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A Study on End Group Characterization of Poly(phenacyl methacrylate) Polymer Produced by Free Radical Polymerization

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Free-radical homopolymerization and copolymerization of phenacyl methacrylate (PAMA) with methyl methacrylate (MMA) was done using 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator in 1,4-dioxane at 60°C. ^{1}H-NMR and FT-IR spectroscopy confirmed the existence of OCH_2 and CH signals and unsaturated structure and CN stretch at the chain end of low molecular weight poly(phenacyl methacrylate) [poly(PAMA)], respectively. The six-membered ring with both ester and ether at the end group was detected by ^{1}H-NMR. In the poly(PAMA), the end groups formed due to chain transfer reactions were found in large concentrations. The mechanism of the formation of end groups has been presented. The behavior of free radical polymerization of PAMA was compared with that of phenoxycarbonylmethyl methacrylate (PCMMA). The molecular weight distribution of the homo and copolymers was determined using gel permeation chromatography. Thermal properties of the polymers were determined using differential thermal analysis (DTA) and thermogravimetric analysis (TGA).

Keywords: free radical polymerization; end group characterization

1 Introduction

Knowledge of end groups in polymers is important in understanding the mechanism of polymerization and degradation. Precise knowledge about the end groups also helps in understanding the mechanism of polymerization particularly the termination and chain transfer reactions (1). The properties of polymers are determined largely by the backbone structure, the end groups also significantly influence the bulk properties of the polymers. The nature of the end group affects thermal stabilities of polymers (2, 3). Traditionally, methods such as ^{1}H-NMR, ^{13}C-NMR, infrared (FT-IR), ultraviolet-visible (UV-VIS) spectroscopies and elemental analysis techniques were used to determine the mode of chain termination in free radical polymerization. Acrylic polymers are commercially popular because of their high clarity and transparency coupled with their resistance to sunlight. To meet the growing demand for acrylics, new improved speciality grades are constantly bearing formulated for new applications (4). It is possible to obtain materials prossesing high thermal properties. Thus, the stereoeffects depend on the monomer structures (5). An enhancing stereoeffect may be effective in view of the syndiotacticity for methacrylates, with a relatively bulk side group such as the phenacyl, benzyl bulk. Bulk substituents increase the glass transition temperature (Tg) because of the increased rotation barrier around the backbone bonds (6–10).

In our a previous study (11), we discussed lactone formation produced at chain ends via atom transfer radical polymerization of phenacyl methacrylate between 70°C–100°C. In this paper, we describe a transformation reaction in the growing chain during traditional free radical polymerization method that has not been reported previously. Poly(PAMA) with low molecular weight characterized by ^{1}H-NMR, GPC techniques showed that it has chain ends with a cyclic structure contained both ester and an etheric group. We have investigated various end groups of poly(PAMA) via ^{1}H-NMR and other techniques such as FT-IR. This formation in poly(PAMA) was compared with that of poly(phenoxycarbonylmethyl methacrylate) [poly(PCMMA)] bearing a phenoxycarbonyl group instead of phenylcarbonyl group in the polymer side group. Furthermore, changing of the chain ends increasing with MMA units in poly(PAMA-co-MMA) was investigated.

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2 Experimental

2.1 Materials

Methyl methacrylate (MMA, Aldrich) was vacuum-distilled after washing with 5% NaOH aqueous solution just before polymerization. 2,2′-Azobisizobutyronitrile (AIBN) was recrystallized from a chloroform-methanol mixture. Prior to polymerization, all solvents, monomers and other reagents were degassed by argon purging.

2.2 Characterization Techniques

Infrared spectra were obtained on a Mattson 1000 FTIR spectrometer. NMR spectra were recorded on Bruker Spektrsopin Avance DPX-400 Ultra Shield 400 MHz High Performance Digital FT-NMR and a Jeol FX 90Q 90 MHz NMR at room temperature in $CDCl_3$. The DTA curves were obtained using a Shimadzu DTA-50 instrument with programmed heating at 20°C/min. Thermogravimetric analysis (TGA) measurements were carried out under a nitrogen flow with a TGA-50 thermobalance at a heating rate of $10^\circ C\ min^{-1}$. Gel Permeation Chromatography (GPC) analyses were carried out using a high pressure liquid chromatography pump with Agilent 1100 system equipped with a vacuum degasser, a refractive index dedector. Tetrahydrofurane (THF) was the carrier solvent at a flow rate of 1 mL/min at room temperature. The instrument was calibrated with linear polystyrene standards.

