Evaluation of the Spacer Effect on Adamantane-Containing Vinyl Polymer T_g's

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ABSTRACT: Two new adamantane-containing methacrylates having methylene and phenyl spacers between the adamantane and the methacrylate were synthesized: 1-adamantylmethyl methacrylate (AdMMA, **1**) and 4-(1-adamantyl)phenyl methacrylate (AdPMA, **2**). The homopolymer of **1** had a T_g of 201 °C while **2** showed a T_g of 253 °C. Copolymers of both monomers with styrene (St) showed significant T_g increases over PSt. The incremental increase obtained with AdPMA per adamantane unit is the highest of all vinyl monomers reported to date, to the best of our knowledge, with a value of 2.2 °C/mol %. Both sets of copolymers showed higher incorporation of adamantane monomers in the copolymer than the feed, with reactivity ratios calculated to be r_1(St) = 0.22 and r_2(AdPMA) = 1.52 and r_1(St) = 0.94 and r_2(AdMMA) = 1.54.

Introduction

Adamantane (tricyclo[3.3.1.1^{3,7}]decane) is a very symmetric tricyclic hydrocarbon with three fused chair-form cyclohexane rings in a diamond lattice structure. This compound is thermodynamically very stable,[1] plus it has unusual effects on polymer behavior. Polymers having adamantane as a pendant group or in the backbone show enormous changes in their physical and chemical properties.[2−4] Our group has been studying the effects of adamantane substitution on physical, thermal, and mechanical properties of a variety of polymer families ranging from acrylates to phenolics.[5] Incorporation of adamantane as a pendant group increases the T_g of the parent polymer significantly for both condensation polymers and vinyl polymers.[2,6−8] Although it is intuitive that large pendant groups tend to have such an effect due to the reduced chain mobility (boat anchor effect), the magnitude of increase is surprisingly high for adamantane. Polymers from ester derivatives of ethyl α-hydroxymethyl acrylate are examples of this effect. The 1-adamantanoate ester had a T_g of 214 °C (M_n = 319 000 g/mol) while the benzoate had 130 °C (M_n = 112 000 g/mol) and acetate only 49 °C (M_n = 610 000 g/mol).[5] Many adamantane derivatives also exhibit enhanced thermal stability because of reduced ease of elimination reactions of substituents at the bridgehead position compared to those of a typical tertiary carbon.[2,5]

There are two patents[9,10] describing adamantane-incorporating vinyl monomers, which are basically formulations for specific applications such as photosensors, and several publications[2,11] mostly studying the polymerization kinetics. Here we focus on adamantane-containing methacrylate esters with different spacers varying in length and rigidity, phenylene and methylene, between the adamantane and the polymer backbone. Homopolymers and copolymers of both monomers with styrene were synthesized and analyzed. Thermal properties were investigated and compared with those of adamantyl methacrylate homopolymer[2] which has direct methacrylate ester linkage to the adamantane group (no spacer).

Experimental Section

Materials. All chemicals were purchased from Aldrich Chemical Co. unless specified otherwise. Methacryloyl chloride and styrene were distilled and stored under N_2 in a refrigerator. Triethylamine (TEA), THF, and benzene were distilled from CaH_2, and xylene was distilled from sodium metal. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol/water (50/50 v/v) and then dried at room temperature under vacuum with P_2O_5. Diethyl ether, methacrylic anhydride, and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) were used as received. 4-(1-Adamantyl)phenol was synthesized by reaction of 1-bromoadamantane and phenol using a literature method.[12]

Measurements. Solution ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer at 300.133 and 75.47 MHz frequencies, respectively, with standard acquisition parameters. DSC analyses were performed on a TA instrument 2920 with heating rates of 10 °C/min under nitrogen. A TA Instrument 2960 was used for TGA analysis in N_2 and air with heating rates of 20 °C/min. Molecular weights and molecular weight distributions were estimated relative to polystyrene standards using size-exclusion chromatography (SEC) with THF solvent and four styrene gel mixed-bed columns (7.5 mm i.d. × 300 nm, 10 μm particle diameter, American Polymer Standard Corp., Mentor, OH). FTIR spectra were obtained on an ATI-Mattson Galaxy 5020 spectrometer on KBr pallets or on polymer thin films cast from methylene chloride. Elemental analysis was carried out by MHW Laboratories, Phoenix, AZ, and Quantitative Technologies Inc. (QTI), Whitehouse, NJ.

