

# Synthesis and Characterization of Functional Copolymers of Citronellol and Acrylamide

A. K. Srivastava, Prachi Pandey, Garima Mishra

Department of Chemistry, H. B. Technological Institute, Kanpur 208 002, India

Received 18 January 2006; accepted 16 April 2006

DOI 10.1002/app.24883

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The radical copolymerization of citronellol with acrylamide in xylene at  $(80 \pm 10)^\circ\text{C}$  for 1 h in the presence of benzoylperoxide follows ideal kinetics with bimolecular termination and results in the formation of an alternating copolymer as evidenced from the values of reactivity ratios as  $r_1$  (acrylamide) = 0.0045 and  $r_2$  (citronellol) = 0.0005, which have been calculated by Kelen-Tüdös method. The overall activation energy is computed as 44 kJ/mol. The IR spectrum of the copolymer shows the presence of bands at  $3427\text{ cm}^{-1}$  due to alcoholic group and  $1710\text{ cm}^{-1}$  due to amide group. The  $^1\text{H}$  NMR spectrum of the copolymer shows peaks between 6.3 and 7 $\delta$  due to amide group ( $> \text{C}=\text{O}$  stretching) and between 7

and 7.7 $\delta$  due to alcoholic group. The values of Mark-Houwink constant for present copolymer system have been evaluated as  $\alpha = 0.33$  and  $K = 2.3 \times 10^{-1}$  with the help of gel permeation chromatography. The Alfrey-Price,  $Q-e$  parameters for citronellol have been calculated as 0.43 and 1.07. The copolymer is highly thermally stable and has a glass transition temperature ( $T_g$ ) of  $102^\circ\text{C}$  as evaluated from differential scanning calorimetry studies. The mechanism has also been elucidated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4908–4914, 2006

**Key words:** citronellol; acrylamide; copolymerization; reactivity ratios; Mark-Houwink constant

## INTRODUCTION

Copolymers of acrylamide (AM) have shown a number of properties lending themselves to variety of industrial applications of growing importance, which are those related to use as water-soluble viscofiers and displacement fluids in enhanced oil recovery. AM has easily been copolymerized with a variety of monomers such as styrene,<sup>1</sup> *N,N*-dimethyl acrylamide,<sup>2,3</sup> and methacrylol derivatives of polyoxotungstates,<sup>4</sup> but few reports<sup>5</sup> are available for the copolymerization of any monoterpenoids. Although much has been published regarding the reactions of terpenes in synthetic organic chemistry, yet their potential applications as monomer in the domain of polymer presence are still scarce. A search of literature reveals that approach of polymer chemist to examine terpenes has been limited to only terpene hydrocarbons, mostly bicyclic monoterpenes like  $\alpha$  and  $\beta$  pinene.<sup>6,7</sup> However, copolymerization of different terpenes have been reported from this lab.<sup>8–16</sup>

Citronellol,  $\text{C}_{10}\text{H}_{20}\text{O}$ , the unsaturated primary alcohol was first prepared by Dodge in 1889 by the reduction of the aldehyde citronellol, which he had isolated

from citronella oil. It is susceptible to polymerization as it contains one double bond and one alcoholic group.

Thus, in the present article it is of great interest to investigate the copolymer of citronellol with AM as a copolymer, and attempts have been made to study the details of the kinetics, mechanism, and characterization of the copolymerization of citronellol with AM in xylene initiated by Benzoylperoxide (BPO) at  $(80 \pm 0.1)^\circ\text{C}$ . Further the copolymers formed are significant due to their nice fragrance, functional properties, and optical activeness.

