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Copolymers of 4-adamantylphenyl methacrylate derivatives with methyl methacrylate and styrene

Lon J. Mathias*, Jennifer Jensen, Kevin Thigpen, John McGowen, Demetrius McCormick, Louis Somlai

Department of Polymer Science, University of Southern Mississippi, P.O. Box 10076, Hattiesburg, MS 39406-0076, USA

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Abstract

Three 4-(1-adamantyl)phenyl methacrylate monomers were synthesized from 4-(1-adamantyl)phenol derivatives which were obtained by Friedel–Crafts alkylation of phenol, 2-methylphenol and 2,6-dimethylphenol with 1-bromoadamantane. Characterization of the monomers by IR, ^{1}H and ^{13}C NMR, GC and elemental analysis confirmed structures and purities. Copolymers of these new monomers with styrene were synthesized using free radical techniques. One series of 4-(1-adamantyl)phenyl methacrylate was also prepared with methyl methacrylate (MMA). Copolymer compositions were evaluated by ^{1}H and ^{13}C solution NMR, and with FTIR. Reactivity ratios were estimated to have values of $r_1 = 0.22$ and $r_2 = 1.51$ for styrene and 4-(1-adamantyl)phenyl methacrylate copolymers; $r_1 = 0.31$ and $r_2 = 2.44$ for styrene and 2-methyl-4-(1-adamantyl)phenyl methacrylate; and $r_1 = 0.97$ and $r_2 = 0$ for styrene and 4-(1-adamantyl)-2,6-dimethylphenyl methacrylate copolymers (J Polym Sci A 3 (1965) 369–87, J Macromol Sci Rev C4 (1970) 281). All homo- and copolymers were characterized using DSC and TGA to determine copolymer composition effects on T_g and thermal stability. The estimated T_g for the homopolymer of 4-(1-adamantyl)phenyl methacrylate was 253°C and the onset of decomposition was 250°C in nitrogen. The homopolymer of 2-methyl-4-(1-adamantyl)phenyl methacrylate had a T_g of 250°C which was at the onset of decomposition in nitrogen. The homopolymer of 4-(1-adamantyl)-2,6-dimethylphenyl methacrylate could not be obtained by free-radical polymerization. 4-(Adamantyl)phenyl methacrylate was incorporated into styrene copolymers at 1–30 mol% and gave T_g increases of ca. 5–60°C over that of polystyrene, respectively. Incorporation of this monomer into MMA copolymers (0.75–35 mol%) resulted in T_g increases of ca. 6–70°C over that of poly(methyl methacylate).

Keywords: Copolymers; 4-Adamantylphenyl methacrylate derivatives; Friedel–Crafts alkylation

1. Introduction

Adamantane (tricyclo [3.3.1.1^{3,7}] decane) is a thermodynamically very stable, highly symmetrical tricyclic hydrocarbon which consists of three fused chair-form cyclohexane rings in a diamond lattice structure [3]. Adamantane-containing polymers have generated a great deal of interest recently due to the fact that pendant adamantanes improve physical properties such as stiffness, glass transition temperature and solubility, and reduce or eliminate crystallinity [4–7]. Several approaches have been utilized to make adamantyl-substituted monomers for both step- and chain-growth systems. Examples include phenolics made from 4-(1-adamantyl)phenol and formaldehyde [8], polymethacrylates made from the adamantanoyl ester derivative of ethyl α-hydroxymethylacrylate [9] and adamantyl methacrylate [10], and poly(*m*-phenylene) incorporating 4-(adamantyl)-1,3-phenylene units [11,12]. Adamantyl-substituted aromatic diols have also been incorporated into poly(ether ether ketone) [13,14], poly(benzylethers) [15] and poly(esters) [16] to give significant T_g increases. This report focuses on the synthesis of new adamantyl substituted methacrylates containing phenyl spacers, their incorporation into methyl methacrylate (MMA) and styrene copolymers based on feed ratios less than 15–30 mol%, and characterization of the polymers obtained.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich Chemical Company unless otherwise stated. 4-(1-Adamantyl)phenol

* Corresponding author. Tel.: +1-601-266-4868; fax: +1-601-266-5504.
E-mail address: lon.mathias@usm.edu (L. Mathias).

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(**1**) was synthesized by reaction of 1-bromoadamantane and phenol using a literature method [17,18]. Intermediate analogs with one *ortho* methyl group (**2**) and two *ortho* methyls (**3**) were synthesized similarly (see below). 2,6-Dimethylphenyl methacrylate was prepared using a previously published procedure [19]. Methacryloyl chloride (MAC), methyl methacrylate (MMA) and styrene (St) were fractionally distilled before use. Triethylamine (TEA), benzene and tetrahydrofuran (THF) were distilled from CaH_2. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Diethyl ether, methacrylic anhydride, *ortho*-cresol, 2,6-dimethylphenol, *ortho*-dichlorobenzene (*o*-DCB) and *sec*-butyl lithuim were used as received. Lupersol 101 [(2,5-dimethyl-2,5-di-(*t*-butylperoxy)hexane] was purchased from Elf Atochem, North America Incorporate and used as received.

2.2. Characterization

FTIR spectra were obtained on an ATI-Mattson Galaxy 5020 spectrometer. ^1H and ^{13}C solution NMR spectra were obtained with a Bruker AC-300 instrument using standard parameters, $CDCl_3$ as solvent and tetramethylsilane as internal standard. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were conducted using TA instruments 2920 and 2960 modules controlled by a Thermal Analyst 2100 data station. DSC scans were run with a 10°C min^{-1} heating rate and nitrogen purge flow of 30 ml min^{-1}. TGA scans were run at 20°C min^{-1} with a nitrogen purge flow of 100 ml min^{-1}. Molecular weights and molecular weight distributions were estimated using size-exclusion chromatography (SEC) with THF solvent and four styrene gel mixed-bed columns (7.5 mm i.d. × 300 mm, 10 μm particle diameter, American Polymer Standard Corporation, Mentor, OH). Number and weight average molecular weights were estimated relative to polystyrene standards. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

2.3. Analysis of copolymer composition

A stock solution of poly(4-(1-adamantyl)phenyl methacrylate) (see below for synthesis) was prepared in chloroform. The solution was allowed to equilibrate for ca. 2 h, then loaded into a liquid IR cell with a 1 mm path-length and the spectrum obtained. The absorbance of the carbonyl at 1749 cm^{-1} was analyzed at several different concentrations (0.005–0.03 M) and a standard Beer's law calibration plot obtained by plotting the measured absorbances vs. known concentrations of polymer solutions. The best fit equation generated through linear least squares analysis was $y = -0.033 + 21.91x$, where x is the molar concentration and the extinction coefficient (21.91) has units of absorbance/concentration.

