Synthesis, Characterization, and Property Evaluations of Copolymers of Diamantyl Methacrylate with Methyl Methacrylate*

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ABSTRACT: This work reports the homo- and copolymerization behavior of previously unknown 4-diamantyl methacrylate (DMA) with vinyl comonomers like methyl methacrylate (MMA); the starting monomer DMA was synthesized in our laboratory using 4-diamantanol and methacryloyl chloride. The structures of the homo- and copolymers were analyzed using NMR techniques. DMA was found to be more reactive than MMA during copolymerization. The reactivity ratios as determined by the Kelen-Tüdos method are $r_{MMA} = 0.58$ and $r_{DMA} = 1.75$. The incorporation of a few mol % of diamantyl units into the PMMA backbone led to a significant increase in its thermal stability and glass transition temperature. The polymers with 15 and 42 mol % of DMA units in the copolymers showed increased T_g values of 126°C and 172°C, respectively. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2109–2115, 2009

Key words: copolymer composition; diamantyl methacrylate; diamodoids; radical polymerization; thermal stability

INTRODUCTION

Diamondoids are cage hydrocarbons with structures resembling the diamond lattice.[1,2] Adamantane **1** is the first member of this family, containing one tricyclic cage. It is followed by diamantane **2** with two cages in its structure, and so on. Diamondoids in general have extraordinary physical as well as chemical properties such as low surface energies, high densities as well as hydrophobicity, thermal stability, and resistance to oxidation.[1,2] These properties led to wide utilization of adamantane, as the most abundant and readily synthesized diamondoid, in polymer chemistry. The effects of adamantane incorporation on the physical, thermal, and mechanical properties of a number of polymer families were investigated.[3–5] Polymers with adamantyl moieties in the main chain or as pendant groups undergo changes in their physical and chemical properties.[6–10] Such functionalizations in particular lead to enhanced thermal stability, e.g., glass transition temperatures (T_g) and decomposition tempera-

tures relative to the parent material.[11] Besides these properties, alicyclic components, in general, provide polymers with high optical transparency and etch resistance, and a number of them were investigated in the form of polyacrylates in view of their application potential. Otsu and coworkers[6] have studied the kinetics of the radical polymerization of 1-adamantyl methacrylate (AdMA) and 3,5-dimethyl-1-adamantyl methacrylate (DMAdMA) with 2-2'-azobis(2-methylpropionitrile) (AIBN) and investigated the properties of the resulting polymers. Nonlinear optical poly(adamantyl methacrylate-methyl vinyl urethane)s were prepared by functionalization of adamantyl methacrylate vinyl isocyanate precursor polymers by Samyn and coworkers.[12] Hada and coworkers[13,29] studied the effect of adamantane containing protecting groups [2-adamantyloxy methyl (AdOM), 2-methyl-2-adamantyl (MAd), 1-methyladamantyloxy methyl (MAdOM), 4-oxo-2-adamantyloxy methyl (OAdOM)] in the methacrylate polymers on lithographic performance and chemical amplification positive-tone resists. Nozaki and coworkers[15] proposed a single-layer resist material that met general requirements of high optical transparency, good dry-etch resistance, and thermal stability, comprised of a polymer containing 2-methyl-2-adamantanol protecting groups. Studies of the properties of the protective groups necessary for good combination with adamantyl moieties in view of lithographic performance were

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*Functionalized nanodiamonds, part 15, for part 14, see ref. 30.

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also performed.[16] Further studies of the synthesis and lithographic properties of resist formulations based on a copolymer containing 2-methyladamantyl methacrylates were carried out by Kudo and coworkers.[14]

It was pointed out earlier that increasing the bulkiness of the substituents in polymers is very effective for increasing T_g, and this is especially true for cyclic alkyl groups.[17] In the present work, we investigate for the first time the homo- and copolymerizability of the previously unknown 4-diamantyl methacrylate (**4**, DMA), synthesized from the next member of the diamondoid family, i.e., diamantane (**2**), with vinyl comonomers like methyl methacrylate (**5**, MMA). We characterize the structure of the copolymers, investigate their properties, and study the effect of incorporation of different numbers of diamantyl units in the PMMA backbone on their thermal stabilities and glass transition temperatures.

