Homopolymer and Copolymers of 4-Cyanophenyl Acrylate with Glycidyl Methacrylate: Synthesis, Characterization, Thermal Properties, and Determination of Monomer Reactivity Ratios

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ABSTRACT: The acrylic monomer, 4-cyanophenyl acrylate (CPA), was synthesized by reacting 4-cyanophenol dissolved in methyl ethyl ketone (MEK) with acryloyl chloride in the presence of triethylamine as a catalyst. The homopolymer and copolymers were synthesized by using free-radical techniques. Characterization by FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopic analysis confirms the chemical structure. The solubility of the polymers was tested in various polar and nonpolar solvents. The polydispersity index values of polymers suggest a strong tendency for chain termination by disproportionation in all cases, and the tendency increases with the increasing GMA content in the feed. The initial decomposition temperatures for poly(GMA) (188°C), poly(CPA-*co*-GMA) (280°C), and poly(CPA) (290°C) reveal that the thermal stability of the copolymer increases with an increase in CPA content. DSC analysis showed T_g for poly(CPA) (25°C), poly(GMA) (74°C), and copolymer (0.4007 : 0.5993) (39°C) indicates that T_g of the copolymers decreases with the increase in CPA content. The copolymer composition was determined using ^{1}H NMR spectra. The monomer reactivity ratios were determined by the application of linearization methods such as Fineman-Ross (r_1 = 0.5806, r_2 = 0.6651), Kelen-Tudos (r_1 = 0.5442, r_2 = 0.6472), and extended Kelen-Tudos methods (r_1 = 0.5372, r_2 = 0.6352). The reactivity ratio values indicate that the copolymerization has a tendency to alternation. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1523–1530, 2008

Key words: 4-cyanophenyl acrylate; copolymerization; ^{1}H NMR; reactivity ratios; glycidyl methacrylate; thermal studies

INTRODUCTION

There exists today a strong demand for functional polymers in the commercial market for industrial applications. The synthesis of specially designed homopolymers and copolymers, having pendant functional groups, is a topic of continued research. Polymers containing polar substituents such as cyano groups are actively used in widespread of industrial applications[1–6] and also for the development of advanced materials, because of the large dipole moment arising from the polar substituent (CN).[7] Aromatic polymers are known as a class of high-temperature resistant polymers, possessing properties such as high-tensile strength, high glass transition temperatures, etc.[8–11] The presence of the oxirane group in glycidyl methacrylate (GMA) polymers, and copolymers favor further chemical modification for various applications such as leather adhesives,[12–15] pharmaceutical use for drug delivery,[16,17] pressure sensitive adhesives,[18] dental composites,[19] superabsorbents,[20] nonlinear optical material,[21] etc.

Estimation of copolymer composition and determination of monomer reactivity ratios of its constituents assume the importance in evaluating end applications of copolymers. The main aim in commercial copolymerization is to achieve a narrow composition as much as possible. Knowledge about the monomer reactivity ratios would be very helpful in achieving this narrow composition. ^{1}H NMR spectroscopy plays a dominant role in the understanding of polymer stereochemistry and has been established a powerful tool for the determination of tacticity, sequence distribution, and for the estimation of copolymer composition because of its simplicity, rapidity, and sensitivity.[22–27]

The synthesis of 4-cyanophenyl acrylate (CPA) copolymer systems for the determination of reactivity ratios has not been reported by *Chemical Abstracts*. Thus, this newly designed functional copolymer will form an important class of materials for industrial applications. In these views of importance, the current research was carried out to synthesize and characterize the homopolymer and copolymers of CPA with GMA. The thermal properties, monomer reactivity ratios, and its copolymerization parameters describing the monomer sequence distribution along the copolymer chains in whole range of compositions were also reported.

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EXPERIMENTAL

Materials

4-Cyano phenol (Wako Chemical Industries, for synthesis) was used as received. GMA (Wako Chemicals) was purified by distillation under reduced pressure. Benzoyl peroxide (BPO, Aldrich) was recrystallized from chloroform-methanol (1 : 1) mixture. Triethylamine, acrylic acid, and benzoyl chloride (Wako) were used as received from Wako. All the solvents were purified by distillation before their use.

