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Copolymerization of 4-cyanophenyl methacrylate with methyl methacrylate: Synthesis, characterization and determination of monomer reactivity ratios

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Summary

A novel methacrylic monomer, 4-cyanophenyl methacrylate (CPM) was synthesized by reacting 4-cyanophenol dissolved in methyl ethyl ketone (MEK) with methacryloyl chloride in the presence of triethylamine as a catalyst. Copolymers of CPM with methyl methacrylate(MMA) at different composition was prepared by free radical solution polymerization at 70 ± 1°C using benzoyl peroxide as initiator. The copolymers were characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. The solubility of the polymers was tested in various polar and non polar solvents. The molecular weight and polydispersity indices of the copolymers were determined using gel permeation chromatography. The glass transition temperature of the copolymers increases with increase in mole fraction of MMA content. The thermal stability of the copolymer increases with increases in mole fraction of CPM content in the copolymer. The copolymer composition was determined by using ^{1}H-NMR spectroscopy. The monomer reactivity ratios estimated by the application of linearization methods such as Fineman-Ross ($r_1 = 2.524 \pm 0.038$, $r_2 = 0.502 \pm 0.015$), Kelen-Tudos ($r_1 = 2.562 \pm 0.173$, $r_2 = 0.487 \pm 0.005$) and extended Kelen-Tudos methods ($r_1 = 2.735 \pm 0.128$, $r_2 = 0.492 \pm 0.002$).

Introduction

There exists today a strong demand for functional polymers for industrial applications in the commercial market. The use of special designed homopolymers and copolymers, having pendant functional groups on the main chain, is a topic of continued research. The incorporation of two different monomers, having physical or chemical properties, in the same polymer molecule in varying proportions leads to the formation of new materials. Cyanoacrylates are widely used in adhesive industries and are well known as “superglues”. Advantages of these adhesives are include; extreme rapidity of cure under light pressure, high tensile and shear strength of the bonds, low fire, no toxic hazards and ease of applications [1-3]. Polymers containing polar substituent groups such as cyano groups are actively used in the development of advanced materials [4], because cyano group is responsible for large dipole moment and high electron affinity [5,6].

Cyanoacrylates are adhesives which are nowadays widely used in the glass and metal industry, in the electronic industry, in medicine and wide range of household appliances [7]. The herbicidal activity of cyanoacrylates has been the subject of intense interest for past decades [8]. As cyanoacrylates are bacteriostatic [9], they have also found potential applications as 'hybrid' cement in medicine and dentistry [10].

Aromatic acrylates and methacrylates are highly reactive monomers due to the presence of aromatic ring and thus form an interesting class of polymers. Poly(phenyl methacrylates) possesses high tensile strength; high thermal stability and their glass transition temperatures are higher than their corresponding acrylate polymers, due to the presence of α-methyl group on their main chain. Poly (methyl methacrylate) is a versatile, hard, rigid, transparent plastic materials and having good weathering resistance, which finds various avenues of industrial applications, especially in automobile and coating materials. Copolymerization of methyl methacrylate (MMA) with suitable vinyl monomers such as alkyl methacrylates has also been carried out for modifying the properties of the polymer [11-12]. A combination of all these features makes this functional copolymer as an important class of material for advanced applications.

The elucidation of copolymer structure (copolymer composition, monomer sequence distribution) and kinetics (propagation rate coefficients) are the major concerns for the prediction of copolymer properties and the correlation between structure and properties. 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. In the past few decades, ^{1}H-NMR spectroscopy plays a dominant role in understanding of polymer stereochemistry and has been established as a powerful tool for the determination of tacticity, sequence distribution and as well as for the estimation of copolymer composition because of its simplicity, rapidity and sensitivity [13-19].

