Free-Radical Copolymerization of [(4-Isopropyl phenyl) oxycarbonyl] Methyl Methacrylate with Acrylonitrile and Methyl Methacrylate

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ABSTRACT: Results of investigations on the synthesis and characterization of free-radical copolymerization of [(4-isopropylphenyl) oxycarbonyl] methyl methacrylate (IP-POMMA), monomer (M_2) with acrylonitrile (AN), and methyl methacrylate (MMA), monomers (M_1) in $CHCl_3$ solution at 60°C with AIBN as initiator are presented. Fourier transform infrared, ^{1}H-NMR, and elemental analyses techniques were used to identify of polymers. Reactivity ratios were calculated according to the general copolymerization equation using Kelen–Tüdös and Fineman–Ross linearization methods, yielding $r_{AN} = 0.60$ plusmn; 0.14 and $r_{IPPOMMA} = 0.94 \pm 0.28$ for the AN/IPPOMMA system; $r_{MMA} = 0.76$ plusmn; 0.30 and $r_{IPPOMMA} = 1.08$ plusmn; 0.52 for the MMA/IPPOMMA system. The thermal properties of the polymers were studied by thermogravimetric analysis and differential scanning calorimetry. In addition, solubility parameters, inherent viscosities, and densities of polymers were determined. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2331–2338, 2003

Key words: Radical polymerization; thermogravimetric analysis (TGA); differential scanning calorimetry (DSC); monomers

INTRODUCTION

The use of raw materials from renewable sources has been the focus of the attention of a great number of scientific research groups all over the world during the last three decades. Nowadays a strong demand exists for "functional polymers" with very specific properties. In polymer science the improvement of the mechanical properties has been at the center of interest for many years, but today special electrical and optical properties of polymers are receiving increasing interest. Functional groups give a polymer structure a special character substantially different from the inherent properties of the basic polymer chain.[1] In recent years some comprehensive work has been published on functional monomers and their polymers.[2,4]

The use of polymeric systems based on acrylic derivatives as biomaterials for clinical applications has increased during the last two decades because of their excellent biocompatibility and long-term stability.[5] Many efforts have been directed toward the development of monomeric systems that have lower shrinkage when polymerization occurs than does the traditional methyl methacrylate. This characteristic seems to be connected with the molar volume of the corresponding compounds.[6,7] It has been demonstrated that large, glassy molar-volume methacrylates correspond to heterocyclic and cyclic derivatives, having a considerable effect on the glass-transition temperature (T_g) of the corresponding polymers.[8,9]

Acrylate and methacrylate polymers have figured prominently in the development of soft tissue–compatible materials[10] and orthopedic[11] and dentalcements.[12] Acrylate- and methacrylate-activated vinyl esters are readily polymerized by free-radical polymerization (FRP) to form linear, branched, or network polymers.[13] The hydrophilic/hydrophobic balance, charge type, and concentration in the polymer may be adjusted by simple copolymerization of acrylate or methacrylate monomers bearing different substituents.[14–18]

A knowledge of copolymer composition is an important step in the evaluation of their utility. Copolymer composition and distribution are dependent on reactivity ratios. The most common mathematical model of copolymerization is based on finding the relationship between the composition of copolymers and the composition of the monomer feed in which the monomer reactivity ratios are the parameters to be determined.[19,20] Calculation of the monomer reactivity ratios requires mathematical treatment of experimental data on the compositions of copolymers and monomer feed mixtures.

In this article we report the synthesis of a new methacrylic monomer derived from the reaction of 4-isopropyl phenyl acetylchloride with sodium

methacrylate as well as its free-radical copolymerization behavior.

EXPERIMENTAL

Materials

4-isopropylphenol and chloroacetylchloride (Merck, Darmstadt, Germany) were used as received. Ethanol, methanol, acetonitrile, chloroform, and benzene were freshly distilled over molecular sieves prior to use. Formic acid, n-heptane, diethyl ether, 1,4-dioxane, and sodium methacrylate (Aldrich, Milwaukee, WI) were used as received. Acrylonitrile (Fluka, Deisenhofen, Germany) and methyl methacrylate (Aldrich) were freed from inhibitor by dilute NaOH solution and were dried over calcium hydride, then purified by standard procedures. 2,2′-Azobisisobutyronitrile (Aldrich) was recrystallized from a chloroform and ethanol mixture and dried under vacuum for 24 h.

