

Kinetics and Monomer Reactivity Ratios of *N*-Vinylpyrrolidone and α -Terpineol

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ABSTRACT: The radical copolymerization of α -terpineol with *N*-vinylpyrrolidone (*N*-VP) in dioxane at $(80 \pm 0.1)^\circ\text{C}$ for 1 h in the presence of benzoylperoxide follows ideal kinetic and results in the formation of random copolymer as evidenced from the value of reactivity ratios as r_1 (*N*-VP) = 0.23 and r_2 (α -terpineol) = 0.025, which have been calculated by the Kelen-Tüdös method. The overall activation energy is computed to be 28 kJ/mol. The FTIR spectrum of

the copolymer shows the presence of bands at 3507 cm^{-1} due to alcoholic group and 1717 cm^{-1} due to $> \text{C}=\text{O}$ group. The Alfrey-Price parameters for α -terpineol has been calculated as 0.024 and -2.66 . © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 476–481, 2007

Key words: kinetics; reactivity ratios; copolymerization; α -terpineol; *N*-vinylpyrrolidone

INTRODUCTION

N-vinylpyrrolidone is best characterized and most widely studied monomer. A search of literature reveals that work on its copolymerization with several vinylmonomers such as 2-hydroxyethylmethacrylate,¹ glycidylmethacrylate,² vinylcyclohexane,³ methacrylate,⁴ vinylacetate⁵ is voluminous. However, it is almost devoid of reports regarding copolymerization of *N*-VP with terpenoids although in recent years, the copolymerization of monocyclic monoterpenoids as functional comonomer has been achieved to yield new class of functional polymers.^{6–12} The incorporation of functional groups into polyolefins is very useful and general method of modifying the chemical and physical properties of corresponding polymers.¹³ Depending on number and nature of the anchored functions, properties such as solubility, thermal and surface properties, hydrophilic/lipophilic balance, or degradation kinetics can be modified.^{14–16} Here, an attempt has been made to study the kinetic and mechanism of copolymerization of α -terpineol (a monocyclic monoterpenoid, containing one double bond and one alcoholic group) with *N*-vinylpyrrolidone in dioxane initiated by benzoylperoxide (BPO) at 80°C . Furthermore, the copolymer formed is significant due to the functional properties.

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EXPERIMENTAL

Materials

N-vinylpyrrolidone (*N*-VP) (Merck-Schuchar'dt)^{17,18} and other solvents were purified by usual methods. α -Terpineol¹⁹ ($M = 154\text{ g/mol}$ 0.9 kg/L) boiling point = 103°C , refractive index²⁰ $n_D = 1.43$, was used after fractional distillation. Benzoylperoxide (BPO) was recrystallized twice from methanol followed by drying under vacuum.

Polymerization procedure

The dilatometric technique has been used to follow the copolymerization runs under nitrogen blanket. The polymerization was carried out at $(80 \pm 0.1)^\circ\text{C}$ for 1 h and the copolymer(s), precipitated with methanol and dried under vacuum. It was then refluxed with tetrahydrofuran to remove poly(*N*-VP). The copolymer was dried to constant weight and percent conversion was calculated. The rate of polymerization (R_p) was calculated from the slope of the graph between percent conversion and time.

Characterization

Viscosity measurements were made with an Ubbelohde suspension level viscometer at $(30 \pm 0.5)^\circ\text{C}$. The spectral analysis FTIR and ^1H NMR were recorded with Perkin-Elmer 599B (with KBr pellets) and Varian 100HA Jeol 400 LA Spectrometer, respectively. The thermogravimetric analysis (TGA) runs were carried out by using V5.1A Dupont 2100 analyzer, sample weight $\sim 10\text{ mg}$, at a heating rate $10^\circ\text{C}/\text{min}$.