2.3 Synthesis of Phenacyl Methacrylate (PAMA)

Phenacylmethacrylate (PAMA) was synthesized by the reaction of phenacylbromide and sodium methacrylate in the presence of hydroquinone at 85–90°C. It was distilled under vacuum (bp: 174°C at 15 mmHg)

IR (cm^{-1}, the most characteristic bands): 1736 (C=O stretch in ester), 1638 (C=C in the vinyl group), 1605 (C=C stretch in aromatic ring).

^{13}C-NMR ($CDCl_3$, δ ppm): 17.8 (CH_3), 66.3 (CH_2 adjacent to keto carbonyl), 133.3 (CH_2=), 166.9 (C=O in ester), 192.3 (C=O in keto group).

^1H-NMR ($CDCl_3$, δ ppm): 1.98 (s,3H), 5.62 (s, 1H), 6.22 (s, 1H, olefinic proton), 6.9–7.3 (5H, aromatic ring protons).

2.4 Synthesis of Phenoxycarbonylmethyl Methacrylate (PCMMA)

Phenoxycarbonyl methyl methacrylate was synthesized by the reaction of phenoxycarbonyl bromomethane with sodium methacrylate by using triethylbenzylammonium chloride (TEBAC)(Aldrich) as a phase transfer catalyst and distilled under vacuum (bp: 162°C at 5 mmHg).

IR (cm^{-1}, the most characteristic bands): 1784 (C=O stretch adjacent to phenoxy), 1730 (C=O stretch), 1638 (C=C stretch in the vinyl group), 1592 (C=C stretch in aromatic ring) ^1H-NMR ($CDCl_3$, δ ppm): 2.03 (s,3H), 5.72 (s, 1H olefinic proton), 6.29 (s, 1H olefinic proton), 6.9–7.4 (aromatic ring protons).

2.5 Free-radical Homopolymerization of PAMA and PCMMA

The homopolymers were synthesized by pre-radical solution polymerization with 2,2′-azobis(isobutyronitrile) as the initiator, in 1,4-dioxane. Typically, the polymerization was carried out in the oil bath at 60°C for 24 h. After the desired time, the reaction tubes were immediately lifted out of the oil bath and cooled to room temperature and then the viscous solutions were precipitated into ethanol. Both polymers were filtered and dried and once again precipitated into ethanol after a concentrated solution was produced in dichloromethane. Then, the copolymers were dried at 60°C for 24 h.

2.6 Free-radical Copolymerization of PAMA with MMA

Three copolymers of PAMA with MMA were prepared in 1,4-dioxane at 60°C in the presence of AIBN. Predetermined amounts of the monomers, AIBN and the solvent were mixed in a polymerization tube. The mixture was degassed about 10 min with argon and kept in a thermostated oil bath at 60°C. After the desired time, the mixture was cooled to an ambient temperature. The copolymers were precipitated into excess ethanol and purified by reprecipitation, and then the copolymers were dried at 60°C for 24 h.

3 Results and Discussion

3.1 Spectroscopic and GPC Characterization

The ^1H-NMR enlarged spectrum (Figure 1) of poly(PAMA) obtained by free radical polymerization indicates the characteristc signals at 7.8 ppm (ortho protons in benzene ring of the phenacyl group), 7.5 ppm (para proton in benzene ring of the phenyl), 7.4 ppm (metha protons in benzene ring of the phenacyl group), 5.3 ppm (methylene protons in the side chain of the repeated units) and 2.5–1.0 ppm (methylene and methyl proton in the main chain). The presence of very small signals at 4.7 (b) and 3.7 ppm (c) turned our attention towards the chain ends, and then a six-membered ring for the chain ends was suggested. The signals at 4.7 ppm and 3.7 ppm are in good agreement with esteric methylene and etheric methyn protons in the six-membered ring, respectively. The ^1H-NMR enlarged spectrum suggests the possible presence of olefinic proton at 6.2 ppm. This olefinic proton may be due to one in the vinylidene end group, perhaps the signal of the other proton of the group overlaps with that of the -OCH_2- moiety in the repeat unit. A low intensive band at 2200 cm^{-1} in FT-IR spectrum of poly(PAMA) (Figure 2) corroborates the CN group in the