Measurements

The IR spectra of the monomer and copolymers were recorded on a Mattson 1000 FTIR spectrometer. The ^{1}H-NMR spectra of the monomer and copolymers were recorded in $CDCl_3$ with tetramethylsilane as the internal standard using a Jeol FX-90 Q NMR spectrometer. Elemental analyses were carried out by a LECO-932 microanalyzer Thermal analysis was performed in a nitrogen atmosphere at a heating rate of 10°C/min. Thermogravimetric data were obtained by using a Shimadzu DSC-50 instrument and a TGA-50 thermobalance. The inherent viscosity of a 1% (w/v) solution of polymer in chloroform was determined at 25°C using an automated Ubbelohde viscometer.

Monomer synthesis

The first, 4-isopropylphenylacetyl chloride, was prepared by reacting 4-isopropylphenol with chloroacetylchloride using K_2CO_3.[21] The monomer, [(4-isopropyl phenyl) oxycarbonyl] methyl methacrylate, was synthesized as follows: a mixture of 4-isopropylphenylacetyl chloride (1 mol), sodium methacrylate (1.1 mol) in 100 mL of acetonitrile, and triethylbenzylammonium chloride (TEBAC) (0.1 mol) as a phase transfer catalyst beter[31] and NaI (0.1 mol) as acatalyst was taken in a two-necked round-bottom flask equipped with a magnetic stirrer and thermometer and was heated to 85°C. In a reflux condenser in the presence of 100 ppm hydroquinone as inhibitor, the reaction was continued for an additional 24 h. The reaction mixture was cooled to room temperature and transferred to a separating funnel and washed sequentially with distilled water, 5% NaOH solution, and diethyl ether.

The organic layers were collected and dried over anhydrous $MgSO_4$ overnight. Diethyl ether was evaporated, and the resulting monomer purified by recrystallization from ethanol (yield 85%).

IR (neat), cm^{-1}: 3000–3100 ($=$C—H in aromatic ring), 2960, 2922, 2865 (aliphatic C—H), 1635 ($CH_2=$C—), 1605, 1526, 1450 (aromatic, C$=$C), 1740 (ester carbonyl), 1725 (oxycarbonyl ketone carbonyl), 1150 (C—O—C), 848, 790, 710 (aromatic C—H def. out-of-plane).

1H-NMR (δ, ppm): 6.9–7.3 (aromatic ring protons), 6.2 and 5.6 ($CH_3=$,vinilic protons), 4.8 (OCH_3—C$=$O protons), 2.8 (C$\underline{H}$(CH$_3$)$_2$ protons), 1.2 and 1.3 (CH(C$\underline{H}$$_3$)$_2$ protons), 1.9 ($CH_3=$C protons).

Copolymerization

Copolymerization of IPPOMMA with AN and MMA using different proportions of IPPOMMA was carried out in glass ampoules under an N_2 atmosphere in chloroform solution with AIBN (1%) as an initiator. The reacting components were degassed by threefold freeze-thawing cycles and then immersed in an oil bath at 60°C $\pm$ 0.1°C for a given reaction time. For estimating monomer reactivity ratios, copolymerization experiments were terminated at less than 10% conversion. The copolymers were separated by precipitation in ethanol and reprecipitated from acetone solution. The polymers were purified by reprecipitation to avoid the formation of homopolymers. The polymers were finally dried over a vacuum to a constant weight.

Determination of physical parameters

Some physical parameters of the polymers, such as density (d), solubility parameter (δ), and inherent viscosity (η_{inh}), were determined in the study. The densities of the polymers were determined experimentally by the flotation method[22] at 25°C using a mixture of methanol and formic acid as the floating agent and many glass beads of known densities. The solubility parameters of the polymers were determined by using a titration method[22] at 25°C from a solubility test using $CHCl_3$ as solvent and n-heptane and ethanol as nonsolvents. The inherent viscosities of 1% (w/v) solutions of the polymers in $CHCl_3$ were determined at 25°C using an Ubbelohde viscometer. These values are shown in Table I. The solubility parameter and density values of the copolymers were between those of the homopolymers. These values were influenced by their composition.

RESULTS AND DISCUSSION

As shown in Scheme 1, we propose a new route for a new methacrylate monomer.

TABLE I
Some Physical Parameters of Polymers

Sample	d (g/cm³)	η_{inh} (dI/g¹)	δ (cal/cm³)^{1/2}
Poly(IPPOMMA)	1.03	0.48	11.2
Poly(AN)	1.19	0.40	13.0
Poly(MMA)	1.20	0.41	9.5
54.0% AN (by mole)	1.15	0.42	12.2
38.0% AN (by mole)	1.10	0.45	11.8
19.0% AN (by mole)	1.08	0.46	11.5
55.0% MMA (by mole)	1.16	0.43	9.8
44.0% MMA (by mole)	1.12	0.44	10.4
14.0% MMA (by mole)	1.05	0.46	10.8

Characterization of monomer and its polymer

The ^{1}H-NMR spectrum of the monomer and its homopolymer are shown in Figure 1(a,b), respectively. The ^{1}H-NMR spectra of the monomers have the characteristic peaks of the monomeric units.