Analysis of Copolymer Compositions. Copolymer compositions of polymers in the poly(St-*co*-AdMMA) series were determined by ^{1}H NMR integration of methyl peak of AdMMA units relative to the aromatic protons of styrene units. Gated proton-decoupled ^{13}C NMR integration was utilized to analyze the copolymer composition of the poly(St-*co*-AdPMA) series. To maximize signal-to-noise, samples were prepared in as high 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.

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A second technique used to analyze copolymer composition of the poly(St-*co*-AdPMA) series was FTIR. A stock solution of poly(AdPMA) was prepared in chloroform. The solution was allowed to equilibrate for ca. 2 h and then loaded into a liquid IR cell with a 1 nm path length, and the spectrum was obtained. Serial dilutions were carried out to give different concentrations of 0.005−0.003 M, and the absorbance of the carbonyl at 1749 cm^{-1} was analyzed at each dilution. A standard Beer's law calibration plot was obtained by plotting the measured absorbances versus known concentrations of homopolymer solutions. The best-fit equation generated through linear least-squares analysis was $y = -0.033 + 21.91x$ in which x is the molar concentration and the extinction coefficient (21.91) has units of abs L/mol. To determine the amount of AdPMA units present in the copolymers, solutions of copolymers of known concentrations were prepared and analyzed by FTIR as indicated above, and comonomer contents were calculated on the basis of the measured absorbances using the Beer's law relationship.

Monomer Synthesis. *1-Adamantylmethyl Methacrylate (AdMMA, **1**).* 1-Adamantanemethanol (7.86 g, 47.05 mmol), TEA (5.7 mL, 40.48 mmol), and DMAP (1.23 g, 9.93 mmol) were dissolved in dry THF (20 mL) in a 50 mL three-necked round-bottomed flask equipped with an addition funnel under nitrogen. The contents were chilled in an ice bath. Freshly distilled methacryloyl chloride (5.2 mL, 53.22 mmol) was added slowly from the addition funnel with continuous stirring. Immediate formation of a white precipitate was observed. The reaction mixture was allowed to warm slowly to room temperature over 1.5 h and stirred overnight. Progress of the reaction was followed with gas−liquid chromatography (GC). Insoluble salts were filtered after the reaction mixture was diluted with 50 mL of THF. The solvent was removed on a rotary evaporator. Ether was added to the remaining viscous liquid, which was then extracted with 0.1 N HCl, 0.1 N NaOH, water, and saturated NaCl solution. The organic phase was dried over anhydrous Na_2CO_3 and filtered, and the ether was removed on a rotary evaporator to give a colorless viscous liquid which solidified in the refrigerator to a white solid (**1**); yield 9.01 g, 82%. Pure compound was obtained after column chromatography over silica gel with 97.5 hexanes/2.5 ethyl acetate eluent; 99.7% purity by GC; mp 39 °C. IR (CH_2Cl_2 cast film on NaCl window): 2904, 2848, 1718, 1637, 1452, 1294, 1162, 937 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.5 (s), 1.7 (m), 1.9 (s), 3.7 (s), 5.5 (s), 6.1 (s) ppm. ^{13}C NMR ($CDCl_3$): δ 18.5, 28.2, 33.5, 37.17, 39.5, 74.3, 125.2, 136.8, 167.7 ppm.

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88%, H, 9.46%. Found: C, 77.08%; H, 9.53%.

*4-(1-Adamantyl)phenyl methacrylate (AdPMA, **2**).* A three-necked 300 mL round-bottomed flask equipped with an addition funnel and mechanical stirrer was charged with 4-(1-adamantyl)phenol (100 g, 0.438 mol) and methacrylic anhydride (88.7 g, 0.575 mol) dissolved in 1000 mL of diethyl ether at 0 °C. Aqueous NaOH (35 g, 0.876 mol in 100 mL of water) was added dropwise to the solution from the addition funnel and stirring continued for 12 h. The mixture was transferred to a separatory funnel and washed with water until a neutral pH was observed, followed by extraction with saturated aqueous NaCl. A precipitate was obtained by removal of ether with a rotary evaporator. Recrystallization from absolute ethanol gave white crystals; yield 110 g, 80%; purity 99.6% by GC; mp 121−125 °C. ^1H NMR ($CDCl_3$): δ 7.3 (d), 7.0 (d), 6.3 (s), 5.7 (s), 2.2 (s), 2.0 (s), 1.9 (s), 1.7 (s). ^{13}C NMR ($CDCl_3$): δ 165.9, 148.6, 135.9, 126.9, 125.8, 120.8, 43.1, 36.6, 35.5, 28.6, 18.3.

