively. Later, Lim was copolymerized with maleic anhydride by Doiuchi et al.[12] Recently, it was copolymerized with acrylonitrile[13] and MMA,[14] but it has never been used as a monomer in a ternary system. Therefore, this article for the first time highlights the synthesis and characterization of a terpolymer of Lim with Sty and MMA in xylene with BPO as a radical initiator at $80 \pm 0.1°C$ for 2 h.
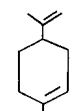
Limonene

Sample	$[BPO] \times 10^3$ (mol/L)	Conversion (%)	$R_p \times 10^6$ (mol/L s)	$[\eta]$ (dL/g)[a]
1	5.16	7.53	4.20	0.17
2	10.33	9.7	5.39	0.11
3	15.49	11.01	6.51	0.09
4	20.66	14.03	7.65	0.065
5	25.82	16.29	8.47	0.03

[Sty] = 1.514 mol/L, [MMA] = 1.575 mol/L, [Lim] = 0.735 mol/L, terpolymerization temperature = 80 ± 0.1°C, terpolymerization time = 120 min.
[a] Temperature = 25 ± 0.2°C.

EXPERIMENTAL

Materials

The vinyl monomers and the solvents were purified by standard methods.[15] Lim (Fluka; bp = 176–177°C, d = 0.8411, $[\alpha]_d^{20}$ = 113 ± 2) was used after fractional distillation. BPO (mp = 104°C) was recrystallized twice with chloroform.

Polymerization procedure

The solution terpolymerization in xylene was carried out with a dilatometric apparatus for 120 min at 80 ± 0.1°C under an inert atmosphere of nitrogen. The terpolymers were precipitated with acidified methanol and dried to a constant weight; they were then refluxed with cyclohexane, acetonitrile, and toluene to remove the homopolymers and copolymers. The terpolymers were again dissolved in xylene and reprecipitated with methanol and dried to a constant weight to calculate the percentage conversion. The
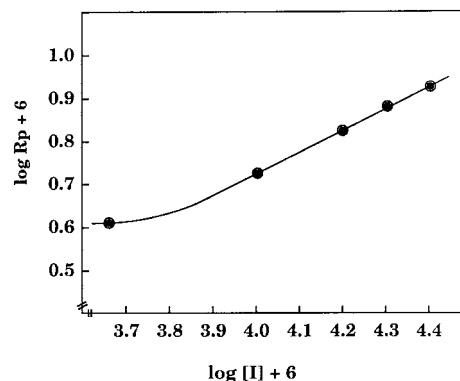

Figure 1 Relationship between R_p and [BPO] with the constant values [Sty] = 1.514 mol/L, [MMA] = 1.575 mol/L, [Lim] = 0.735 mol/L, terpolymerization temperature = 80 ± 0.1°C, and terpolymerization time = 2 h.

rate of polymerization (R_p) was calculated from the slope of linear plot of the percentage conversion versus time plot.

The intrinsic viscosities [η's] of the terpolymers were measured in benzene at 25 ± 0.1°C with an Ubbelohde viscometer and are expressed in deciliters per gram. The Fourier transform infrared (FTIR) and ^{1}H-NMR spectra were recorded with a PerkinElmer 599 B (with kBr pallets) with dimethylformamide as the solvent and a Varian 100 HA Jeol 400 LA spectrophotometer with CDCl$_3$ as the solvent and tetramethylsilane as an internal reference, respectively.

RESULTS AND DISCUSSION

The effect of [BPO] on R_p was studied through the variation of its concentration from 0.516×10^{-2} to 2.58

TABLE II
Effect of Comonomer(s) on R_p

Sample	[Sty] (mol/L)	[MMA] (mol/L)	[Lim] (mol/L)	Conversion (%)	$R_p \times 10^6$ (mol l^{-1}s^{-1})	$[\eta]$ (dL/g)[a]
6	0.216	1.575	0.735	9.5	3.89	0.02
7	0.865	1.575	0.735	10.4	5.19	0.051
3	1.514	1.575	0.735	11.01	6.51	0.09
8	2.163	1.575	0.735	12.3	7.75	0.175
9	2.81	1.575	0.735	14.9	8.70	0.21
10	1.514	0.225	0.735	9.7	4.12	0.03
11	1.514	0.9	0.735	10.3	5.30	0.044
3	1.514	1.575	0.735	11.01	6.51	0.09
12	1.514	2.25	0.735	12.9	9.31	0.16
13	1.514	2.925	0.735	15.1	10.47	0.23
14	1.514	1.575	0.147	14.16	6.77	0.19
15	1.514	1.575	0.441	12.7	6.61	0.12
3	1.514	1.575	0.735	11.01	6.51	0.09
16	1.514	1.575	1.029	10.15	6.45	0.048
17	1.514	1.575	1.158	9.6	6.3	0.030