The main evidence of polymer formation is certainly the disappearance of some characteristic signals of the double bond in the spectra, which was effectively observed in our case. Thus, two bands vanished in the IR spectrum: the absorption band at 920 cm^{-1} assigned to the C—H bending of geminal =CH$_2$, and the stretching vibration band at C=C at 1630 cm^{-1}. From ^{1}H-NMR spectroscopy the formation of the polymer is also clearly evident from the vanishing of the two singlets at 6.2 and 5.6 ppm of the vinyl protons and the appearance of the broad signal at 1.3–1.4 ppm, assigned to an aliphatic —CH$_2$— group. All the other spectroscopic signals for the macromolecule appeared in a normal mode.

Characterization of poly(IPPOMMA-*co*-AN) (a) and poly(IPPOMMA-*co*-MMA) (b)

The constituent monomeric units of the copolymers are as follows (Scheme 2):

The FTIR spectrum of poly(AN-*co*-IPPOMMA) is shown in Figure 2. The keto and ester-carbonyl groups of the IPPOMMA unit have sharp bands at 1690 and 1740 cm^{-1}, respectively. The bands at 848 and 790 cm^{-1} correspond to the bending vibrations of C–H and C–C, respectively; which also explain the disubstituted aromatic nature of the IPPOMMA unit. The band at 2230 cm^{-1} (—CN in the acrylonitrile units) is the most characteristic for the copolymers.

The ^{1}H-NMR spectra of the copolymers have the characteristic peaks of the monomeric units. The ^{1}H-NMR spectra (Fig. 3) of poly(MMA-*co*-IPPOMMA) show resonances at 6.9–7.4 ppm, corresponding to the phenyl ring protons of IPPOMMA units. The signals at 4.6–4 9 ppm are a result of the OCH$_2$ group of IPPOMMA. The CH protons of the isopropyl group may be assigned 2.7–3.0 ppm. The methyl protons of the IPPOMMA unit appear at 1.7–2.0 ppm. A group of signals between 1.2 and 1.4 ppm may be assigned to (CH$_3$)$_2$ protons of the isopropyl group. A group of signals between 0.8 and 1.1 ppm may be assigned to CH$_2$— and —CH— protons in the backbone. The signals at 3.4–3.8 ppm are a result of the OCH$_3$ group of the MMA unit.
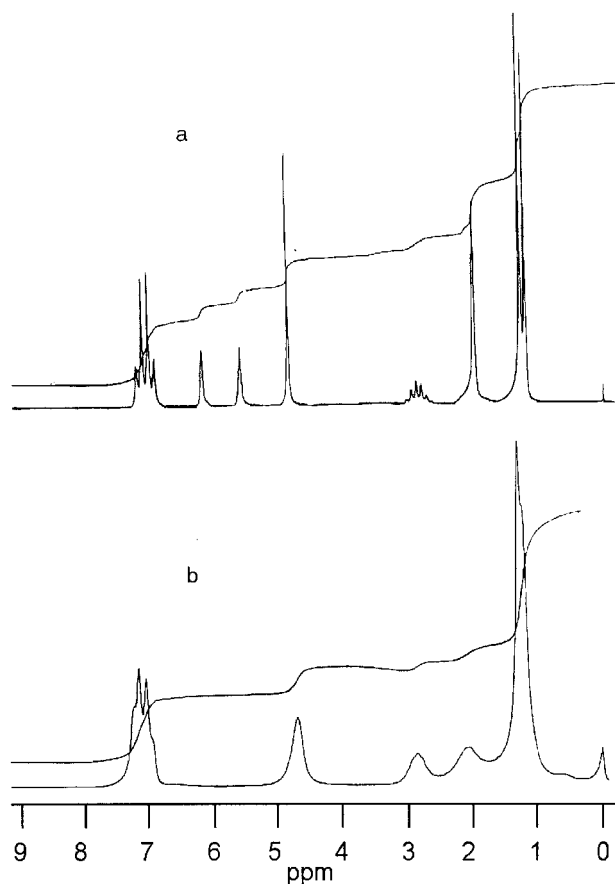

(1)

(2)

Scheme 1

Figure 1 ^{1}H-NMR spectrum of (a) monomer and (b) its polymer.

