Functional Copolymer of Geraniol and Acrylonitrile: Synthesis and Characterization

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ABSTRACT: The radical copolymerization of acyclic terpene namely geraniol [GER] with acrylonitrile [AN] in DMF at $(70 \pm 0.1)°C$ for 1 h, using benzoylperoxide (BPO) as an initiator has been carried out under inert atmosphere of nitrogen. The kinetic expression for reaction is $R_p \propto [BPO]^{0.5} [AN]^{1.0} [GER]^{1.0}$. The IR spectrum of the copolymer shows bands at 3432 and at 2244 cm^{-1} due to —OH group of GER and —CN group of AN, respectively. The ^{13}C-NMR spectrum shows peaks at 73–75 δ ppm and 116–120 δ ppm due to —OH group of GER and —CN group of AN, respectively. The thermogravimetric analysis and differential scanning calorimetry study shows that copolymer is thermally stable up to 407°C and has glass transition temperatures (T_g) 56°C. The reactivity ratios r_1 (AN) and r_2 (GER) have been calculated as 0.05 and 0.005, respectively. The Alfrey-Price Q-e parameter for GER has been calculated as 0.094 and −2.0, respectively. The molecular weights of the copolymers have been evaluated by gel-permeation chromatography. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 892–899, 2008

Key words: geraniol; acrylonitrile; functional; FTIR spectrum; glass transition temperature

INTRODUCTION

Chemical diversity in natural products is an immensely rich source of new pharmaceutical agrochemicals, industrial raw materials, and other economically important chemicals. Among the various class of natural products, the terpene has occupied a special position because of its biological and commercial applications.[1,2] A search of literature reveals that in the recent years the terpenes have been copolymerized with different vinyl monomer yielding optically active[3,4] and functional polymers[4–12] by our laboratory, i.e., limonene-*co*-vinyl acetate,[3] linalool-*co*-acrylamide,[4] citronellol-*co*-vinyl acetate,[5] linalool-*co*-acrylonitrile,[6] linalool-*co*-styrene,[7] α-terpineol-*co*-styrene,[8] α-terpineol-*co*-methyl methacrylate,[9] limonene-*co*-styrene,[10] linalool-*co*-methyl methacrylate,[11] and limonene-*co*-acrylonitrile.[12]

Acrylonitrile (AN) has found its way into great variety of polymeric compositions based on its polar nature and reactivity. AN copolymerizes readily with electron donor and electron acceptor monomers such as styrene,[13] butadiene,[14] vinyl acetate,[15] N-vinyl pyrrolidone,[16] etc., which are used as barrier films, laminater, viscosity modifier, environmentally degradable polymers, plasticizer, artificial organs, etc., but less work has been published with terpene viz. linalool-*co*-acrylonitrile[6] and limonene-*co*-acrylonitrile,[12] citronellol-*co*-acrylonitrile,[17] containing such functional groups as hydroxyl ones.

The incorporation of functional groups into polyolefins is very useful and general method of modifying the chemical and physical characteristics of corresponding polymers. Depending on the number and nature of anchored functions, properties, hydrophilic/lyophilic balance or degradation, kinetics can be drastically modified. Some comprehensive work has been published on functional polymers,[18,19] describing the modification of hydroxyl functions.[20,21] GER-*co*-AN could also be very useful because it may be used to graft numerous functions through its hydroxyl group.

Thus in this study, copolymer bearing different organic functions can be prepared by chemical modifications of the pendent—hydroxyl group. It establishes the preparation of specific polymers allowing the modifications of the physio-chemical properties of the initial copolymer, leading to new tailor-made polymers.

EXPERIMENTAL

The acrylonitrile (AN)[22] (Ranbaxy) and solvent (DMF)[23] were purified by usual method. Geraniol (GER) (Fluka) (bp = 103°C, R.I. = 1.4562) was used after fractional distillation. Benzoylperoxide (BPO) was recrystallized twice from chloroform and then dried *in vacuo*.