TABLE I
Effect of Initiator and Monomer Concentration on the Rate of Copolymerization of α -Terpineol and *N*-Vinylpyrrolidone

Sample	[BPO] (10^3 mol L^{-1})	$[\alpha\text{-Terpineol}]$ (mol L^{-1})	[<i>N</i> -VP] (mol L^{-1})	% conv	R_p ($10^6 \text{ mol L}^{-1} \text{ s}^{-1}$)	$[\eta]$ (dL g^{-1})
1	2.03	0.907	1.57	2.62	3.4	0.042
2	6.09	0.907	1.57	5.4	4.23	0.040
3	10.16	0.907	1.57	9.15	6.77	0.037
4	14.20	0.907	1.57	13.00	7.19	0.033
5	18.29	0.907	1.57	17.00	11.0	0.027
6	10.16	0.907	0.31	4.7	2.13	0.021
7	10.16	0.907	0.94	8.4	4.77	0.024
8	10.16	0.907	2.20	11.0	12.15	0.031
9	10.16	0.907	2.83	14.5	16.46	0.035
10	10.16	0.19	1.57	4.31	7.3	0.019
11	10.16	0.58	1.57	7.3	2.86	0.022
12	10.16	1.36	1.57	10.1	8.30	0.026
13	10.16	1.75	1.57	13.2	13.83	0.029

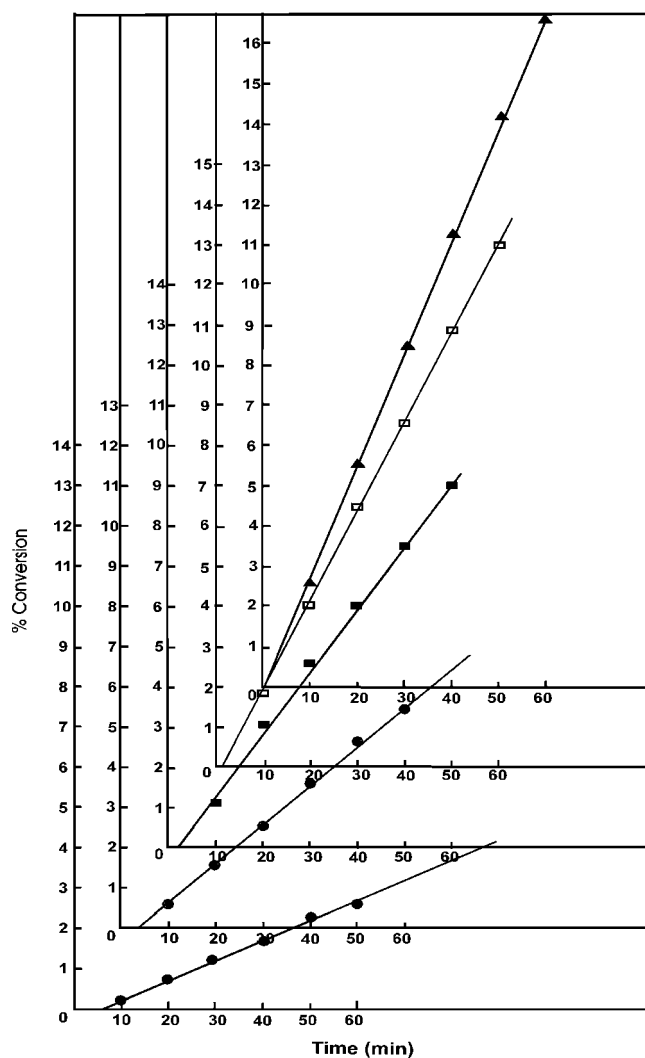


Figure 1 Time conversion plot in copolymerization of $[\alpha\text{-terpineol}]$ and [*N*-VP]. $[\alpha\text{-terpineol}] = 0.907 \text{ mol/L}^{-1}$, [*N*-VP] = 1.57 mol/L^{-1} , copolymerization time = 1 h; copolymerization temperature = 80 ± 0.1 [BPO] = $2.03 \times 10^{-3} \text{ mol/L}^{-1}$; 6.09×10^{-3} ; $10.16 \times 10^{-3} \text{ mol/L}^{-1}$; $14.20 \times 10^{-3} \text{ mol/L}^{-1}$; $18.29 \times 10^{-3} \text{ mol/L}^{-1}$.

RESULTS AND DISCUSSION

Some monomers do not undergo homopolymerization because of steric hindrance,^{21,22} low stabilization energy between monomers and free radicals in the transition state,²³ excessive chain transfer,²⁴ termination of cyclization, such as 1,2 disubstituted ethylene,²⁵ maleic anhydride, fumarates, and vinyl ethers. α -terpineol also does not homopolymerize under experimental conditions.