[BPO] = 15.49×10^{-3} mol/L, terpolymerization temperature = 80 ± 0.1°C, terpolymerization time = 2 h.
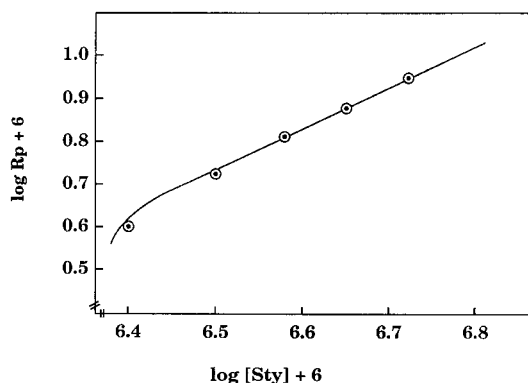[a] Temperature = 25 ± 0.2°C.

Figure 2 Relationship between R_p and [Sty] with the constant values [BPO] = 15.49 × 10^{-3} mol/L, [MMA] = 1.575 mol/L, [Lim] = 0.735 mol/L, terpolymerization temperature = 80 ± 0.1°C, and terpolymerization time = 2 h.

× 10^{-2} mol/L, with the monomer ratio [MMA/Sty + Lim] kept constant at 0.7003 mol/L (Table I). R_p was a direct function of [BPO]. The initiator exponent, calculated from the linear portion of the slope of the plot of log R_p versus log [BPO], was 0.5 ± 0.02 (Fig. 1).

The effect of monomer concentration on R_p is summarized in Table II. The results revealed that the R_p was a direct function of [Sty] and [MMA] and an inverse function of [Lim]. The exponent values, calculated from the linear portion of the slope of log R_p versus log [monomer] in all three cases was unity (Figs. 2–4).

The decrease in R_p with increasing [Lim] might have been due to the penultimate unit effect:[16]

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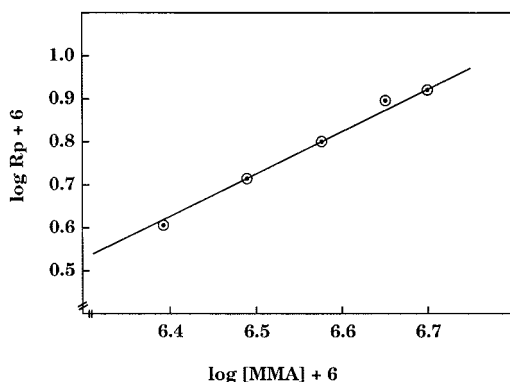

Figure 3 Relationship between R_p and [MMA] with the constant values [BPO] = 15.49 × 10^{-3} mol/L, [Sty] = 1.514 mol/L, [Lim] = 0.735 mol/L, terpolymerization temperature = 80 ± 0.1°C, and terpolymerization time = 2 h.
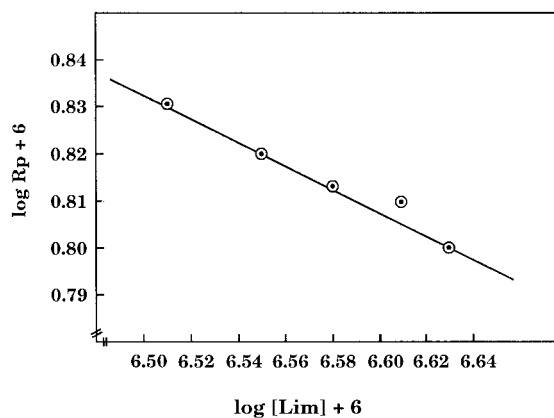

Figure 4 Relationship between R_p and [Lim] with the constant values [BPO] = 15.49 × 10^{-3} mol/L, [Sty] = 1.514 mol/L, [MMA] = 1.575 mol/L, [Lim] = 0.735 mol/L, and terpolymerization temperature = 80 ± 0.1°C.

where M_1 is MMA, M_2 is Sty + Lim, $\delta_1 = (2k_{t11}/k_{11})^{1/2}$, $\delta_2 = (2k_{t22}/k^2_{t22})^{1/2}$, and $\phi = (K_{t12}/2k_{t11}k_{t22})^{1/2}$.

From the experimental data, the value of ϕ was calculated as 3.55. It was more than unity, indicating that the penultimate unit effect was applicable[17,18] in this system.

Polymerization was also carried out at 70, 75, 85, and 90°C to evaluate the overall energy of activation. R_p was a direct function of the temperature, and the overall energy of activation as calculated from the slope of the Arrhenius plot was 26 kJ mol/L (Fig. 5).