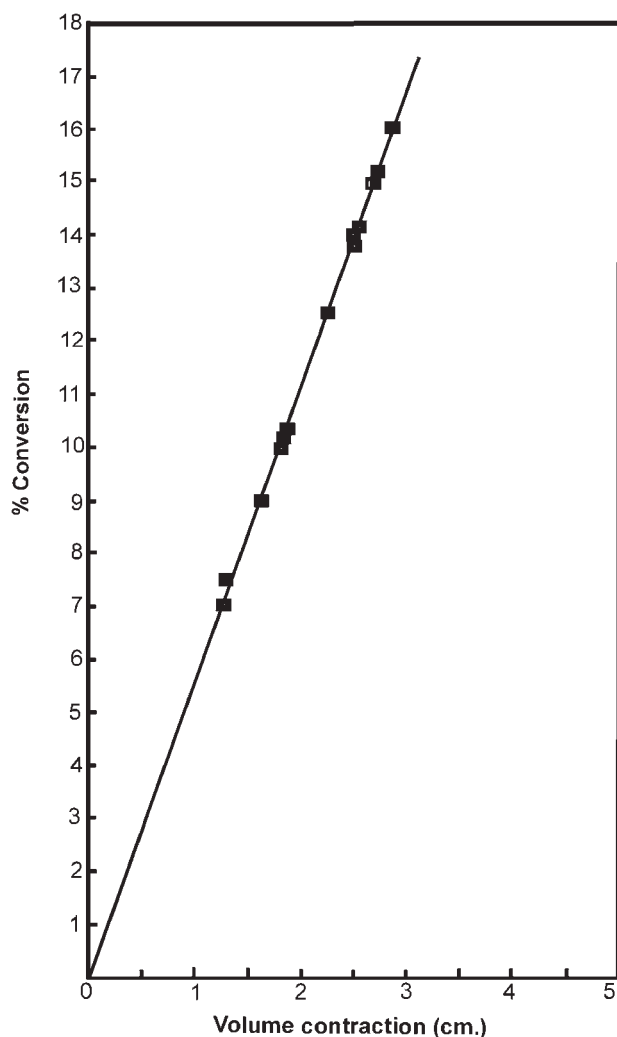*Correspondence to:* A. K. Srivastava (akspolym@rediffmail.com).

Figure 1 Relationship between percent conversion versus volume contraction. Copolymerization time = 1 h, copolymerization temperature (70 ± 0.1) °C.

Polymerization procedure

All the reactions were performed in dilatometer (Cap. dia. 2 mm, Cap. length 9.5 cm, bulk capacity 2.5 mL) using [BPO] from 4.13×10^{-3} mol L^{-1} to 15.15×10^{-3} mol L^{-1}, [GER] from 0.19 to 1.68 mol L^{-1} and [AN] 0.503 to 4.52 mol L^{-1} in DMF at (70 ± 0.1)°C for 60 min under oxygen free condition to limit the percentage conversion up to 16% (Fig. 1). The copolymer(s) isolated by precipitation into acidified methanol and dried *in vacuo* were refluxed with dioxane to remove polyacrylonitrile, and no weight loss was observed. Finally, the copolymer(s) were dried to constant weight. The rate of polymerization (R_p) was calculated from the slope of graph between percent conversion and time (min).

Intrinsic viscosities of the copolymers were measured in DMF at (30 ± 0.2)°C using Ubbelohde viscometer. FTIR, ^{1}H-NMR, ^{13}C-NMR spectral analysis were recorded with Perkin-Elmer 599 B (with KBr

pellets), and Varian 100 HA JEOL 400 LA spectrometer using CDCl$_3$ as solvent and TMS as an internal reference, respectively. Differential scanning calorimetry (DSC) was carried out on DuPont V4.1C Model 2000 at the heating rate 10°C min^{-1} under nitrogen atmosphere and gel permeation chromatography studies were made with E. Merck RI-L-7490 instrument using styragel column and tetrahydrofuran as elution solvent.

RESULT AND DISCUSSION

There are series of monomers, such as maleic anhydride, fumarates, vinyl ethers, and 1,2 disubstituted ethylene which do not homopolymerize because of steric hindrance,[24,25] low stabilization energy of the propagation transition state,[26] and excessive chain transfer.[27] Geraniol (GER) too does not homopolymerize under experimental condition.

The kinetics of copolymerization has been studied by varying benzoylperoxide [BPO] from 4.13×10^{-3} mol L^{-1} to 15.15×10^{-3} mol L^{-1}, keeping [GER] and acrylonitrile [AN] constant at 0.93 and 2.5 mol L^{-1}, respectively. The reaction proceeds with short induction period of 1–4 min. The R_p is a direct function of [BPO] and the exponent value, determined from the slope of the plot of the dependence of log R_p versus log [BPO], is 0.5 ± 0.01 (Fig. 2, Table I).