The kinetics of copolymerization has been studied by varying [BPO] from $2.03 \times 10^{-3} \text{ mol/L}^{-1}$ to $18.29 \times 10^{-3} \text{ mol/L}^{-1}$; keeping the concentration of α -terpineol and *N*-vinylpyrrolidone kept constant at 0.907 and 1.57 mol/L^{-1} (Table I), respectively. The reaction proceeds with short induction period of about 3–1 min. (Fig. 1). It is concluded that the R_p is a direct function

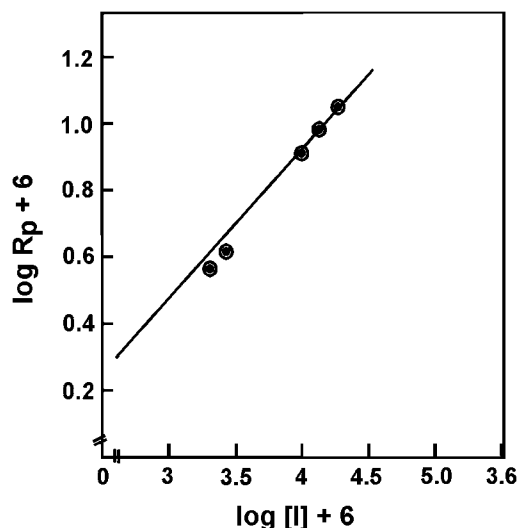


Figure 2 Relationship between the rate of copolymerization and [BPO]; $[\alpha\text{-terpineol}] = 0.97 \text{ mol/L}^{-1}$, [*N*-VP] = 1.57 mol/L^{-1} ; copolymerization time = 1 h, copolymerization temperature = $(80 \pm 0.1)^\circ\text{C}$.

of the initiator concentration and the exponent value of the initiator, obtained from a linear graph of $\log R_p$ vs. $\log [\text{BPO}]$ is 0.5 ± 0.01 (Table I; Sample 1–5, Fig. 2).

The effect of $[\alpha\text{-terpineol}]$ on the R_p has been studied by variation in the $[\alpha\text{-terpineol}]$ from 0.19 mol/L^{-1} to 1.75 mol/L^{-1} , since the $[\text{N-VP}]$ and $[\text{BPO}]$ were kept constant at 1.57 and $10.16 \times 10^{-3} \text{ mol/L}^{-1}$, respectively. The R_p is directly proportional to the $[\alpha\text{-terpineol}]$ (Table I; Sample 10–13, Fig. 3). The plot between $\log R_p$ vs. $\log [\alpha\text{-terpineol}]$ is linear, the slope gives order of reaction in unity.

The effect of the $[\text{N-VP}]$ on the R_p has also been studied with variation in the $[\text{N-VP}]$ from 0.31 to 2.83 mol/L^{-1} , since the $[\alpha\text{-terpineol}]$ and $[\text{BPO}]$ were kept constant at 0.907 and $10.16 \times 10^{-3} \text{ mol/L}^{-1}$, respectively. The R_p is directly proportional to the $[\text{N-VP}]$ (Table I; Sample 6–9, Fig. 4). A plot between $\log R_p$ vs. $\log [\text{N-VP}]$ is linear, the slope gives order of reaction is 1 ± 0.03 .

Effect of temperature

The rate of copolymerization increases with increasing temperature. The overall activation energy computed from the slope of Arrhenius plot²⁶ of $\log R_p$ versus $1/K$ is 28 kJ/mol (Fig. 5).