AN Units

IPPOMMA Units

(a)

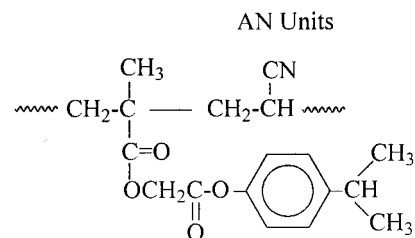MMA Units

IPPOMMA Units

(b)

Scheme 2

Copolymer compositions

Copolymerization of IPPOMMA with AN in chloroform solution was studied for a molar fraction of IPPOMMA from approximately 0.80 to 0.25 in the feed. The amounts of monomeric units in the copolymers were determined by elemental analysis. The plot of the mole fraction of IPPOMMA in feed (M_2) versus that of IPPOMMA in copolymer (m_2) is shown in Figure 4(a).

The composition of the monomeric units in poly(IP-POMMA-*co*-MMA) was determined from the assignment of distinct and well-separated resonance peaks in the ^{1}H-NMR spectra. Thus, the mole fraction of IPPOMMA in the copolymer was determined from the ratio of the integrated values of the intensities of the aromatic protons of IPPOMMA (6.9–7.4 ppm) and the methoxy protons (3.6 ppm) of MMA units.

Let m_1 be the mole fraction of IPPOMMA and $m_1 = (1 - m_2)$ that of the MMA unit:
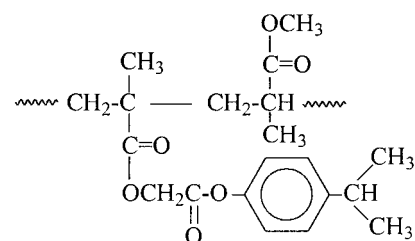
$$\frac{\text{Integrated intensities of aromatic protons } (I_A)}{\text{Integrated intensities of methoxy protons } (I_m)} = \frac{4m_2}{3m_1} = C \quad (1)$$

On simplicification:

$$m_2 = \frac{3C}{3C + 4} \quad (2)$$

From eq. (2) the mole fraction of IPPOMMA in the copolymers was determined.
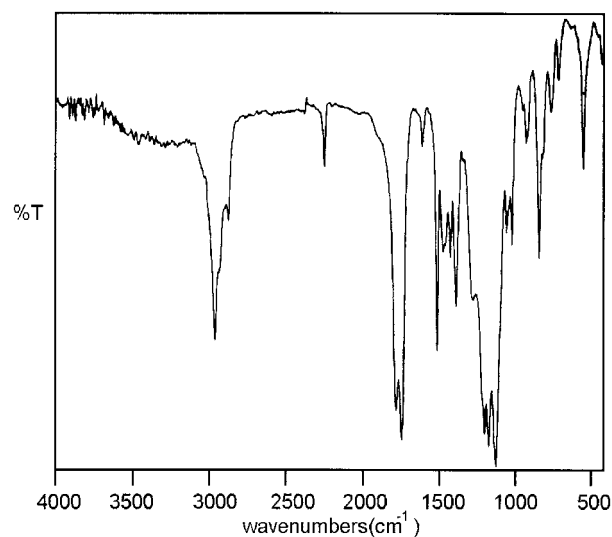

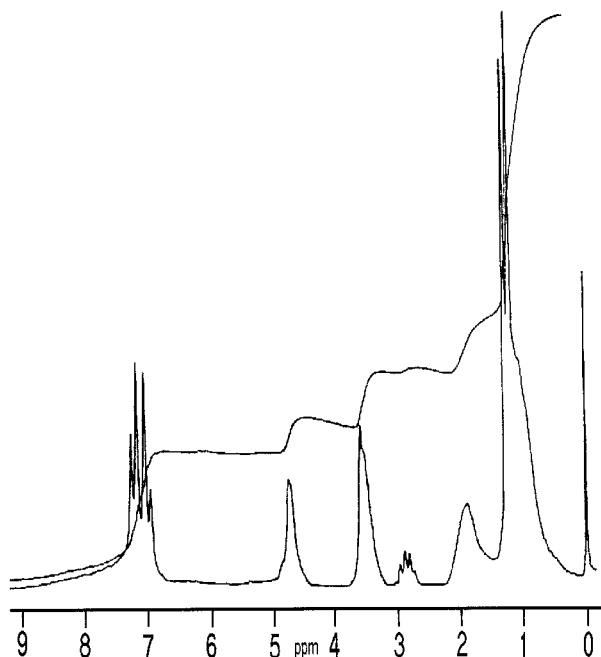**Figure 2** FTIR spectrum of poly(AN-*co*-IPPOMMA) (44.00: 56.00) mol %.