Characterization of the terpolymer

FTIR spectroscopy

As shown in Figure 6, the assignments (KBr pellets) were C—H stretching due to the phenyl protons of Sty
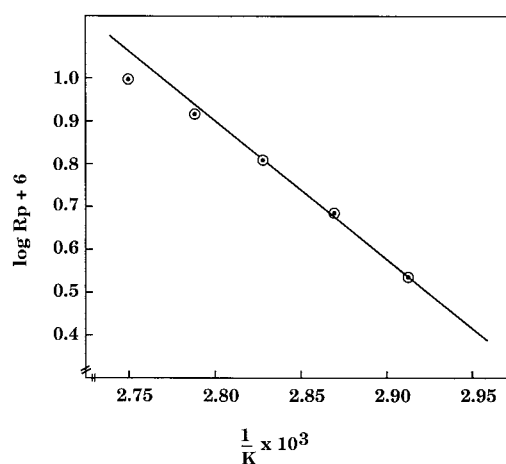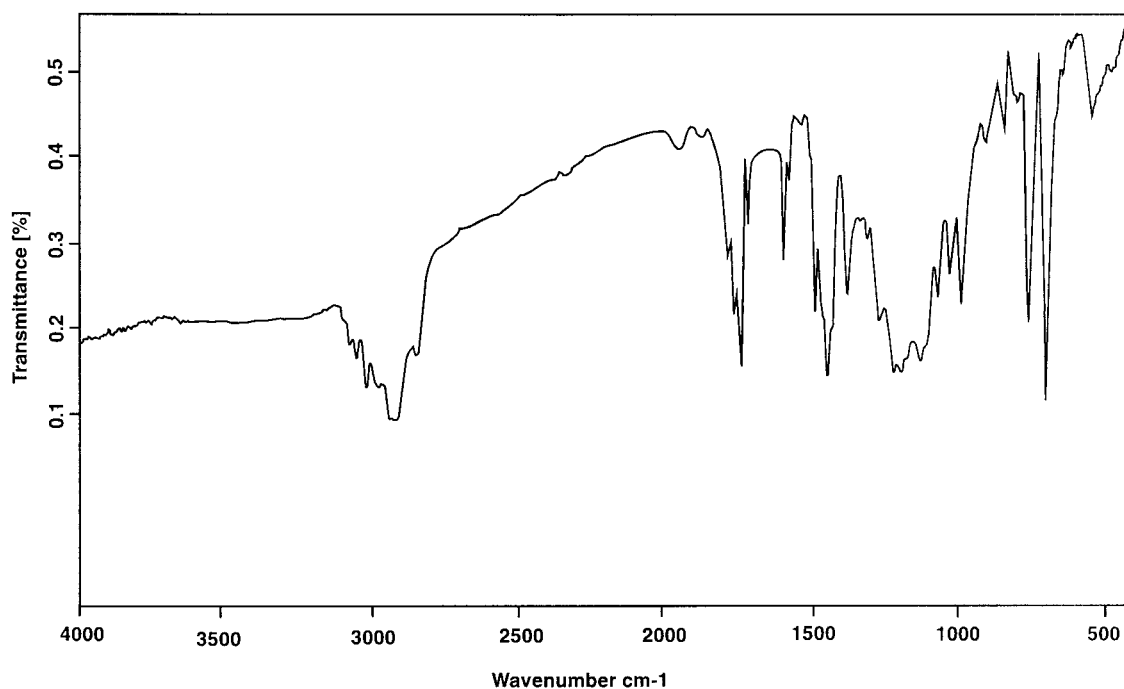

Figure 5 Arrhenius plot for activation energy.

Figure 6　FTIR spectrum of the terpolymer (sample 3).

at 3025–3082 cm^{-1}, C—H stretching due to the trisubstituted olefinic of protons of Lim at 2851–2984 cm^{-1}, C—H bending vibrations at 699–759 cm^{-1}, the ester group of MMA at 1728 cm^{-1}, and C=C stretching due to the trisubstituted olefinic of protons of Lim at 1688 cm^{-1}.