Characterization of the copolymer

FTIR spectroscopy

The FTIR spectrum of the copolymer shows bands at 3507 cm^{-1} due to $-\text{OH}$ stretching vibrations of $\alpha\text{-terpineol}$, at 1452 cm^{-1} a band assigned to $\text{C}-\text{H}$ bending vibrations, at 1279 cm^{-1} due to $\text{C}-\text{N}$ ring stretching

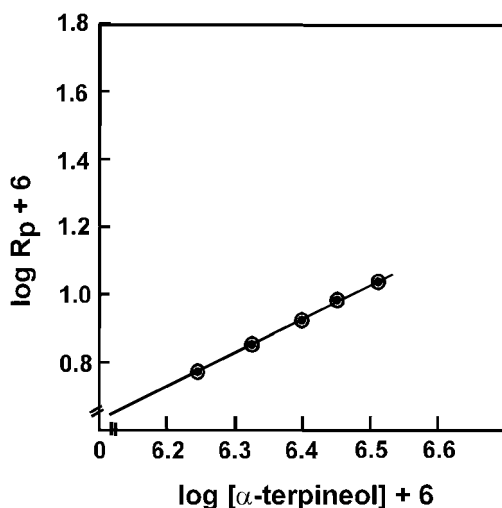


Figure 3 Relationship between the rate of copolymerization and $[\alpha\text{-terpineol}]$ with constant $[\text{N-VP}] = 1.57 \text{ mol/L}^{-1}$, $[\text{BPO}] = 10.16 \times 10^{-3} \text{ mol/L}^{-1}$; copolymerization time = 1 h , copolymerization temperature = $(80 \pm 0.1)^\circ\text{C}$.

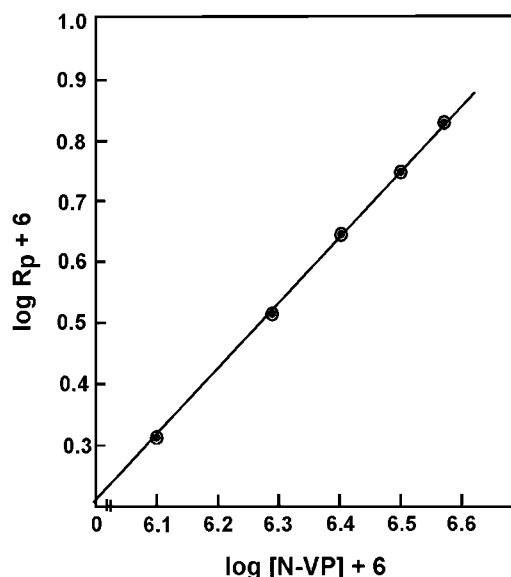


Figure 4 Relationship between the rate of copolymerization and $[\text{N-VP}]$ with constant $[\alpha\text{-terpineol}] = 0.907 \text{ mol/L}^{-1}$; $[\text{BPO}] = 10.16 \times 10^{-3} \text{ mol/L}^{-1}$; copolymerization time = 50 min , copolymerization temperature = $(80 \pm 0.1)^\circ\text{C}$.

vibrations, at 600 cm^{-1} due to $\text{C}-\text{H}$ out of plane ring bending vibration, at 1420 cm^{-1} due to $-\text{OH}$ bending vibration, 3051 cm^{-1} due to $\text{C}-\text{H}$ stretching vibrations and at 1717 cm^{-1} due to normal $>\text{C}=\text{O}$ stretching vibration of N-VP units (Fig. 6).

^1H NMR 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 related phenomena of intermolecular exchange and hydrogen bonding. The appearance of signals in the

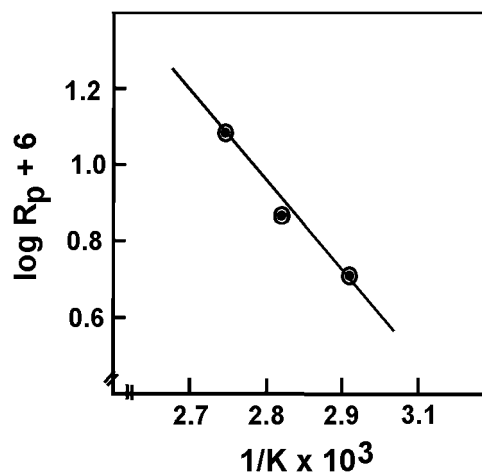


Figure 5 Arrhenius plot of rate polymerization versus polymerization temperature; $[\text{BPO}] = 10.16 \times 10^{-3} \text{ mol/L}^{-1}$; $[\alpha\text{-terpineol}] = 0.97 \text{ mol/L}^{-1}$, $[\text{N-VP}] = 1.57 \text{ mol/L}^{-1}$ copolymerization time = 1 h .