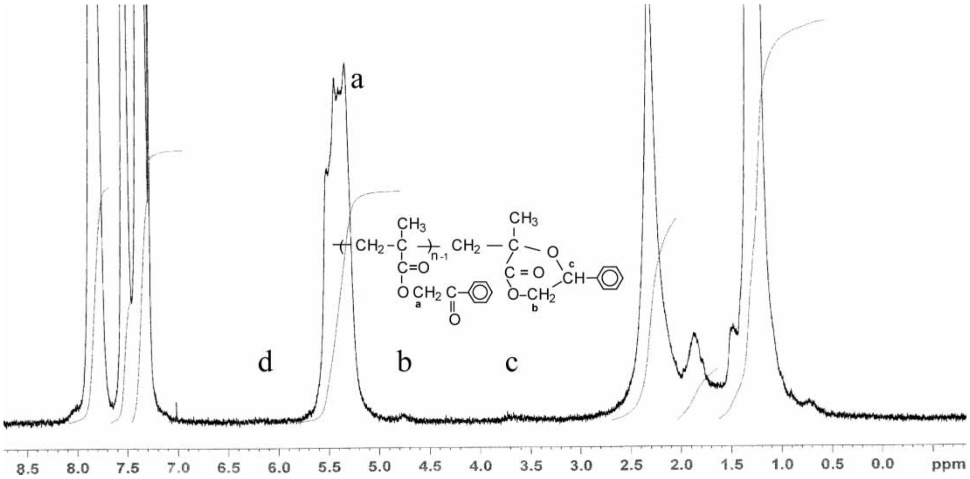


Fig. 1. ^{1}H-NMR spectrum of poly(PAMA) (Mn = 2800).

isobutyronitrile group coming from the initiator at the other end of the chain.

Mn values and polydispersities of the polymers prepared in this study are listed in Table 1, and some of the GPC profiles are shown in Figure 3. GPC curves of all the polymers are unimodel. Poly(PAMA) has a relatively low molecular weight (Mn = 2800, Table 1, Entry 1).

To investigate the effect of methyl methacrylate on the polymerization of PAMA, the copolymers were prepared in various feed ratios of PAMA to MMA. GPC data (as b and c in Figure 3) showed that Mn of the copolymer produced also increased (Table 1, Mn = 4100–15200) as MMA units increased in the copolymerization system. GPC curve (as d in Figure 3) showed that Mn of poly(MMA) prepared via free radical polymerization is 107000. The Mn values of the copolymers were decreased with the increase of the PAMA units in copolymer, as was seen in Figure 4. On the other hand, to assess the role of the phenacyl side group in decrease, the molecular weight, poly(PCMMA) bearing phenoxycarbonyl group instead of the phenylcarbonyl group in side chain, was prepared in the same conditions with those of poly(PAMA). This poly(PCMMA) indicates a Mn value of 50000 (Figure 5, Table 1). This value is much higher than that of poly(PAMA). The Mn value of poly(1-phenoxycarbonylethyl methacrylate), poly(1-PCEMA), given in the recent work (12) was 110200.

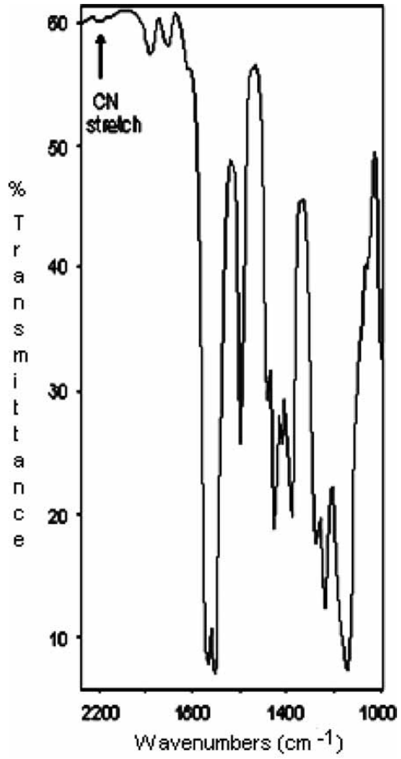


Fig. 2. FT-IR spectrum of poly(PAMA).