EXPERIMENTAL PART

Materials

The synthesis of 4-diamantanol (**3**) was carried out as described in our previous article[18] from diamantane (**2**), which can readily be synthesized from Binor-S[19,20] but is also available commercially.[21,22] Commercially available methacryloyl chloride (Alfa Aesar) was used for the monomer synthesis without purification. MMA (BASF, 99%) and anisole (Acros, 99%) were dried over calcium hydride, distilled, and stored under argon. Dichloromethane (DCM, BASF), methanol (BASF), and ethanol (BASF) were purified by distillation. 2,2′-Azobis(2-methylpropionitrile) (AIBN, Riedel-de Haën, 98%) was recrystallized from ethanol.

Instrumentation

The values for the average molecular weights M_n and the weight average molecular weights M_w of the polymers were determined by gel permeation chromatography (GPC) using a Knauer system equipped with a PSS-SDV (10 μm) 50 × 8 mm^2 column and two columns 600 × 8 mm^2 at 25°C, a differential refractive index detector, and a UV photometer using THF as eluent at a flow rate of 0.8 mL/min. Poly (methyl methacrylate) standards were used for calibration.

^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on Bruker Avance 300 A and Avance 300 B spectrometers, respectively, using CDCl$_3$ as solvent.

Mettler thermal analyzers having 851 TG and 821 DSC modules were used for the thermal characterization of the polymers. Indium and zinc standards were used for temperature and enthalpy calibration of the 821 DSC module. Differential scanning calorimetry (DSC) scans were recorded in a nitrogen atmosphere (flow rate = 80 mL/min) at a heating respectively cooling rate of 10°C/min. The glass transition temperature (T_g) was determined at the inflection point of the observed shift in the base line of the second heating cycle of a DSC scan. Thermal stabilities were determined by recording thermogravimetric (TG) traces in a nitrogen atmosphere (flow rate = 50 mL/min) using powdered samples. A heating rate of 10°C/min and a sample size of 10 ± 2 mg were used in each experiment.

Synthesis of 4-diamantyl methacrylate DMA (4)

Triethylamine (20.35 mL, 146.83 mmol) was added dropwise to a stirred suspension of 4-diamantanol (**3**, 20.00 g, 97.89 mmol) in DCM (220 mL) at 0°C under argon. After 5 min of stirring, the solution of methacryloyl chloride (14.7 mL, 151.73 mmol) in DCM (70 mL) was added to the reaction mixture. The resultant mixture was allowed to come to ambient temperature and stirred overnight. The organic layer was washed with water, aqueous sodium hydroxide (10%), water, brine, and dried over MgSO$_4$. After removal of the solvent, the residue was purified by column chromatography on SiO$_2$ (pentane/ CH$_2$Cl$_2$ 9 : 1) to give DMA (**4**, 24.2 g, 91%) as a colorless solid, m. p. 70–74 °C.

^{1}H NMR (200 MHz, CDCl$_3$): 5.96 (m, 1 H), 5.43 (m, 1 H), 2.09 (m, 6 H); 1.94 (m, 3 H), 1.86 (m, 3 H), 1.75 (m, 4 H), 1.71 (m, 6 H).

^{13}C NMR (50 MHz, CDCl$_3$): 166.5 (C), 138.0 (C), 124.2 (CH$_2$), 79.7 (C), 41.5 (CH$_2$), 39.7 (CH), 37.0 (CH$_2$), 36.4 (CH), 25.5 (CH), 18.3 (CH$_3$).