The effect of [AN] on the R_p has been studied by varying [AN] from 0.503 to 4.52 mol L^{-1}, keeping [GER] and [BPO] constant at 0.93 mol L^{-1} and
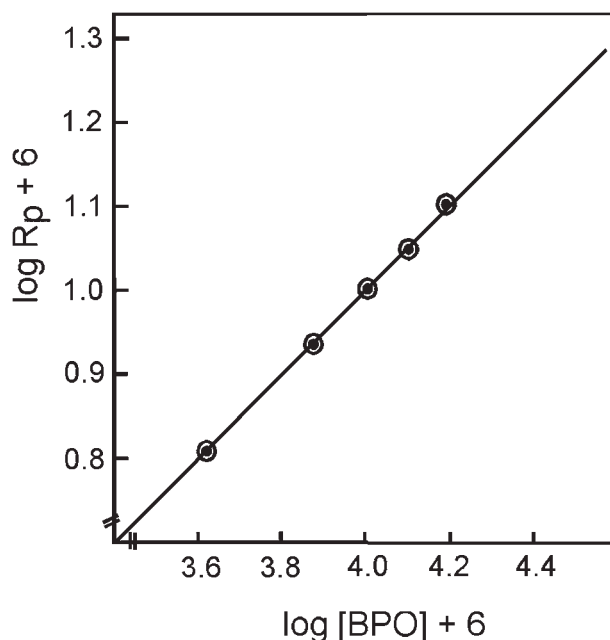

Figure 2 Relationship between the rate of poylmerization and [BPO] with constant [GER] = 0.93 mol L^{-1}, [AN] = 2.5 mol L^{-1}, copolymerization time = 1 h, copolymerization temperature (70 ± 0.1) °C.

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TABLE I
Effect of Concentration of Initiator and Comonomer(s) on the Rate of Polymerization

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Sample	[BPO] $\times 10^3$ (mol L^{-1})	[AN] (mol L^{-1})	[GER] (mol L^{-1})	Conv. (%)	$R_p \times 10^6$ (mol L^{-1} s^{-1})	η_{int} (dLg^{-1})
1	4.13	2.5	0.93	7.5	7.89	0.033
2	6.88	2.5	0.93	10.2	10.9	0.028
3	9.64	2.5	0.93	12.6	12.6	0.026
4	12.4	2.5	0.93	14.0	14.1	0.020
5	15.1	2.5	0.93	16.0	15.8	0.017
6	9.64	0.503	0.93	7.0	4.8	0.012
7	9.64	1.5	0.93	10.2	8.5	0.018
8	9.64	3.52	0.93	14.1	16.6	0.021
9	9.64	4.52	0.93	15.2	20.7	0.025
10	9.64	2.5	0.19	9.0	9.8	0.011
11	9.64	2.5	0.56	10.3	11.2	0.016
12	9.64	2.5	1.3	13.9	14.2	0.022
13	9.64	2.5	1.68	15.0	15.9	0.027

Copolymerization time = 1 h.
Copolymerization temp. = (70 ± 0.1)°C.

9.64×10^{-3} mol L^{-1}, respectively. Similarly, the effect of [GER] on the R_p has been studied by varying [GER] from 0.19 to 1.68 mol L^{-1}, keeping [AN] and [BPO] constant at 2.5 mol L^{-1} and 9.64×10^{-3} mol L^{-1}, respectively. The plots of log R_p versus log [AN] and log [GER] are linear and the slopes of which give order unity in both cases (Figs. 3 and 4).

Effect of temperature

The polymerization runs were also carried out at 65 and 75°C to evaluate the activation energy using Arrhenius equation. The overall energy of activation has been computed as 38 kJ mol^{-1} (Fig. 5).

Characterization

Fourier transform infrared spectroscopy

The symmetrical and asymmetrical bending vibration due to —CH_3 occurs at 1335 and 1458 cm^{-1}, respectively. The band at 1335 cm^{-1} due to methyl is very stable in position when the methyl group is attached to another carbon atom.
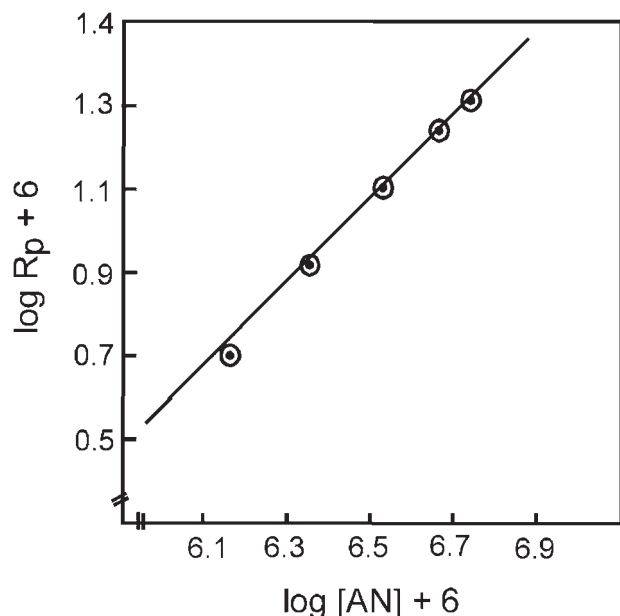