Synthesis of CPA

Acryloyl chloride was prepared from acrylic acid and benzoyl chloride using the procedure of Stampel et al.[28] For the synthesis of CPA, 4-cyano phenol (10 g, 0.084 mol), MEK (250 mL), and triethylamine (11.7 mL, 0.084 mol) were combined in a three-necked RB flask. A mechanical stirrer was attached to the center neck, a dropping funnel with pressure equalizing arrangement was attached to the second neck, and a guard tube was attached to the third neck. The RB flask was placed in an ice bath and the contents were stirred well at 0–5°C. Acryloyl chloride (6.8 mL, 0.084 mol) dissolved in 20 mL of MEK was taken in a dropping funnel and added drop wise with constant stirring. After the addition, the reaction mixture was allowed to be stirred in cold condition for 2 h and then at room temperature for 1 h. Then the precipitated triethylammonium chloride was filtered off, and solvent in the filtrate was removed using a rotary evaporator. The residue was dissolved in ether, washed twice with 0.1% solution of NaOH, and then with distilled water. The ether solution was dried using anhydrous Na_2SO_4. Finally, the ether solution was evaporated to obtain a residue, which was distilled under reduced pressure, providing a yield of 65% of crude CPA.

The monomer was examined by FTIR and ^{1}H NMR spectra, with IR cm^{-1} exhibiting absorptions at 3104 and 3078 (=C—H), 2996 and 2951 (C—H stretching), 2232 (CN stretching), 1747 (C=O), 1634 (CH_2=C), 1604 and 1512 (aromatic C=C), 1368 (CH_3 symmetrical bending), 1179 (C—O), and 826 (C—H out of plane bending), confirming the chemical structure. The ^{1}H NMR (ppm) with 7.72 and 7.30 (aromatic protons), 6.33 and 6.08 (CH_2=C), 5.89 (=CH—) also confirmed the structure.

Homopolymerization

One gram of monomer CPA and 50 mg of BPO free-radical initiator were dissolved in 10 mL of MEK in a polymerization tube, and oxygen-free nitrogen was purged through a solution for about 20 min. Then the solution was thermostated at 70°C ± 1°C; after 8 h, the polymer was precipitated in excess of methanol. The polymer was purified by repeated reprecipitation by methanol from MEK solution. Then the polymer was dried in vacuum at 50°C.

Copolymerization

Predetermined quantities of CPA, GMA, MEK, and BPO were placed in a standard polymerization tube, and the mixture was flushed with oxygen-free nitrogen for 20 min. Then the tube was tightly sealed and immersed in an oil bath at 70°C ± 1°C. The copolymer conversions were restricted to less than 10% to follow a copolymer equation. After the required time, the reaction mixture was poured into excess methanol. The precipitated polymer was filtered off and purified by repeated reprecipitation from MEK solution using methanol. Finally, the polymer was dried in vacuum at 50°C for 24 h.

Solubility studies

Solubility of the polymers was tested in various polar and nonpolar solvents. About 5–10 mg of the polymer was added to about 4 mL of the solvent in a test tube and kept overnight. The solubility of the polymers was observed after 24 h.