3.2 *The Formation Mechanism of End Group*

To the best of our knowledge, the reasons for a very low Mn of poly(PAMA) prepared by the free radical polymerization method using AIBN has not been reported to date. Increasing the molecular weight of the copolymer while increasing MMA content in the PAMA and MMA copolymers, and reaching the high molecular weight of poly(PCMMA) produced by free radical polymerization, directed us to

Table 1. The results of the molecular characterization of the polymers prepared by free radical polymerization method

Entry		M_n(GPC)	M_w/M_n	Tg (°C)
1	Poly(PAMA)	2800	1.07	107
2	Poly(PAMA80%-co-MMA)	4100	1.07	108
3	Poly(PAMA50%-co-MMA)	8100	1.45	—
4	Poly(PAMA20%-co-MMA)	15200	1.59	112
5	Poly(MMA)	107000	1.62	122
6	Poly(PCMMA)	50000	1.67	83
7	Poly(1-PCEMA)[12]	110200	1.63	96

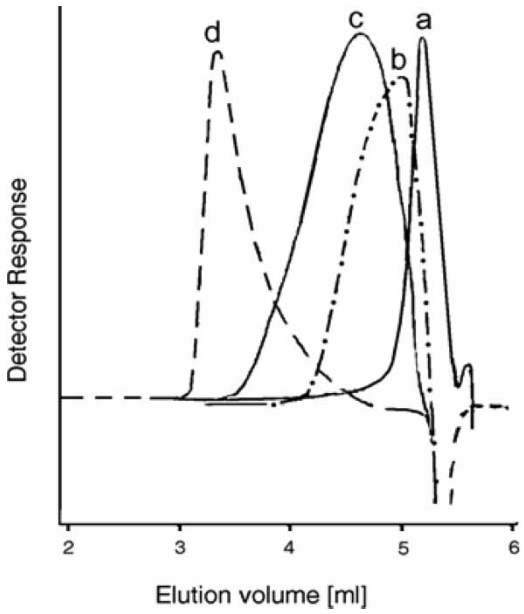


Fig. 3. GPC curves of polymers prepared via free radical polymerization; a) Poly(PAMA), b) Poly(PAMA50%-co-MMA), c) Poly(PAMA20%-co-MMA), d) Poly(MMA).

investigate why free radical polymerization of PAMA gives very low molecular weight

The formation of poly(PAMA) with relatively low molecular weight during free radical polymerization of PAMA results in rapid termination of growing chain radicals. The experimental data indicate that the phenacyl side group has an important role in this termination. When the phenoxy carbonyl group in Scheme 2 is changed with the phenacyl group as illulstrated in Scheme 1, it was synthesized poly (PCMMA) with high molecular weights. A termination mechanism preventing the sufficient growth of chains has been suggested as showed in Scheme 1. In this mechanism, the radical at the chain end catches carbonyl oxygene in the phenacyl group, and a cyclization occurs. So, an unpaired electron passes on carbon atom which is directly adjacent to phenyl ring, that is, a benzylic radical is formed. An unpaired electron of the new radical can form on two ortho and one para carbons of phenyl ring, which is stabilized by resonance. Benzylic form of this cyclic radical may catch a hydrogen radical from end group of another growing chain. Such as termination gives two poly(PAMA) molecules, which are one end a having six-membered ring and the other with an unsaturated end. The signal at 4.7 ppm (esteric methylene protons) and 3.7 ppm (etheric methyn proton) in ^{1}H-NMR protons spectrum of poly(PAMA) is strong evidence for formation of the cyclic end group. In addition, olefinic proton signal at 6.2 ppm is an evidence for unsaturated structures at the chain end. On the other hand, the presence of an equilibrium between a chain with cyclic radical end and a growing chain reduces concentration of the growing chain radicals. This may cause a controlled growing up of the chains. As a matter of fact, a very low polydispersity ($Mw/Mn = 1.07$) of poly(PAMA) prepared by free radical polymerization confirms this approach.