The synthesis of 4-cyanophenyl methacrylate (CPM) monomer nor its copolymer system with MMA for the determination of reactivity ratios has not been reported by Chemical Abstracts. In continuation of our efforts, we synthesized this novel polymeric material for industrial applications. The present work is undertaken with a view to develop suitable leather adhesives based on activated acrylates. The present research work describes the synthesis of free radical copolymerization of 4-cyanophenyl methacrylate (CPM) of with methyl methacrylate and characterization by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. Determination of copolymer composition was achieved by ^{1}H-NMR spectroscopy and monomer reactivity ratios measured by Fineman-Ross (F-R) [20], Kelen-Tudos (K-T) [21] and extended Kelen-Tudos (Ext.K-T) [22] methods. The thermal properties of the polymers were analysed by TGA and DSC.

Experimental

Materials

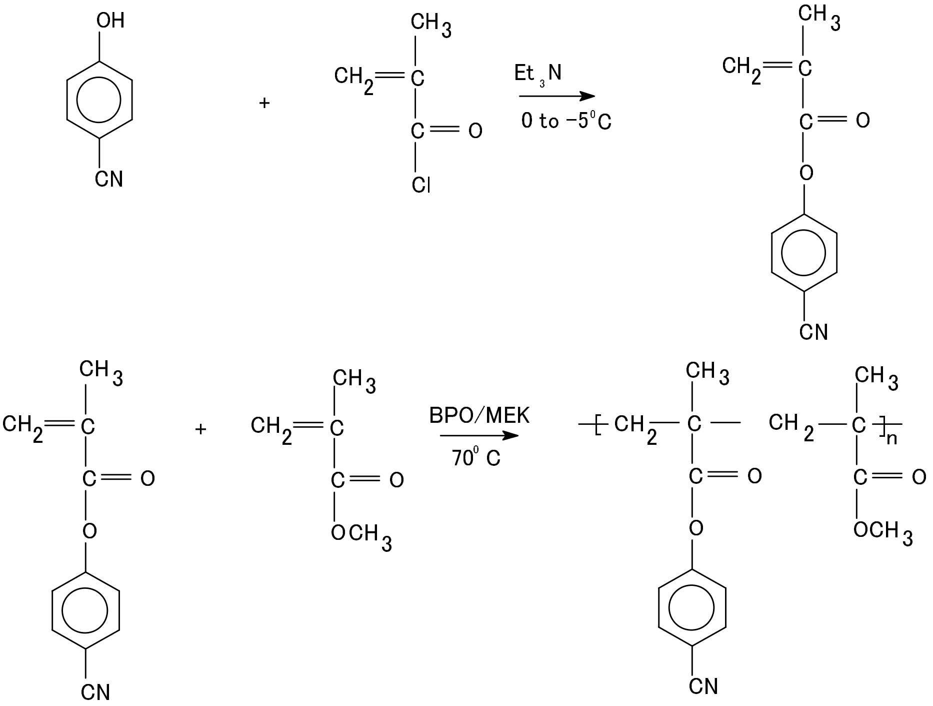
4-Cyano Phenol (Wako Chemical Industries, for synthesis) was used as received. MMA (Wako Chemicals) was purified by distillation under reduced pressure. Benzoyl peroxide (Aldrich) was recrystallised from a chloroform-methanol (1:1) mixture. Triethyamine, Methacrylic acid and Benzoyl chloride were used as such as received from Wako. All the other solvents were purified by distillation prior to their use.

Synthesis of 4-cyanophenyl methacrylate(CPM)

Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride utilizing the procedure of Stampel et al [23]. For the synthesis of CPM, 4-cyano phenol (10g, 0.084 mol), methyl ethyl ketone(250ml) and triethylamine (11.7 ml, 0.084 mol) were taken in 3-necked round bottomed (RB) flask. The RB flask was placed in an ice bath and the contents were stirred well at 0-5°C. Methacryloyl chloride (8.2 ml, 0.084mol) 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 the solvent in the filtrate was removed using a rotary evaporator. The residue was dissolved in ether and was washed twice with 0.1% solution of NaOH and then with distilled water. The ether solution was dried using anhydrous Na_2SO_4. The ether solution was evaporated to get a residue which was distilled under reduced pressure, providing a 75 % yield of crude CPM. The reaction scheme for the synthesis of CPM is shown in scheme 1.

