

Synthesis and Characterization of Functional Copolymers of Citronellol with Butylmethacrylate Initiated by Benzoyl Peroxide

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ABSTRACT: Benzoyl peroxide (BPO)-initiated free radical copolymerization of citronellol with butylmethacrylate (BMA) in xylene at $80^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ under the inert atmosphere of nitrogen has been studied. The kinetics expression is $R_p \propto [I]^{0.5 \pm 0.27} [\text{citronellol}]^{1.0 \pm 0.13} [\text{BMA}]^{1.0 \pm 0.18}$. The overall activation energy has been calculated as 65 kJ/mol. Bands at 3436 and 1732 cm^{-1} in the FTIR spectrum of the copolymer(s) have indicated the presence of hydroxy, ester group of citronellol and butylmethacrylate, respectively. The $^1\text{H-NMR}$ spectrum shows peaks at 7.0–7.7 δ due to $-\text{OH}$ proton of citronellol and at 3.2–4.0 δ due to $-\text{OCH}_2$ proton of butylmethacrylate. The molecular weight M_v and η_{int} of the copolymers have been measured with the help of gel permeation chromatography in tetrahydrofuran

at 25°C to calculate Mark-Houwink constants as $K = 2.68 \times 10^{-4}$ and $\alpha = 0.34 \pm 0.40$. The alternating nature of the copolymer is confirmed by reactivity ratios r_1 (BMA) = 0.023 ± 0.004 and r_2 (Citronellol) = 0.0025 ± 0.22 . The Alfrey-Price $Q-e$ parameters for citronellol have been calculated as $Q_2 = 0.13$ and $e_2 = -1.28$. Thermal decompositions of copolymer are evaluated with the help of thermal gravimetric analysis technique. The mechanism of copolymerization has been elucidated. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2601–2608, 2009

Key words: activation energy; gel permeation chromatography; kinetics (polym.); radical polymerization; thermogravimetric analysis

INTRODUCTION

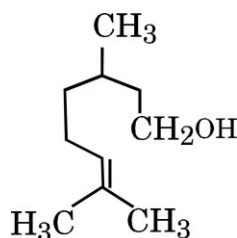
Despite the limitations of scientific knowledge and understanding, it proved possible for an empirical technology to arise and grow, based upon natural polymers having novel compositions with unique and useful properties. Such materials have been prepared by modifying existing polymer(s) through copolymerization. Today, equipped with experience gained over the years, it seems variety of comonomers is required to tailor in polymer properties. The synthesis of copolymer(s) of terpenes is one of the connecting links in this series. A search of literature reveals that attempts have been made by chemists to develop a substitute for polyterpenes from petroleum distillates,¹ but no such substitute has been developed yet, as most of the terpenes do not undergo homopolymerization because of steric hin-

drance,² low stabilization energy between monomers and free radicals in transition state,³ excessive chain transfer,⁴ and termination of cyclization as in case of 1,2-disubstituted ethylene,⁵ except α,λ -pinene(s), which have been polymerized by Ziegler-Natta^{6,7} as well as Lewis acid catalysts.⁸ Thus, literature is almost devoid of radical polymerization of terpenes, except few recent contributions from our laboratory, i.e., geraniol-*co*-acrylonitrile/benzoyl peroxide (BPO)/ 70°C ,⁹ limonene-*co*-vinylacetate/AIBN/ 65°C ,¹⁰ α -terpineol-*co*-*N*-vinylpyrrolidone/BPO/ 80°C ,¹¹ linalool-*co*-butylmethacrylate/BPO/ 80°C ,¹² linalool-*co*-acrylamide/BPO/ 75°C ,¹³ linalool-*co*-acrylonitrile/BPO/ 75°C ,¹⁴ geraniol-*co*-styrene/BPO/ 80°C ,¹⁵ limonene-*co*-acrylonitrile/BPO/ 70°C ,¹⁶ limonene-*co*-methyl methacrylate/BPO/ 80°C ,¹⁷ limonene-*co*-styrene/AIBN/ 80°C ,¹⁸ α -terpineol-*co*-butyl methacrylate/BPO/ 80°C ,¹⁹ α -terpineol-*co*-methyl methacrylate/AIBN/ 80°C .²⁰ These terpenoids are useful as novel monomers and have great relevance because they yield optically active and functional copolymer(s). Therefore, the field of polymers of terpenoids is a very challenging area of green chemistry with unlimited future prospects.