To determine the amount of 4-(1-adamantyl)phenyl methacrylate units present in the copolymers, solutions of copolymers of known concentrations were prepared, analyzed by IR as indicated above, and comonomer contents calculated based on the measured absorbances using the Beer's law relationship.

A second technique used to analyze copolymer composition was gated proton-decoupled ^{13}C NMR. To maximize signal-to-noise, samples were prepared in as high a concentration as possible while still allowing flow. The delay in acquisition time was set to 30 s, which allowed sufficient time for all nuclei to relax between scans. The quaternary peaks on the aromatic ring located ipso to both the oxygen and adamantane moieties were integrated relative to the quaternary carbon on the styrene aromatic ring. Integration values were calculated using both Bruker supplied software and GRAMS/32 software (Galactic Industries; Salem, New Hampshire); essentially identical results were obtained.

3. Precursor synthesis

3.1. 2-Methyl-4-(1-adamantyl) phenol (*2*)

A 500 ml three-neck round-bottom flask equipped with nitrogen inlet and outlet (to a solution of 1N KOH to trap evolved HBr gas) was charged with 1-bromoadamantane (40 g, 0.186 mol) and *o*-cresol (23 ml, 0.223 mol) in 60 ml *o*-DCB. The mixture was then heated to 70–80°C and held at this temperature until reaction was complete (as determined by GC). The mixture was cooled, filtered and the precipitate recrystallized from methanol to give a white crystalline powder; purity 100% by GC, yd 41.5 g, 60%; mp 136–138°C; ^1H NMR ($CDCl_3$): δ 7.31 (s), 7.08 (t), 6.7 (d), 4.5 (s), 2.3 (s), 2.14 (s), 1.88 (d), 1.75 (d); ^{13}C NMR ($CDCl_3$): δ 151.37, 143.88, 127.55, 123.32, 12.06, 114.52, 43.34, 36.77, 35.43, 28.99, 16.09.

Anal. calcd for $C_{17}H_{19}O$: C, 84.25%; H, 9.15%; Found: C, 84.48%; H, 8.90%.

3.2. 2,6-Dimethyl-4-(1-adamantyl) phenol (*3*)

A 250 ml three-neck round-bottom flask equipped with nitrogen inlet and outlet (to a solution of 1N KOH to trap evolved HBr gas) was charged with 1-bromoadamantane (20.0 g, 93 mmol) and 2,6-dimethylphenol (13.62 g, 111 mmol) in 40 ml of *o*-DCB. The reaction was heated to reflux (170–180°C) and held at this temperature until reaction was complete as indicated by GC. The mixture was cooled, filtered and the precipitate recrystallized from a mixture of hexanes and methylene chloride (95:5) to give a white crystalline solid; purity 100% by GC, yd 14 g, 60%; mp 166–169°C; ^1H NMR ($CDCl_3$): δ 6.95 (s), 4.48 (s), 2.24 (s), 2.07 (s), 1.87 (d), 1.70 (s); ^{13}C NMR ($CDCl_3$): δ 149.97, 143.03, 124.82, 122.88, 43.29, 36.71, 35.20, 28.92, 16.21.

Anal. calcd for $C_{18}H_{21}O$: C, 84.32%; H, 9.40%; Found: C, 84.21%, 9.48%.

4. Monomer synthesis

4.1. 4-(1-Adamantyl)phenyl methacrylate (**4**)

A three-neck 3000 ml round-bottom flask equipped with an addition funnel and mechanical stirrer was charged with **1** (100 g, 0.438 mol) and methyacrylic anhydride (88.7 g, 0.575 mol) dissolved in 1000 ml of diethyl ether at 0°C. NaOH (35 g, 0.876 mol) was dissolved in 100 ml of water and slowly added dropwise to the stirred solution via the addition funnel. The reaction was stirred for 12 h. The mixture was then transferred to a seperatory funnel and washed with water until a neutral pH was obtained for the aqueous phase. The organic phase was then washed with two 500 ml portions of saturated NaCl solution. The ether was removed under reduced pressure and the precipitate recystallized from absolute ethanol to give a white crystalline solid; purity 99.6% by GC, yd 110 g, 85%; mp 121–125°C; ^{1}H NMR ($CDCl_3$): δ 7.38 (d), 7.06 (d), 6.32 (s), 5.72(s), 2.27 (s), 2.09 (s), 1.90(s), 1.77(s); ^{13}C NMR ($CDCl_3$): δ 165.95, 148.68, 135.94, 126.92, 125.82, 120.83, 43.15, 36.66, 35.59, 28.65, 18.33.

Anal. calcd for $C_{20}H_{24}O_2$: C, 81.05%; H, 8.16%; Found: C, 81.24%; H, 7.97%.

4.2. 2-Methyl-4-(1-adamantyl)phenyl methacrylate (**5**)

A three-neck 250 ml round-bottom flask equipped with nitrogen inlet and outlet to trap hydrogen gas was flame-dried twice. The flask was charged with **2** (6.3 g, 26.35 mmol), 30 ml of THF and three spatula tips of a 60% NaH dispersion in mineral oil (ca. 3.0 g). Once the phenoxide ion was generated (as evident by cessation of hydrogen gas evolution), methacroyl chloride (5 ml, 44.1 mmol) was dripped in slowly. A small amount (1 ml) of TEA was added to trap any HCl present. The addition funnel was then washed with an additional 20 ml of THF. The reaction was kept in the ice bath for 45 min, then filtered. THF was removed under reduced pressure. The product was recrystallized from methanol to give a white powder; purity 100% by GC, yd 5.31 g, 65%; mp 120–123°C; ^{1}H NMR ($CDCl_3$): δ 7.29 (s), 7.21 (d), 7.00 (d), 6.34(s), 5.73(s), 2.23(s), 2.17(s), 1.89(s), 1.76(s); ^{13}C NMR ($CDCL_3$): δ 165.38, 148.61, 146.99, 135.72, 128.94, 127.41, 126.62, 123.18, 121.02, 43.05, 36.59, 35.65, 28.78, 18.22, 16.23.

Anal. calcd for $C_{21}H_{26}O_2$: C, 81.51%; H, 8.14%; Found: C, 81.32%, H, 8.36%.

4.3. 2,6-Dimethyl-4-(1-adamantyl)phenyl methacrylate (**6**)

The procedure used was the same as above for **5**. The product was then recrystallized from methanol to yield a white crystalline powder; purity 100% by GC, yd 4.78 g, 63%; mp 158°C; ^{1}H NMR ($CDCl_3$): δ 7.04 (s), 6.36 (s), 5.73 (s), 2.13 (s), 2.08 (s), 1.88 (s), 1.76 (s); ^{13}C NMR ($CDCl_3$): δ 1.65, 148.61, 145.93, 135.71, 129.33, 126.77, 125.15, 43.22, 36.78, 35.74, 28.95, 18.47, 16.56.