Figure 3 Relationship between the rate of poylymerization and [AN] with constant [GER] = 0.93 mol L^{-1}, [BPO] = 9.64×10^{-3} mol L^{-1}, copolymerization time = 1 h, copolymerization temperature (70 ± 0.1) °C.

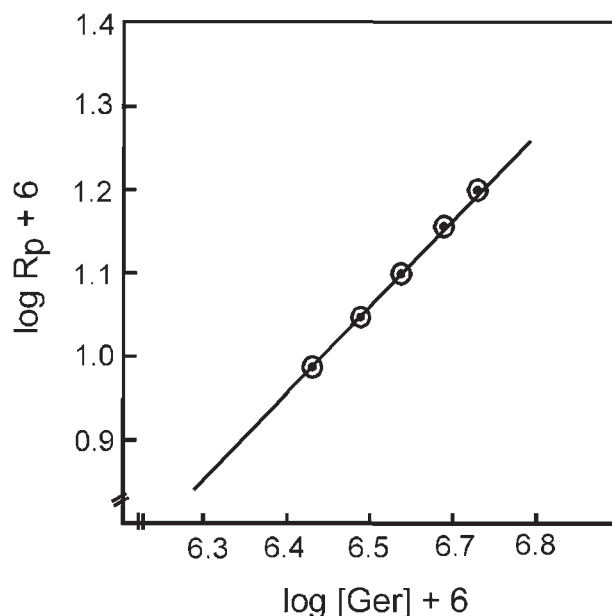**Figure 4** Relationship between the rate of poylymerization and [GER] with constant [AN] = 2.5 mol L^{-1}, [BPO] = 9.64×10^{-3} mol L^{-1}, copolymerization time = 1 h, copolymerization temperature (70 ± 0.1) °C.
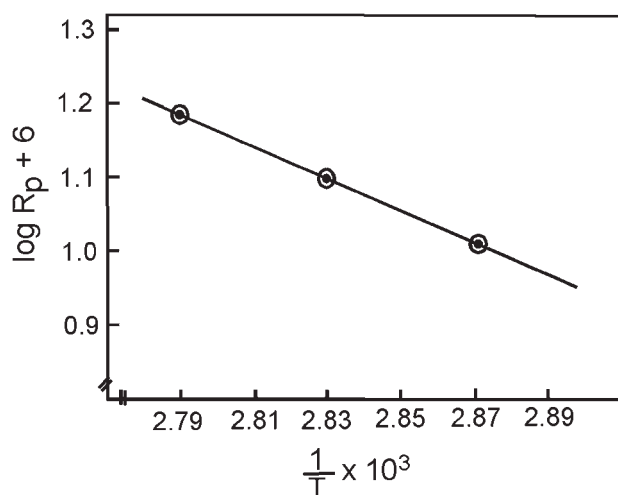
Figure 5 Arrhenius plot of R_p versus the polymerization temperature [BPO] = 9.64×10^{-3} mol L^{-1}, [AN] = 2.5 mol L^{-1}, [GER] = 0.93 mol L^{-1}, copolymerization time = 2 h.

The absorption of —CH$_2$ twisting and wagging vibration is observed in the region 1378–1020 cm^{-1}. Thus, a series of bands in this region arise from the methylene groups, which is characteristic for long chain.

The bands at 3432 and 2244 cm^{-1} are due to —OH group of GER and —CN group of AN, respectively, indicating the incorporation of both monomers in the copolymer (Fig. 6).