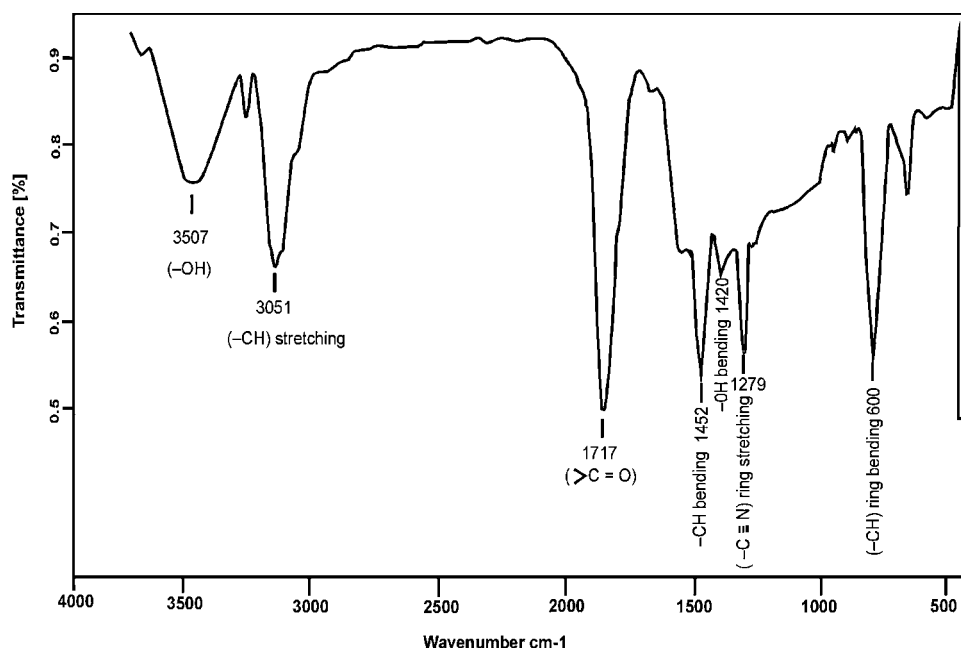


Figure 6 FTIR spectrum of the copolymer (Sample 3).

NMR spectra, that are due to hydroxyl protons with the species of small molecular weight, where intermolecular association is not hindered, generally resonate in the region of 3.3 δ for hydroxyl protons of methanol and at 5.4 δ for hydroxyl proton of ethanol.²⁷ However, with many large molecules, the hydroxyl protons often resonate near 8 δ , even at relatively high concentrations, partially due to steric effect and partially due to resonance stabilization. Therefore, the peaks for hydroxyl protons of α -terpineol appear in the range of 7.2–7.7 δ in the NMR spectra of α -terpineol as well as in the copolymer of α -terpineol and *N*-VP [Fig. 7(a,b)].

The NMR spectrum of α -terpineol [Fig. 7(a)] shows singlet at 7.2–7.7 δ (1H, OH); singlet at 0.9 δ (3H, CH₃); multiplet at 1.3–2.3 δ (2H, CH₂); triplet at 1.8–2.5 δ (1H, CH); triplet at 5.1–5.4 δ due to olefinic bond.

The NMR spectrum of *N*-VP¹ [Fig. 7(b)] shows multiplets at 1.2–2.8 δ (2H, CH₂); doublet at 3.7 δ (1H, CH).

¹H NMR spectra of the copolymer shows disappearance of peak at 5.1–5.4 δ (triplet) due to olefinic protons of α -terpineol; at 3.7 δ (doublet) due to olefinic bond in *N*-VP and appearance of additional peak at 2.5 δ (singlet) and 3.0 δ (triplet) of methyl and methylene protons of *N*-VP [Fig. 7(c)].