Anal. calcd for ($C_{22}H_{28}O_2$): C, 81.45%; H, 8.70%; Found: C, 81.46%, H, 8.50%.

5. Homopolymer synthesis

5.1. Poly(4-(1-adamantyl)phenyl methacrylate

A large thick-walled test tube was charged with **4** (6.82 g, 22.94 mmol), AIBN (0.034 g, 0.5 wt%) and benzene (30 ml). The tube was sealed with a rubber septum and air removed with three freeze/evacuate/thaw cycles followed by a purge with nitrogen. The tube was placed in a 60°C oil bath, reacted to high conversion as shown by viscosity increase to gellation and precipitated into CH_3OH; yd 4.14 g, 61%.

5.2. Poly(2-methyl-4-(adamantyl)phenyl methacrylate)

A small thick-walled test tube was charged with **5** (0.1589 g, 0.52 mmol). The tube was sealed with a rubber septum and air removed with three freeze/evacuate/thaw cycles followed by a purge with nitrogen. The tube was placed into a 120°C oil bath. A small test tube was charged with lupersol 101 (0.015 g; 10 wt%) and *o*-dichlorobenzene (1 ml). Once the monomer had melted, the initiator solution was added (0.1 ml; 1 wt%). The solution vitrified within 30 min. The solid polymer was dissolved in CH_2Cl_2 and precipitated into hot CH_3OH; yd 0.075 g, 47%.

5.3. Poly(2,6-dimethylphenyl methacrylate)

A dried 50 ml three-neck flask purged with N_2 was placed in a dry ice/isopropanol bath (−78°C). 2,6-Dimethylphenyl methacrylate (1.0 g; 5.3 mmol) in 5 ml of dry THF was added via a syringe followed by *sec*-BuLi (1.3 M solution in cyclohexane) (0.4 ml; 0.52 mmol). After stirring for 20 min, a noticeable viscosity increase occurred and three drops (ca. 0.024 ml) of degassed methanol was added to quench the reaction. The resulting polymer was then precipitated into 250 ml methanol, filtered and dried under reduced pressure at 100°C for 24 h; yd 0.65 g, 65%.

5.4. General copolymer synthesis

A large thick-walled test tube was charged with styrene (4.0 g, 40 mmol), monomer **6** (0.8 g, 2.46 mmol), AIBN (0.02 g, 0.5 wt%) and benzene (20 ml). The tube was sealed with a rubber septum and air removed with three freeze/evacuate/thaw cycles followed by a purge with nitrogen. The tube was placed in a 60°C oil bath and held there for times ranging from 2–4 h. Polymerization was stopped at a conversions of less than 15% by precipitation into CH_3OH. The obtained polymers were dissolved in either CH_2Cl_2 or THF and reprecipitated into CH_3OH to insure all monomer had been removed. Due to limited solubility of the

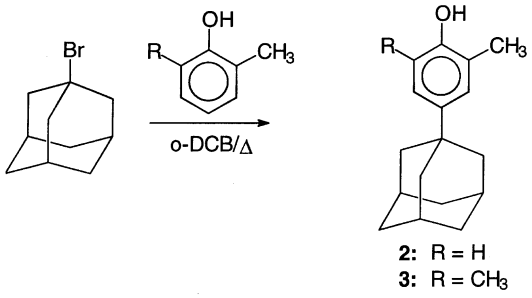

Fig. 1. Precursor synthesis using 1-bromoadamantane and hindered phenols.

methylated phenol monomers, their copolymers were precipitated into hot CH_3OH. This method was applied to all monomers (**4**–**6**) and copolymers with styrene and MMA. ^1H NMR was used to confirm complete removal of unreacted monomer and solvent, and TGA to evaluate thermal stability. All the copolymers were analyzed by SEC to determine the molecular weights. Quantitative NMR and IR were used to determine composition, and DSC to determine T_gs.

6. Results and discussion

6.1. Monomer synthesis

The methyl-substituted adamantyl phenols (**2** and **3**) were readily synthesized via Freidel–Crafts alkylation of *ortho*-cresol and 2,6-dimethylphenol with 1-bromoadamantane analogous to the synthesis of 4-(1-adamantyl)phenol (Fig. 1) [17,18]. All reactions proceeded without added catalyst. To obtain exclusive *para* substitution to the oxygen on *ortho*-cresol, the reaction temperature was kept below 80°C. There was no evidence of adamantyl incorporation at the *ortho* position by GC or NMR, although adamantyl substitution of phenols in the *ortho* position is possible under certain conditions [20–22].

Monomer **4** was synthesized under phase transfer conditions (Fig. 2) using **1** and methacrylic anhyride. Compounds **5** and **6** were much more difficult to obtain due to steric

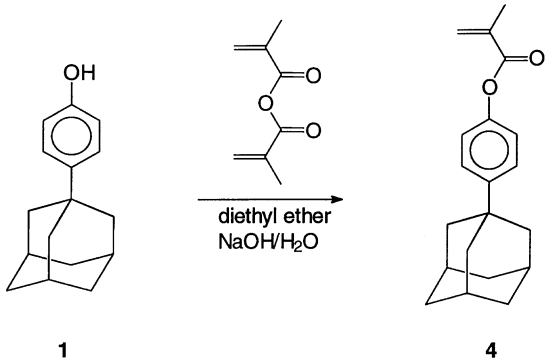

Fig. 2. Monomer **4** synthesis using (**1**) and methacrylic anhydride.

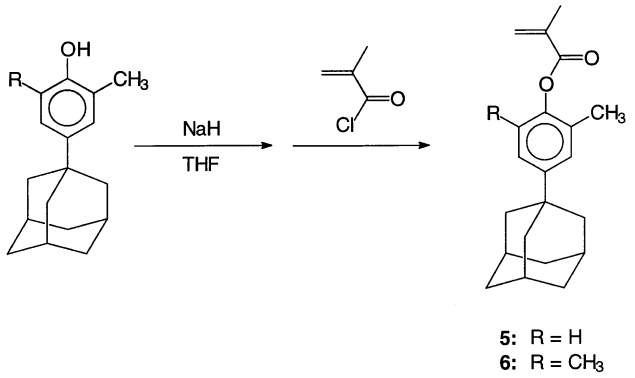

Fig. 3. Monomer **5** and **6** synthesis using **2** and **3** plus methacroyl chloride.

hindrance by the methyl substituents. They were synthesized by first generating the phenoxide anions through addition of NaH to solutions of compounds **2** and **3**, followed by reaction with excess methacryoyl chloride (Fig. 3).