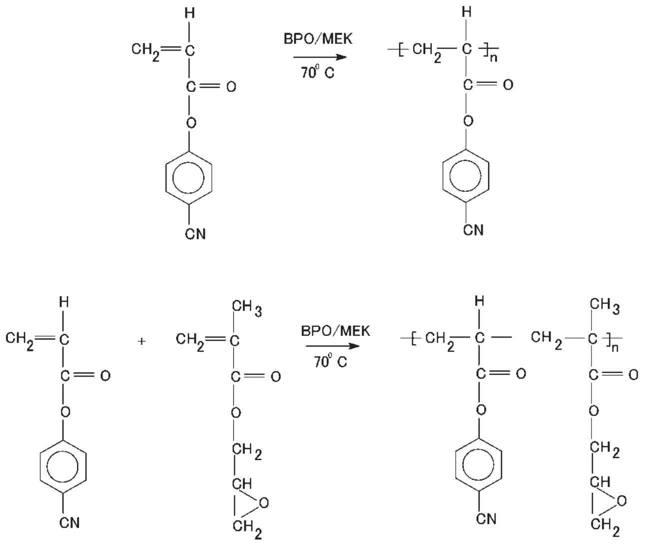
Measurements

Infrared spectra were recorded with a Shimadzu FTIR spectrophotometer as KBr pellets. ^{1}H NMR spectra of the monomer and all the polymer samples were run on a JEOL 400 MHz FT-NMR spectrophotometer at room temperature using $CDCl_3$ solvent and TMS as an internal standard, respectively. The proton-decoupled ^{13}C NMR spectrum was run on the same instrument operating at 100 MHz at room temperature, and the corresponding chemical shifts were recorded under similar conditions. The molecular weights (M_w and M_n) were estimated using Shimadzu Gel Permeation Chromatography, in which tetrahydrofuran was used as an eluent with polystyrene standards for calibration. Thermogravimetric analysis was performed with Shimadzu Thermal Analyzer at a heating rate of 10°C/min under nitrogen atmosphere. The glass transition temperature was determined with Shimadazu DSC Differential Scanning Calorimeter at a heating rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Synthesis of polymers

Poly(CPA) and its copolymers were obtained by the free-radical solution polymerization at 70°C ± 1°C in



Scheme 1 Synthesis of poly(CPA) and poly(CPA-*co*-GMA).

MEK solvent using BPO as the initiator. The mole fractions of CPA ranging from 0.15 to 0.9 in the feed were studied in wide composition intervals. The reaction time was then selected in trials to give conversions less than 10% to satisfy the differential copolymerization equation. The monomeric units of the copolymer are shown in Scheme 1. The composition data of the feed and copolymers are given in Table I.

The homopolymer and the copolymers were soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene, and xylene. It is insoluble in *n*-hexane and alcohol-containing solvents such as methanol and ethanol.

Characterization of polymers

The FTIR spectrum of poly(CPA) shows a absorption peaks at 3104 and 3068 cm^{-1} corresponding to C—H stretching of the aromatic ring. The absorption peaks at 2975, 2938, and 2803 cm^{-1} are attributed to the unsymmetrical and symmetrical C—H stretching of methylene and methyl groups. The strong intense band at 2230 cm^{-1} is due to CN stretching. The ester carbonyl stretching is observed at 1758 cm^{-1}. The ring-stretching vibrations of aromatic nuclei are observed at 1602, 1499, and 1450 cm^{-1}. The C—H deformation of methyl group is seen at 1380 cm^{-1}. The peak at 1167 cm^{-1} corresponds to C—O stretching. The C—H of plane-bending vibrations of the aromatic nuclei is observed at 842 and 757 cm^{-1}.

The ^{1}H NMR spectrum of poly(CPA) shows that the chemical shifts of the aromatic protons were shifted up to field, and they appear at 7.72 and 7.01 ppm. The broad resonance signal (multiplet) at 2.79 to 1.21 ppm is due to backbone methylene and α-methyl group protons. The absence of active group ($CH_2{=}CH$) signals between 6.33 and 5.90 ppm confirms the completion of polymerization of CPA monomer.

The proton-decoupled ^{13}C NMR spectrum of poly(CPA) shows a resonance signal at 176.98 ppm corresponding to the carbonyl carbon. The aromatic carbon attached to the oxygen atom gave signal at 150.07 ppm. The aromatic carbons attached to cyano group gave signals at 134.15. The other aromatic carbons gave signal at 128.84 and 117.49 ppm. The backbone methylene and methyne carbons gave signals at 54.17 and 48.84 ppm.

The FTIR spectrum of the copolymer poly(CPA-*co*-GMA) (0.4007 : 0.5993) is shown in Figure 1. It shows a peak at 3104 and 3064 cm^{-1} corresponding to the C—H stretching of the aromatic system. The symmetrical and asymmetrical stretching due to the methyl and methylene groups is observed at 2995, 2948, and 2801 cm^{-1}. The intense band at 2230 cm^{-1} is due to CN stretching. The peaks at 1750 and 1727 cm^{-1} are attributed to the ester carbonyl stretching of CPA and GMA units. The aromatic C=C stretching vibrations are observed at 1602, 1558, and 1499 cm^{-1}. The C—O links in the ester of CPA and GMA units show signals at 1169, 1208, and 1341 cm^{-1}, respectively. The C—H of plane-bending vibrations of the aromatic nuclei is observed at 845 and 759 cm^{-1}.