Copolymer composition and reactivity ratios

To calculate the reactivity ratios, the α -terpineol content has been calculated from the peak area of hydroxy protons in ¹H NMR and *N*-VP content from nitrogen percent by the elemental analysis of the copolymer samples (Table II). The Kelen-Tüdös²⁰

approach is used for evaluation of reactivity ratios, r_1 (*N*-VP) and r_2 (α -terpineol) for the monomer according to:

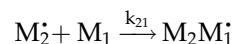
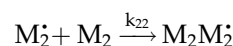
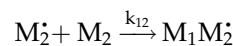
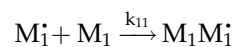
$$\eta = r_1 \xi - \frac{r_2(1 - \xi)}{\alpha}$$

where $\eta = \frac{G}{(\alpha+H)}$ and $\xi = \frac{H}{\alpha+H}$ the transformed variables G and H are given 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 α is calculated by the square root of the product of the lowest and highest values of H for the copolymerization series. The graphical evaluation for *N*-VP/ α -terpineol yield values of $r_1 = 0.23$ and $r_2 = 0.025$ (Fig. 8; Table III).



$M_1 = N$ -VP and $M_2 = \alpha$ -terpineol; $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$.

By the values of r_1 and r_2 , it is clear that r_1 and r_2 are less than one 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 zero, which shows that the probability of propagation reaction 22 is much less. Therefore, a chain ending with M_2 will add only M_1 due to the fact that no homopolymerization of M_2 takes place.

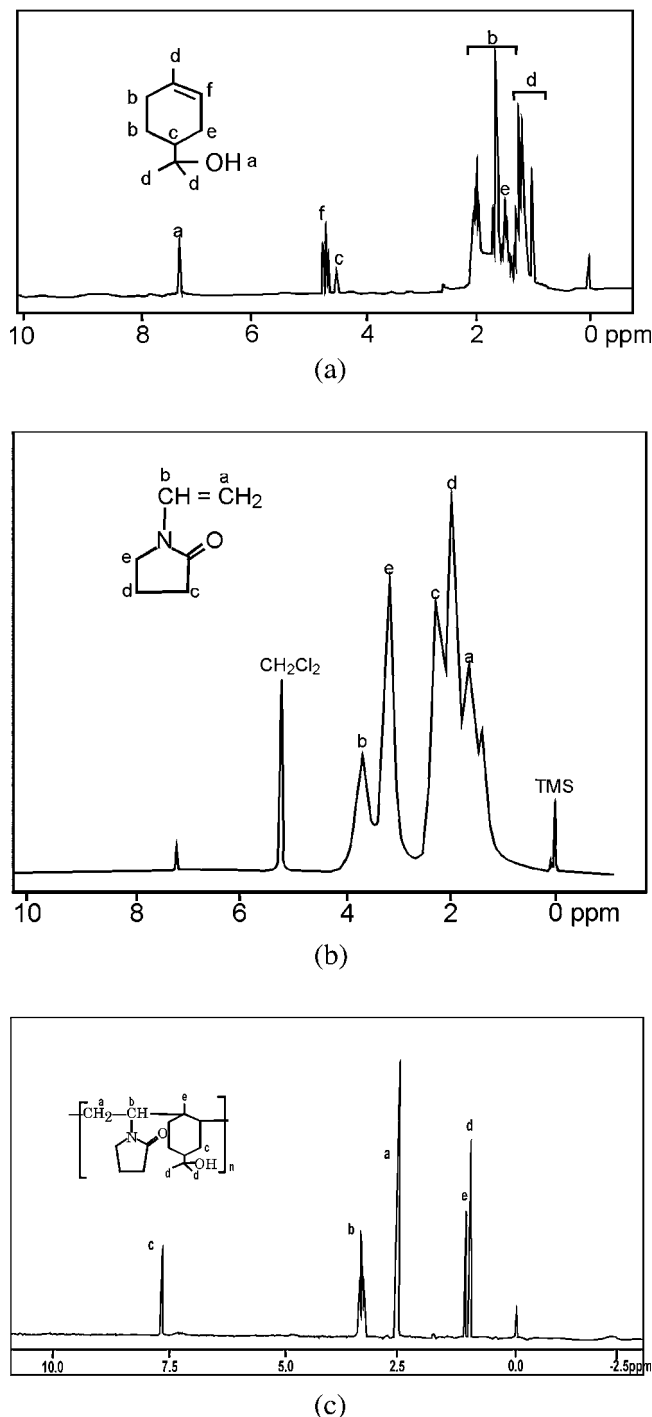


Figure 7 ¹H NMR Spectra of α-terpineol (a), N-VP (b), and the copolymer (c) (Sample 3).