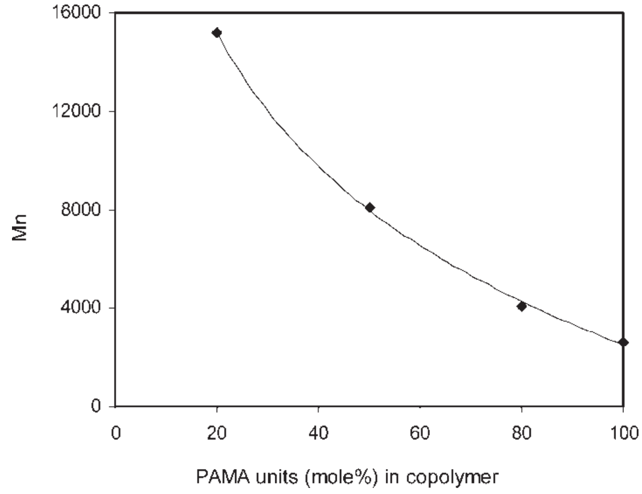


Fig. 4. Mn plot vs. PAMA unit (as mol%) in copolymer.

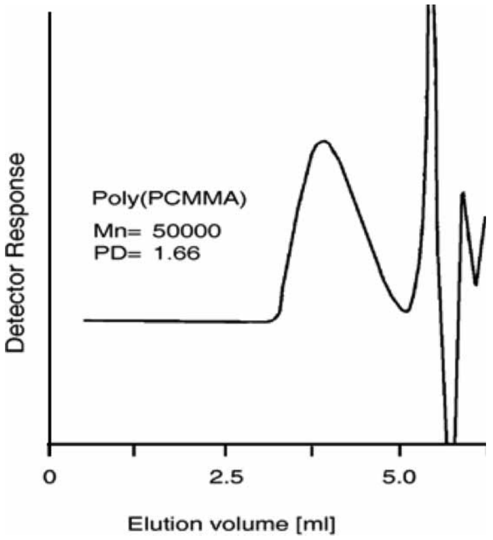
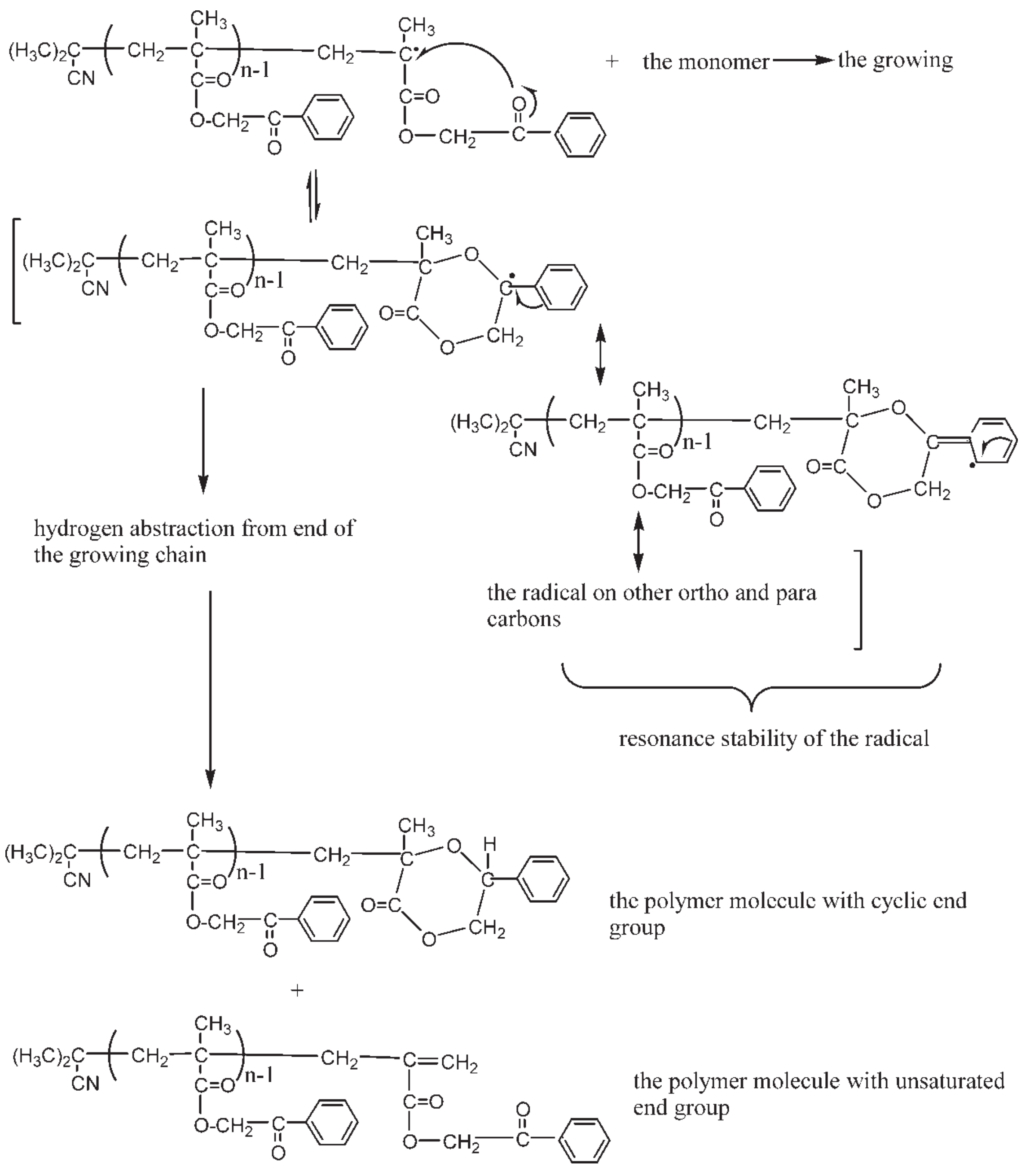