The ^{1}H NMR spectrum of the copolymer of poly (CPA-*co*-GMA) (0.4007 : 0.5993) is shown in Figure 2. The chemical shift assignments for the copolymers

TABLE I
Composition Data for Free-Radical Polymerization of CPA(1) with GMA(2) in EMK Solution at 70°C ± 1°C

Copolymer	M_1[a]	Conversion (%)	Integral height (I_{Ar})	Peak (I_{Ali})	C	m_1[b]
1	0.1554	8.45	6.577	72.251	0.0910	0.1962
2	0.3598	7.90	4.000	18.051	0.2216	0.3991
3	0.5071	7.78	4.000	17.956	0.2228	0.4007
4	0.6493	8.52	4.000	15.094	0.2650	0.4526
5	0.7984	8.14	4.000	7.300	0.5479	0.6993
6	0.8985	8.84	4.000	4.734	0.8448	0.8522

[a] M_1 is the mole fraction of CPA in the feed.
[b] m_1 is the mole fraction of CPA in the copolymer.

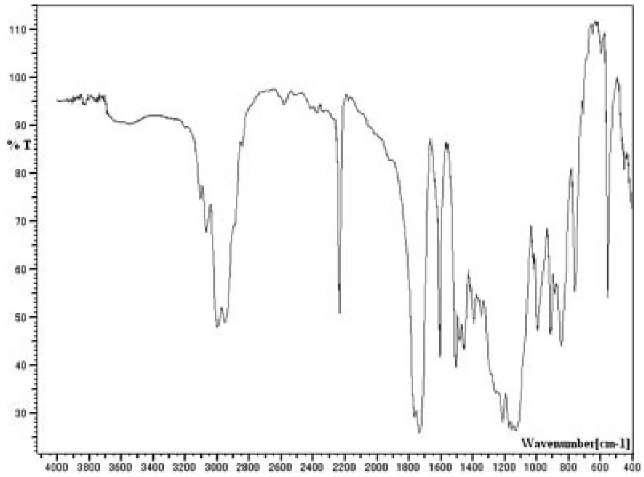


Figure 1 FTIR spectrum of poly (CPA-*co*-GMA) (0.4007 : 0.5993).

were based on the chemical shifts observed for the respective homopolymers. The aromatic protons show signal between 7.72 and 7.16 ppm. The spectrum showing two signals at 4.35 and 3.80 ppm is due to the ester —CH_2O group. The peak at 3.23 ppm corresponds to methyne proton of the epoxy group. The methylene protons of the epoxy group show signals at 2.84 and 2.64 ppm. Because of the existence of tacticity, the resonance signals (multiplet), corresponding to the methylene group of the polymer backbone, are observed between 210 and 1.56 ppm. The α-methyl group of CPA and GMA units shows signal at 1.26 and 0.88 ppm.

The proton decoupled of ^{13}C NMR spectrum of poly(CPA-*co*-GMA) (0.4007 : 0.5993) is shown in Figure 3. It shows resonance signals at 176.98 and 176.05 ppm and is due to the ester carbonyl carbon of CPA and GMA units. The aromatic carbon attached to the oxygen atom shows signal at 150.07 ppm. The aromatic carbons attached to cyano group gave signals at 134.15 ppm. The other aromatic carbon signals are observed at 128.84 (C_5, C_9) and 117.49 ppm (C_6, C_8). The cyano group shows signal at 122.54 ppm. The methyleneoxy group flanked between the carbonyl group, and the epoxy group gave signal at 65.93 ppm. The epoxy ring methyne and methylene carbon of GMA unit give signals at 48.99 and 45.16 ppm, respectively. The signals due to the backbone methylene, methyne, and tertiary carbon atoms are observed at 54.17, 48.84, and 44.69 ppm. The α-methyl group of GMA units shows a resonance at 18.90 ppm.

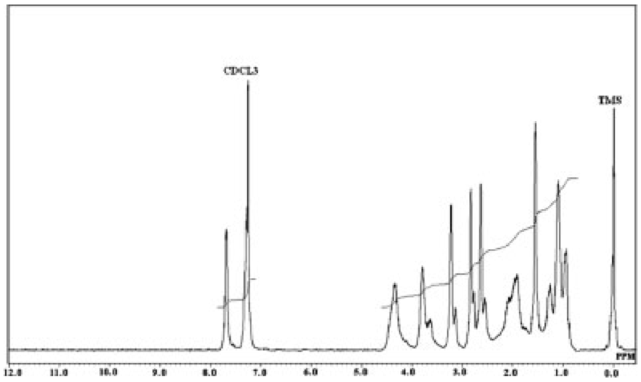


Figure 2 ^1H NMR spectrum of poly (CPA-*co*-GMA) (0.4007 : 0.5993).