## EXPERIMENTAL

### Materials

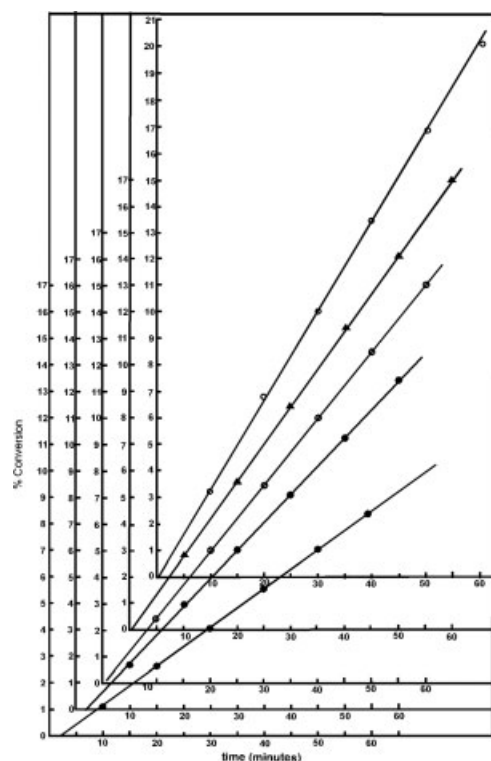
Acrylamide (AM) (Merck-Schuchardt) was recrystallized from methanol and vacuum-dried at room temperature prior to use (m.p.  $83.5\text{--}84.5^\circ\text{C}$ ).

Citronellol,<sup>17,18</sup> (E. Merck) boiling point =  $1100^\circ\text{C}$ , refractive index  $n_{20^\circ/\text{D}}$  1.4562, specific rotation ( $[\alpha]_{200/\text{D}}$ ; +4), was used after fractional distillation. Benzoylperoxide (BPO) was recrystallized twice from methanol followed by drying under vacuum. Other solvents were purified by usual method.<sup>19,20</sup>

### Polymerization procedure

A dilatometer technique (dia = 2 mm, Cap length = 9.5 cm, capacity = 2.5 mL) has been used to follow

Correspondence to: A. K. Srivastava (akspolym@rediffmail.com).



**Figure 1** The conversion plot for the copolymerization of citronellol and AM. [Citro] =  $1.28 \text{ mol l}^{-1}$ , [AM] =  $2.1 \text{ mol l}^{-1}$ ; Copolymerization time = 1 h; Copolymerization temperature =  $(80 \pm 1)^\circ\text{C}$ . [BPO] – ● =  $2.06 \times 10^{-3} \text{ mol l}^{-1}$ ; ○ =  $4.13 \times 10^{-3} \text{ mol l}^{-1}$ ; ⊗ =  $6.19 \times 10^{-3} \text{ mol l}^{-1}$ ; ▲ =  $8.26 \times 10^{-3} \text{ mol l}^{-1}$ ; ○ =  $10.33 \times 10^{-3} \text{ mol l}^{-1}$ .

the copolymerization runs under oxygen free conditions. The polymerization mixture was prepared by taking both comonomers along with BPO. Polymerization was continued up to 1 h to limit the conversion range between 5 and 20% at  $(80 \pm 0.1)^\circ\text{C}$ . The polymer was isolated with acidified methanol and dried under vacuum. It was then treated with water to remove polyacrylamide (PAM). Finally, the copolymer was dried to constant weight and present conversion was calculated. The rate of polymerization ( $R_p$ ) was calcu-

**TABLE I**  
Effect of Initiator Concentration on the Rate of Copolymerization on the rate of Citronellol and Acrylamide

Sample	[BPO] ( $10^3 \text{ mol l}^{-1}$ )	Conversion (%)	$R_p$ ( $10^6 \text{ mol l}^{-1}\text{s}^{-1}$ )
1	2.06	8.4	4.46
2	4.13	12.4	6.19
3	6.19	15.0	7.5
4	8.26	17.1	8.7
5	10.33	20.3	10.0

[Citronellol] =  $1.28 \text{ mol l}^{-1}$ ; [AM] =  $2.1 \text{ mol l}^{-1}$ ; Copolymerization time = 1 h; Copolymerization temperature =  $(80 \pm 0.1)^\circ\text{C}$ .

lated from the slope of the graph between percent conversion and time.