Figure 3 ^{1}H-NMR spectrum of poly(MMA-co-IPPOMMA) (38.00 : 62.00) mol %.

The plot of the mole fraction of IPPOMMA in feed (M_2) versus that of IPPOMMA in copolymer (m_2) is shown in Figure 4(b).

Determination of monomer reactivity ratios

The monomer reactivity ratios for the copolymerization of IPPOMMA with AN and MMA were determined from the monomer feed ratios and the copolymer composition. The Fineman–Ross (FR)[23] and Kelen–Tüdös (KT)[24] methods were used to determine the monomer reactivity ratios. The relationship between mole percentage of IPPOMMA incorporated into the copolymers and the comonomer feed ratio is shown in Figure 4(a,b), respectively.

The data were analyzed by the Fineman–Ross, method where r_1 and r_2 represent the slope and the intercept of eq. (3), respectively. Typical plots are shown in Figure 5(a,b), respectively. In the Kelen–Tüdös equation the least-squares method was used throughout the calculations for the determination of the slopes and intercepts. Averaged values were used to construct theoretical composition curves. The fit with the experimental points was rather good. The Kelen-Tüdös plots for the two systems are presented in Figure 6(a,b). The intercept of the line at $\xi = 1$ is equal to r_1 and that at $\xi = 0$ is equal to r_1/α[25] from eq. (4):
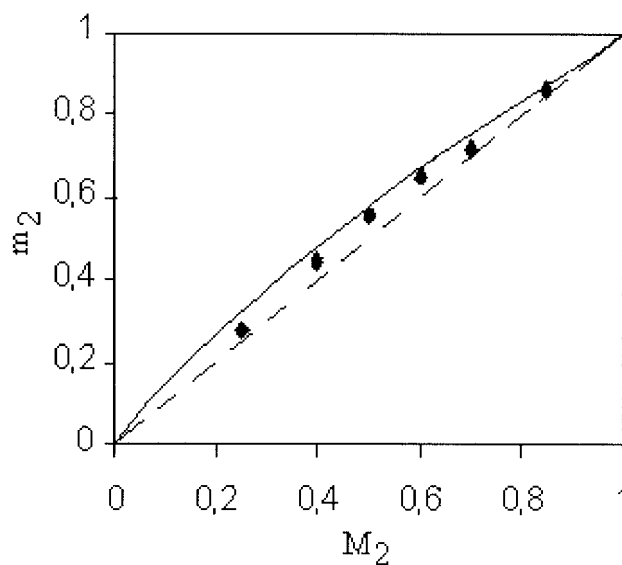
$$X(Y - 1)/Y = X^2/Yr_1 - r_2 \qquad (3)$$

$$\eta = G/(F + \alpha), \xi = F/(F + \alpha) \qquad (4)$$

and α is an arbitrary constant [$\alpha = (F_{maxs}F_{mins})^{0.5}$].

The following values were found: $r_1 = 0.54 \pm 0.17$, $r_2 = 0.89 \pm 0.30$ (Fineman–Ross), $r_1 = 0.66 \pm 0.11$, $r_2 = 0.98 \pm 0.26$ (Kelen–Tüdös) of copoly(AN–IPPOMMA) system; $r_1 = 0.77 \pm 0.26$, $r_2 = 1.09 \pm 0.49$ (Fineman–Ross), $r_1 = 0.75 \pm 0.34$, $r_2 = 1.06 \pm 0.55$ (Kelen–Tüdös) of copoly(MMA–IPPOMMA) system. For copolymerizations of IPPOMMA with AN and
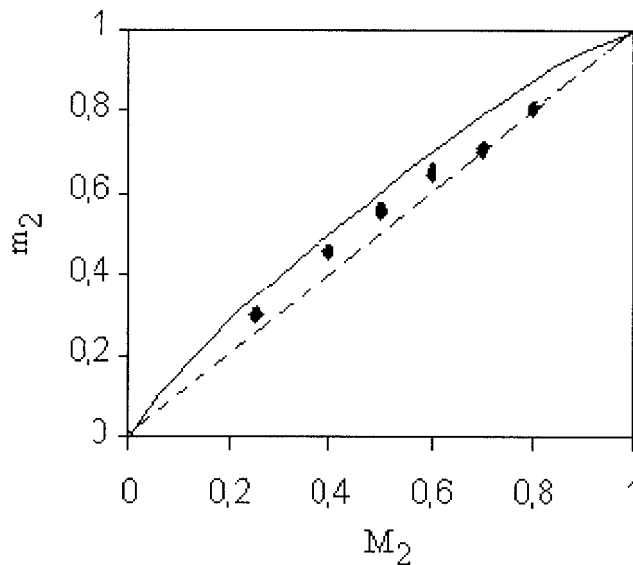
(a)