CPM monomer was further examined by FT-IR and ^{1}H-NMR spectra, with FT-IR cm^{-1} exhibiting absorptions at 3103 and 3062 (=C-H), 2991 and 2950 (C-H stretching), 2229 (CN stretching), 1738 (C=O), 1635 (CH_2=C), 1608 and 1513 (aromatic C=C), 1380 (CH_3 symmetrical bending), 1222 (C-O), 822 (C-H out of plane bending), confirming chemical structure.

^{1}H-NMR (ppm) with 7.70 and 7.34 (aromatic protons), 6.34 and 5.98 (CH_2=C), 2.05 (α-methyl) also confirmed the structure.



Scheme 1. Synthesis of CPM and poly (CPM-co-MMA).

Copolymerization

Free radical solution polymerization was utilized for synthesizing the copolymers. Appropriate quantities of CPM, MMA, MEK and BPO were placed in a standard polymerization tube. The reaction mixture was deoxygenated by passing a nitrogen gas for 20 min. The tube was then tightly sealed and immersed in an oil bath at 70 ± 1°C. The polymerization time was carefully controlled to obtain low conversions(less than 10%) in order to follow the copolymer equation. After the desired time, the reaction mixture was cooled to room temperature and resulting polymer solution was poured very slowly into a excess methanol. The obtained solid polymers were purified by continuous reprecipitation by methanol from MEK solution. Finally, the polymer was dried in vacuum at 50°C for 24 h. The monomeric units of the copolymer are shown in scheme 1.

Solubility studies

Solubility of the polymers was tested in various polar and non-polar organic solvents. About 5-10 mg of the polymer was added to 5 ml of the solvent in a standard test tube and kept overnight. The solubility of the polymers was observed after 24 h.

Measurements

Infrared spectra were recorded with Jasco 460 FT-IR spectrophotometer as KBr pellets. ^{1}H-NMR spectra of the monomer and all 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 a Shimadzu Gel Permeation Chromatography, where tetrahydrofuran was used as the eluent and polystyrene standard for calibration. Thermogravimetric analysis of the samples was performed with a Shimadzu Thermal Analyzer under a nitrogen atmosphere at a heating rate of 10°C/min. The glass transition temperature was determined with a Shimadazu Differential Scanning Calorimeter at a heating rate of 10°C/min under nitrogen atmosphere.

Results and discussion

Synthesis of polymers

Poly(CPM) and its copolymers were synthesized by using free radical solution polymerization technique by taking different mole fractions of CPM in the feed ranging from 0.15 to 0.9 (Table 1). The reaction time was selected between 15 min and 30 min to give conversions less than 10%, in order to satisfy the differential copolymerization equation. The copolymers were found to soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene and xylene. It is insoluble in n-hexane and hydroxyl-group containing solvents such as methanol and ethanol.

Table 1 Composition data for free radical polymerization of CPM(1) with MMA(2) in EMK solution at 70 ± 1°C

Copolymer	M_1^a	Conversion (%)	Integral height I_{Ar}	peak I_{Ali}	C	m_1^b	M_w/M_n	T_g (°C)
1	0.1553	8.90	4.000	25.084	0.1595	0.2849	1.90	104
2	0.3548	9.36	4.101	11.230	0.3652	0.5734	1.88	104
3	0.4989	9.15	4.000	8.034	0.4979	0.7250	1.84	104
4	0.6418	7.82	4.000	6.762	0.5915	0.8195	1.80	103
5	0.7769	7.95	4.000	6.288	0.6361	0.8613	1.82	103
6	0.8968	8.64	4.000	5.679	0.7044	0.9218	1.79	103

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

Characterization of polymers

The FT-IR spectrum of the copolymer poly(CPM-co-MMA) (0.7250: 0.2750) is shown in Fig. 1. The spectrum confirms the structure of the copolymer in all aspects. The absorption peaks at 3106 and 3070 cm^{-1} are due to the C-H stretching of the aromatic system. The two bands at 2994 and 2842 cm^{-1} are assigned to the symmetrical and asymmetrical stretching due to methyl groups. The sharp intense band at 2231 cm^{-1} is due to CN stretching. The peaks at 1750 and 1735 cm^{-1} are attributed to the ester carbonyl stretching of CPM and MMA moieties. The C-O links in the ester of CPM and MMA units show strong absorption in the range signals at 1389-1205 cm^{-1}, respectively. The C-H out of plane bending vibrations of the aromatic nuclei are observed at 844 and 746 cm^{-1}. The absence of absorption peak around 1640 cm^{-1} indicates the participation of vinyl group in the copolymerization.