Citronellol ($\text{C}_{10}\text{H}_{20}\text{O}$), an optically active acyclic monoterpenoid includes one alcoholic group, was first prepared by Dodge in 1889:

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Citronellol

It is susceptible to copolymerization as it contains one double bond, however, it has been used as comonomer with vinyl acetate²¹ and styrene.²² To the best of our knowledge, no reports on its copolymerization with butylmethacrylate (BMA) are available in literature; although the latter has been used as a comonomer with different vinyl monomers like methyl methacrylate,²³ styrene,²⁴ and vinyl acetate.²⁵

BMA-based products have a number of industrial applications in the area of lubricating oil, hydraulic fluid additives, surface coatings, impregnates, adhesives, paints, binders, and floor polishes.

The incorporation of functional groups of citronellol into polyolefins may be an interesting approach to modify the chemical and physical characteristics of their copolymers. Therefore, we have undertaken this study to describe the kinetics and mechanism of copolymerization of citronellol with BMA initiated by BPO in xylene at $80^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ for 1 h. The values of the Mark-Houwink constants, K and α , have been evaluated, and the thermal properties of the copolymer are reported. Further, the copolymers formed are significant because of their nice fragrance and functional properties.

EXPERIMENTAL

Materials

BMA (Merck-Schuchardt, Hohenbrunn, Germany) and other solvents were purified by the usual methods published elsewhere.²⁶ Citronellol (Merck-Schuchardt) ($M = 156.27$ g/mol), 1 L = 0.86 kg, b.p. = 103°C , refractive index (n_D^{20}) = 1.4562, specific rotation ($[\alpha]_D^{20} = +4^{\circ}$ – 5°) was used after fractional distillation. BPO was recrystallized twice from methanol followed by drying under vacuum.

Polymerization procedure

The copolymerization of citronellol with BMA was carried out at $80^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ in xylene using dilatometer to determine conversion under an inert atmosphere of nitrogen. The copolymers were precipitated with acidified methanol and dried under vacuum.

Then, the copolymers were refluxed with toluene to remove the poly (BMA) when no detectable weight loss was observed. Finally, the copolymer was dried to constant weight and the percentage conversion was calculated. The rate of polymerization (R_p) was calculated from the slope of the graph between the percentage conversion versus time plots.

Characterization of copolymers

The FTIR (with KBr pellets) and $^1\text{H-NMR}$ [using CDCl_3 as a solvent and tetra methylsilane (TMS) as an internal reference] spectra were recorded with a Perkin-Elmer 599B and a Bruker DRX-300 MHz spectrometer, respectively. Gel permeation chromatography (GPC) studies were done with E. Merck RI-L-7490. The elution solvent was tetrahydrofuran (THF) at a temperature of 25°C . Thermal gravimetric analysis (TGA) was carried out on Perkin-Elmer thermal analyzer, sample weight (20 mg, and at a heating rate $10^{\circ}\text{C}/\text{min}$ under the nitrogen atmosphere.

RESULTS AND DISCUSSION

There are a series of monomers, such as maleic anhydride, fumarates, maleates, α -methyl styrene, and vinyl ethers, that do not homopolymerize but are often used as comonomers.²⁷ Citronellol does not undergo homopolymerization under experimental conditions but has a tendency to copolymerize.

The kinetics of copolymerization was carried out by varying the concentration of initiator (BPO), monomer(s), and temperature. The maximum conversion was limited to 18.7%, and the polymerization proceeded with a short induction period of 3 ± 1 min. The results of the kinetic investigations are illustrated in Table I and Figures 1–4.

The effect of [BPO] was studied by varying [BPO] from (1.37×10^{-3} to 6.89×10^{-3} mol/L), keeping the [citronellol] and [BMA] constant at 0.73 and 1.5 mol/L (Table I). It is clear that R_p is a direct function of [BPO], and the exponent value of BPO, determined from the slope of linear plot of $\log R_p$ vs. \log [BPO], is 0.5 ± 0.27 (Fig. 1).

$$R_p \propto [\text{BPO}]^{0.5 \pm 0.27} \quad (1)$$

The calculated value of goodness of fit, i.e., R_2 value (regression coefficient), obtained from Figure 1, is close to 1 (~ 0.97).