^{1}H-Nuclear magnetic resonance spectroscopy

The chemical shifts of protons attached to elements other than carbon like —OH, —NH, and —SH to a greater or lesser extent are influenced by related phenomenon of intermolecular exchange and hydrogen bonding. The appearance of signals in ^{1}H-NMR spectra due to —OH protons with the species of small molecular weight, where intermolecular association is not hindered generally resonates in the
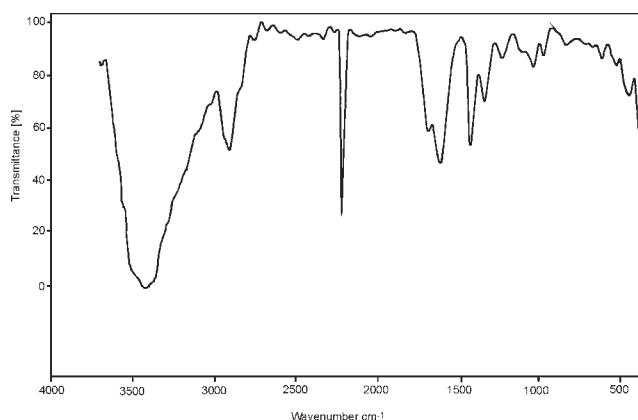

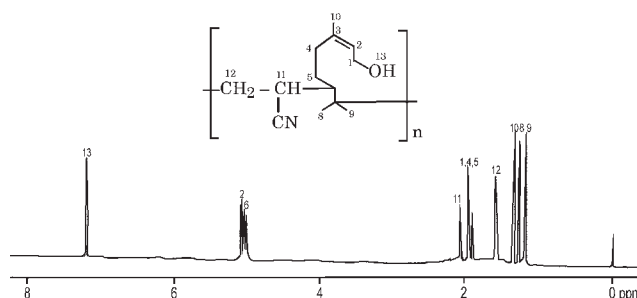**Figure 6** FTIR spectra of the copolymer (sample-3).

Figure 7 ^{1}H-NMR spectrum of the copolymer (sample-3).

region of 3–5.5 δ ppm (hydroxyl protons of CH$_3$—OH appears at 3.3 δ ppm whereas that of C$_2$H$_5$OH appears at 5.4 δ.[28] However, with many large molecules, the hydroxyl protons often resonate 8 δ ppm even at relatively high concentration, partially due to steric effect.[29] Therefore, we have assigned the peak of —OH group in the range of 7.0–7.5 δ ppm in the ^{1}H-NMR spectra of GER as well as copolymer of (GER-co-AN) GER and AN (Fig. 7).

^{13}C-Nuclear magnetic resonance spectroscopy

^{13}C-NMR spectrum of the copolymer [GER-co-AN] (Fig. 8) shows the signals at 14–18 δ ppm, 29–35 δ ppm, and 35–45 δ ppm due to —CH$_3$ —CH$_2$, and —CH, respectively. The nitrile carbon (—CN) of AN appeared at 116–120 δ ppm and —C—OH group at 73–75 δ ppm.[30]

Differential scanning calorimetry

The DSC curve indicates the glass transition temperature (T_g) of GER-co-AN as 56°C (Fig. 9). The value is in agreement with those reported in literature for other terpenes copolymer with vinyl monomers.[4–6] The T_g value of copolymer of linalool with AN (LIN-co-AN)[6] is 50°C, which close to the T_g value of [GER-co-AN].
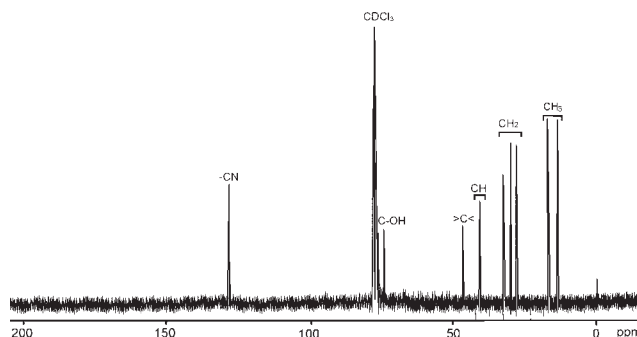