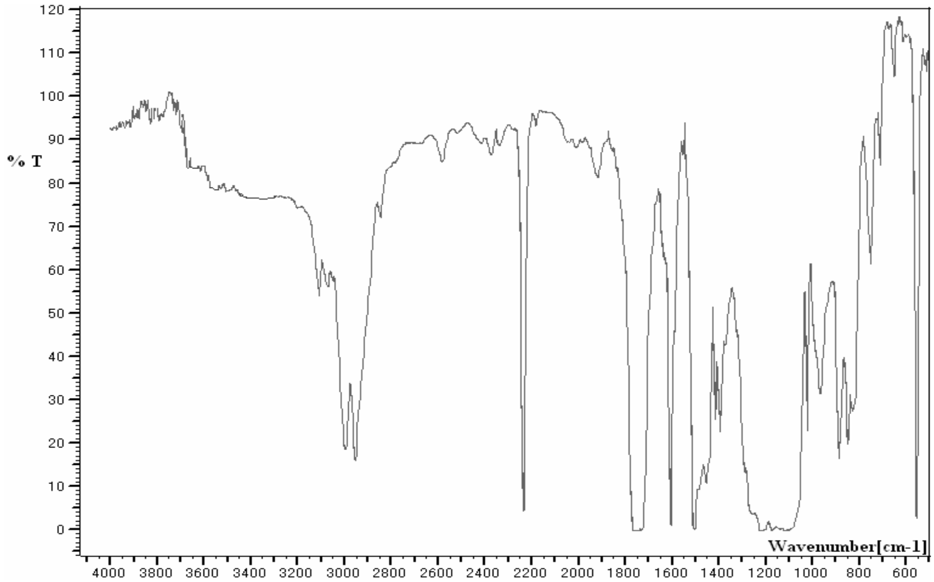


Figure 1. FT-IR spectrum of poly(CPM-co-MMA) (0.7250 : 0.2750)

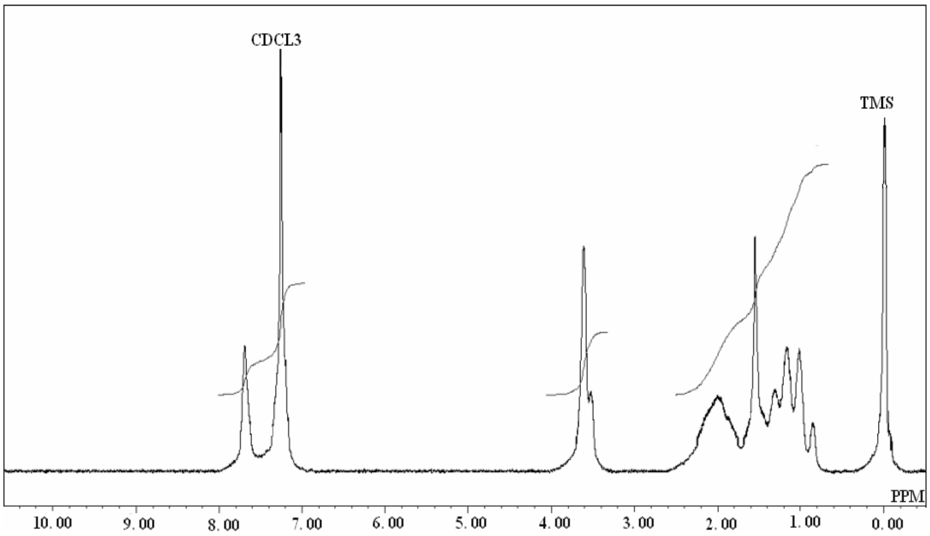


Figure 2. ^{1}H-NMR spectrum of poly(CPM-co-MMA) (0.7250 : 0.2750)

The ^{1}H-NMR spectrum of the copolymer of poly (CPM-co-MMA) (0.7250 : 0.2750) is shown in Fig. 2. It is consistent with its chemical structure. The aromatic protons show a signals between 7.69 and 7.17 ppm. The methoxy proton resonance of the MMA unit appears at 3.62 ppm. The broad resonance signals between 2.14-0.76 ppm are due to the existence of tacticity of backbone methylene groups and the α-methyl group.