6.2. Polymer synthesis

The homopolymer of 4-(1-adamantyl)phenyl methacrylate (**4**) was synthesized from a 1 M benzene solution of monomers using 0.5 wt% AIBN as initiator at 60°C. It was quenched at 61% conversion by precipitation into CH_3OH. 2-Methyl-4-(1-adamantyl)phenyl methacrylate did not polymerize in solution using AIBN as the initiator at 60°C. The homopolymer of 2-methyl-4-(1-adamantyl)-phenyl methacrylate (**5**) was synthesized in bulk at 120°C using 1% lupersol 101 (added as a 10% *o*-DCB solution) which has a half-life of 10 h at this temperature. The polymer vitrified within 30 min of adding initiator. Homopolymers of **4** and **5** were soluble in $CHCl_3$, THF, and CH_2Cl_2 but not in CH_3OH or acetone.

Despite repeated efforts, we were unable to make the homopolymer of **6** in bulk or in solution using conventional free radical techniques. 2,6-Dimethylphenyl methacrylate has been reported to hompolymerize at 60°C in bulk using dilauroyl peroxide as initiator [23], and we have confirmed this. Due to steric hindrance and sites for chain transfer to monomer, the rates of polymerization were very slow and only low molecular weights were obtained (intrinsic viscosity (η) of 0.12), SEC molecular weight of 22,000). However, **6** did not hompolymerize in the bulk using this method even at 150°C (the melting point of monomer) or in solution using AIBN as initiator at 60 or 30°C. Apparently, the high temperature needed to melt the adamantyl-substituted monomer raised the rates of chain transfer and termination so that they competed effectively with polymerization. The melt temperature may also be above the ceiling temperature, which would also limit or stop propagation. 2,6-Dimethyl-4-(1-adamantyl)phenyl methacrylate did homopolymerize anionically in THF at −78°C using *sec*-BuLi as the initiator, although low conversion and low molecular weight material was obtained. Surprisingly,

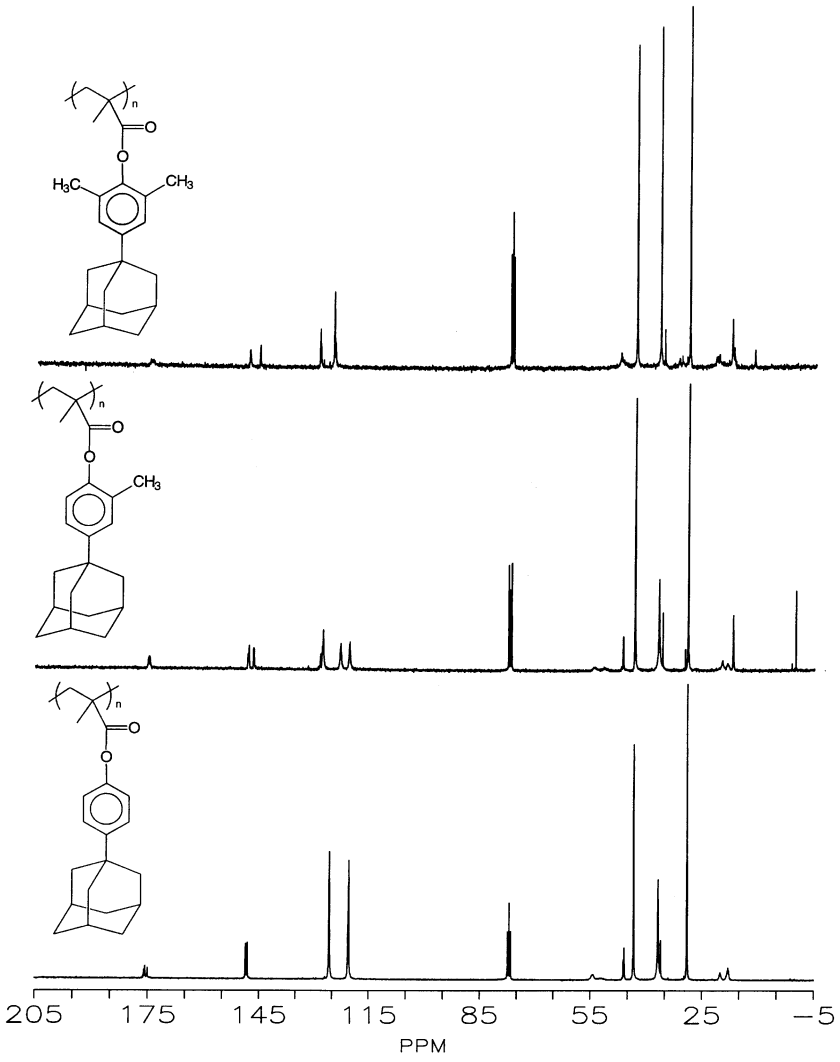

Fig. 4. ^{13}C NMR spectra of poly(4-(1-adamantyl)phenyl methacrylate) (bottom), poly(2-methyl-4-(1-adamantyl)phenyl methacrylate) (middle), poly(4-(1-adamantyl)-2,6-dimethylphenyl methacrylate) (top).

copolymerizations proceeded normally, and **6** was readily incorporated into a series of copolymers.

The copolymers of all three monomers were synthesized in benzene because of limited solubility of the adamantylphenyl methacrylate monomers in MMA and styrene. Early attempts of copolymerizations to moderate conversion indicated a high incorporation of 4-(1-adamantyl)phenyl methacrylate relative to the feed. Therefore, all of the copolymerizations were quenched at less than 15% conversion to control compositional drift during reactions.

Table 1
Molecular weight data, conditions, and thermal analysis of homopolymers

Polymer	Conditions	% Conversion	M_n[a]	M_w[b]	Peak MW[c]	MWD	T_g	Td[d]
PAdPHMA	1 M benzene 0.5% AIBN	90	55.0	250	170	4.5	253	260
PAdOCMA	Bulk; 1% Lupersol	47	89.2	401	290	4.5	250	250
PAdDMPMA	1 M THF; 10% *sec*-BuLi	36	–[e]	–	–	–	227	260
PDMPMA (model-compound	1 M THF 10% *sec*-BuLi	65	15.1	17	18.8	1.12	196	220

[a] $M_n/10^3$.
[b] $M_w/10^3$.
[c] Peak Max/10^3.
[d] Onset of decomposition.
[e] Not soluble in THF.