General procedure for homopolymerization of 4-diamantyl Methacrylate (4) in solution

A dry Schlenk tube equipped with a magnetic stir bar was charged with DMA (**4**, 272.4 mg, 1 mmol) and a solution of 2,2′-azobis(2-methylpropionitrile) in anisole (1 mL, c$_{AIBN}$ = 10 mmol/L) in a counter flow of argon. The flask was sealed and three freeze-pump-thaw cycles were performed to remove oxygen. The Schlenk tube was immersed in a preheated oil bath at 60°C. After 6 h, the polymerization was stopped by cooling the Schlenk tube in liquid nitrogen. The reaction mixture was then diluted with DCM (2 mL), precipitated from methanol (100 mL), and collected by filtration. Yield: 254 mg (93%). M_n = 94,000, M_w/M_n = 2.74. $T_{5\%}$ = 276°C.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.2–0.9 (m, 24 H, polymer backbone and diamantyl side chain).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 177.1, 80.1, 79.9, 46.5, 46.5, 41.5, 39.8, 37.1, 36.5, 25.5, 17.9.

TABLE I
Homopolymerization of Diamantyl Methacrylate (4, DMA) at 60°C Using 2,2′-Azobis(2-methylpropionitrile) (AIBN) as Initiator for Different Intervals of Time ([M]/[In] = 100 : 1)

Sample	Reaction time/min	Conversion/%	$M_n \times 10^{-5}$	M_w/M_n
1	30	31	2.1	1.9
2	60	47	1.7	2.0
3	120	69	1.4	1.9
4	240	83	1.4	2.2
5	360	93	1.0	2.7

General procedure for copolymerization of 4-diamantyl methacrylate (4) and methyl methacrylate (5) in solution

A dry Schlenk tube equipped with a magnetic stir bar was charged with DMA (**4**, 500.2 mg, 1.84 mmol), MMA (**5**, 196.0 µL, 1.84 mmol), anisole (3.55 mL) and a solution of 2,2′-azobis(2-methylpropionitrile) in anisole (120.0 µL, $c_{AIBN} = 0.306$ mol/L) in a counter flow of argon. The Schlenk flask was sealed and three freeze-pump-thaw cycles were performed to remove oxygen. The tube was heated in an oil bath at 60°C for 1 h and then cooled in liquid nitrogen to stop further polymerization. The copolymer was precipitated from methanol (100 mL) and collected by filtration. Yield: 179 mg (26%). $M_n = 127,000$, $M_w/M_n = 1.93$. $T_{5\%} = 251°C$.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.59 (bs, 3 H, —OCH$_3$), 2.2-0.8 (m, 46 H, polymer backbone and diamantyl side chain).

Different copolymers were made by changing the feed ratio of the two comonomers in the feed, the details are given in Table I.

RESULTS AND DISCUSSION

In the present study, homopolymerization and copolymerization of DMA (**4**) and MMA (**5**) was carried out under conventional free radical polymerization reaction conditions with AIBN as a radical initiator at 60°C (Fig. 1).

The homopolymer of **4** was soluble in common organic solvents like chloroform, tetrahydrofuran, and dimethylformamide. The polymer structure was investigated by NMR spectroscopy and representative ^{1}H and ^{13}C NMR spectra of homo DMA (PDMA) in CDCl$_3$ are shown in Figure 2. The ^{1}H NMR spectrum shows peaks of aliphatic protons in the lower ppm region at 0.9–2.2 ppm; the ^{13}C NMR spectrum of the homopolymer shows the presence of characteristic carbonyl carbon (1) and quaternary carbon (2) of diamantyl units and absence of peaks of unsaturated vinyl groups at 124 and 138 ppm characteristic for corresponding DMA monomer.
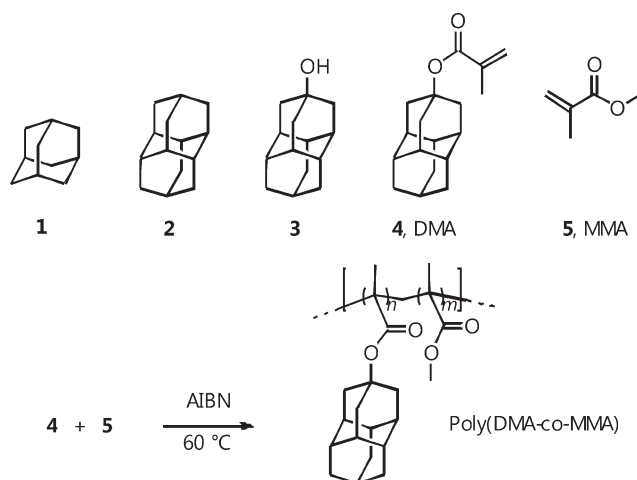