The proton decoupled of ^{13}C-NMR spectrum of poly(CPM-co-MMA) (0.7250 : 0.2750) is shown in Fig. 3. It shows resonance signals at 176.56 ppm and 167.75 ppm are due to the ester carbonyl carbon of CPM and MMA units. The aromatic carbon attached to the oxygen atom shows signal at 153.82 ppm. The aromatic carbons attached to cyano

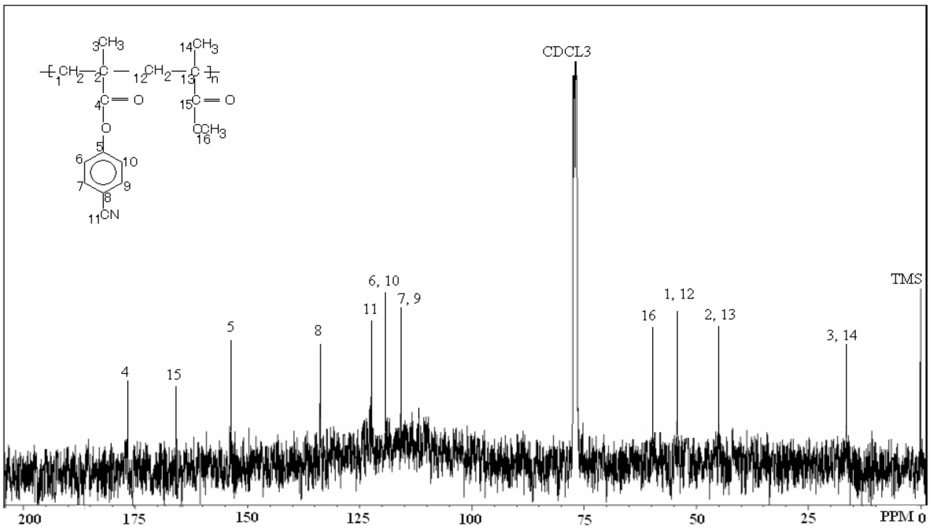


Figure 3. ^{13}C-NMR spectrum of poly(CPM-co-MMA) (0.7250 : 0.2750)

group gave a signal at 133.61 ppm. The other aromatic carbon signals are observed at 122.19 (C_6, C_{10}) and 119.96 ppm(C_7, C_9). The cyano group shows a signal at 122.19 ppm. The methoxy carbon signal of MMA unit was observed at 58.45 ppm. The signals due to the backbone methylene and tertiary carbon atoms are observed at 54.25 and 44.89 ppm. The α-methyl group of both the monomer units shows a resonance signal at 16.55 ppm.

Molecular weights

The weight average, number average molecular weights (M_w, M_n) and polydispersity index (M_w/M_n) values of poly(CPM), poly(MMA) and six copolymer samples were estimated by gel permeation chromatography (Table 1). The polydispersity indices of poly(CPM) and poly(MMA) are 1.70 and 1.84 respectively. The theoretical value of M_w and M_n for polymers produced via radical recombination and disproportionation is 1.5 and 2.0, respectively [24]. In the homopolymerization of MMA the growing chains undergoes chain termination by disproportionation [25]. The polydispersity values of poly(MMA) and poly(CPM) suggest that the tendency for chain termination by disproportionation is greater for MMA than CPM. The values of M_w/M_n of the copolymers ranges from 1.79 to 1.90, also suggests that in the copolymerization the chain also termination takes place mainly by disproportionation, which is predominate over coupling.