Fig. 5. GPC curve of poly(PCMMA).

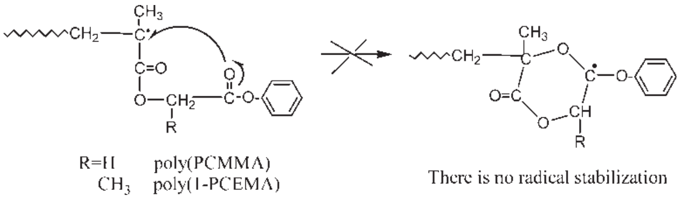
Reaching high molecular weights (Table 1) of poly(MMA), poly(PCMMA) and poly(1-PCEMA) (12) prepared under the same conditions as that of poly(PAMA) indicate that the cyclization does not occur at their growing chain ends. Side chain structures of poly(PCMMA) and poly(1-PCEMA) are especially similar to that of poly(PAMA), except for oxygen atom between the carbonyl group and phenyl ring. In cases of poly(PCMMA) and poly(1-PCEMA), the possible radicals corresponding to the cyclic radical produced at the end of growing phenacyl chain do not have the resonance stability because passing on phenyl ring of the radical is hindered by oxygene bonded to phenyl (Scheme 2). The terminal radicals cannot catch oxygen of phenoxycarbonyl in their side chain. So, a cyclization reaction cannot occur at the chain ends.



Sch. 1. The termination mechanism in free radical polymerization of phenacyl methacrylate.

3.3 Differential Termal Analysis (DTA) Measurements

The glass transition temperature is an important physical property to evaulate an amorphous polymer. Based on DTA determination, the poly(PAMA) obtained by traditional free radical polymerization exhibits a Tg at 107°C, whereas that of poly(PCMMA) obtained by the same method exhibits at 83°C. A difference of about 24°C temperature is due to the different free volume, which results in phenoxycarbonyl instead of a phenylcarbonyl group. The glass transition temperatures of the homo and copolymers are collected in Table 1, and DTA curves of poly(PAMA) and poly(MMA) and two the copolymers of PAMA and MMA are illustrated in Figure 6. The copolymer of PAMA and MMA (PAMA/MMA = 20/80, mol/mol) was determined to have a Tg of 112°C. In the case of the other copolymers, a single glass



Sch. 2. The structure showing that there is no end-cyclization in free radical polymerization of PCMMA or 1-PCEMA.

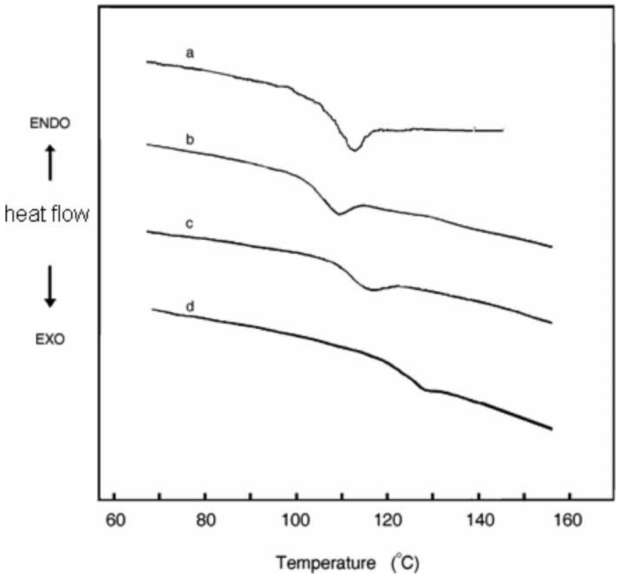


Fig. 6. DTA curves of poly(PAMA) and poly(MMA) and two the copolymers of PAMA and MMA.