(b)

Figure 4 The comonomer–copolymer composition curves for copolymerization of (a) copoly(AN–IPPOMMA) system, (b) copoly(MMA–IPPOMMA) system (m_2: mole fraction of IPPOMMA in copolymer, M_2: mole fraction of IPPOMMA in feed).
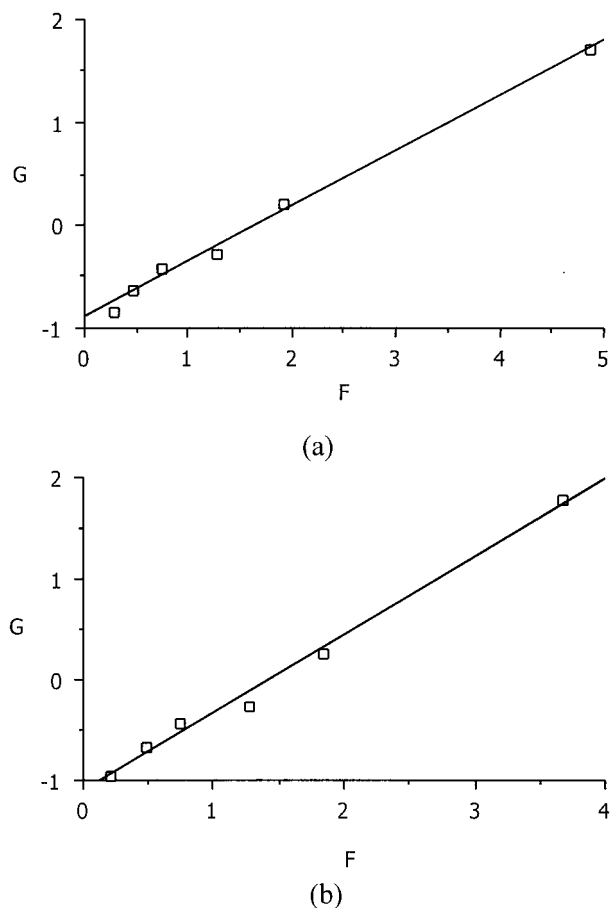
Figure 5 Fineman–Ross plot of (a) copoly(AN–IPPOMMA) system, (b) copoly(MMA–IPPOMMA) system.

MMA, the reactivity ratios obtained from the F–R equation and the K–T equation agreed with each other. All the reactivity ratios calculated from both methods are smaller than unity. The higher r_2 value of IPPOMMA confirms the higher reactivity of IP-POMMA compared with that of AN, and the copolymer sequence will be statistical in structure with more IPPOMMA. IPPOMMA and AN have approximately equal reactivities toward the poly(IPPOMMA) radical, but IPPOMMA has about 1.5 times more reactivity than AN toward the poly(AN) radical. The copolymer will have a statistical arrangement of units in which IPPOMMA will tend to predominate. The higher r_2 value of IPPOMMA confirms its higher reactivity compared with that of MMA. The higher fraction of IPPOMMA in the copolymer indicates that the probability of the IPPOMMA entry into the chain is greater than that of the MMA entry. Thus, the copolymers formed were richer in IPPOMMA. Although the reactivity of growing radicals with the IPPOMMA end was higher toward AN and MMA than IPPOMMA, the reactivities of growing radicals with the AN and MMA ends were higher toward IPPOMMA than AN and MMA. Consequently, in both copolymerizations

the copolymer sequences will be an alternating tendency.