Glass transition temperature (T_g)

The T_g value of poly(CPM), poly(CPM-co-MMA) (0.7250 : 0.2750) and poly(MMA) were found to be 103°C, 104°C and 105°C, respectively. The variation of T_g of copolymers with mole fraction of the CPM unit in the copolymer is shown in Fig. 4 and their data are presented in Table 1. The results clearly indicate that T_g values of the copolymers mainly depend on the composition of the comonomers and its value increases with increase in mole fraction of MMA content in the copolymer.

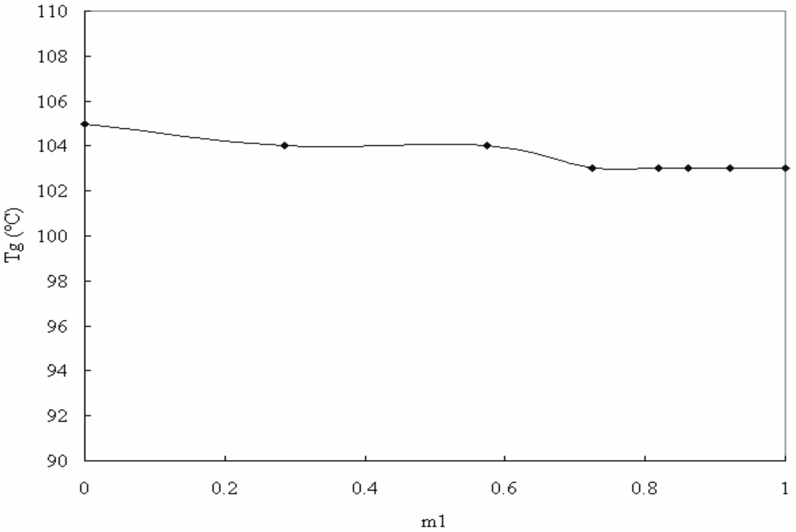


Figure 4. Variation of T_g (°C) with composition of poly(CPM-co-MMA) system

Thermogravimetric analysis

Thermogravimetric analysis was performed in nitrogen atmosphere in order to study the thermal stability of the polymers. TGA curves for poly(CPM) and a sample of poly(CPM-co-MMA) (0.7250 : 0.2750) are shown in Fig. 5. The initial decomposition