Figure 1 The first two members of diamondoid family: adamantane (**1**) and diamantane (**2**); 4-diamantanol (**3**), the starting compound for DMA (**4**) synthesis, and the polymerization reaction under consideration in the present work.

The homopolymerization of DMA monomer was followed in different time intervals (Table I). There was an increase in conversion with time and a high yield of about 93% was achieved already after 6 h. Very high molecular weight was obtained at the start of the reaction followed by a decrease with moderate polydispersities with unimodal GPC curves (Fig. 3). The increase of conversion with time, the very high molecular weight at the start of the reaction, and the polydispersities are in accord with
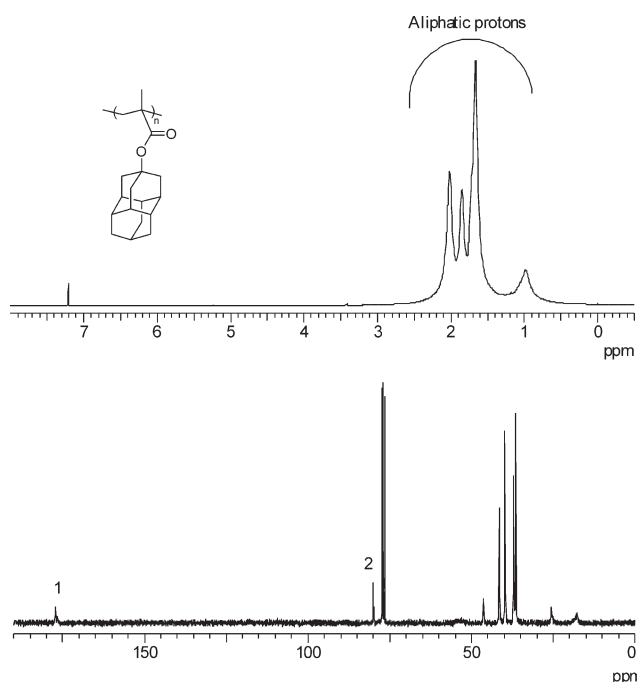

Figure 2 ^{1}H and ^{13}C NMR spectra of homo poly(diamantyl methacrylate) (PDMA) in CDCl$_3$.
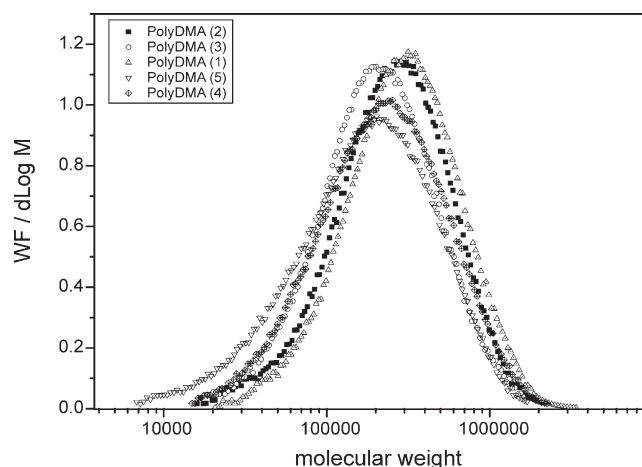
Figure 3 Gel permeation chromatography (GPC) traces of different homo poly(diamantyl methacrylate) (PDMA) obtained at different time intervals (refer for numbers in Table I).

Figure 4 Thermogravimetric TGA trace of homo poly (diamantyl methacrylate) (PDMA) in nitrogen atmosphere.

the conventional free radical polymerization of vinyl monomers. We observed a continuous decrease in molecular weight and increase in the polydispersity with time, which shows slow initiation and increased termination reactions with time.