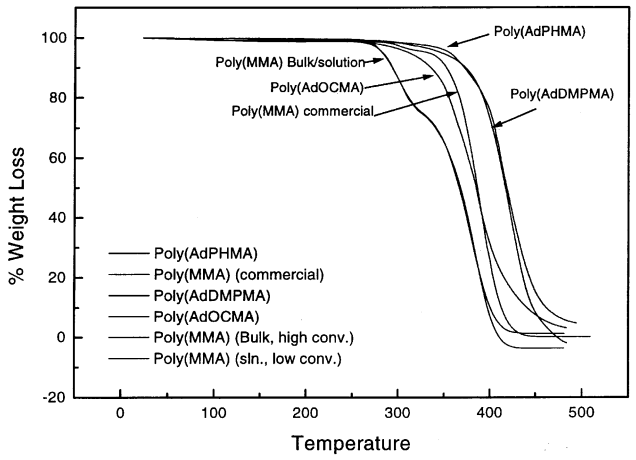

Fig. 5. TGA trace of homopolymers: poly(4-(1-adamantyl)phenyl methacrylate) (—), poly(methayl methacrylate) (commercial) (- - -), poly(4-(1-adamantyl)-2,6-dimethylphenyl methacrylate) (--- ·-), poly(2-methyl-4-(1-adamantyl)phenyl methacrylate (···) and poly(methayl methacrylate) (synthesized in our lab) (-·-·-·-).

7. Polymer characterization

7.1. Homopolymers

Structures of all homopolymers (**4**–**6** plus that of 2,6-dimethylphenyl methacrylate) were confirmed by FTIR, and ^{13}C and ^{1}H NMR. Homopolymer spectra were used to make peak assignments for the copolymers, determine limiting T_g values, and evaluate Beer's law parameters for determination of copolymer compositions by FTIR (Fig. 4).

Molecular weight analysis of the homopolymers of 4-(1-adamantyl)phenyl methacrylate and 2-methyl-4-(1-adamantyl)phenyl methacrylate showed number average values (relative to polystyrene) of 155,000 and 89,000 with polydispersities of 3.2 and 4.5, respectively (Table 1). Analysis of the thermal stability of poly(4-(1-adamantyl)phenyl methacrylate) and poly(2,6-dimethyl-4-(1-adamantyl)phenyl methacrylate) in nitrogen showed a slight improvement over commercial PMMA and a large improvement over PMMA synthesized in our lab in solution using AIBN as an initiator at 60°C (Fig. 5). The thermal stability of poly(2-methyl-4-(1-adamantyl)phenyl methacrylate) was less than that of commercial PMMA and the other homopolymers synthesized. This polymer was synthesized in the bulk at 120°C, which may have increased termination by coupling, incorporating a weak link in the chain which would lead to cleavage and polymer unzipping. The T_g of poly(4-(1-adamantyl)phenyl methacrylate) was estimated to be 253°C, which was at or just below the temperature for onset of decomposition. The T_g of poly(2-methyl-4-(1-adamantyl)phenyl methacrylate) was greater than that of decomposition (ca. 257°C) and only a combined DSC transition was observed. A second scan in the DSC revealed a lower T_g which would be indicative of decomposition or chain unzipping occurring in the first run (Fig. 5 and Table 1).

7.2. Copolymers

The number average molecular weights (relative to polystyrene) for copolymers of 4-(1-adamantyl)phenyl methacrylate and MMA ranged from 35,000 to 75,000 with T_gs of 130–194°C (Table 2). The T_gs are ca. 6–64°C higher than PMMA. This series of copolymers utilized a higher amount of 4-(1-adamantyl)phenyl methacrylate in the feed so a larger increase in T_g was expected. The number average molecular weights for copolymers of 4-(1-adamantyl)phenyl methacrylate and styrene ranged from 70,000 to 172,000. The T_gs of 113–166°C where ca. 10–63°C higher than the T_g of polystyrene (Table 3). The number average molecular weights for copolymers of 2-methyl-4-(1-adamantyl)phenyl methacrylate and styrene ranged from 26,000 to 40,000 and the T_gs from 106 to 133 (Table 4). The number average molecular weights for copolymers of 2,6-dimethyl-4-(1-adamantyl)phenyl methacrylate and styrene ranged from 18,500 to 51,500 and the T_gs from 107 to 142 (Table 5). The T_g increase for the methylated

Table 2
Molecular weight data, composition, and thermal analysis of methyl methacrylate-co-4-(1-adamantyl)phenyl methacrylate

Mol % AdPHMA (Feed)	Mol% AdPHMA (exp)[a]	% Conversion	M_n[b]	M_w[c]	Peak MW[d]	MWD	T_g
0	0	5.6	51.1	97.8	69.8	1.9	124
0.5	0.74	8.0	53.9	100.1	69.1	1.9	130
1.0	1.71	6.0	52.9	99.8	71.4	1.9	137
1.5	2.40	10.0	55.9	114.7	81.0	2.0	139
5.0	8.24	5.6	46.7	112.1	78.2	2.4	145.4
10.0	15.64	3.4	35.9	86.5	56.7	2.4	163.0
15.0	23.03	5.4	40.4	113.5	73.7	2.8	174.5
20.0	31.04	8.0	72.8	220	160	3.0	186.1
22.5	36.59	4.76	62.3	194.7	139.5	3.1	195.8
25.0	34.77	5.9	70.4	233	171.2	3.3	194.0

[a] Calculated by integration of ^{1}H NMR.
[b] $M_n/10^3$.
[c] $M_w/10^3$.
[d] Peak max/10^3.

Table 3
Molecular weight data, composition, and thermal analysis of styrene-co-4-(1-adamantyl)phenyl methacrylate

Mol% AdPHMA (Feed)	Mol%AdPHMA (exp)[a]	Mol% AdPHMA (exp)[b]	% Conversion	M_n[c]	M_w[d]	Peak MW[e]	MWD	T_g
0	0	0	15.7	22.0	36.5	34.2	1.6	103
1.0	5	4.18	4.5	70.9	118.2	100.6	1.7	113.04
2.0	7	8.4	7	70.8	114.6	95.5	1.6	119.58
2.4	9	10.1	6.8	69.6	111.7	94.2	1.6	122.4
6.1	21	18.34	6.3	74.4	117.5	100.9	1.6	140.56
13	33	28.16	5.2	122.3	209.8	178.0	1.7	166.18

[a] Calculated from IR (Beer's law).
[b] Calculated by integration of ^{13}C NMR.
[c] $M_n/10^3$.
[d] $M_w/10^3$.
[e] Peak max/10^3.