The viscosity measurements were made with ubbelohde viscometer at  $\pm 0.5^\circ\text{C}$ . The spectral analysis IR and  $^1\text{H}$  MNR were recorded with Perkin-Elmer 599 B (with KBr pellets) and Varian 100 HA, Jeol LA 400 LA spectrophotometer, respectively. The gel permeation chromatography (GPC) studies were made with water 200 model using THF as solvent. DSC curve was carried out on a DuPont V4.1C Model 2000 at a heating rate  $100^\circ\text{C}/\text{min}$  under nitrogen atmosphere. The monomer reactivity ratios were determined with the help of peak area in the NMR spectra by using Kelen-Tüdös method.<sup>21</sup>

## RESULTS AND DISCUSSION

It has been observed that few monomers do not undergo homopolymerization due to steric hindrance,<sup>22</sup> low stabilization energy between monomer and free radicals in transition state, excessive chain transfer termination of cyclization as in case of 1,2 disubstituted ethylene,<sup>23</sup> maleic anhydride, fumarates, and vinyl ethers. Citronellol too does not homopolymerize under experimental conditions.

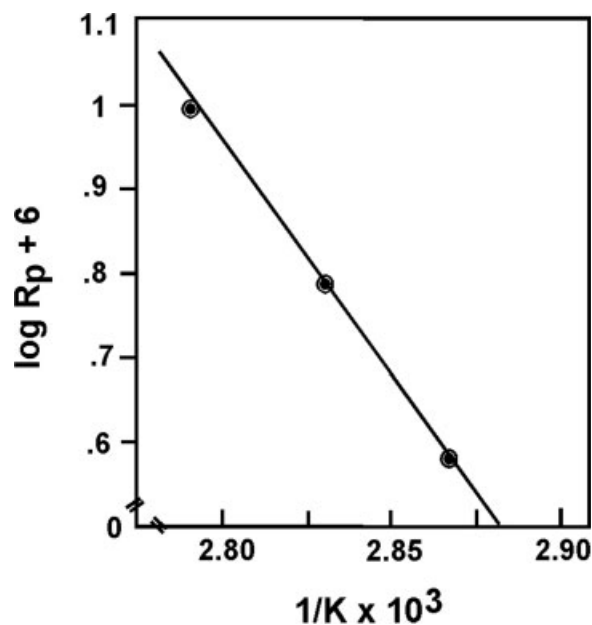
The kinetic of copolymerization has been studied by varying [BPO] from  $2.06 \times 10^{-3}$  to  $10.33 \times 10^{-3} \text{ mol l}^{-1}$ , keeping the concentration of citronellol and AM constant at 1.28 and 2.1  $\text{mol l}^{-1}$ , respectively. The reaction proceeds with short induction period of about  $3 \pm 1$  min. (Fig. 1). It is clear that the  $R_p$  is a direct function of the concentration of initiator and the exponent value of the initiator, obtained from a linear graph of  $\log R_p$  versus  $\log$  concentration of BPO,  $0.5 \pm 0.01$  (Table I).

The effect of [citronellol] on  $R_p$  has been studied by varying [citronellol] from 0.25 to 2.30  $\text{mol l}^{-1}$ , where [AM] and [BPO] were kept constant at 2.1 and  $4.13 \times 10^{-3} \text{ mol l}^{-1}$ , respectively. It is noticed that the  $R_p$  is directly proportional to [citronellol]. A plot between

**TABLE II**  
Effect of Concentration of Comonomer on the Rate of Copolymerization using BPO

Sample	[Citronellol] ( $\text{mol l}^{-1}$ )	[AM] ( $\text{mol l}^{-1}$ )	Conversion (%)	$R_p$ ( $10^6 \text{ mol l}^{-1}\text{s}^{-1}$ )
6	0.258	2.1	9.03	4.3
7	0.769	2.1	10.02	5.2
2	1.28	2.1	12.4	6.1
8	1.79	2.1	14.7	7.0
9	2.30	2.1	17.4	8.3
10	1.28	0.7	7.7	3.7
11	1.28	1.4	9.8	4.7
12	1.28	2.8	15.1	7.2
13	1.28	3.5	22.4	10.7

[BPO] =  $4.13 \times 10^{-3} \text{ mol l}^{-1}$ ; Copolymerization time = 1 h; Copolymerization temperature =  $(80 \pm 0.1)^\circ\text{C}$ .



**Figure 2** Arrhenius plot of rate of polymerization versus polymerization temperature; [BPO] =  $4.13 \times 10^{-3}$  mol l $^{-1}$ , [Citro] = 1.196 mol l $^{-1}$ ; [AM] = 2.1 mol l $^{-1}$ ; Copolymerization time = 1 h.