Figure 8 ^{13}C-NMR spectrum of the copolymer (sample-3).
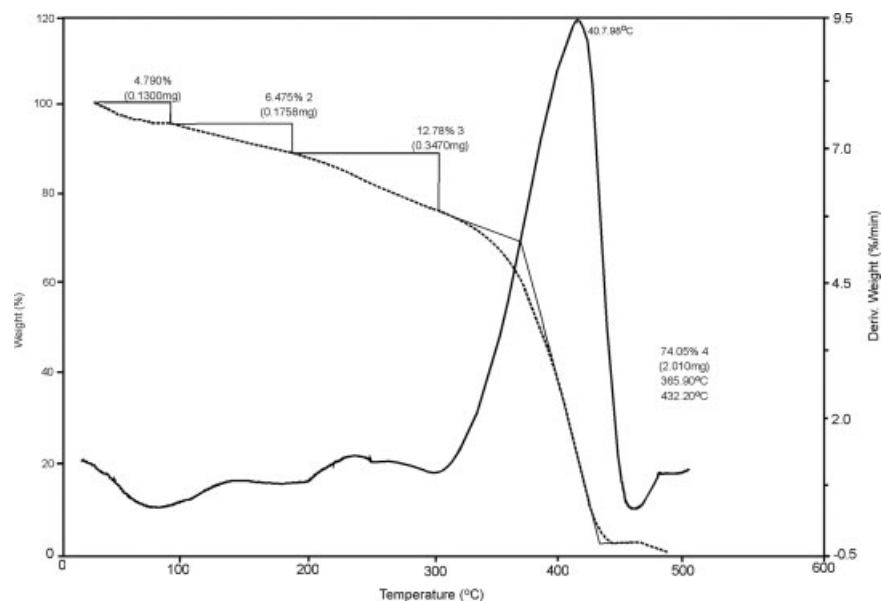
Figure 9   TGA curve of the copolymer (sample-3).

Thermogravimetric analysis

TGA curve of the copolymer (Fig. 10) exhibits weight loss with temperature. The thermal behavior data are as follows:

a. Onset of major weight loss 305.52°C, completion of major weight loss 465°C.
b. Total weight loss in the range of 50–455°C is 95%.

c. Weight loss at different temperature has been calculated by plotting perpendicular between % weight and temperature is as follows:

i 50–100°C = 1.5%
ii 100–200°C = 7%
iii 200–300°C = 13%
iv 300–450°C = 64.6%

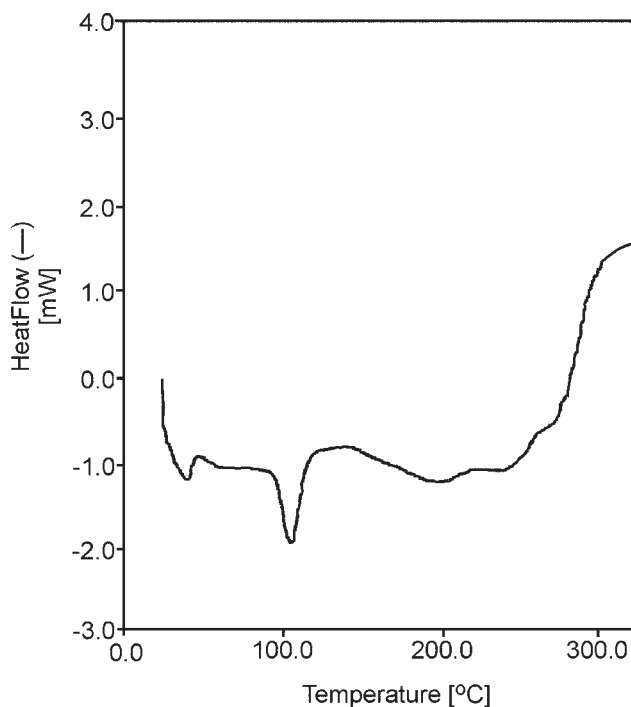d. Almost total decomposition of polymer occurred at 407°C.

A comparison of TGA curve of the [GER-*co*-AN] has also been made with [LIN-*co*-AN].[6]

The TGA curve of [LIN-*co*-AN] exhibits major weight loss at 425°C, while [GER-*co*-AN] has major weight loss at 465°C. The total decomposition of [LIN-*co*-AN] occurred at 403°C, while [GER-*co*-AN] shows total decomposition at 407°C. This indicates that thermal stability of both copolymers is almost similar.

Gel permeation chromatography

The Table IV shows the number average molecular weight $(\overline{M}_n)$ and weight molecular average weight $(\overline{M}_w)$ of the polymer samples.

Copolymer composition and values of reactivity ratios

The composition of the copolymer(s) (Table II) has been evaluated from the high resolution ^{1}H-NMR and elemental analysis. The relative peak area at

Figure 10   DSC curve of the copolymer (sample-3).