The thermal stability of PDMA was probed using thermogravimetric analysis (Fig. 4). The homopolymer showed two-step degradation with very high thermal stability. The temperature for 5% weight loss ($T_{5\%}$) of the homopolymer was ca. 276°C. The first step showed a weight loss of about 40% and the major weight loss took place at the second step starting from ca. 350°C with T_{max} (temperature at which maximum weight loss occurs) 370°C. The first polymer member of diamondoids series, poly(adamantyl methacrylate) (PAdMA) showed an initial decomposition temperature of 254°C and T_{max} of 304°C. That is, PDMA showed an increased thermal stability over AdMA. Attempts to determine the glass transition temperature of the homo PDMA using differential scanning calorimetry were not successful and no glass transition was seen before 250°C, i.e., before the first decomposition temperature of the polymer. This could be a result of the very high T_g, which lies above the decomposition temperature of the polymer.
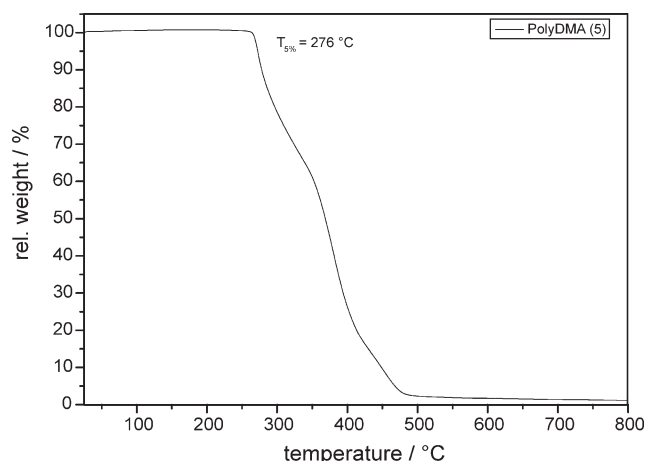
The homopolymer is found to be film forming and we were able to prepare transparent films in solvents such as THF and CHCl$_3$; the films were very brittle and could not be handled without breaking.

A series of copolymers of DMA (**4**) with MMA (**5**) were made by changing the molar ratio of the two monomers in the initial feed (Table II). The structural characterizations of the copolymers were done in CDCl$_3$ using NMR spectroscopic techniques. The representative ^{1}H NMR spectra of the copolymers are shown in Figure 5 (Table II). The characteristic signals of both **4** and **5** were seen in the spectra of all the copolymers. The methoxy protons of **5** appear at 3.6 ppm while the other aliphatic protons of **5** and **4** overlap in the lower ppm region at 0.8–2.2 ppm. We determined the copolymer compositions from ^{1}H NMR spectra using the peak intensities I_{OMe} of the methoxy protons at 3.6 ppm (characteristic of MMA units) and the total intensities I_{total} of aliphatic proton peaks at 0.8–2.2 ppm using the following formula:

$$[MMA]/[DMA] = \frac{1_{-OCH_3}/3}{\left(\frac{I_{total} - 5}{24}\right)}$$

The aliphatic proton signal in the ^{1}H-NMR-spectra at 0.8–2.2 ppm of poly(DMA-co-MMA) includes all

TABLE II
Copolymerization of Diamantyl Methacrylate (4, DMA) with Methyl Methacrylate (5, MMA) at 60°C Using 2,2′-Azobis(2-methylpropionitrile) (AIBN) as Initiator for 1 h