Thermal analysis

Differential scanning calorimetry (DSC) was performed at a heating rate of 10°C/min under a nitrogen atmosphere. A plot of copolymer composition versus glass-transition temperatures of the copolymers is shown in Figure 7(a,b). The T_g values of poly(IP-POMMA), poly(AN), and poly(MMA) obtained under the same conditions with the copolymers were found at 87°C, 120°C, and 105°C, respectively. The T_g values of all the copolymers were between those of the homopolymers of the same monomers, which is predicted by the dotted line in Figure 7(a,b). When the mole fraction of IPPOMMA in the copoly(IPPOMMA-AN) changed from 0.81 to 0.30, the T_g value changed from 91°C to 110°C. The chain flexibility of poly(IP-POMMA) was higher than that of poly(AN). This means that the free volume in poly(IPPOMMA) was
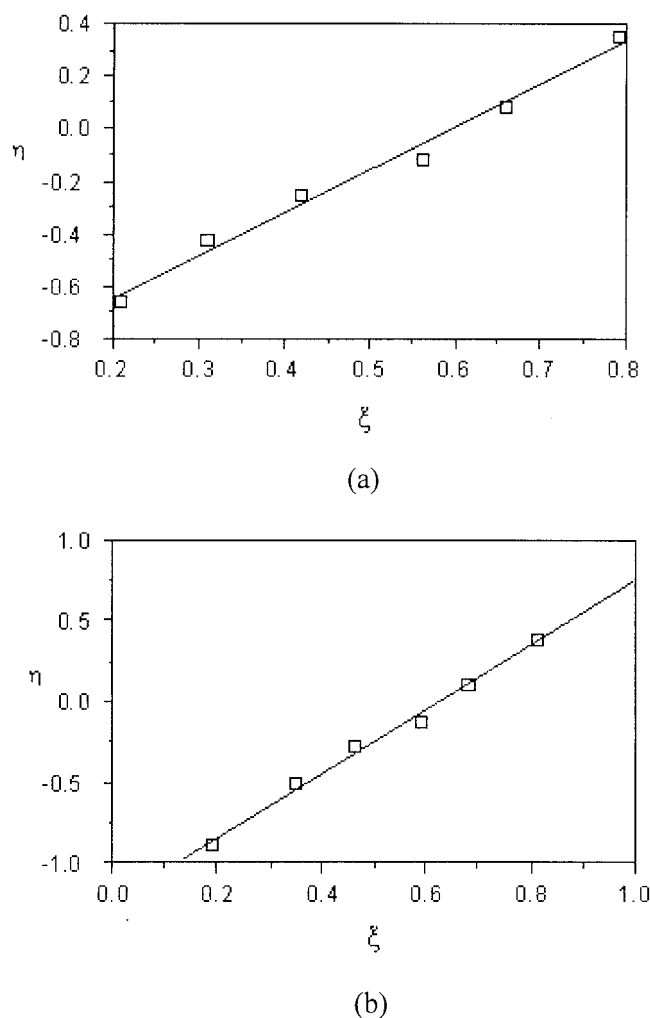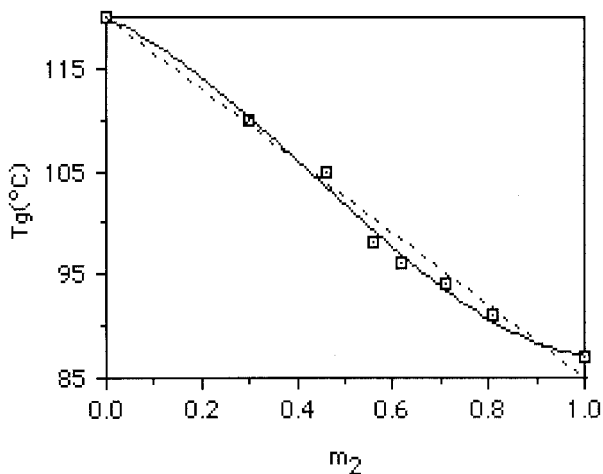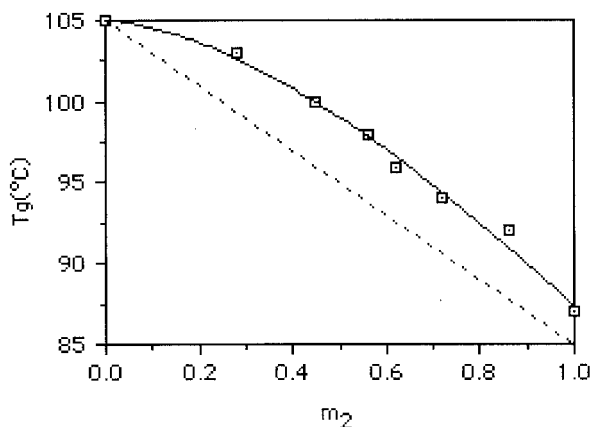

Figure 6 Kelen–Tudos plot of (a) copoly(AN–IPPOMMA) system, (b) copoly(MMA–IPPOMMA) system.