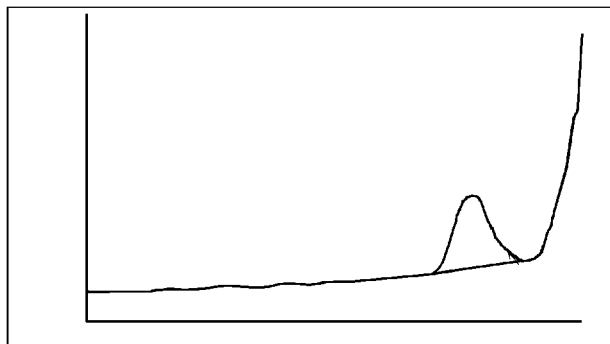
$\log R_p$  and  $\log[\text{citronellol}]$  is linear, the slope of which gives the following relationship (Table II):

$$R_p \propto [\text{citronellol}]^{1.0}$$

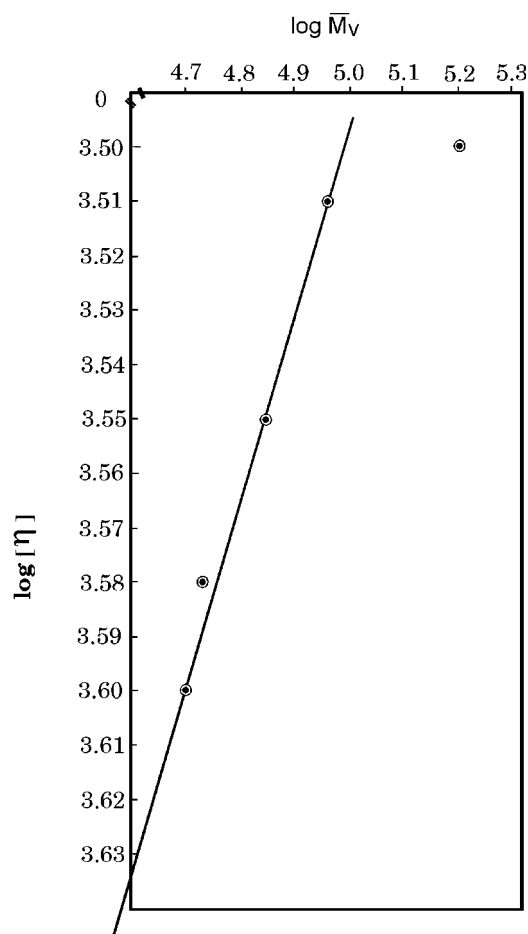
The effect of [AM] on the  $R_p$  has been studied by varying [AM] from 0.7 to 3.5 mol l $^{-1}$ , where [citronellol] and [BPO] were kept constant at 1.28 and  $4.13 \times 10^{-3}$  mol l $^{-1}$ , respectively. It is noticed that the  $R_p$  is directly proportional to [AM]. A plot between  $\log R_p$  and  $\log[\text{AM}]$  is linear, the slope of which gives the following relationship (Table II):

$$R_p \propto [\text{MMA}]^{1.0}$$

The intrinsic viscosity of the copolymers increase with increase in comonomer concentration. Further, the termination is bimolecular in nature as the linear



**Figure 3** GPC graph of the copolymer (Sample 2).



**Figure 4** Plot of  $\log[\eta]$  versus  $\log M_v$ .

plot between the reciprocal of  $\eta_{\text{int}}$  against the square root of BPO concentration passes through origin.

The rate of copolymerization increases with increase in temperature and the overall activation energy is computed as 44 kJ mol $^{-1}$  from the slope of Arrhenius plot<sup>24</sup> of  $\log R_p$  versus  $1/T$  (Fig. 2).

The Mark Houwink equation

$$[\eta] = k[M]^\alpha$$

**TABLE III**  
GPC Parameters of the Copolymerization of Citronellol with AM using BPO as Initiator

Sample	$[\eta]$ ( $10^4$ Poise)	$M_v$
12	3.08	91,725
13	3.16	162,382
9	2.81	70,658
2	2.60	53,787
3	2.50	50,390

[BPO] =  $4.13 \times 10^{-3}$  mol l $^{-1}$ ; Copolymerization time = 1 h; Copolymerization temperature =  $(80 \pm 0.1)^\circ\text{C}$ ; Viscosity temperature =  $25^\circ\text{C}$ .