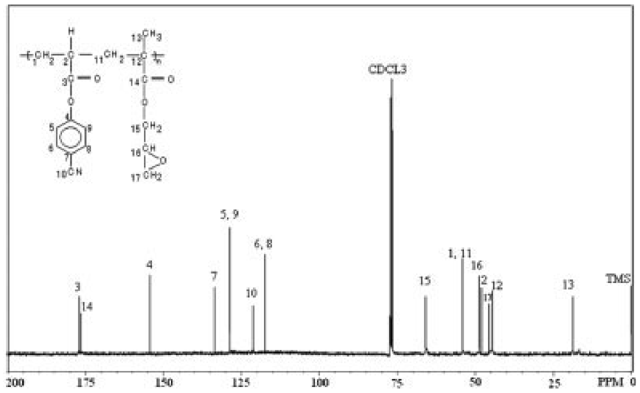


Figure 3 ^{13}C NMR spectrum of poly(CPA-*co*-GMA) (0.4007 : 0.5993).

Molecular weights

The number–average and weight–average molecular weights of poly(CPA) and poly(GMA) and six polymer samples of copolymers, determined by Gel Permeation Chromatography, are given in Table II. The polydispersity indices of poly(CPA) and poly(GMA) are 1.65 and 1.97, respectively. The theoretical value of M_w and M_n for polymers produced via radical recombination and disproportionations are 1.5 and 2.0, respectively.[29] In the homopolymerization of GMA, the growing chains undergo chain termination by disproportionation.[30] The polydispersity values of poly(GMA) and poly(CPA) suggest that the tendency for chain termination by disproportionation is greater for GMA than CPA. The values of M_w/M_n in

TABLE II
Molecular Weight Data for Homo and Copolymers of CPA-GMA

Polymer	m_1[a]	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n
Poly(CPA)	1.0000	3.98	2.41	1.65
Poly(CPA-GMA)	0.1962	3.80	1.98	1.92
	0.3991	3.76	2.00	1.88
	0.4007	3.75	2.02	1.86
	0.4526	3.61	1.98	1.82
	0.6993	3.18	1.76	1.81
	0.8522	3.10	1.72	1.80
Poly(GMA)	0.0000	4.02	2.04	1.97

[a] m_1 is the mole fraction of CPA in the copolymer.

TABLE III
DSC and TGA Data for CPA-GMA Copolymer System

Polymers	m_1	T_g (°C)	*IDT*[a] (°C)	Temp (°C) 10%	Weight loss 90%
Poly(GMA)	0.0000	74	188	263	375
	0.3991	41	270	294	400
Poly(CPA-GMA)	0.4007	39	280	310	412
	0.4526	31	285	318	420
Poly(CPA)	1.0000	25	290	326	424

[a] IDT is the initial decomposition temperature.

copolymerization are also known to depend on chain termination in the same way as in homopolymerization. The values of M_w/M_n of the copolymers also suggest that in copolymerization, the chain termination takes place predominantly by disproportionation than coupling.

Glass transition temperature (T_g)

The glass transition temperatures (T_g) of the copolymers were determined using differential scanning calorimetry, and their data are presented in Table III. All the copolymers show a single T_g, indicating the absence of a mixture of homopolymers or the formation of a block copolymer. The T_g of poly(CPA) is 25°C and that of poly(GMA) is 74°C. The variation of T_g of copolymers with mole fraction of the CPA unit in the copolymer is shown in Figure 4. It has been observed that the T_g of the copolymers displayed a sudden drop in the composition range between 0.4 and 0.5 mol fraction, and this is due to the composition drift in the copolymerization. Thus, DSC results clearly indicate that the T_g values of the copolymers mainly depend on the composition of comonomers, and its value decreases with the increase in CPA content.

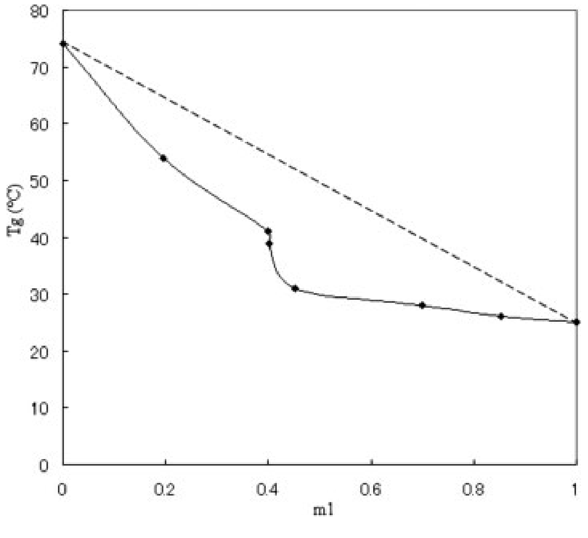


Figure 4 Variation of T_g (°C) with composition of poly (CPA-*co*-GMA) system.