The effect of [citronellol] on the R_p has been studied by varying [citronellol] from 0.18 to 1.84 mol/L, keeping [BMA] and [BPO] constant at 1.5 and 2.75×10^{-3} mol/L, respectively (Table I). It is noticed that R_p is directly proportional to [citronellol]. A plot between $\log R_p$ and \log [citronellol] is linear; the

TABLE I
Effect of [BPO] and [comonomer(s)] on the Rate of Copolymerization of Citronellol with BMA

Sample no.	[BPO] × 10 ³ (mol/L)	[Citronellol] (mol/L)	[BMA] (mol/L)	Conversion (%)	R _p × 10 ⁶ [mol/(L s)]
1	1.37	0.73	1.5	7.9	5.01
2	2.75	0.73	1.5	13.7	11.15
3	4.13	0.73	1.5	14.9	14.1
4	5.50	0.73	1.5	16.0	14.9
5	6.89	0.73	1.5	17.9	17.7
6	2.75	0.18	1.5	10.6	7.76
7	2.75	0.55	1.5	12.4	9.54
8	2.75	1.30	1.5	15.0	13.8
9	2.75	1.84	1.5	16.7	16.6
10	2.75	0.73	0.63	6.1	3.9
11	2.75	0.73	1.0	9.5	7.9
12	2.75	0.73	2.51	15.9	14.4
13	2.75	0.73	3.13	18.7	18.6

Copolymerization time = 1 h; copolymerization temperature = 80°C ± 0.1°C.

slope of which gives the following relationship (Fig. 2):

$$R_p \propto [\text{citronellol}]^{1.0 \pm 0.13} \quad (2)$$

The goodness of fit, i.e., R_2 value (regression coefficient), obtained from Figure 2, is calculated as 0.99.

The effect of [BMA] on the R_p has been studied by varying [BMA] from 0.63 to 3.13 mol/L, keeping [citronellol] and [BPO] constant at 0.73 and 2.75×10^{-3} mol/L, respectively (Table I). The R_p is a direct function of [BMA]. A plot between $\log R_p$ and \log [BMA] is linear, the slope of which gives the following relationship (Fig. 3):

$$R_p \propto [\text{BMA}]^{1.0 \pm 0.18} \quad (3)$$

The goodness of fit, i.e., R^2 value (regression coefficient), obtained from Figure 3, is calculated as 0.98.

The polymerization was also carried out at 75 and 85°C to evaluate the energy of activation because no

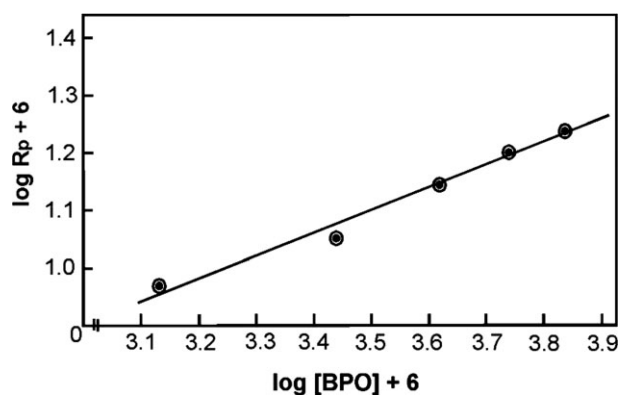


Figure 1 Relationship between the rate of copolymerization and [BPO]; [citronellol] = 0.73 mol/L; [BMA] = 1.5 mol/L; copolymerization time = 1 h; copolymerization temperature = 80°C ± 0.1°C.

significant polymerization occurs below 75°C. R_p increases with increasing polymerization temperature. The overall activation energy, calculated from the linear Arrhenius plot,²⁸ is 65 kJ/mol (Fig. 4).

Characterization of copolymers

Fourier transform infrared spectroscopy

The FTIR spectra of the copolymer show bands at 3436 cm^{-1} for the alcoholic group of citronellol and at 1732 cm^{-1} for ester group of BMA. This confirms the copolymer formation (Fig. 5).