Table 4
Molecular weight data, composition, and thermal analysis of styrene-co-2-methyl-4-(1-adamantyl)phenyl methacrylate

Mol% AdOCMA (Feed)	Mol% AdOCMA (exp)[a]	Mol% AdOCMA (exp)[b]	% Conversion	M_n[c]	M_w[d]	Peak MW[e]	MWD	T_g
0	0	0	15.7	22.0	36.5	34.2	1.66	103
0.17	.59	–[f]	10.57	28.2	43.8	39.3	1.55	105.9
0.35	1.16	–	11.40	27.1	43.6	38.5	1.61	107.7
0.67	–[f]	–	11.86	26.7	46.4	37.5	1.73	108.2
0.85	–	0.65	10.17	28.1	45.0	40.8	1.60	109.9
1.56	4.45	1.32	9.57	26.7	42.2	38.5	1.58	112.2
2.47	–	–	10.37	40.5	55.4	46.1	1.37	114.4
3.27	9.85	–	10.16	33.4	52.8	46.1	1.58	117.8
4.79	13.98	7.99	14.38	31.5	50.8	43.4	1.61	124.1
6.32	17.12	12.47	13.79	42.1	57.1	49.0	1.36	128.4
7.76	–	14.52	14.52	34.3	57.2	47.8	1.66	132.6

[a] Calculated from IR (Beer's law).
[b] Calculated by integration of ^{13}C NMR.
[c] $M_n/10^3$.
[d] $M_w/10^3$.
[e] Peak max/10^3.
[f] Not able to accurately estimate mol% incorporation.

Table 5
Molecular weight data, composition, and thermal analysis of styrene-co-4-(1-adamantyl)-2,6-dimethylphenyl methacrylate

Mol% AdDMPMA (Feed)	Mol % AdDMPMA (exp)[a]	Mol% AdDMPMA (exp)[b]	% Conversion	M_n[c]	M_w[d]	Peak MW[e]	MWD	T_g
0	0	0	15.7	22.0	36.5	34.2	1.65	103
0.17	–[f]	–[f]	11.35	24.0	42.9	37.8	1.78	107.1
0.33	–	–	12.41	18.5	31.6	29.5	1.71	108.0
0.65	0.67	–	9.11	35.4	64.0	65.7	1.80	109.1
0.81	1.12	1.57	13.13	24.8	41.3	38.3	1.66	109.3
1.29	1.55	2.76	14.33	19.0	32.6	31.5	1.71	110.3
1.60	1.83	3.08	10.88	28.1	45.6	39.4	1.62	113.9
2.22	–	5.23	12.71	30.1	45.1	41.1	1.50	117.6
3.13	–	6.58	12.35	29.7	47.0	40.8	1.58	121.7
4.64	4.93	7.93	12.50	36.0	52.0	48.1	1.44	127.5
6.07	6.42	10.06	8.51	51.5	86.7	76.2	1.68	136.7
7.45	7.05	11.4	13.70	31.9	52.3	47.8	1.64	137.1
8.81	7.61	15.25	15.70	33.8	52.2	48.7	1.54	142.4

[a] Calculated by FTIR (Beer's Law).
[b] Calculated by integration of ^{13}C NMR.
[c] $M_n/10^3$.
[d] $M_w/10^3$.
[e] Peak max/10^3.
[f] Not able to accurately estimate mol% incorporation.

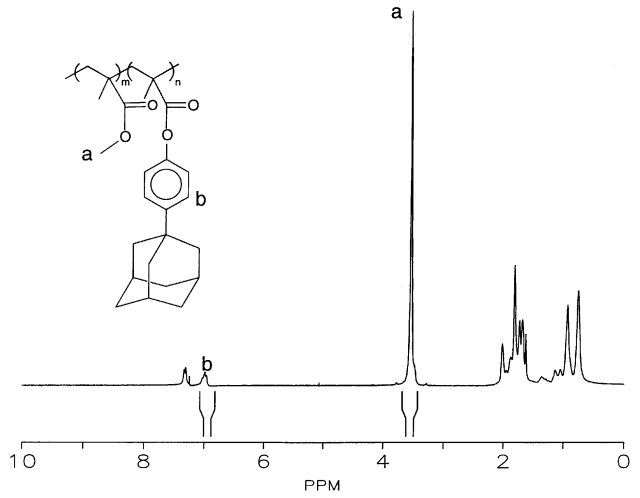

Fig. 6. ^{1}H proton NMR of methyl methacrylate-co-4-(1-adamantyl)phenyl methacrylate (showing integrated peaks).

phenols was similar (ca. 3–30°C). It was found that 2,6-dimethyl-4-(1-adamantyl)phenyl methacrylate was much less reactive and a smaller amount of incorporation into the copolymer, showed a comparable increase in T_g (in comparison to the other 2 styrene copolymers).

7.3. Copolymer composition

To determine compositions, the copolymers were analyzed by FTIR, ^{13}C and ^{1}H NMR. Copolymers of MMA and 4-(1-adamantyl)phenyl methacrylate were analyzed by ^{1}H NMR, using methoxy protons integrated relative to the aromatic protons (Fig. 6). The experimental values obtained indicated that the adamantyl monomer was incorporated at a much higher rate than present in the feed.

The homopolymer of 4-(1-adamantyl)phenyl methacrylate was synthesized and analyzed by FTIR at various concentrations to develop a Beer's law plot. By measuring the aborbance of the carbonyl of the various styrene copolymers at 1750 cm^{-1}, the incorporation of the adamantyl monomer could be determined. The copolymers were also analyzed by ^{13}C gated decoupled NMR. The quaternary phenyl carbons were integrated relative to the quaternary carbon on styrene ipso to the backbone carbon (Fig. 7). The values obtained were close but not identical to those obtained by FTIR. Because FTIR is a more sensitive technique, it was possible to measure absorbances of the carbonyl at lower concentrations. Although very concentrated samples and long acquisition times were used for ^{13}C NMR, the quaternary carbon peaks were weak and it was difficult to distinguish them from baseline noise. Fig. 8 is a plot comparing values obtained by both techniques. Both methods confirmed higher incorporation of the adamantyl monomer than in the feed.

To slow down the reactivity of the adamantyl monomer, and evaluate the effect of additional phenyl substitutions on polymer properties, *ortho* methyl groups were added to the phenyl moiety. A homopolymer of 2-methyl-(1-adamantyl)-phenyl methacrylate was synthesized and analyzed by FTIR at various concentrations to obtain a Beer's law plot for the carbonyl peak. Styrene copolymers were analyzed by FTIR and ^{13}C gated decoupled NMR. For the latter, the quaternary carbon ipso to the oxygen was integrated relative to the quaternary carbon on styrene ipso to the backbone carbon. Both methods indicated a higher incorporation of this adamantyl monomer than in the feed, although, slightly less than the unsubstituted adamantyl monomer.