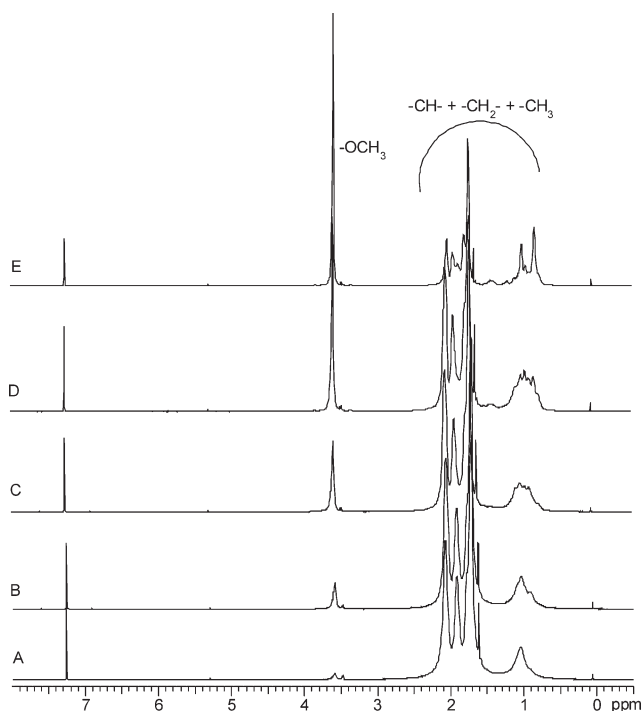| Sample	Feed ratio [MMA]/[DMA] Molar ratio	Copolymer ratio [MMA]/[DMA] Molar ratio	Conversion/%	$M_n \times 10^{-5}$	M_w/M_n
A	0.111	0.066	41	1.96	1.87
B	0.429	0.232	35	1.59	1.90
C	1.000	0.580	26	1.27	1.93
D	2.335	1.348	19	1.01	1.98
E	9.003	5.310	15	0.70	2.20

Figure 5 ^{1}H NMR spectra of copolymers poly(diamantyl methacrylate-co-methyl methacrylate) poly(DMA-co-MMA) in CDCl$_3$: Copolymer ratio [MMA]/[DMA] Molar ratio (A) 0.066, (B) 0.232, (C) 0.580, (D) 1.348, and (E) 5.310.

Figure 7 Gel permeation chromatography (GPC) traces of different copolymers poly(diamantyl methacrylate-co-methyl methacrylate) poly(DMA-co-MMA) in THF: Copolymer ratio [MMA]/[DMA] Molar ratio (A) 0.066, (B) 0.232, (C) 0.580, (D) 1.348, and (E) 5.310.

protons of the DMA monomer, that are 24, and the backbone protons of the MMA monomer, that are five, taking into account that the backbone protons of the MMA monomer also contribute to the signal area of the aliphatic proton signal at 0.8–2.2 ppm.