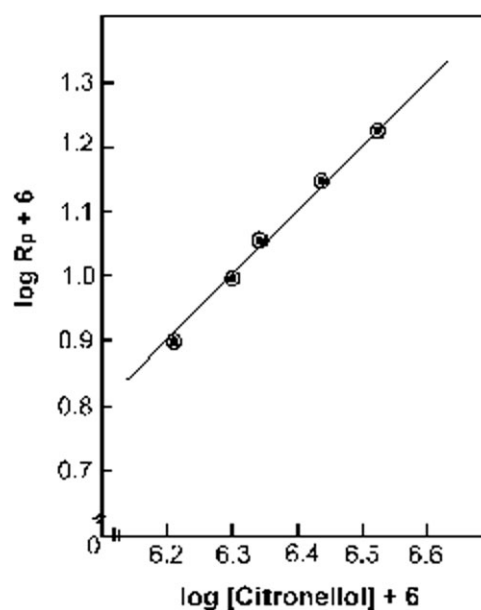


Figure 2 Relationship between the rate of copolymerization and [citronellol] with constant [BMA] = 1.5 mol/L; [BPO] = 2.75×10^{-3} mol/L; copolymerization time = 1 h; copolymerization temperature = 80°C ± 0.1°C.

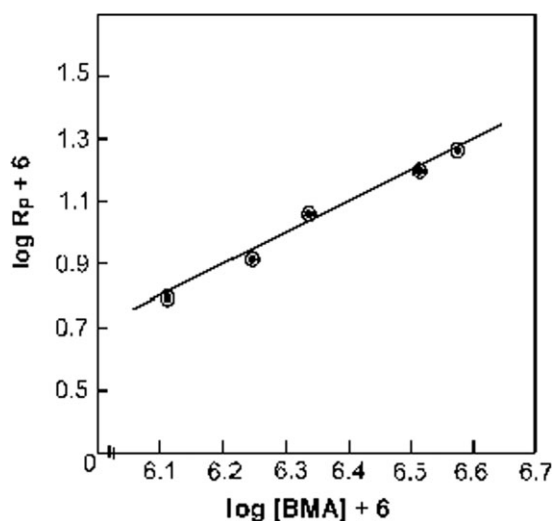


Figure 3 Relationship between the rate of copolymerization and [BMA] with constant [citronellol] = 0.73 mol/L; [BPO] = 2.75×10^{-3} mol/L; copolymerization time = 1 h; copolymerization temperature = $80^\circ\text{C} \pm 0.1^\circ\text{C}$.

Nuclear magnetic resonance spectroscopy

The chemical shifts of protons, attached to elements other than carbon such as $-\text{OH}$, $-\text{NH}$, and $-\text{SH}$, to a greater extent or lesser extent, are influenced by the related phenomena of intermolecular exchange and hydrogen bonding. The signals appearing in the $^1\text{H-NMR}$ spectra that are due to $-\text{OH}$ (hydroxyl protons) with species of small molecular weight, where intermolecular association is not hindered, generally resonate in the region of 3.0–5.5 δ (the hydroxyl protons of CH_3-OH appear at 3.3 δ , whereas those of $\text{C}_2\text{H}_5\text{OH}$ appear at 5.4 δ).²⁹ However, with many large molecules, the hydroxyl protons often resonate at 8.0 δ , even at relatively high

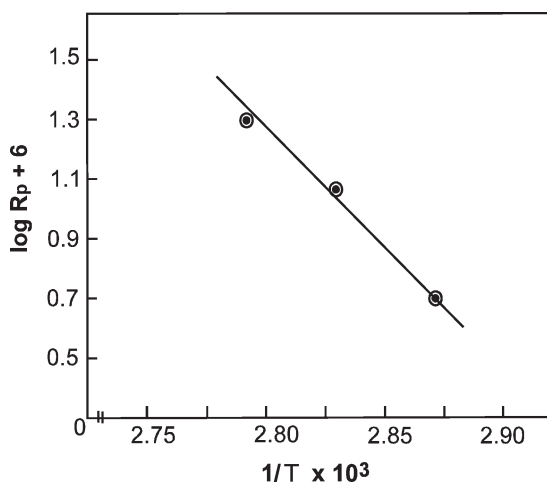


Figure 4 Arrhenius plot of the rate of polymerization versus polymerization temperature; [BPO] = 2.75×10^{-3} mol/L; [citronellol] = 0.73 mol/L; [BMA] = 1.5 mol/L; copolymerization time = 1 h.