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

Polymer Synthesis. *Poly(styrene).* Two different homopolymerizations of styrene were performed: one with 0.1 mol % AIBN at 50 °C and one with 0.3 mol % AIBN at 60 °C. Both polymerizations were done in sealed tubes after three freeze/evacuate/thaw cycles. Polymer was precipitated into CH_3OH after noticeable viscosity increase. The filtered product was reprecipitated from THF and then methylene chloride into CH_3OH, filtered, and dried in vacuo.

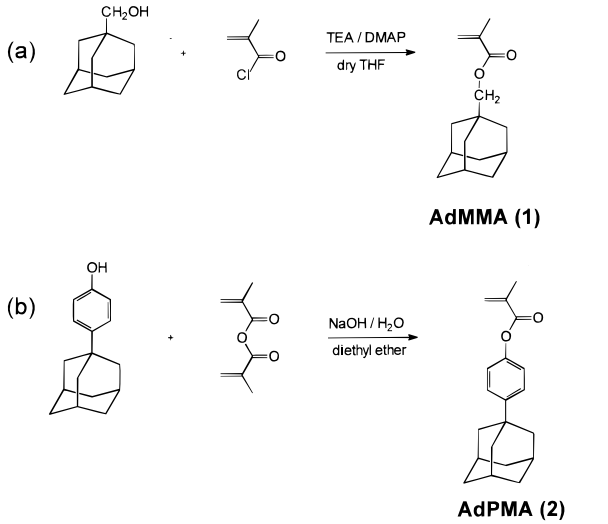

Figure 1. Synthesis of (a) AdMMA (**1**) and (b) AdPMA (**2**).

Poly(1-adamantylmethyl methacrylate) (Poly(AdMMA)). Monomer **1** (0.83 g, 3.53 mmol) was homopolymerized with AIBN (2.6 mg, 0.45 mol %) from 40 wt % solution in xylene at 62 °C in a 25 mL round-bottomed flask which was first sealed and subjected to three freeze/evacuate/thaw cycles followed by a N_2 purge. Polymer was precipitated into CH_3OH, then reprecipitated from methylene chloride into CH_3OH, and dried to give a white powder; yield 0.48 g, 58%. ^1H NMR (CD_2Cl_2): δ 0.8−1.0 (br d) 1.5−1.9 (m), 3.4 (br s). ^{13}C NMR ($CDCl_3$): δ 15.7, 17.6, 28.3, 33.0, 37.2, 39.8, 45.0−45.5, 54.7, 69.2, 177.4, 178.0, 178.3 ppm.

Poly(4-(1-adamantyl)phenyl methacrylate) (Poly(AdPMA)). Monomer **2** (6.82 g, 22.94 mmol) was homopolymerized with AIBN (0.034 g, 0.9 mol %) as a 1 M solution in benzene at 60 °C in a sealed tube after three freeze/evacuate/thaw cycles followed by a N_2 purge. Polymer was isolated by precipitation into CH_3OH and then reprecipitated from CH_2Cl_2 into acetone to give a fine white powder; yield 4.14 g, 61%. ^1H NMR ($CDCl_3$): δ 1.4−1.5 (br d), 1.7−1.8−2.0 (m), 2.3 (br s); 7.0 (s), 7.2 (s). ^{13}C NMR ($CDCl_3$): δ 17.7, 19.8, 28.8, 35.8, 36.6, 43.2, 45.7−45.9, 54.2, 120.4−120.5, 125.7, 148.2, 148.7, 175.1, 175.4, 175.8, 176.1 ppm.

Copolymer Synthesis. Styrene (St)−AdMMA copolymers were synthesized in bulk using 0.1 mol % AIBN, while St−AdPMA copolymers were obtained from 1 M benzene solution with 0.5 wt % (0.32−0.39 mol %) AIBN. All polymerizations were thermally initiated at 60 °C after the sealed reaction tubes were subjected to freeze/evacuate/thaw cycles followed by a nitrogen purge. All polymers were precipitated into CH_3OH and reprecipitated at least twice from methylene chloride or THF into CH_3OH. All thermal analyses were conducted after samples were dried in a vacuum at 50 °C overnight. Yields for copolymers were usually kept low (<20% conversion) to minimize compositional drift. Several copolymers were allowed to go to higher conversions, however, for comparison.