TABLE II
Composition of Copolymers

Sample	Molar ratio in the monomer feed [N-VP]/[α-terpineol]	% conv	Mole fraction in the copolymer composition	
			[N-VP]	[α-Terpineol]
7	0.96	8.4	0.50	0.49
9	0.89	14.5	0.50	0.48
3	1.61	9.15	0.20	0.80
11	2.68	7.3	0.33	0.66
13	2.92	13.2	0.26	0.73

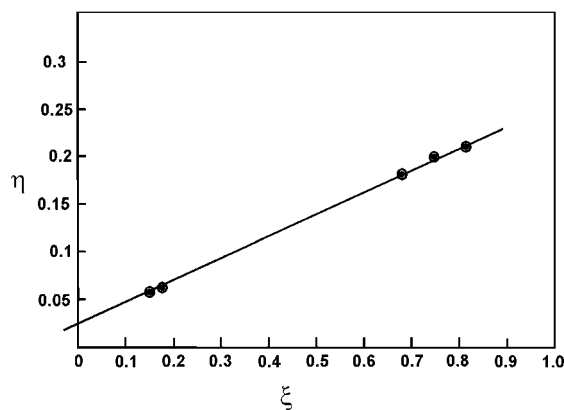


Figure 8 Kelen Tüdös plot of [α-terpineol] and [N-VP] for determination of reactivity ratios.

The value of e_2 and Q_2 has been calculated by using $e_1 = -1.17$ and $Q_1 = 0.093$ assuming for N-VP by following Alfrey-Price equation.³⁰

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

$$Q_2 = Q_1 / r_2 \exp[-e_1(e_1 - e_2)]$$

Q_2 value, less than one indicates that reactivity of α-terpineol is lower than that of N-VP.

Thermal gravimetric analysis

The TGA curve for copolymers (Fig. 9) exhibits weight loss with temperature.^{28,29} The thermal behavior data are as follows:

1. Onset major weight loss 163.27°C, completion of major weight loss 340°C.
2. Weight loss in the range 50–400°C = 20.43%.
3. The volatilization temperature is 190°C.

TABLE III
Reactivity Parameters

r_1	r_2	$r_1 r_2$	Q_2	e_2
0.23	0.025	0.005	0.024	-2.66

For N-VP, $e_1 = -1.17$ and $Q_1 = 0.093$.

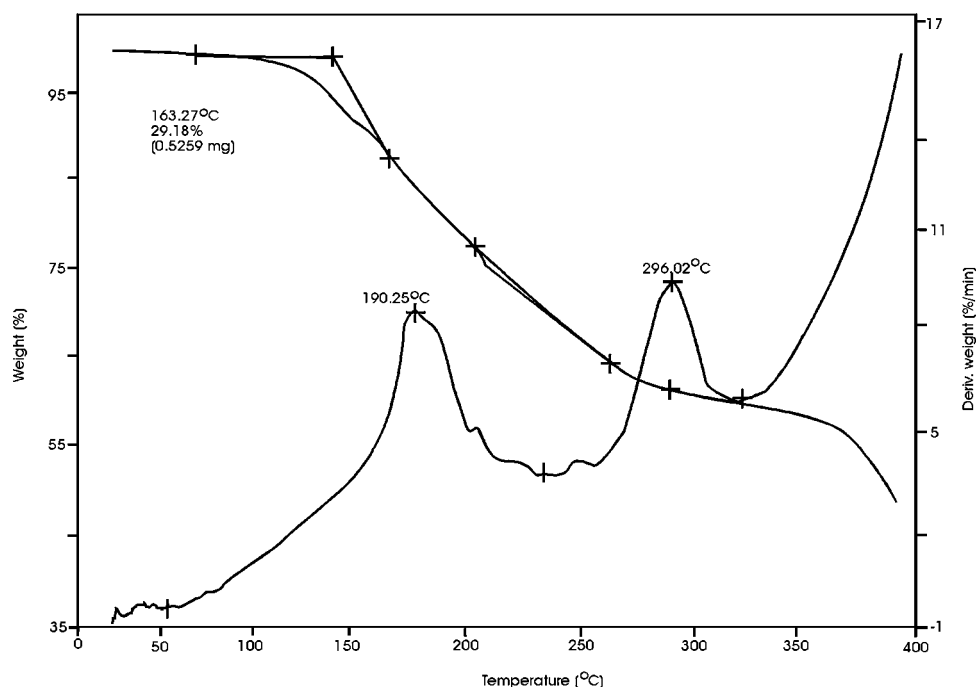


Figure 9 TGA curve of the copolymer (Sample 3).