transition temperatures is detected in the DTA thermograms. Such a transition is slightly moved toward higher temperature with increasing in percentage MMA in the copolymer. This shift is probably due to introduction of the MMA units in the PAMA chain. It is also important to remark that Tg increase as Mn value of copolymer increase.

3.4 Thermal Behaviors

The thermogravimetric curves for poly(PAMA), poly(MMA) and one copolymer prepared by free radical polymerization, which are obtained from room temperature to 500°C at a heating rate of 10°C/min under nitrogen flow, are given in Figure 7 as compared with that of poly(PCMMA) prepared under the same conditions. The thermogravimetric behavior of polymer depends on its structure and type of substituents in the main chain and side group. The effect on traditional free radical polymerization of side groups in the PAMA and PCMMA monomers was discussed in Section 3.1. So, TG and FT-IR analyses were carried out to discern the behavior of side groups during degradation of poly(PAMA) and poly (PCMMA). Thus, apparently, the thermal degradation of poly(PAMA) involves a mass loss with two stages, according to the TG curve in Figure 7: the first is associated with the first stage of the degradation reaction in the backbone of poly(PAMA). On the other hand, decomposition at low temperature implies that has an unsaturated end group generates a radical unzipping of the polymer chains via the chain transfer process. The second stage is attributed to the degradation by either the chain scission in the branches or the random scission of the backbone. In the case of the copolymer of PAMA and MMA, the introduction of MMA into the chain decreases the weight loss of the first step, which might be an indication that a MMA located between two PAMA units is stabilized relative to PAMA units. Poly(PCMMA) showed two stages of weight loss. The first step is between 213°C and 320°C. The second stage is between 325°C and 370°C. Poly(PAMA) and poly(PCMMA) were partially degraded. For this purpose, both polymers on different salt plates were partially degraded under argon at a heating rate

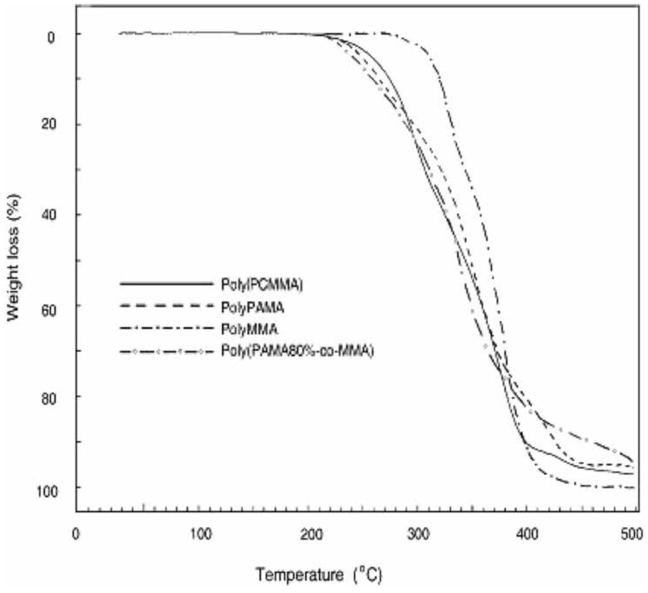


Fig. 7. The thermogravimetric curves for poly(PAMA), poly (MMA), one copolymer, poly(PCMMA) (heated 10°C/min heating rate under nitrogen atmosphere).