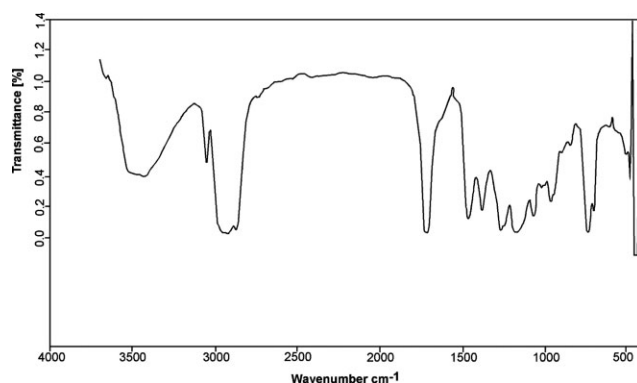


Figure 5 FTIR spectrum of citronellol-BMA copolymer (sample 2).

concentration, partially because of steric effects³⁰ and partially due to resonance stabilization. Therefore, we have assigned the peaks of the $-\text{OH}$ group in the range of 7.0–7.7 δ in the $^1\text{H-NMR}$ spectra of copolymers of BMA and citronellol.^{21,22} The copolymers show the triplet at 3.2–4.0 δ which are due to the $(-\text{OCH}_2)$ protons of BMA.³¹ These characteristic signals of the two monomers clearly showed their presence in the copolymer (Fig. 6).

Gel permeation chromatography

The Mark-Houwink equation $[\eta] = K[M]^\alpha$ relates the intrinsic viscosity $[\eta]$ of a polymer to its molecular weight $[M]$ through empirical constants K and α . A typical GPC curve is shown in Figure 7. The standard procedure for measuring these constants requires M_v and $[\eta]$ of polymer samples, which are measured by GPC (Table II). The two constants K and α of the empirical Mark-Houwink expression were evaluated from the intercept and the slope of the plot of $\log M_v$ versus $\log [\eta]$ (Fig. 8) for copolymer samples and the following relationship is established:

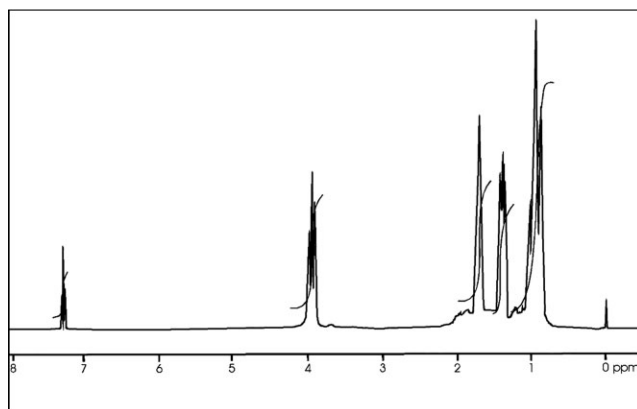


Figure 6 $^1\text{H-NMR}$ spectrum of citronellol-BMA copolymer (sample 2).

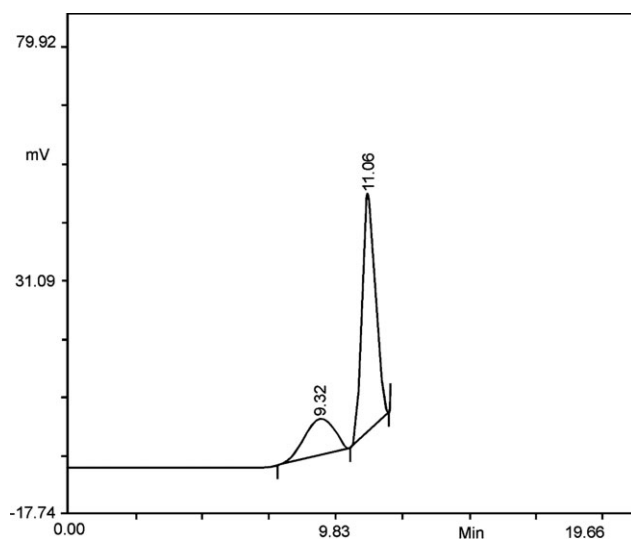


Figure 7 GPC graph of citronellol-BMA copolymer (sample 2).

$$[\eta](\text{dL/g}) = 2.68 \times 10^{-4} M_v^{0.34 \pm 0.40} \text{ in THF at } 25^\circ\text{C} \quad (4)$$

The statistical analysis, i.e., goodness of fit (R^2 value), obtained from Figure 8, is 0.93.