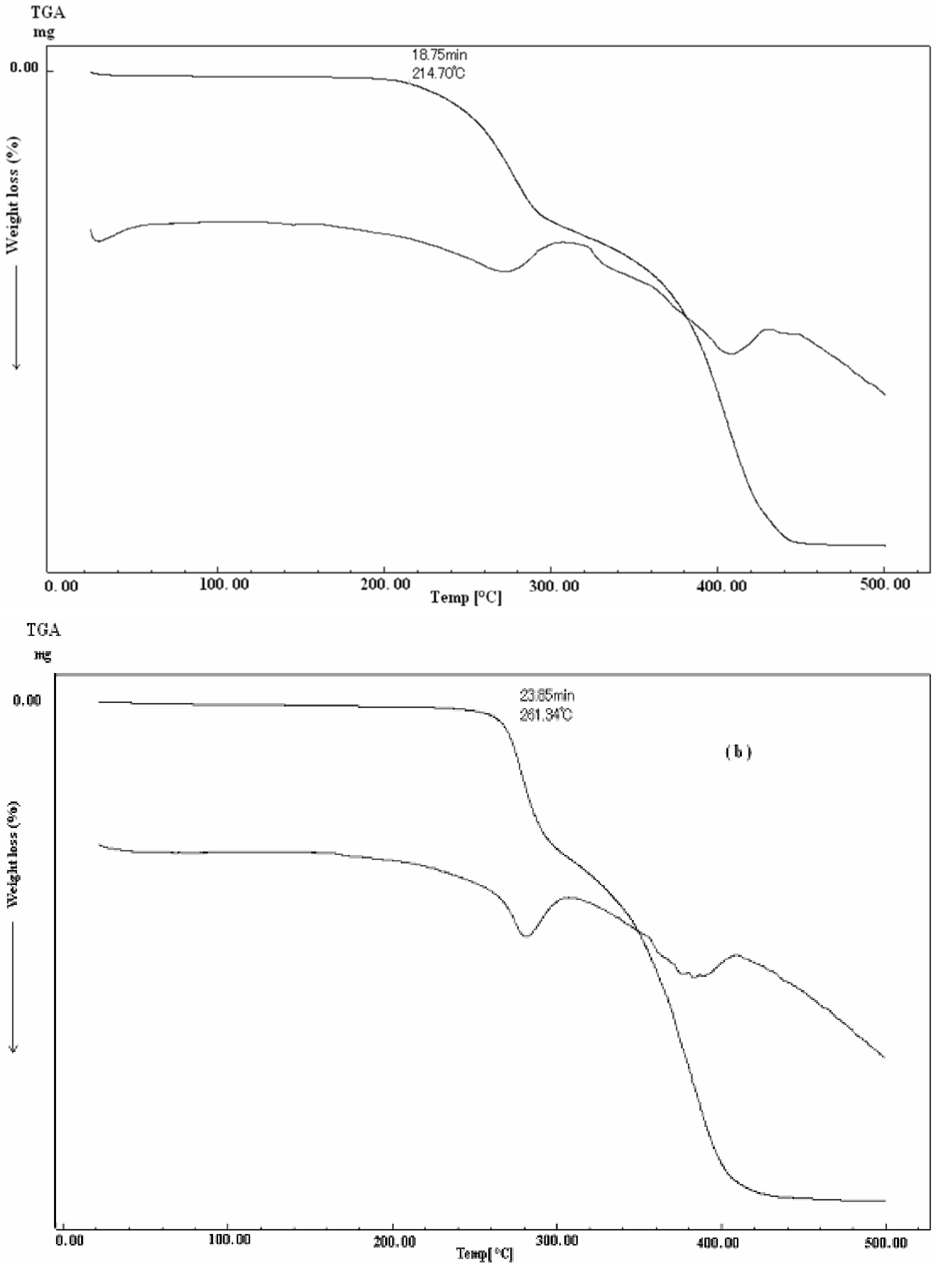


Figure 5. TGA curves (a) poly(CPM-co-MMA) (0.7250 : 0.2750), (b) poly(CPM)

temperature (IDT) of poly(CPM), poly(CPM-co-MMA) and poly(MMA) [26] are 261, 215, and 105°C. The thermograms clearly indicates that poly(CPM) and poly(CPM-co-MMA) undergo two stages decomposition, where as poly(MMA) undergo single stage decomposition. The decomposition temperature range also mainly depends upon the monomer constituents in the copolymer. Thus, the thermograms clearly indicate that the thermal stability of the copolymer increases with the increase of CPM content in the copolymer chain.

Copolymer composition

The average composition of monomer units in the copolymer was determined from the corresponding ^{1}H-NMR spectra. The assignment of the resonance peaks in ^{1}H-NMR spectrum leads to accurate evaluation of each monomeric content incorporated into the copolymer chains. Thus, the mole fraction of CPM in the copolymer was calculated by measuring the integrated peak height of aromatic protons of CPM to that of total aliphatic protons in the copolymer. The mole fraction of the monomeric units in the copolymer was determined by the following equation:

$$\begin{aligned} C &= \frac{\text{Integral peak height of aromatic protons}}{\text{Integral peak height of total aliphatic protons}} \\ &= \frac{4m_l}{5m_l + 8(1-m_l)} \end{aligned} \qquad (1)$$

This on simplification gives

$$m_l = \frac{8C}{4+3C} \qquad (2)$$

where m_l is the mole fraction of CPM and 1-m_l be that of MMA. This equation is based on the fact, that there are four aromatic protons and five aliphatic protons in