Results and Discussion

Monomer **1** was synthesized from methacryloyl chloride and 1-adamantanylmethanol in the presence of TEA and DMAP (Figure 1a). The reaction gave methacrylic anhydride as a byproduct. The addition of DMAP accelerated the reaction and decreased the amount of anhydride formed. Product (AdMMA) was successfully purified by column chromatography. AdPMA (**2**) was synthesized in high yield under phase transfer conditions using methacrylic anhydride and 4-(1-adamantylphenol) and purified by recrystallization from ethanol (Figure 1b). Both monomers were obtained in high purity and characterized by standard NMR and FTIR techniques.

Table 1. Molecular Weight, Composition, and Thermal Characteristics of Poly(AdMMA) and Poly(St-*co*-AdMMA)

AdMMA									
feed	copolymer[a]								
mol %	mol %	wt %	conv[b] (%)	M_n[f]	M_w[f]	P_{max}[f]	PDI[c]	T_g (°C)[d]	T_{dec} (%)[e]
0			22	190	269	275	1.4	107	356
9.87	10.51	20.9	20	239	291	305	1.2	118	308
28.83	31.89	51.3	15	154	245	245	1.6	142	315
49.99	58.84	79.28	18	288	270	470	1.6	160	322
70.05	75.00	87.09	10	61.4	109	98.2	1.77	168	322
100			58	98.7	182	135.7	1.8	201	235

[a] Calculated by ^{1}H NMR integration. [b] Conversion calculated gravimetrically. [c] Polydispersity index = M_w/M_n. [d] Reported as inflection point of the second DSC trace at a heating rate of 10 °C/min in N_2. [e] Reported as the onset of decomposition recorded by TGA at a heating rate of 20 °C/min in N_2. [f] Values $\times 10^3$ g/mol.

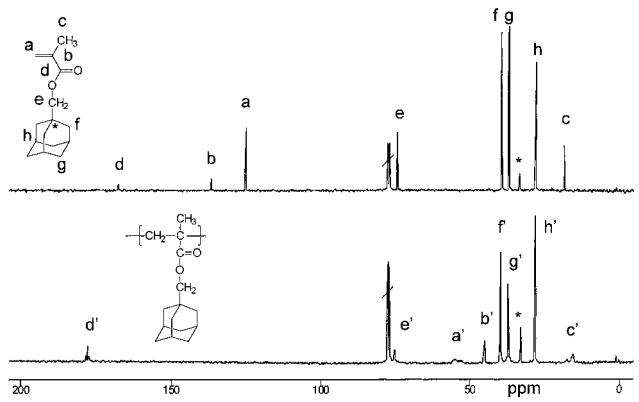

Figure 2. ^{13}C NMR of AdMMA (**1**) (top) and poly(AdMMA) (bottom).

All homo- and copolymers were synthesized free radically using AIBN as initiator. Structures of all polymers were confirmed by solution NMR spectroscopy (^{1}H and ^{13}C) and FTIR analysis of solvent-cast films. The homopolymer of AdMMA showed M_n of 98 000 and M_w of 182 000 with a peak maximum at 135 700 and M_w/M_n value of 1.8 (Table 1). Solution ^{1}H and ^{13}C NMR analysis showed disappearance of vinyl protons and carbons at 5.55−6.12 and 125.2−136.8 ppm, respectively, and the appearance of backbone methylene protons at ca. 1.65 ppm and carbons at 59.0 ppm (Figure 2). The NMR results showed more syndiotactic triad than atactic (comparison of α $-CH_3$ peaks at 15.9 and 17.8 ppm) and no measurable isotactic content, similar to PMMA. Poly(AdMMA) had a T_g of 201 °C, which is lower than that of poly(AdMA) (no T_g was reported below decomposition at 254 °C)[2] but 100 °C higher than that of poly(methyl methacrylate) (105 °C)[15] and poly(*tert*-butyl methacrylate) (98 °C).[15] Such large T_g enhancement can be explained by factors such as decreasing chain mobility and increasing rotational barrier upon incorporation of the bulky adamantane moiety. However, the extent of enhancement is very dramatic. The difference between poly(AdMMA) and poly(AdMA) can be attributed to the methylene spacer between the adamantane and the backbone which is providing more motional freedom and flexibility over the former.