From the copolymer composition diagram (Table II), we conclude that the copolymers for each feed composition were rich in DMA. This shows the higher reactivity of the DMA monomer as compared with MMA during copolymerization. Also, reactivity
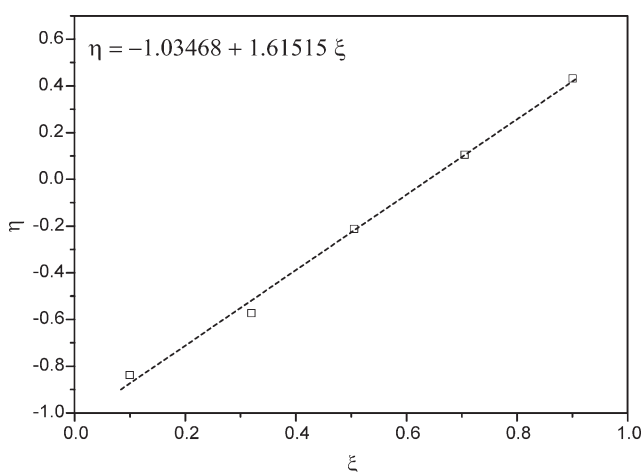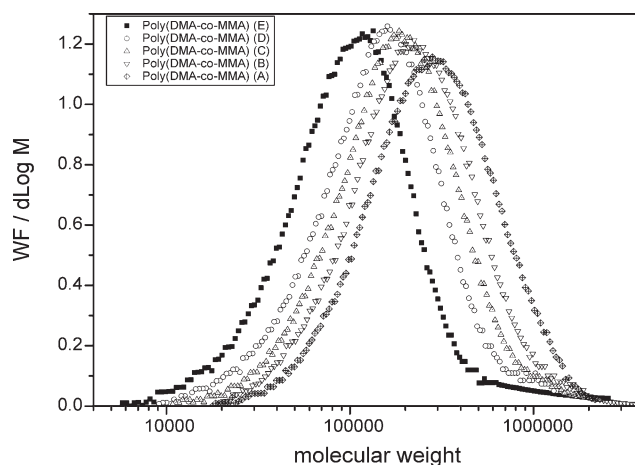
ratios for **4** and **5** were determined using the Kelen-Tüdos method[23] and a corresponding plot is shown in Figure 6; values determined are: $r_{MMA} = 0.58$ and $r_{DMA} = 1.75$. The reactivity ratio values also show an increased tendency of both DMA and MMA radicals to react with DMA monomers as compared with their reaction with **5**. DMA radicals are expected to be less reactive in terms of recombination or disproportionation as compared with MMA radicals, because of the presence of the rigid and bulky diamantyl cages. As a result, there is an increased tendency of DMA radical formation. The same behavior regarding increased reactivity of either dialkyl fumarates or AdMA due to the bulky ester groups was reported by Otsu and coworkers.[6]
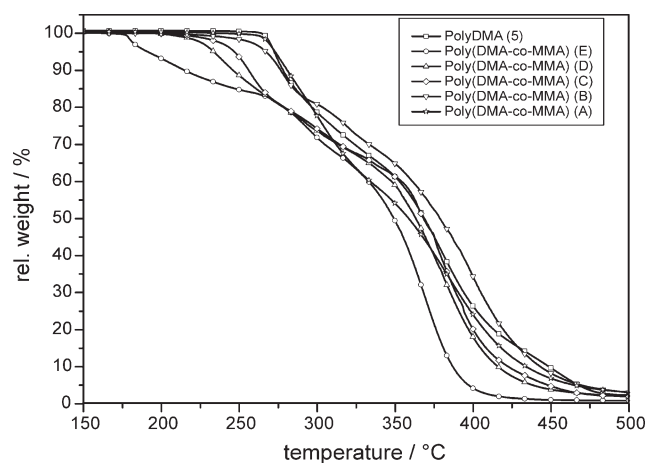

$$\eta = -1.03468 + 1.61515\,\xi$$

Figure 6 Kelen-Tüdos plot for copolymerization of diamantyl methacrylate (**4**) with methyl methacrylate (**5**).

Figure 8 Thermogravimetric trace of different copolymers poly(diamantyl methacrylate-co-methyl methacrylate) poly(DMA-co-MMA): Copolymer ratio [MMA]/[DMA] Molar ratio (A) 0.066, (B) 0.232, (C) 0.580, (D) 1.348, (E) 5.310.

Sample	Copolymer ratio [MMA]/[DMA] Molar ratio	$T_{5\%}$ (temperature for 5% weight loss)/°C	T_{max} (temperature of maximum weight loss) /°C			T_g (glass transition temperature)/°C
			$T_{max\ 1}$	$T_{max\ 2}$	$T_{max\ 3}$	
A	0.066	277	—	300	395	—
B	0.232	271	280	320	400	—
C	0.580	251	260	320	390	—
D	1.348	237	240	315	380	172
E	5.310	195	220	280	370	126

A very systematic trend was also seen for the molecular weight of the copolymers as determined by the GPC technique (Table II, Figure 7). All GPC curves were unimodal but the molecular weight decreased with an increase in the amount of **5** in the copolymers. This can also be very nicely rationalized by the increased number of termination reactions, like recombination and disproportionation, with an increase in the amount of **5** in the copolymers as the ester groups of **5** are more flexible relative to **4**. This increase in termination reactions is also reflected in the slight increase in polydispersities, showing broadness in the chain distribution size, with increased amount of MMA (**5**) in the copolymers.