Copolymers of 4-(1-adamantyl)-2,6-dimethylphenyl methacrylate and styrene were analyzed by ^{13}C NMR to determine composition, using two methods of integration (using Bruker and GRAMS software) were utilized to confirm the values. Fig. 9 is a plot comparing the two integration techniques, the values obtained were comparable. The copolymers were also analyzed by FTIR, since it was not possible to get high conversion or high molecular

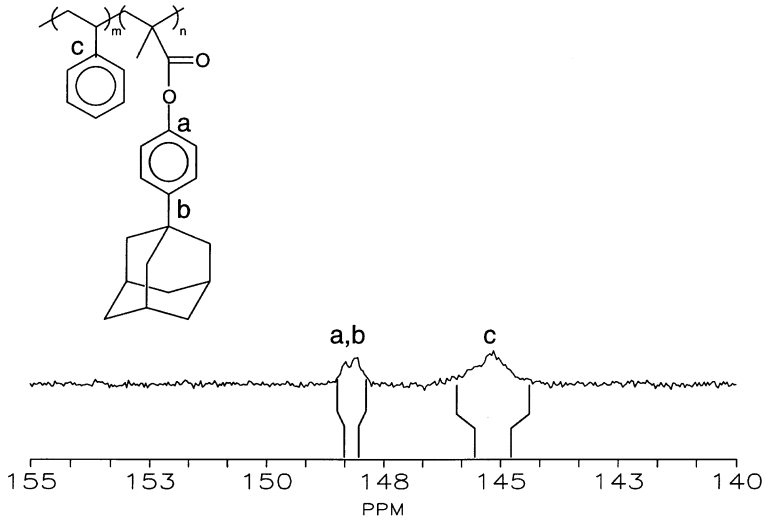

Fig. 7. ^{13}C NMR of styrene-co-4-(1-adamantyl)phenyl methacrylate (showing integrated peaks).

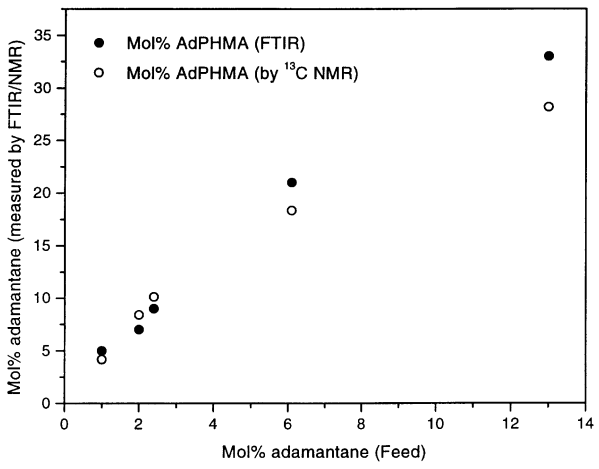

Fig. 8. Plot of mole percent 4-(1-adamantyl)phenyl methacrylate by FTIR (●), mole percent 4-(1-adamantyl)phenyl methacrylate by ^{13}C NMR (○) versus mole percent adamantane in the feed.

weights of the homopolymer of 4-(1-adamantyl)-2,6-dimethylphenyl methacrylate, the homopolymer of 2,6-dimethylphenyl methacrylate was used to obtain a Beer's law plot. The absorbances of the carbonyl for each copolymer were used to calculate the incorportion of adamantane monomer. For this series of polymers, the amount of adamantane found in the copolymer was slightly more than that of the feed, indicating a significant decrease in reactivity compared to the *mono*-methyl and unsubstituted monomers.

The addition of *ortho* methyl clearly slows down the radical reactivity as seen by comparing a plot of feed versus incorporation of the copolymers of styrene with the three adamantyl monomers (Fig. 10). Reactivity ratios were estimated for these copolymers based on just composition values.

7.4. Monomer reactivity ratios

While there are several methods available to determine reactivity ratios [24,25], the Mortimer–Tidewell method [1,2] was utilized. The molar feed values and copolymer composition values (as determined by ^{1}H NMR for MMA copolymers and Beer's Law for styrene copolymers) were used in the calculations. The values calculated were r_1 (MMA) = 0.591 and r_2 (4-(1-adamantyl)phenyl methacrylate) = 1.92. Copolymers with styrene for the three monomers (4–6) respectively, gave r_1/r_2 values: 0.22/1.51, 0.31/ 2.441, and 0.97/0. In comparing the first two styrene copolymers, clearly the addition of one *ortho* methyl group does not appear to decrease the reactivity. In Fig. 10 (plot of feed vs. composition), it appears that the reactivity is slightly lower, however the calculated r_2 values for 2-methyl-4-(1-adamantyl)phenyl methacrylate are slightly higher than calculated for the unsubstituted methacrylate. This could be attributed to the fact that a narrower sample selection (0.5–17 mol%) was used in the calculation of reactivity ratios as compared to 5–33 mol% for the unsubstituted methacrylate. The calculated r_2 value for

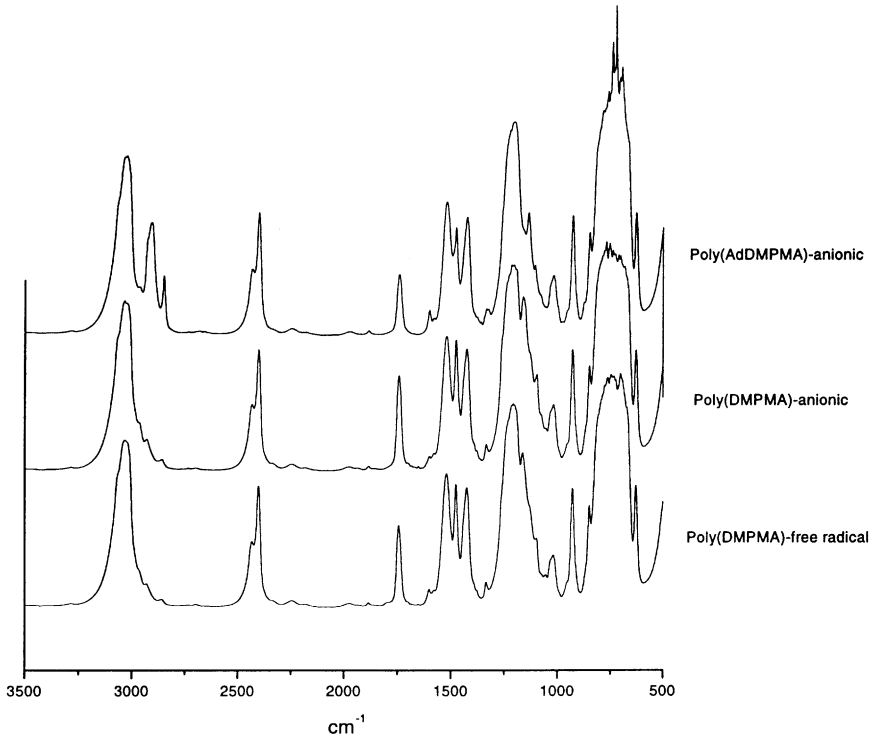

Fig. 9. Plot of mole percent 4-(1-adamantyl)phenyl methacrylate integrated by BRUKER software (●), Mole percent 4-(1-adamantyl)phenyl methacrylate integrated by GRAMS software (○) versus mole percent adamantane in the feed.