Thermal gravimetric analysis

A TGA curve for the copolymer (Fig. 9) exhibits weight loss with temperature.^{32,33} The decomposition of the copolymer started from 250°C. The thermal behavior data are as follows:

- Onset of major weight loss occurs at 250°C, and completion of major weight loss occurs at 450°C.
- The total weight loss is 98% in the range 50–480°C.
- The weight loss at different stages of temperature are as follows:
 - 50–200°C = 31%
 - 200–480°C = 95%
- Almost total volatilization of the copolymer occurred at 385°C.

TABLE II
GPC Parameters of the Copolymerization of Citronellol with BMA

Sample no. (Table I)	$[\eta] \times 10^4$	$\bar{M}_v \times 10^4$
7	3.14	9.73
11	3.91	20.4
2	4.50	32.5
8	5.41	60.2
12	5.72	72.3

Elution solvent: tetrahydrofuran (THF); viscosity temperature = 25°C.

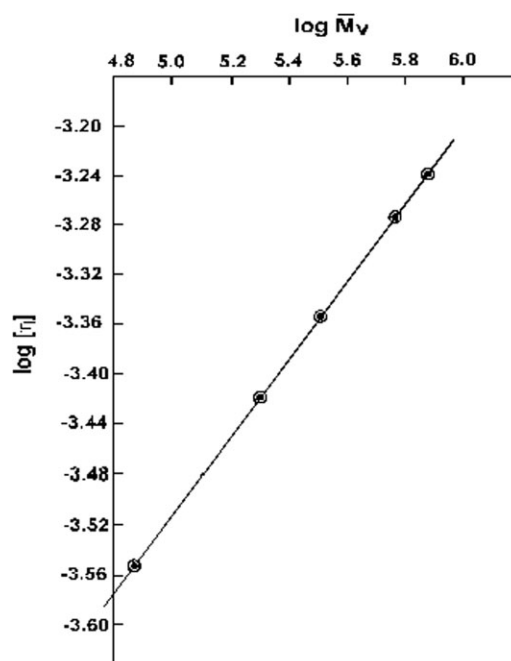


Figure 8 Plot of $\log [\eta]$ versus $\log M_v$ (Mark-Houwink curve): $[\text{BPO}] = 2.75 \times 10^{-3} \text{ mol/L}$; copolymerization time = 1 h; copolymerization temperature = $80^\circ\text{C} \pm 0.1^\circ\text{C}$.

The TGA data show a weight loss of 3.1% as the temperature increased to 200°C, which is attributed to the loss of absorbed water.^{34,35} The range of temperature above 200°C and up to 480°C are the regions of major weight loss and appear because of the extensive degradation of the copolymer backbone chain.

Copolymer composition and reactivity ratios

$^1\text{H-NMR}$ analysis has been used to calculate the copolymer composition. The relative peak of resonance at 3.2–4.0 δ due to $-\text{OCH}_2$ protons of BMA³¹ and

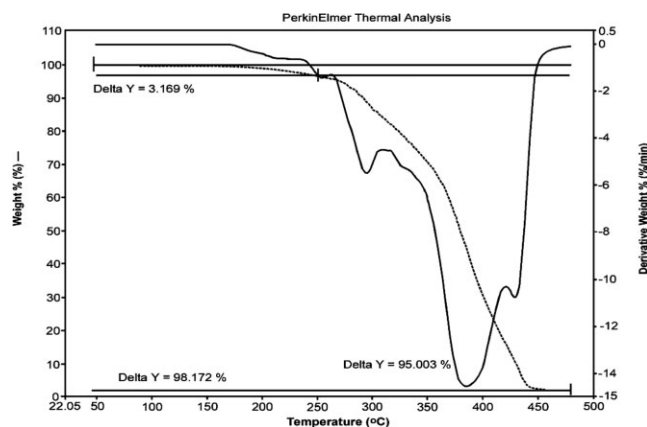


Figure 9 TGA thermogram of citronellol-BMA copolymer performed at $10^\circ\text{C}/\text{min}$ (sample 2).