The effect of incorporating diamantyl units into the PMMA hydrocarbon chain on the thermal stability and glass transition temperature of PMMA was also investigated. The degradation of PMMA prepared by radical polymerization generally proceeds in two or three steps.[24] In the present work, PMMA prepared under similar conditions with radical initiator showed three-step degradations. The steps at lower temperatures (T_{max} 180°C and 295°C) are assigned to the weak linkages and chain end initiated thermal degradations. The step at T_{max} about 371°C is a result of the random chain scission. Incorporation of low mol % (15 mol %) of DMA onto the PMMA backbone (Fig. 8) led to three-step degradation but with increased $T_{5\%}$, (temperature at which 5% weight loss took place) to 195°C which is an indication of increased thermal stability. T_{max} (temperature at which maximum weight loss occurs) for the first step also increases ($T_{max1} = 220$°C). With high mol % of **4** in the copolymers (> 40 mol %) thermal degradation took place in two-three steps depending upon the composition (Table III). The degradation steps of PMMA at T_{max} 180°C and 371°C were shifted to much higher values. As is shown in the literature[25–28] attempts to improve thermal stability of PMMA were made by incorporating N-substituted maleimides, bis-maleimides, itaconimides, and cardanyl acrylate etc. In the present study, we observe that even incorporation of very low mol % (around 15 mol %) of the DMA units onto the PMMA backbone lead to increased thermal stability with increased $T_{5\%}$ and T_{max} for each step of degradation. Glass transition temperatures were evaluated for each polymer (Table III, Fig. 9) using the differential scanning calorimetry technique. Like in the case of homo PDMA, copolymers having higher mol % of DMA (> 60%) did not show any glass transition temperature up to 250°C. The polymers with 15 and 42 mol % of DMA units in the copolymers showed increased T_g values of 126°C and 172°C, respectively (Fig. 9) due to increased stiffness of the polymer chains.

CONCLUSIONS

We prepared PDMA homopolymer and copolymers poly(DMA-co-MMA), and their structures were analyzed by a variety of techniques. Different mol % of diamantyl units can be incorporated onto the poly (methyl methacrylate) backbone by free radical copolymerization. DMA was found to be more reactive than MMA during copolymerization. The reactivity ratios as determined by the Kelen-Tüdos
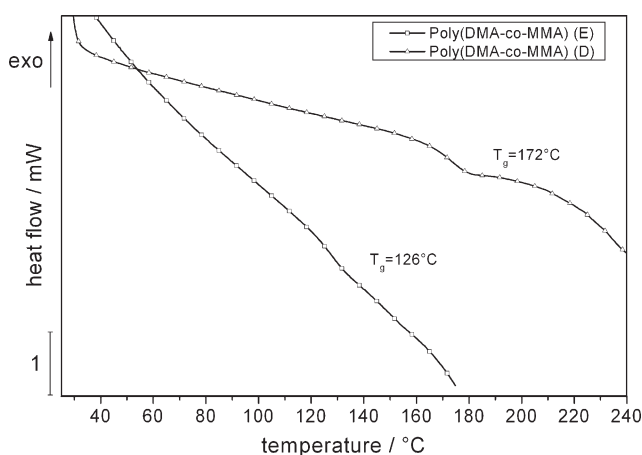
Figure 9 Differential scanning calorimetric traces of different copolymers poly(diamantyl methacrylate-co-methyl methacrylate) poly(DMA-co-MMA).

method are $r_{MMA} = 0.58$ and $r_{DMA} = 1.75$. Incorporation of low mol % of diamantyl units into the PMMA backbone lead to an increase in its thermal stability and glass transition temperature. Hence, this provides a simple method of improving the thermal properties of poly(methyl methacrylate)s. Like polymers with adamantyl units, diamantyl containing polymers, inspite being tertiary alkyl esters, proved to be highly thermally stable materials. To propose materials for industrial applications, it is necessary to compare the optical and mechanical properties of the diamantyl based polymers with that of poly(methyl methacrylate). This part of the work is in progress in our laboratories.

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