(a)

(b)

Figure 7 Plot of glass-transition temperature versus copolymer composition of (a) copoly(AN–IPPOMMA) system, (b) copoly(MMA–IPPOMMA) system (m_2: mole fraction of IPPOMMA in copolymer).

higher than that in poly(AN). Therefore, an increase of T_g as a function of the number of AN units in the copolymer is an expected result. Similar results were observed for poly(IPPOMMA-co-MMA). When the mole fraction of IPPOMMA in the copolymer changed from 0.86 to 0.28, the T_g value changed from 92°C to 103°C.

The thermal stability of the copolymers was studied by programmed thermogravimetric analysis over a temperature range from room temperature to 500°C under a nitrogen atmosphere [see Fig. 8(a,b)].

The thermal stabilities of two copolymers were between those of the corresponding homopolymers. The residue at 450°C for the IPPOMMA-AN copolymers increased with increasing AN units, whereas the IPPOMMA-MMA copolymers had very low residues. Intramoleculer cyclization between nitrile groups in the AN units was restricted by the IPPOMMA units

that were present between the AN units in the copolymer. This caused the amount of residue to decrease with increasing IPPOMMA content. Although thermal degradation of most of the poly(methacrylic ester) began with a depolymerization process,[26] thermal degradation of poly(AN) began with a nucleophilic addition reaction between the nitrile groups.[26–28] Most reports in the literature have been in agreement that the initial reaction is nucleophilic attack at a nitrile followed by cyclization to an extended conjugated structure.[29,30] This means that the thermal stability of the copolymers will increase on incorporation of AN. Our results are in agreement. The TGA curves of poly(IPPOMMA-co-AN) showed that the thermal stability of IPPOMMA was increased by the incorporation of AN.
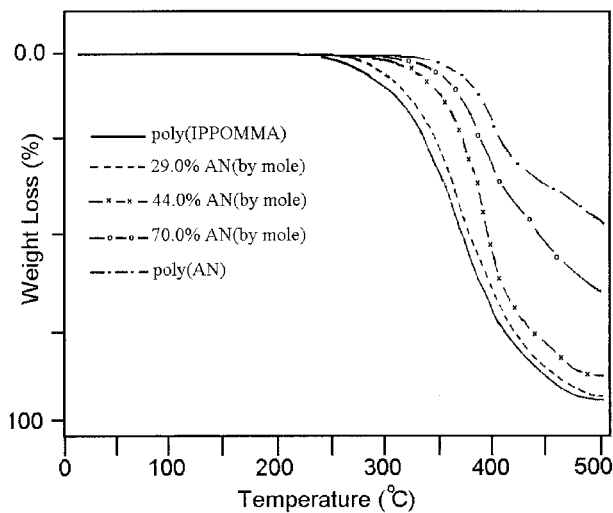
(a)
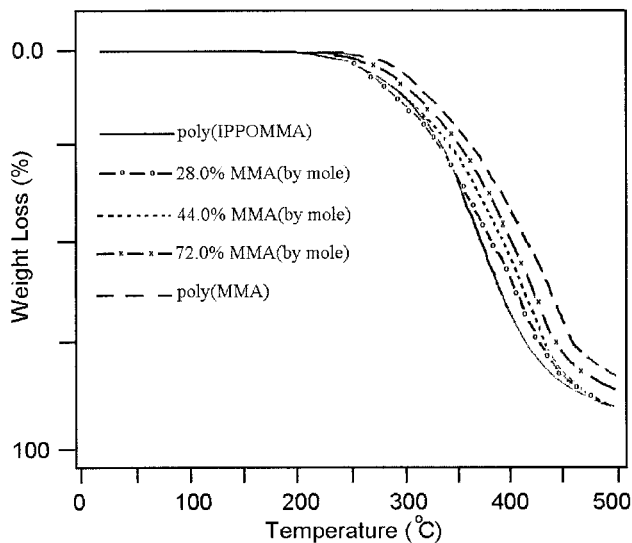
(b)

Figure 8 TGA curves of the polymers (heating rate 10°C/min under a nitrogen atmosphere).

CONCLUSION

As our aim was to engineer a multipurpose functionalized monomer, the synthesis of a chiral prototype molecule that could easily polymerize—because of the presence of the double bond in the methacrylate moiety—and then display second-order nonlinearities as a monomer and polymers was the driving force of this work.

[(4-Isopropylphenyl) oxycarbonyl] methyl methacrylate (IPPOMMA) was synthesized and characterized. Copolymers of IPPOMMA with AN and MMA having different copolymer compositions were prepared. The reactivity ratio values were discussed. The reactivity ratio values derived from the F–R and K–T methods were in good agreement with each other. The reactivity of IPPOMMA was greater than AN and MMA, which means the copolymer is always richer in IPPOMMA units.

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