CONCLUSIONS

The *N*-VP has been successfully copolymerized with α -terpineol, and results in the formation of random copolymers. The copolymer contains pendant alcoholic group, which is significant for a functional copolymer.

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References

- Liu, Z. F.; Rimmer, S. *Macromolecules* 2002, 35, 1200.
- Faragalla, M. M.; Hill, D. J. T.; Whittaker, A. K. *Polymer* 2002, 47, 421.
- Sanchez-Chaves, M.; Martinez, G.; Madruga, E. L.; Fernandez-Monreal, C. *J Polym Sci Part A: Polym Chem* 2002, 40, 1192.
- Gatica, N.; Gargallo, L.; Radic, D. *Eur Polym J* 2002, 38, 1371.
- Brar, A. S.; Kaur, R. *J Polym Sci Part A: Polym Chem* 2002, 40, 2225.
- Pandey, P.; Srivastava, A. K. *Polym Int* 2001, 50, 937.
- Pandey, P.; Srivastava, A. K. *Ind J Chem* 2003, A42, 68.
- Pandey, P.; Srivastava, A. K. *J Polym Sci Part A: Polym Chem* 2002, 40, 1243.
- Pandey, P.; Srivastava, A. K. *Eur Polym J* 2002, 38, 1709.
- Shukla, A.; Srivastava, A. K. *J Macromol Sci Chem* 2003, 40, 61.
- Yadav, S.; Srivastava, A. K. *J Polym Sci Part A: Polym Chem* 2003, 41, 81.
- Yadav, S.; Srivastava, A. K. *J Polym Res* 2002, 9, 265.
- Vogel, O. *J Macromol Sci Pure Appl Chem* 1996, A33, 963.
- Arshady, R. *J Macromol Sci Rev Macromol Chem Phys* 1992, C32, 10.
- Akelah, A.; Moet, A. *Functionalized Polymers and Their Applications*; Thomson Press: New Delhi, 1990.
- Bicak, N.; Senkal, B. F. *React Funct Polym Sci* 1996, 29, 123.
- Overberger, C. G.; Yamamoto, N. *J Polym Sci Part A-1: Polym Chem* 1966, 4, 3101.
- Vogel, A. I. *A Text Book of Practical Organic Chemistry*, 5th ed.; Longman: London, 1994; p 395.
- Inoue, S. *J Chem Soc Chem Commun* 1994, 1036.
- Kelen, T.; Tüdös, F. *J Macromol Sci Chem Ed* 1975, 9, 1.
- Harm, G. M. *Copolymerization*; Interscience: New York, 1964.
- Mayo, F. R.; Lewis, F. M.; Walling, C. *Faraday Discuss Sci* 1947, 2, 285.
- Hayashi, K. *J Polym Sci* 1956, 20, 537.
- Joshi, R. M. *Macromol Chem* 1962, 55, 35.
- Miller, M. L. *The Structure of Polymer*; Reinhold: London, 1968; p 450.
- Bhatnagar, U.; Srivastava, A. K. *Polym Int* 1991, 25, 13.
- Jackman, L. M.; Sternhell, S. *Application of NMR Spectroscopy in Organic Chemistry*; 1970; Vol. 2, pp 3-7, 215, 216.
- Gronowski, A.; Wojtczak, Z. *J Therm Anal Cal* 1983, 2, 233.
- Balcerowiak, W.; Hetper, J.; Beres, J.; Olkoswka, J. *J Therm Anal Cal* 1977, 11, 101.
- Gronowski, A.; Wojtczak, Z. *Macromol Chem* 1985, 186, 139.