NMR

The ^{1}H-NMR spectra of the terpolymers (Fig. 7) showed a singlet at 5.0–5.6 δ and a multiplet at 3.9–4.4 δ and 7.3–8.1δ due to the trisubstituted olefinic
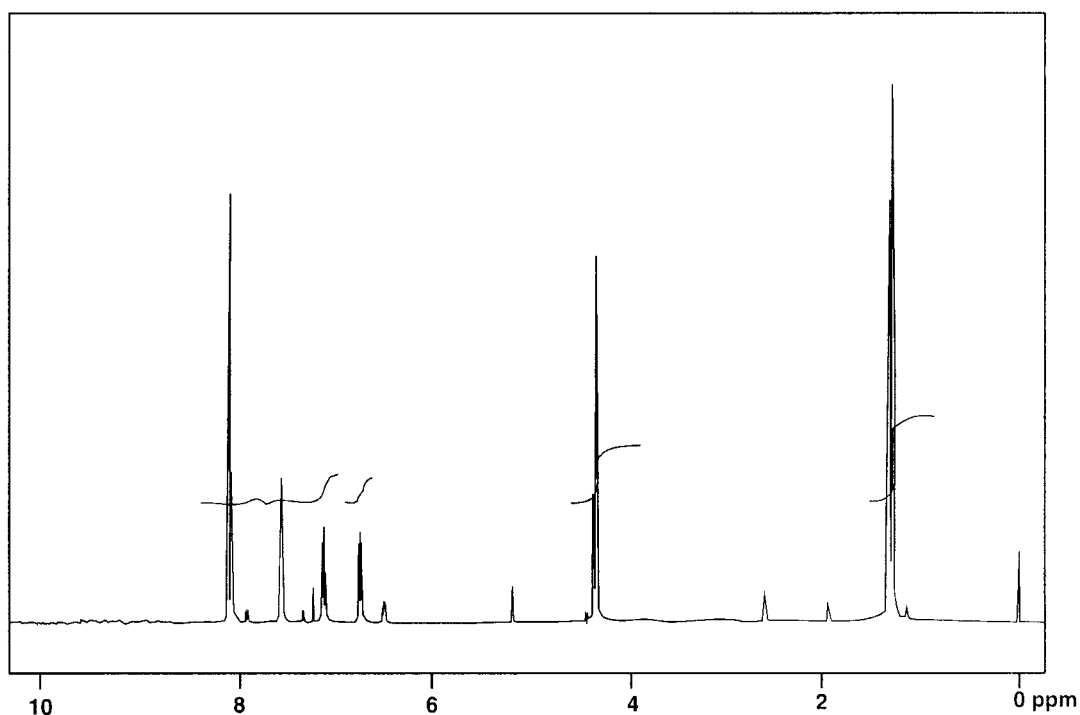
Figure 7　^{1}H-NMR spectrum of the terpolymer (sample 3).

TABLE III
Terpolymer Composition

Sample	Monomer feed $\frac{MMA}{Sty + Lim}$ (F)	Polymer feed $\frac{MMA}{Sty + Lim}$ (f)	Molar fraction of MMA in the terpolymer	Molar fraction Sty in the terpolymer	Molar fraction of Lim in the terpolymer	η	ξ
3	0.7003	1.13	0.53	0.31	0.16	0.1017	0.548
7	0.984	1.19	0.54	0.33	0.123	0.134	0.695
8	0.544	1.05	0.51	0.35	0.136	0.0403	0.440
11	0.400	1.02	0.507	0.34	0.15	0.01525	0.305
12	1.00	1.28	0.56	0.26	0.178	0.2798	0.686
15	0.8056	1.15	0.53	0.31	0.15	0.1138	0.612
16	0.619	1.09	0.516	0.32	0.155	0.072	0.4956

($-CH=CH-CH_2$) protons of Lim, the $-OCH_3$ protons of MMA, and the $-C_6H_5$ protons of Sty, respectively. The peaks at 6.5 and 7.95 ppm may have been due to the presence of impurities.

Terpolymer composition (Table III) and reactivity ratios (r_1 and r_2)

The relative peak areas at 3.9–4.4, 7.3–8.1, and 5.0–5.5 δ due to $-OCH_3$, $-C_6H_5$ and the trisubstituted olefinic protons of MMA, Sty, and Lim, respectively, were used to calculate the reactivity ratios with the Kelen–Tüdos method.[19] The slope of the plot (least squares method) of η versus ξ gave values of r_1 (MMA) = 0.33 and r_2 (Sty + Lim) = 0.06 (Fig. 8).

CONCLUSIONS

A functional terpolymer of Lim, Sty, and MMA was synthesized via free-radical polymerization. The pen-
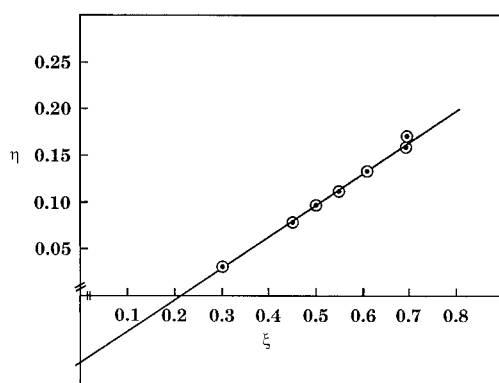

Figure 8 Kelen–Tüdos plot for the determination of the reactivity ratios.

ultimate unit effect was assumed in this system, as R_p decreased as [Lim] increased and the value of ϕ was more than unity.

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