TABLE IV  
Composition of Copolymers

Sample	Molar ratio in monomer feed [AM]/[Citronellol]	Conversion (%)	Molar ratio in copolymer composition [AM]/[Citronellol]
2	1.64	12.4	1.01
11	1.09	9.8	1.01
12	2.18	15.1	1.02
7	2.73	10.0	1.03
8	1.17	14.7	1.01

relates the intrinsic viscosity  $[\eta]$  of a polymer to its molecular weight  $[M]$ , which is used to calculate the empirical constant  $K$  and  $\alpha$ . A typical GPC curve is shown in Figure 3. The value of  $K$  and  $\alpha$  are determined from the intercept and the slope of the plot between  $\log M_v$  versus  $\log[\eta]$  for copolymers (Fig. 4). The values of  $K$  and  $\alpha$  are  $2.3 \times 10^{-4}$  and 0.33, respectively, (Table III).

#### Characterization of copolymer

##### Infrared spectroscopy

The IR spectra of the copolymer shows bands at  $3427 \text{ cm}^{-1}$  for alcoholic group of citronellol and at  $1710 \text{ cm}^{-1}$  for amide group of AM. (Fig. 5).

##### Nuclear magnetic resonance spectroscopy

The peaks of  $-\text{OH}$  group<sup>25</sup> are in the range of  $7\delta$  to  $7.7\delta$  in the NMR spectra of citronellol as well copolymer of citronellol and AM.

The NMR spectra of pure citronellol (I) and those of copolymers (II) (Fig. 6) shows following peaks.

I	(1H, OH)	Triplet	7-7.7 $\delta$
	(3H, CH <sub>3</sub> )	Triplet	0.9 $\delta$
	(2H, CH <sub>2</sub> )	Multipet	1.2-2.2 $\delta$
II	(1H, CH)	Multipet	1.8-2.2 $\delta$
	(1H, OH)	Triplet	7-7.7 $\delta$
	(3H, CH <sub>3</sub> )	Triplet	1 $\delta$
	(2H, CH <sub>2</sub> )	Multipet	1.2-2.2 $\delta$
	(1H, CH)	Singlet	1.8-2.2 $\delta$
	(2H, OCNH <sub>2</sub> )	Singlet	6.3-7 $\delta$

##### Differential scanning calorimetry

The DSC curve indicates the glass transition temperature ( $T_g$ ) of citronellol-*alt*-acrylamide as  $102^\circ\text{C}$  (Fig. 7).

##### Thermal analysis

The typical TGA curve for copolymer (Fig. 8) exhibits weight loss with temperature.<sup>26,27</sup> The thermal behavior data are as follows:

- Onset of major weight loss  $359.52^\circ\text{C}$ ; completion of major weight loss  $440^\circ\text{C}$ .