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TABLE II
Copolymer Composition

Sample	Monomer feed [AN]/ [GER]	Mole fraction of AN in copolymer	Comonomer ratio [AN]/ [GER]
7	1.61	0.516	1.07
8	3.70	0.540	1.21
3	2.68	0.536	1.18
11	4.46	0.546	1.24
12	1.92	0.530	1.12

7.0–7.5 δ ppm due to —OH group of GER and %N due to cyanide group of AN by elemental analysis, has been used to calculate the monomer reactivity ratios r_1 (AN) 0.05 and r_2 (GER) 0.005, respectively, using Kelen-Tüdos method[31] (Fig. 11 and Table III).

Alfrey-Price parameter (Q-e scheme)

Gronowski and Wojtczak[32,33] derived a semiquantitative relationship to compute the reactivity ratios of various monomers. The method deals with the resonance stabilization and polarization characteristics of a monomer and predicts its reactivity behavior with reference to another monomer radical M_1. The rate constants for the propagation reaction can be written as

$$k_{12} = P_1 Q_1 / \exp(-e_1 e_2)$$

where P_1 denotes a factor characterizing the state of the radical M_1 at the growing chain end, Q_2 indicates the resonance ability and, hence, the measure of the reactivity of the monomer M_2, e_1, and e_2 refer to the polarization characteristics of monomer M_1 and M_2 and also to those of the radicals M_1 and M_2, respectively.
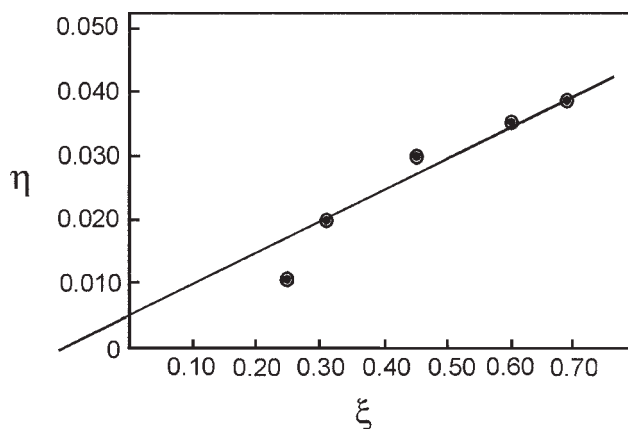
$$k_{11} = P_1 Q_1 / \exp(-e_1 e_2)$$

Figure 11 Kelen-Tüdos plot for the determination of reactivity ratios.

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TABLE III
Reactivity Parameter

r_1	r_2	$r_1 r_2$	Q_2	E_2
0.05	0.005	0.00025	0.094	−2.0

$e_1 = 1.2$.
$Q_1 = 0.060$.

now, $r_1 = k_{11}/k_{12}$ can be rewritten as

$$r_1 = \frac{P_1 Q_1 \exp(-e_1 e_1)}{P_1 Q_1 \exp(-e_2 e_2)} \text{ or } r_1 Q_1 / Q_2 \exp(-e_1(e_1 - e_2))$$

and $r_2 Q_2 / Q_1 \exp(-e_2(e_2 - e_1))$

In the copolymerization systems the widely differing e values have tendency to form alternating copolymers.

The e_2 and Q_2 values for GER (Table III) were calculated by using $e_1 = 1.2$ and $Q_1 = 0.060$ for AN[34] using following equations:

$$e_2 = e_1 \pm (\log r_1 r_2)^{0.5}$$
$$Q_2 = Q_1 / r_1 \exp(-e_1(e_1 - e_2))$$

In the present system, the widely differing e values for both monomers ($e_{AN} = 1.2$, $e_{GER} = -2.0$) suggest that copolymerization has a tendency toward the formation of alternating copolymer, as also suggested by the copolymer composition data (Table III).

Mechanism

  i. Copolymer(s), formed is an unsaturated polymer since it decolorizes Baeyer's regent.