Thermogravimetric analysis

The TGA data for the homopolymers and copolymers of CPA and GMA are given in Table III. TGA curves for poly(GMA), poly(CPA), and a sample of poly (CPA-*co*-GMA) (0.4007 : 0.5993) are shown in Figure 5. The initial decomposition temperature (IDT) of poly(CPA), poly(CPA-*co*-GMA), and poly(GMA) are 290, 280, and 188°C. The thermograms clearly indicate that poly(CPA) and poly(CPA-*co*-GMA) undergo two-stage decomposition. This behavior can be explained by assuming the following mechanism.

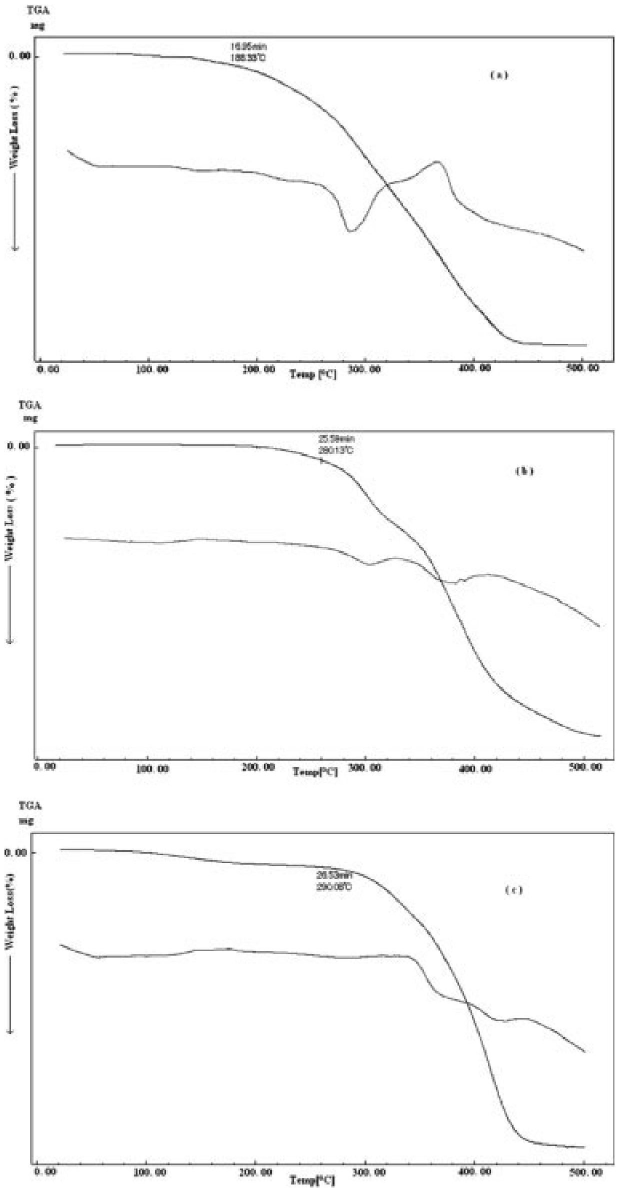


Figure 5 TGA curves (a) poly(GMA), (b) poly(CPA-*co*-GMA) (0.4007 : 0.5993), and (c) poly(CPA).

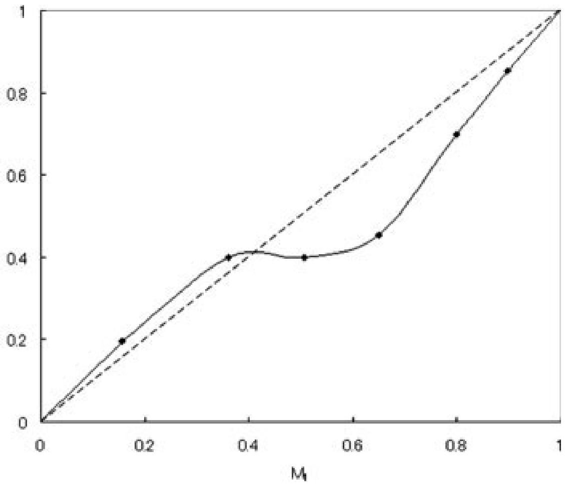


Figure 6 Copolymer composition diagram of poly(CPA-*co*-GMA).