TABLE III
Composition of Citronellol-BMA Copolymers

Sample no.	Molar ratio in monomer feed [BMA]/[citronellol]	Conversion (%)	Mole fraction of [BMA] in copolymer	Molar ratio in copolymer [BMA]/[citronellol]
8	1.15	15.0	0.508	1.035
11	1.37	9.5	0.510	1.040
2	2.05	13.7	0.512	1.054
7	2.72	12.4	0.516	1.060
12	3.44	15.9	0.520	1.085

7.0–7.7 δ due to $-\text{OH}$ protons of citronellol^{21,22} in the $^1\text{H-NMR}$ spectrum allows the estimation of the copolymer composition (Table III). The Kelen-Tüdös³⁶ approach is used for the evaluation of reactivity ratios, r_1 (BMA) and r_2 (citronellol), for the monomer pair as follows:

$$\eta = r_1\xi - r_2(1 - \xi)/\alpha$$

where $\eta = G/(\alpha + H)$ and $\xi = H/(\alpha + H)$.

The transformed variables G and H are given by

$$G = \frac{[\text{M}_1]/[\text{M}_2][(d[\text{M}_1]/d[\text{M}_2]) - 1]}{d[\text{M}_1]/d[\text{M}_2]} \quad (5)$$

$$H = \frac{([\text{M}_1]/[\text{M}_2])^2}{d[\text{M}_1]/d[\text{M}_2]}$$

The parameter α is calculated by taking the square root of the product of the lowest and highest values of H for the copolymerization series. The graphical evaluation for BMA/Citronellol (least square method), yields values of $r_1 = 0.023 \pm 0.004$ and $r_2 = 0.0025 \pm 0.022$. The product of r_1r_2 is nearly 0, which is the sign of alternating copolymerization. The goodness of fit, i.e., R^2 value calculated, from the Figure 10, is 0.99. The statistical calculation for Kelen-Tüdös plot shows residual analysis in terms of residual values. These residual values are calculated as -0.0000265 , -0.0000675 , -0.000275 , -0.0002275 , -0.0000400 , respectively, from the Kelen-Tüdös plot (Fig. 10).

The Q - e parameters for citronellol have been calculated by using $e_1 = 0.78$ and $Q_1 = 0.51$ for BMA by the following Alfrey-Price equations.^{37,38}

$$e_2 = e_1 \pm (\log r_1r_2)^{0.5}$$

$$Q_2 = Q_1/r_1 \exp[-e_1(e_1 - e_2)] \quad (6)$$

These equations express r_1 and r_2 in terms of constants; Q and e are assumed to be characteristic of each monomer. Q is related to the extent of resonance stabilization in the monomer, i.e., its reactivity, and e is related to the polarity of the double bond. It has been found that strong alternating copolymers are formed when comonomers with

widely differing polarities react with each other. The value of $Q_2 = 0.13$ and $e_2 = 1.28$ for citronellol have been calculated from our data. Thus, an alternating copolymerization is suggested from the large difference between e values of both comonomers.

Mechanism

The oxidation of citronellol with KMnO_4 has yielded results of considerable value in the elucidation of the constitution and nature of alcohol. Tiemann and Semmler³⁹ observed that when citronellol was oxidized with a 1% solution of KMnO_4 , followed by a chromic acid mixture, acetone was always found among the oxidation products, a fact that regarded the evidence in favor of breaking of a double bond.

Furthermore, Kotz and Steche⁴⁰ studied the oxidation of citronellol with great care; they treated this alcohol with BPO and obtained in this manner, after hydration of the oxide, a glycerol, which can be represented by the following scheme:

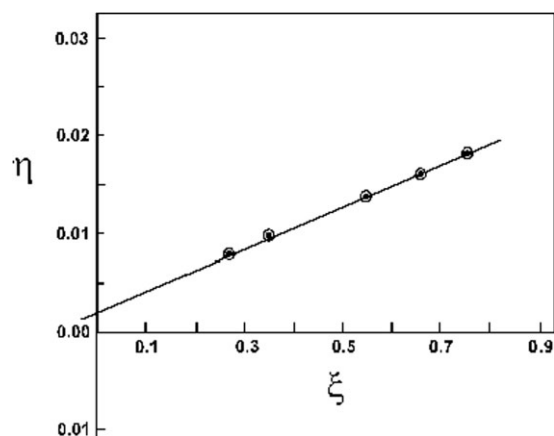
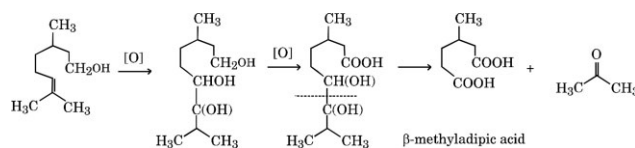
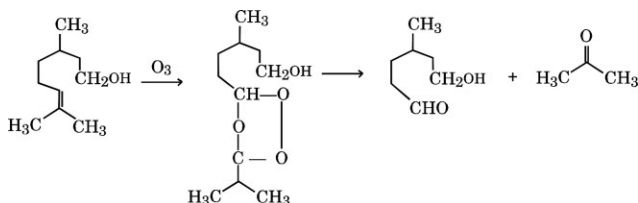
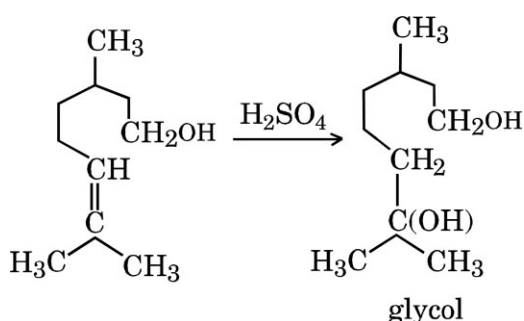


Figure 10 Kelen-Tüdös plot of copolymer for the determination of reactivity ratios.

Confirmation of the view that alcohol citronellol has the tendency to lose the π electron has been furnished by a study of the oxidation products resulting from the action of ozone. Harries and Himmelmann,^{41,42} who first studied this reaction, showed that both acetone and formaldehyde were obtained by the decomposition of the ozonides, the course of the reaction may be indicated as follows:

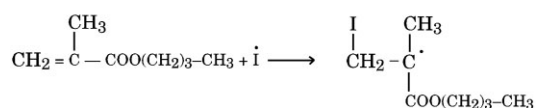
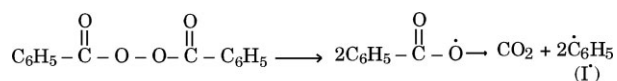


Tiemann and Schmidt^{43,44} also found that when citronellol was shaken with diluted H_2SO_4 , a glycol was formed.

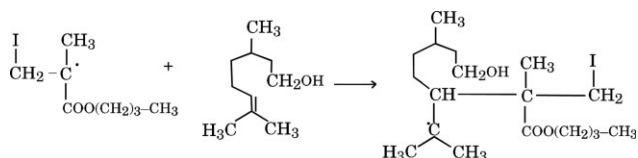


Based on this reaction, it is clear that $>C=C<$ is more susceptible than an alcoholic $O-H$ bond and, therefore, the π bond takes part in polymerization. The various step of mechanism are as follows:

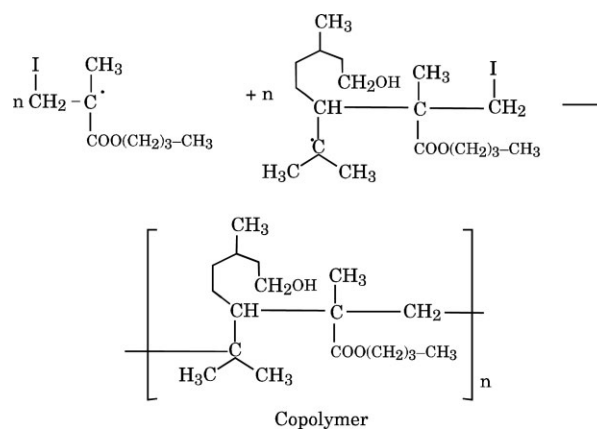
Initiation:



Propagation:



Termination:



CONCLUSION

Poly(citronellol-*alt*-BMA) has been synthesized via free radical solution polymerization using BPO as a radical initiator. The system follows kinetics expression: $R_p \propto [I]^{0.5} [\text{citronellol}]^{1.0} [\text{BMA}]^{1.0}$, and the energy of activation is evaluated as 65 kJ/mol. The molecular weight of copolymers and Mark-Houwink constants $K = 2.68 \times 10^{-4}$ and $\alpha = 0.34$ were evaluated with the help of GPC. The copolymer is thermally stable. The copolymer contains a pendant alcoholic group, which is significant as a functional polymer.

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