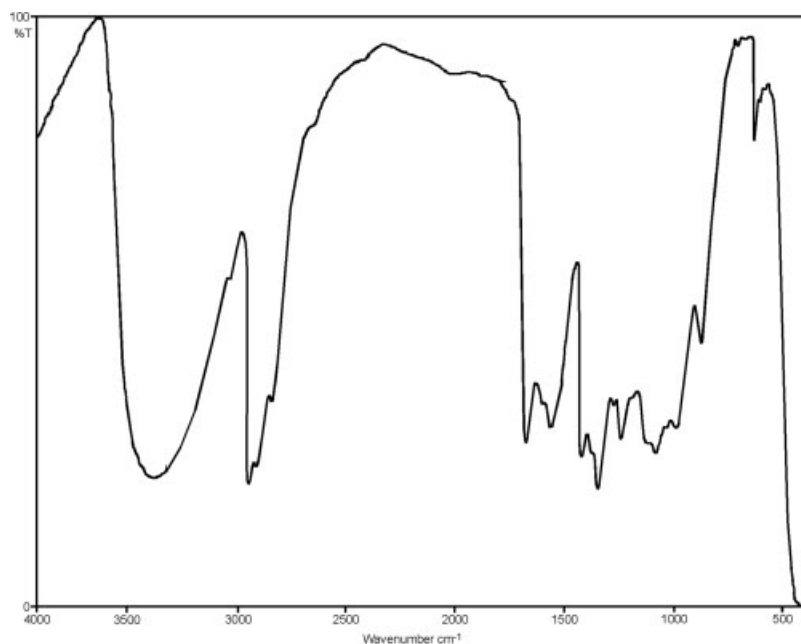
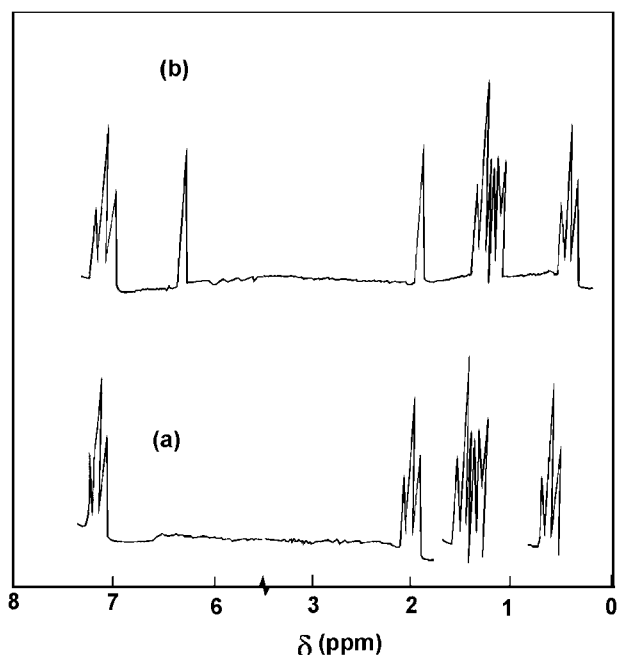


Figure 5 IR spectrum of the copolymer (Sample 2).



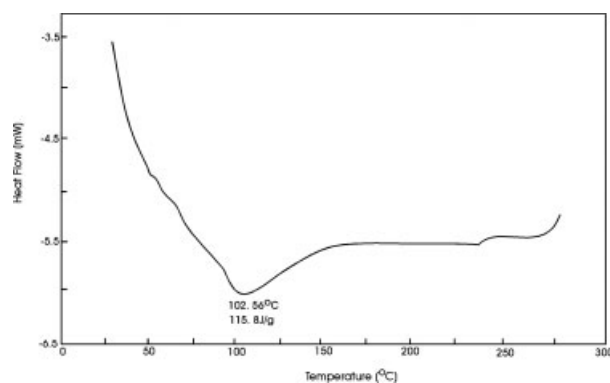
**Figure 6** NMR spectrum of (a) monomer citronellol and (b) copolymer using Sample 2.

- b. Total weight loss in the range 35–455°C = 94.84%  
 c. Weight loss at a given range  
 i. (25–150)°C – 2%  
 ii. (200–360)°C – 4%  
 iii. (360–455)°C – 94.84%

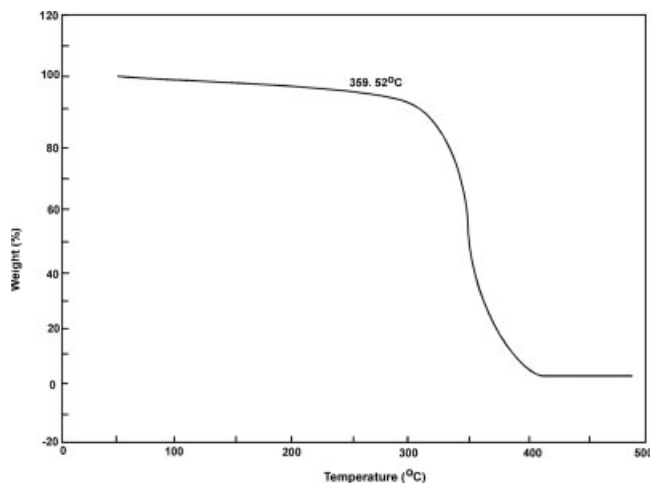
#### Copolymer composition and values of reactivity ratios