Poly(AdPMA) was obtained with a M_n of 55 000, M_w of 250 000, and peak maximum at 170 000 (Table 2). Polymerization was confirmed by the disappearance of vinyl protons and carbons at 5.7−6.3 and 126.8−135.9 ppm, respectively, and the appearance of backbone methylene hydrogen and carbon peaks at 2.3 and 54.2

Table 2. Molecular Weight, Composition, and Thermal Characteristics of Poly(AdPMA) and Poly(St-*co*-AdPMA)

AdPMA (mol %)								
	copolymer							
feed	IR[a]	NMR[b]	conv[c] (%)	M_n[f]	M_w[f]	P_{max}[f]	PDI[d]	T_g (°C)[e]
0.0			15.7	22	36.5	34.2	1.6	103
1.0	5	4.18	4.5	70.9	118.2	100.6	1.7	113
2.0	7	8.4	7	70.8	114.6	95.5	1.6	119
2.4	9	10.1	6.8	69.6	111.7	94.2	1.6	122
6.1	21	18.34	16.3	74.4	117.5	100.9	1.6	140
13.0	33	28.16	5.2	122.3	209.8	178.0	1.7	166
100			90	55.0	250	170	4.5	253

[a] Calculated from FTIR. [b] Calculated by ^{13}C NMR integration. [c] Conversion calculated gravimetrically. [d] Polydispersity index = M_w/M_n. [e] Reported as inflection point of the second DSC trace at a heating rate of 10 °C/min in N_2. [f] Values $\times 10^3$ g/mol.

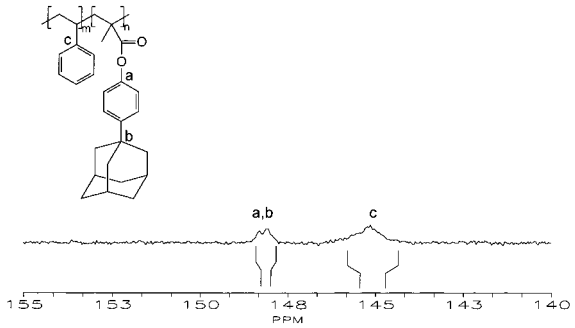

Figure 3. ^{13}C NMR of substituted aromatic carbon peaks of poly(St-*co*-AdPMA).

ppm in the ^{1}H and ^{13}C NMR spectrum. It was difficult to ascertain the tacticity by ^{1}H NMR because the intense adamantyl proton peaks, observed in the same region of the spectrum, masked the backbone methylene and methyl groups. However, the methyl peaks in the ^{13}C NMR spectrum showed two prominent peaks for atactic and syndiotactic triads (19.8 and 17.7 ppm, respectively) for α $-CH_3$ carbons (spectrum not shown) in about the same ratio as for PMMA and poly(AdMMA). The T_g of poly(AdPMA) was observed at 253 °C, which is very close to the decomposition temperature. Comparison with poly(phenyl methacrylate) (T_g = 110 °C)[15] shows a 143 °C increase in T_g upon addition of adamantane to the phenyl ring. The phenyl spacer between the adamantane and the backbone imparts a 52 °C enhancement over the methylene spacer due to its more rigid structure. A similar effect is evident for poly(AdMA) in which elimination of the spacer group raises the T_g to above the decomposition temperature (254 °C).[2]

Poly(AdPMA) and poly(St-*co*-AdPMA) copolymers with 1−13 mol % AdPMA in the feed were prepared from benzene solutions due to the low solubility of AdPMA in styrene. Conversions were kept below 20%. Polymers with molecular weights between 70 000 and 122 000 (M_n) were obtained with polydispersities of 1.6−1.7. Two different methods were used to determine the compositions of the St−AdPMA copolymers: ^{13}C gated-decoupled NMR and FTIR. Using the ^{13}C gated-decoupled NMR method, the peaks corresponding to the carbons ipso to both oxygen and adamantane moieties of the AdPMA units were integrated relative to the quaternary carbon on the styrene aromatic ring (Figure 3). Although long acquisition times and concentrated samples were used for the analysis, the quaternary carbon peaks were weak and difficult to differentiate from the baseline. Therefore, copolymer compositions were also calculated