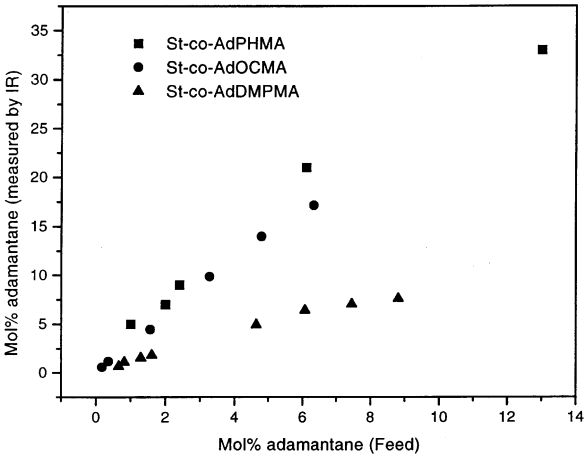

Fig. 10. Plot of mole percent adamantane measured by FTIR, styrene-co-4-(1-adamantyl)phenyl methacrylate (■), styrene-co-2-methyl-4-(1-adamantyl)phenyl methacrylate (●), styrene-co-4-(1-adamantyl)-2,6dimethylphenyl methacrylate (▲) versus mole percent adamantane in the feed.

4-(1-adamantyl)-2,6-dimethylphenyl methacrylate is zero. By definition, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, since this monomer did not homopolymerize under free radical techniques, the rate constant (k_{22}) equals zero making the value of r_2 equal to zero. Evaluation of copolymer compositions clearly indicates incorporation of 4-(1-adamantyl)-2,6-dimethylphenyl methacrylate, therefore, the rate constant (k_{12}) is some value greater then zero, albeit a small value. It appears that the addition of two *ortho* methyl groups slows down the reactivity significantly.

7.5. Glass transition temperatures of copolymers

All of the copolymers had higher T_gs than the parent MMA and St homopolymers and T_gs increased with increasing

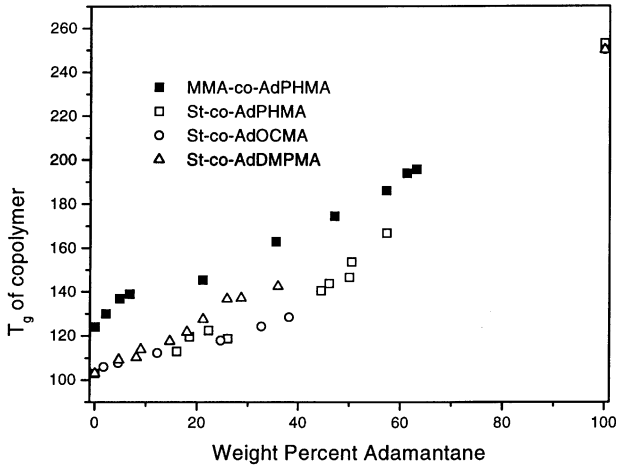

Fig. 11. Plot of T_g versus weight percent adamantane measured by FTIR, methyl methacrylate-co-4-(1-adamantyl)phenyl methacrylate (■), styrene-co-4-(1-adamantyl)phenyl methacrylate (□), styrene-co-2-methyl-4-(1-adamantyl)phenyl methacrylate (○), styrene-co-4-(1-adamantyl)-2,6dimethylphenyl methacrylate (△).

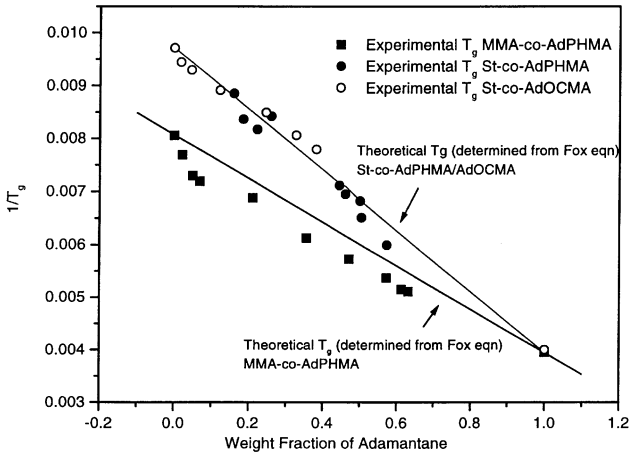

Fig. 12. Plot of reciprocal T_g versus weight fraction of Adamantane. Theoretical T_g (determined from Fox equation) methyl methacrylate-co-4-(1-adamantyl)phenyl methacrylate (- - -), theoretical T_g (determined) from Fox equation) styrene-co-4-(1-adamantyl)phenyl methacrylate and styrene-co-2-methyl-4-(1-adamantyl)phenyl methacrylate (—), experimental T_g of methyl methacrylate-co-4-(1-adamantyl)phenyl methacrylate (■), experimental T_g of styrene-co-4-(1-adamantyl)phenyl methacrylate (●), experimental T_g of styrene-co-2-methyl-4-(1-adamantyl)phenyl methacrylate (○).

incorporation of the adamantyl monomers. What is surprising is that as little as 1 mol% of the adamantyl monomer results in a 10°C increase in T_g (see Tables 2–5). Fig. 11 is a plot comparing T_g with composition of the copolymers.

The Fox equation ($1/T_g = W_{x1}/T_{g1} + W_{x2}/T_{g2}$) was utilized to determine the theoretical T_gs of various copolymer compositions. The T_gs for the copolymers of styrene and adamantylphenyl methacrylate derivatives fall within the range of the Fox predicted T_g; whereas the T_gs for the copolymers of MMA and 4-(1-adamantyl)phenyl methacrylates were higher than predicted (Fig. 12).

8. Conclusions

Three new adamantyl-substituted methacrylate monomers were synthsized and incorporated into a series of copolymers with MMA and styrene resulting in incremental increases in T_g with incorporation of adamantane.

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