The first step of decomposition is due to the loss of CO_2, rupture of weak linkages in backbone pendant group, and thereby volatilization of low-molecular weight species. This process is further followed by the loss of benzene ring, by the breakage of main chains, and volatilization of the cleaved products. Thus, TGA results clearly indicate that the thermal stability of the copolymer increases with rising CPA content in the copolymer.

Copolymer composition

The chemical structure of copolymers may be represented as shown in Scheme 1. The average compositions of the copolymer samples were determined from the corresponding ^1H NMR spectra. The assignment of resonance peaks in the ^1H NMR spectrum leads to the accurate evaluation of each monomeric content incorporated into the copolymer chains. Thus, the mole fraction of CPA in the copolymer was calculated by measuring the integrated peak height of aromatic protons of CPA to that of total aliphatic protons in the copolymer.

The following expression is used to determine the composition of the copolymers. Let m_1 be the mole fraction of CPA and $1 - m_1$ be that of GMA. CPA contains four aromatic protons and three aliphatic protons, and GMA contains 10 aliphatic protons. The following expression is used to determine the composition of copolymers.

$$C = \frac{\text{Intergral peak height of aromatic protons}}{\text{Integral peak height of total aliphatic protons}} = \frac{4m_1}{3m_1 + 10(1 - m_1)} \tag{1}$$

This on simplification gives

$$m_1 = \frac{10C}{4 + 7C} \tag{2}$$

Based on eq. (2), the mole fractions of CPA in the copolymers were determined by measuring the integral peak height of aromatic proton and aliphatic proton signals. Table I gives the values of *C* and the corresponding mole fractions of CPA in the copolymers. The plot of mole fractions of CPA (M_1) in the feed versus that in the copolymer (m_1) is shown in Figure 6. It clearly indicates that the system can form an azeotropic polymerization.

Reactivity ratios

From the monomer feed ratios and the copolymer composition, the reactivity ratios of CPA and GMA were determined by the application of conventional linearization methods, such as Fineman-Ross (F-R),[31] Kelen-Tudos (K-T),[32] and extended Kelen-Tudos (Ext.K-T).[33] The F-R and K-T parameters for the copolymers are presented in Table IV, and those for Ext. K-T are shown in Table V. The values obtained from F-R plot (Fig. 7), K-T, and Ext.K-T plots (Fig. 8) are presented as follows:

Methods	r_1	r_2	
Fineman-Ross	0.5806	0.6651	
Kelen-Tudos	0.5442	0.6472	
Ext.Kelen-Tudos	0.5372	0.6352	
Average	0.5540	0.6492	$r_1 \times r_2 = 0.3597$

TABLE IV
F-R Parameters for CPA-GMA Copolymer

$F = M_1/M_2$	$f = m_1/m_2$	$H = F^2/f$	$G = F(f - 1)/f$	$\eta = G/(\alpha + H)^a$	$\xi = H/(\alpha + H)^a$
0.1840	0.2441	0.1387	−0.5698	−0.3769	0.0918
0.5620	0.6642	0.4755	−0.2841	−0.1537	0.2572
1.0288	0.6686	1.5831	−0.5099	−0.1153	0.5355
1.8514	0.8268	4.1457	−0.3878	−0.0703	0.7512
3.9603	2.3256	6.7441	2.2574	0.2781	0.8309
8.8522	5.7659	13.5905	7.3169	0.4890	0.9082

[a] $\alpha = (H_{max} \times H_{min})^{1/2} = 1.3730$.