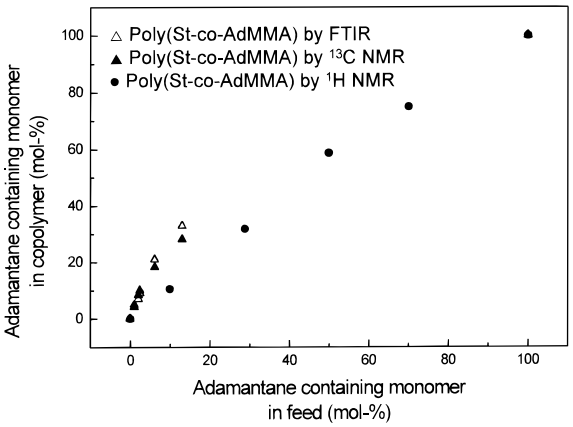

Figure 4. Plot of adamantane monomer content in styrene copolymers versus in the feed.

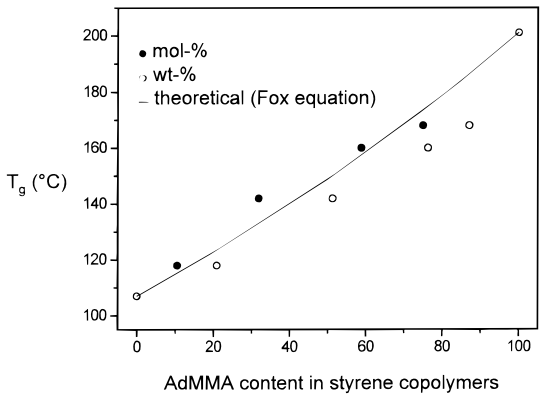

Figure 5. Plot of T_g versus AdMMA content of poly(St-*co*-AdMMA) copolymers.

by FTIR. A Beer's law plot was prepared from the measurements of carbonyl absorbances (1750 cm^{-1}) of poly(AdPMA) at various concentrations. The fraction of AdPMA in the copolymers was then determined using the slope and intercept obtained from this plot. Both methods indicated much higher incorporation of AdPMA than in the feed, indicating a large difference between the reactivities of the two monomers. The Mortimer−Tidewell[13,14] method was used to determine the reactivity ratios for the styrene (M_1) and AdPMA (M_2) system. The values were calculated as r_1(St) = 0.22 and r_2(AdPMA) = 1.52. This is consistent with the behavior of phenyl methacrylate (M_1 = styrene, M_2 = phenyl methacrylate: $r_1 = 0.246$, $r_2 = 0.480$).[15]

Copolymers of AdMMA and styrene were prepared in bulk. Polymerizations were quenched below 20% conversion. Copolymers with molecular weights between 60 000 and 288 000 (M_n) and polydispersities of 1.2−1.7 were obtained with 10−70 mol % AdMMA in the feed (Table 1). Poly(St-*co*-AdMMA) compositions were determined by ^{1}H NMR integration and found to be 10.5−75 mol % AdMMA, indicating slightly higher incorporation of the AdMMA (Figure 4). The difference in reactivity is not as dramatic as for AdPMA. Reactivity ratios for the styrene−AdMMA couple were calculated according to the Mortimer−Tidewell procedure as r_1(St) = 0.94 and r_2(AdMMA) = 1.54. The reactivity ratios of AdMMA and styrene are more similar to styrene and AdMA ($r_1 = 0.54$ (St), $r_2 = 0.62$ (AdMA))[2] than AdPMA−styrene.

All the copolymers with both AdMMA and AdPMA had marked increases in T_g compared to the parent PSt

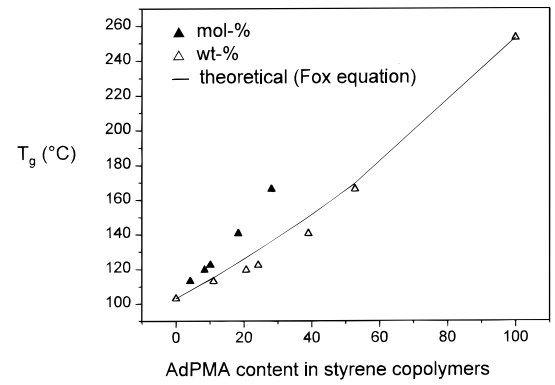

Figure 6. Plot of T_g versus AdPMA content of poly(St-*co*-AdPMA) copolymers.