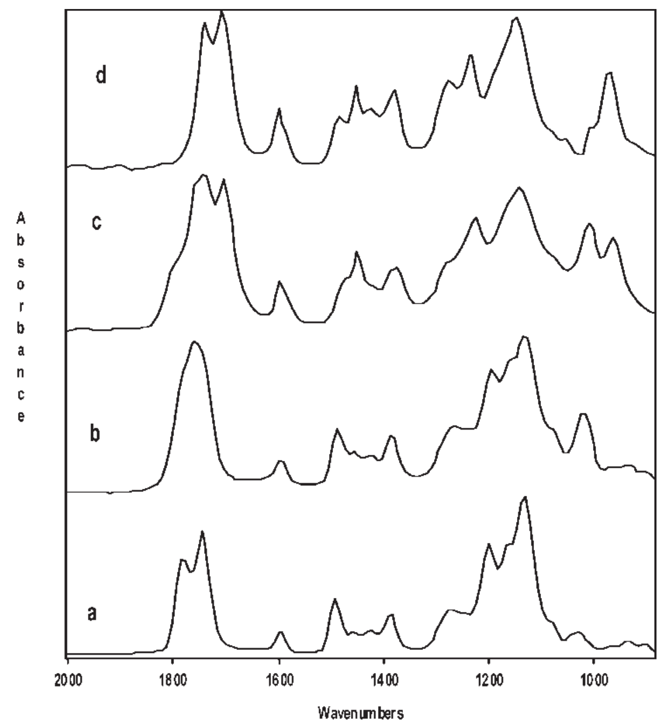


Fig. 8. FT-IR spectra of the partially degraded under argon atmosphere a) orginal poly(PCMMA) b) poly(PCMMA) heated to 320°C, c) poly(PAMA) heated to 270°C, d) original poly(PAMA).

Table 2. TGA data for the polymers

Polymers	T_i^a	$T_{\%50}^b$	%Weight loss at 300°C	%Weight loss at 350°C	%Weight loss at 400°C
Poly(PAMA)	210	350	20	50	20
Poly(MMA)	273	365	3	35	10
Poly(PAMA80%-co-MMA)	195	340	26	62	18
Poly(PCMMA)	213	342	26	54	8

[a] Initial decomposition temperature.
[b] Decomposition temperature at 50% wt loss.

of 10°C/min to 270°C and 320°C, respectively. The polymer films were heated progressively to each temperature and the FT-IR spectra were recorded at each stage and were compared with those of original polymers as in Figure 8. FT-IR spectrum of the poly(PCMMA) heated to 320°C was almost the same as that of the original poly(PCMMA) in spite of a weight loss of about 40%. This implies that poly (PCMMA) depolymerizes to 320°C. When poly(PAMA) was heated to 270°C, FT-IR spectrum of residue (as **c** in Figure 8) showed new bands at 1800, 1763 and 1023 cm^{-1}. These bands are characteristic for a anhydride structure forming as a result of elimination of acetophenone in the side group. The experimental data for poly(PAMA) are consistent with those reported in the literature (13). Although decomposition of poly(PAMA) and poly(PCMMA) began almost at the same temperature, poly(PCMMA) heated up to 320°C gave extensive depolymerization to the monomer being a product of main chain scission, while poly(PAMA) heated up to 270°C presented cyclic anhydride structures as being a product of a side chain reaction.

The volatile product collected during degradation of poly (PCMMA) heated to 320°C showed that the monomer with about 40% mass loss formed according to ^{1}H-NMR (for example 6.6; 6.2 ppm are characteristic for $CH_2{=}C$) and FT-IR analysis (for example, a band at 1638 cm^{-1} is characteristic for C=C stretch), and its yellow residue is dissolved within the solvent such as chloroform, dioxane, dichloromethane. TGA results of the polymers are summarized in Table 2. The TGA data of poly(PCMMA) are compared with those of poly(MMA), poly(PAMA) and poly(PAMA80%-co-MMA).

4 Conclusions

In this work, in free-radical polymerization of PAMA, we have suggested a reason on that the molecular weights can not increase in relatively high values and its polydispersity is very low. The radical in the terminal unit of the growing chain passes to a carbonyl carbon in the phenacyl group and this results in a cyclization. A new cyclic radical has the resonance stability with phenyl ring. This cyclic radical terminates by abstracting one hydrogen atom from the another growing chain end. These processes result in two poly(PAMA) molecules, one with a six-members ring end and the another with an unsaturated end. ^{1}H-NMR, FT-IR and GPC results support such a mechanism.

Thermal studies on poly(PAMA), poly(PAMA-co-MMA)s and poly(PCMMA) were given in detail as a comparison with each other.

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