TABLE V
Extended K-T Parameters for CPA-GMA Copolymer System

	Copolymer system					
Parameters	1	2	3	4	5	6
ζ_2	0.0810	0.0747	0.0927	0.1279	0.1189	0.1275
ζ_1	0.1075	0.0883	0.0602	0.0571	0.0698	0.0830
Z	1.3464	1.1907	0.6382	0.4296	0.5716	0.6352
F	0.1813	0.5578	1.0476	1.9246	4.0686	9.0773
H	0.1347	0.4685	1.6415	4.4799	7.1179	14.2905
G	−0.5614	−0.2820	−0.5193	−0.4032	2.3191	7.5030
η	−0.3960	−0.1610	−0.1776	−0.0700	0.2761	0.4818
ξ	0.0950	0.2675	0.5613	0.7774	0.8473	0.9176

$\alpha = (F_{\max} \times F_{\min})^{1/2} = 1.2829$.

Because the values of r_1 and r_2 are lesser than 1, this suggests that the system gives rise to an azeotropic polymerization at a particular composition viz. 0.41. However the product of r_1 and r_2 is lesser than 1, which clearly indicates that the system forms an alternating copolymer.

CONCLUSIONS

Poly(CPA) and the copolymers of CPA with GMA were synthesized by free-radical solution polymerization techniques. Characterization of poly(CPA) and poly(CPA-*co*-GMA) were performed by FTIR, ^{1}H NMR, and ^{13}C NMR techniques. The homopolymer and copolymers are soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene, xylene, and insoluble in *n*-hexane and hydroxyl-group containing solvents such as methanol and ethanol. Thermogravimetric analysis indicated that the thermal stability of the copolymer increases with the increase of CPA units in the copolymer. The glass transition temperature of the copolymer decreases with the increase in CPA content. The polydispersity index values for poly(CPA), poly(CPA-*co*-GMA), and poly(GMA) suggest a strong tendency for chain termination by disproportionation in all cases, and the tendency increases with increasing GMA content in the feed. The monomer reactivity ratios were determined by three known linearization methods such as F-R, K-T, and Ext.K-T methods and are found to be in good agreement. The r_1 and r_2 values are lesser than 1, and this indicates that the system follows azeotropic polymerization. The product value of r_1 and r_2 is lesser than 1, resulting a strong tendency to alternation.

Thus, this study demonstrates the synthesis, characterization, thermal properties, and determination of monomer reactivity ratios for CPA homopolymers and copolymers with GMA. The application studies of these polymers as functional coatings such as adhesives and antifouling are our future interests.

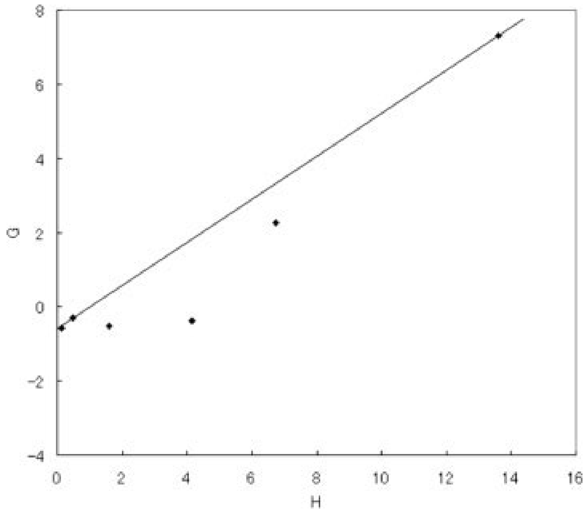


Figure 7 F-R plot for poly(CPA-*co*-GMA) system.

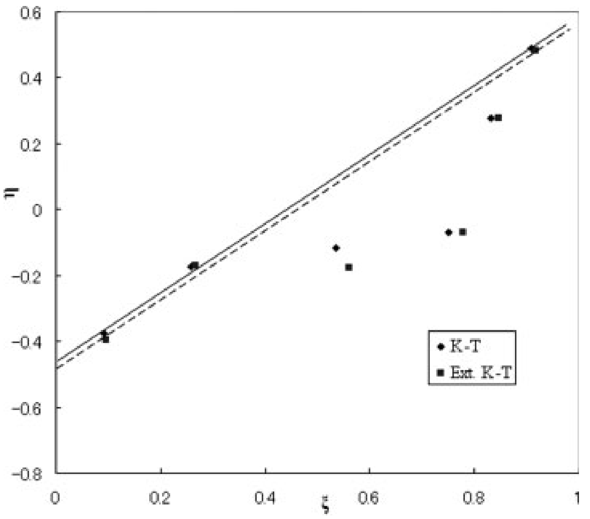


Figure 8 K-T and Ext.K-T plot for poly(CPA-*co*-GMA) system.

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