 ii. It has already been mentioned, that cyclization of GER with dil H_2SO_4 proceeds as follows:
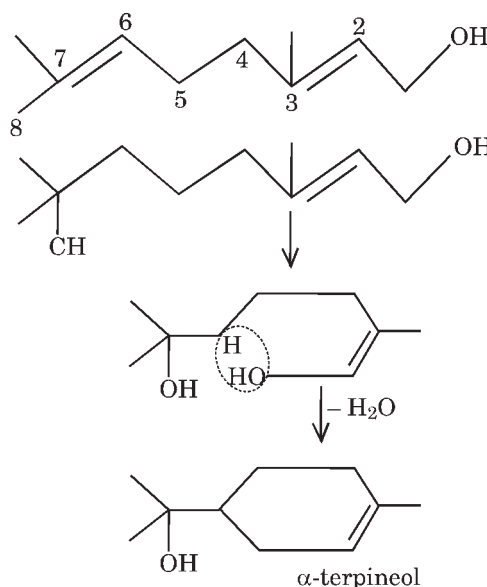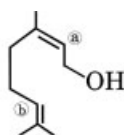
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Sample	M_n	M_w	M_w/M_n
8	12,215	18948	1.55
9	10,274	27,306	2.65
12	9306	22,885	2.46
2	14,299	41,283	2.88
3	11,015	35,007	3.18

iii. There are two possible sites in the GER for the polymerization, the C=C bond between C–2, C–3 and between and C–6 and C–7. The ^{1}H-NMR spectrum of GER shows the peaks of

a) $-CH{=}CH_2$ at 5.0 δ ppm

b) $-C = C{<}$ at 5.4 δ ppm

The ^{1}H-NMR spectrum of copolymer [GER-co-AN] shows that $-CH{=}C{<}$ does not resonate at 5.4–5.5 δ ppm, which indicates indicating the participation of C=C bond present between C–6 and C–7 in copolymerization, while the peak at 4.6–5.1 δ ppm remain present in the copolymers, which gives the positive unsaturation test. Therefore, mechanism for the copolymerization is as follows:
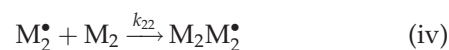
Initiation

As pointed out earlier that GER does not undergo homopolymerization, therefore initiation step consists of decomposition of peroxide to form I and than conversion of AN monomer to AN radical.
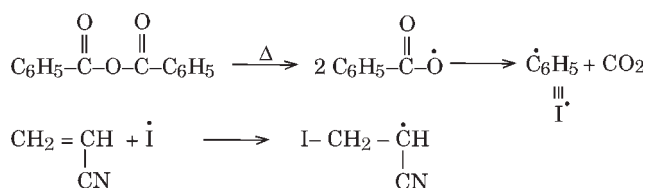

Propagation

In copolymerization the propagation step consists of following steps:

$$M_1^{\bullet} + M_1 \xrightarrow{k_{11}} M_1M_1^{\bullet} \qquad \text{(i)}$$

$$M_1^{\bullet} + M_2 \xrightarrow{k_{12}} M_1M_2^{\bullet} \qquad \text{(ii)}$$

$$M_2^{\bullet} + M_1 \xrightarrow{k_{21}} M_2M_1^{\bullet} \qquad \text{(iii)}$$

$$M_2^{\bullet} + M_2 \xrightarrow{k_{22}} M_2M_2^{\bullet} \qquad \text{(iv)}$$

where M_1 = AN, M_2 = GER

In the present system, step (iv) does not take place since GER does not undergo homopolymerization. Step (iii) does not occur since M_2 is not formed. Therefore, propagation consists of step (i) and (ii) has been removed with solvent treatment in experimental part.
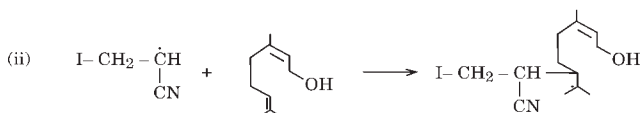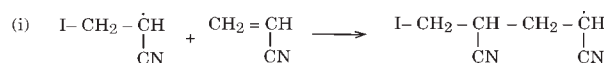
Termination
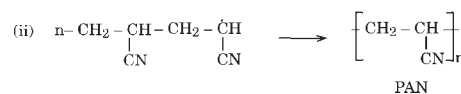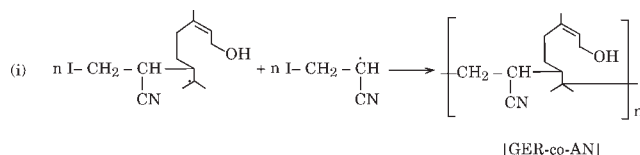
The polyacrylonitrile has been removed with solvent treatment in experimental part. Therefore, finally we get copolymer of GER and AN.

CONCLUSION

Poly[GER-co-AN] has been synthesized via free radical route using BPO as an initiator. The copolymer is thermally stable up to 407 °C and the T_g is 56 °C. The copolymer contains the pendant alcoholic group, which is significant of functional polymer.

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