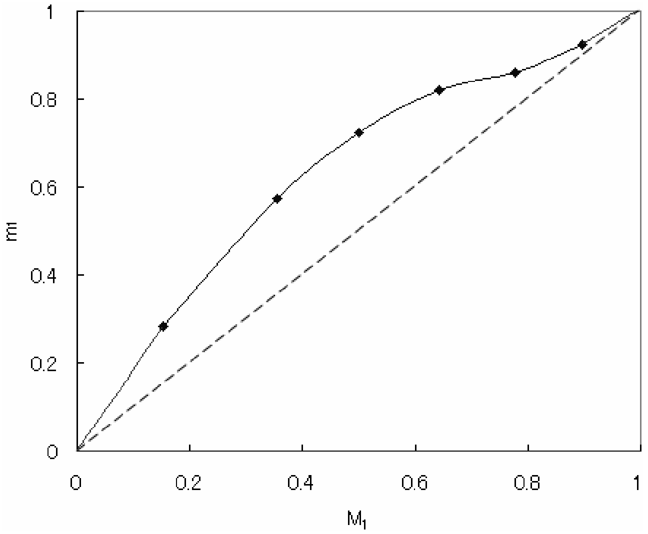


Figure 6. Copolymer composition diagram of poly(CPM-co-MMA)

CPM units, and MMA contains eight aliphatic protons. Based on equation (2), the mole fractions of CPM in the copolymers was determined by measuring the integral peak height of aromatic protons and aliphatic protons signals. The values of “C” and the corresponding mole fractions of CPM in the copolymers are presented in Table 1. The plot of mole fraction of CPM (M1) in the feed versus that in the copolymer (m1) is shown in Fig. 6. The copolymerization curve clearly indicates that the system that the composition of CPM in the copolymer is always higher than that in the feed.

Monomer reactivity ratios

In order understand the copolymerization behavior, the monomer reactivity ratios were calculated by the application of linearization methods, such as Fineman-Ross (F-R), Kelen-Tudos (K-T) and extended Kelen-Tudos (Ext.K-T). The monomer ratio reactivity values determined from F-R, K-T and Ext K-T are presented as follows:

Methods	r_1	r_2	
Fineman-Ross	2.524 ± 0.038	0.502 ± 0.015	
Kelen-Tudos	2.562 ± 0.173	0.487 ± 0.005	
Ext.Kelen-Tudos	2.735 ± 0.128	0.492 ± 0.002	
Average	2.607 ± 0.113	0.494 ± 0.007	r_1x r_2 = 1.288

The r_1 and r_2 values obtained from three methods were in good agreement with each other. Since the value of r_1 is greater than 1 and the value of r_2 is lesser than 1, this suggests the presence of a higher amount of CPM units in the copolymer than in the feed. In this case, the propagation reaction types such as CPM monomer radical add to its own monomer and MMA monomer radical add to CPM monomer will be preferred. Hence, the probability of M_1 monomer entering into the copolymer chain is higher compared to M_2. The copolymer formed will therefore be richer in M_1. However, the product value of r_1 and r_2 is greater than 1 i.e. 1.288, which clearly indicates that the system forms a random copolymer with longer sequences of CPM units in the copolymer chain [14, 17]. Generally the neutral olefin molecules and those olefin molecules containing moderately electron-donating or electron-withdrawing groups favour free radical polymerization. In case of CPM, the electron withdrawing phenyl substituted ester group and electron donating methyl group attached to an olefinic group. Therefore, the net charge of CPM molecule is lesser than the MMA molecule. Hence, the reactivity of the molecule is comparatively high. Further more, the relative reactivity of the co monomers has to be decided not only in terms of the electronic effects but also of the steric effects and the overall polarity of the molecule.

Conclusion

The copolymers of CPM with MMA having different compositions were synthesized by free radical solution polymerization. Characterization of poly (CPM-co-MMA) performed by FT-IR, ^{1}H-NMR and ^{13}C-NMR techniques confirms the chemical structure. The copolymers were 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 in mole fraction of CPM units in the copolymer. The glass transition temperature of the copolymer increases slightly with increase of MMA content. The polydispersity index values for poly(CPM), poly(CPM-co-MMA) and poly(MMA) suggest a strong tendency for chain termination by disproportionation over coupling. The monomer reactivity ratios were derived from F-R, K-T and Ext. K-T methods were in good agreement with each other. The r_1 value is greater than 1 and r_2 value is lesser than 1 indicating that CPM is more reactive than MMA. The value of product r_1 r_2 is greater than 1, which clearly indicates that the system forms a random copolymer with longer sequence distribution of CPM units in the copolymer chain.

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