The relative peak areas of amide and alcoholic protons in the NMR spectra of copolymer have been used to calculate the copolymer composition (Table IV). The Kelen–Tüdös approach is used for evaluation of reactivity ratios  $r_1$  and  $r_2$  for the monomer pair according to

$$\eta = r_1 \xi - \frac{r_2(1 - \xi)}{\alpha}$$



**Figure 7** DSC curve of the copolymer (Sample 2).



**Figure 8** TGA curve of the copolymer (Sample 2).

$$\text{where } \eta = \frac{G}{(\alpha + H)} \quad \text{and} \quad \xi = \frac{H}{\alpha + H}$$

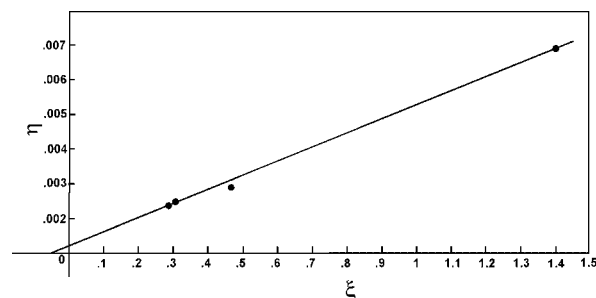
The value of  $\alpha$  is calculated by taking the square root of the product of the highest and the lowest value of  $H$  for copolymerization series. The variable  $G$  and  $H$  are determined by

$$G = \frac{[M_1]/[M_2][d[M_1]/d[M_2] - 1]}{d[M_1]/d[M_2]}$$

$$H = \frac{[M_1]/[M_2]^2}{d[M_1]/d[M_2]}$$

The parameter  $\alpha$  is calculated by taking the square root of the product of the lowest and highest values of  $H$  for copolymerization series. Graphical evaluation for AM/citronellol yield values of  $r_1 = 0.0045$  and  $r_2 = 0.0005$  (Fig. 9) (Table V).

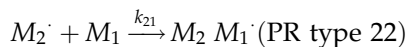
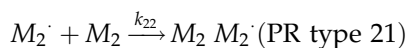
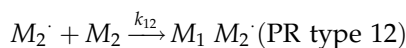
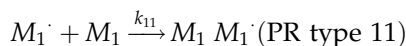
The product of  $r_1 r_2$  is nearly zero, which is a sign of alternating copolymerization.



**Figure 9** Kelen–Tüdös plot of citronellol and AM for determination of reactivity ratio.

TABLE V  
Reactivity Parameters

$r_1$	$r_2$	$r_1 r_2$	$Q_2$	$e_2$
0.0045	0.0005	$2.25 \times 10^{-6}$	0.43	1.07



$M_1 \cdot$  = Acrylamide

$M_2 \cdot$  = Citronellol

$$r_1 = k_{11}/k_{12} \quad \text{and} \quad r_2 = k_{22}/k_{21}$$

By the values of  $r_1$  and  $r_2$ , it is clear that  $r_1$  and  $r_2$  are less than 1, i.e., the propagation reaction type 12 and 21 are preferred to type 11 and 22. The value of  $r_2$  may be taken as nearly zero, which shows that the probability of propagation reaction type 22 is very less or somewhat impossible and hence, a chain ending with  $M_2 \cdot$  will add only a  $M_1 \cdot$  due to the fact that no homopolymerization of  $M_2$  is obtained.

The  $e_2$  and  $Q_2$  values for citronellol were calculated using  $e_1 = 1.30$  and  $Q_1 = 1.18$  assumed for AM using the following equation.

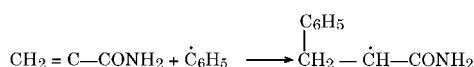
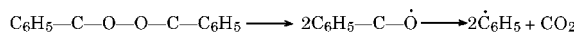
$$e_2 = e_1 \pm (\log r_1 r_2)^{0.5}$$

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

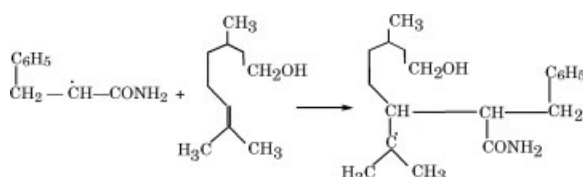
### Mechanism

It has been well reported that  $>C=C<$  is more susceptible than alcoholic O—H bond and therefore  $\pi$  bond takes part in polymerization. The speculative mechanisms are as follows:

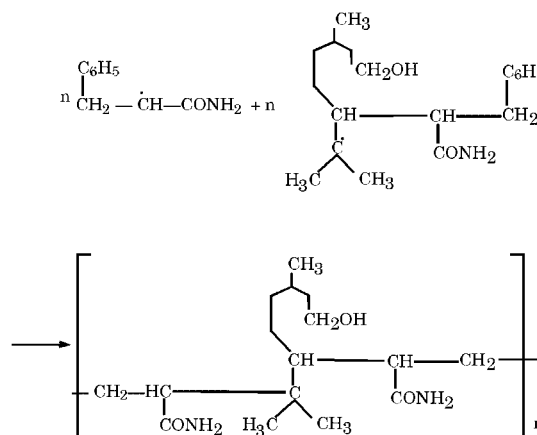
### Initiation



### Propogation



### Termination



### CONCLUSIONS

From the above work it is concluded that citronellol can be successfully copolymerized with AM using radical initiator, resulting in the formation of an alternating copolymer, which has  $T_g$  value as  $102^\circ\text{C}$ . The copolymer contains pendent alcoholic group, which is significant as functional and optically active polymer.

Authors thank Dr. R. P. Singh, Director, Harcourt Butler Technological Institute, Kanpur for providing necessary facilities.

### References

- Bhattacharya, N. S.; Maldas, D. J Polym Sci Polym Chem Edn 1983, 21, 3291.
- Hocking, B. M.; Klimchuk, A. K.; Lowen, S. J Polym Sci Part A: Polym Chem 2000, 38, 3128.
- McCormik, C. L.; Chen, S. G. J Polym Sci Polym Chem Edn 1984, 22, 3633.
- Mayer, R. C.; Thouvenot, R.; Lalot, T. Macromolecules 2000, 33, 4433.
- Shukla, A.; Srivastava, A. K. High Perform Polym 2003, 15, 243.
- Pietila, H.; Sivolo, A.; Seffer, H. J Polym Sci Part A-1: Polym Chem 1970, 3, 727.
- Huet, J. M.; Marechal, E. Comp Rend Acad Sci Paris 1970, 271, 1058.
- Pandey, P.; Srivastava, A. K. J Chem 2003, 42A, 68.
- Pandey, P.; Srivastava, A. K. J Polym Res, to appear.
- Pandey, P.; Srivastava, A. K. Designed Mono Polym 2003, 6, 197.
- Shukla, A.; Srivastava, A. K. J Macromol Sci 2003, 40, 61.
- Yadav, S.; Srivastava, A. K. J Polym Sci Part A: Polym Chem 2003, 41, 1700.
- Sharma, S.; Srivastava, A. K. J Macromol Sci Chem 2003, 40, 593.
- Sharma, S.; Srivastava, A. K. Ind J Chem Tech 2005, 12, 62.
- Sharma, S.; Srivastava, A. K. Eur Polym J 2004, 40, 2235.

16. Pathak, S.; Srivastava, A. K. *Designed Mono Polym* 2005, 8, 409.
17. Dodge, C. J. *Am Chem J* 11, 463 (1989).
18. Inoue, S. *J Chem Soc Chem Commun* 1987, 1036.
19. Overberger, G. C.; Yamamoto, N. *J Polym Sci Part A-1: Polym Chem* 1966, 4, 3101.
20. Vogel, I. A. *A Text Book of Practical Organic Chemistry*; Longman Group: London 1966.
21. Kelen, T.; Tüdös, F. *J Macromol Sci Chem Edn* 1975, 9, 1.
22. Ham, M. G. *Copolymerization*; Interscience: New York, 1964.
23. Miller, L. M. *The Structure of Polymer*; Reinhold Publishing Corporation: London, 1968; p 450.
24. Bhatnagar, U.; Srivastava, A. K. *Polym Int* 1991, 25, 13.
25. In *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Jackman, M. L.; Sterhell, S, Eds; Chapter 3-7, p 215.
26. Gronowski, A.; Wojtczak, Z. *Makromol Chem* 1985, 190, 2063.
27. Wojtczak, Z.; Gronowski, A. *Makromol Chem* 1985, 186, 139.