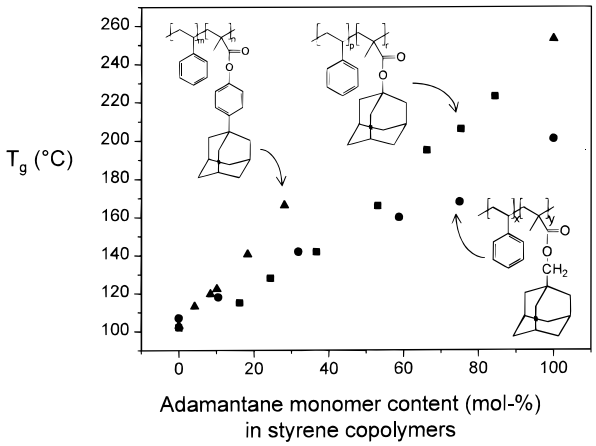

Figure 7. Plot of T_g versus mol % adamantane monomer in poly(St-*co*-AdMMA), poly(St-*co*-AdPMA), and poly(St-*co*-AdMA).[2]

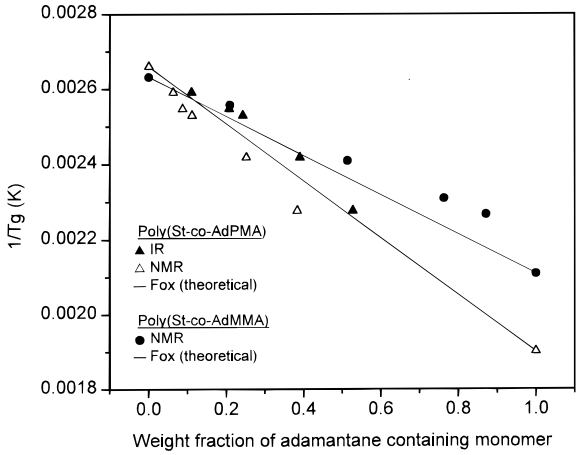

Figure 8. Plot of experimental and theoretical values of $1/T_g$ versus weight fraction of adamantane monomer the copolymers.

(Figures 5 and 6). The T_g's increased almost linearly with increasing AdMMA content (0.88 °C/mol). The incremental increase per monomer unit of AdPMA (2.2 °C/mol) is the highest among any comonomer units of which we are aware. Surprisingly, it is more effective than adamantyl methacrylate (AdMA)[2] in which the adamantane group is closer to the backbone with no spacer (Figure 7). The magnitude of T_g enhancement of AdMMA was comparable to AdMA below 60 mol % incorporation of adamantane monomer. The theoretical T_g's of the copolymers were calculated according to the

Fox equation ($1/T_g = w_1/T_{g1} + w_2/T_{g2}$)[16] (Figures 5, 6, and 8).

Thermal stability of the polymers was investigated by TGA under N_2. Since the elimination at the adamantane bridgehead carbon (the point of attachment) is not favorable, poly(AdMMA) and poly(AdPMA) showed much better stability over other tertiary alkyl methacrylate polymers. For example, poly(*tert*-butyl methacrylate) decomposes between 180 and 200 °C,[17] while onset temperatures for decomposition for poly(AdMMA) and poly(AdPMA) were at 235 and 260 °C, respectively. The lower onset of decomposition of these homopolymers with respect to PSt may be due to the highly substituted bonds formed by bimolecular termination,[2] which can break homolytically and cause polymer unzipping.

Conclusion

1-Adamantylmethyl methacrylate (AdMMA, **1**) and 4-(1-adamantyl)phenyl methacrylate (AdPMA, **2**) monomers were synthesized and polymerized under free radical conditions. The homopolymers displayed about the same syndiotactic and atactic contents as PMMA. Thus, tacticity is not a factor in T_g enhancement of these polymers. T_g's for poly(AdMMA) and poly(AdPMA) were observed at 201 and 253 °C, respectively, showing dramatically enhanced T_g's. Thermal stability was also enhanced over other methacrylate polymers with tertiary alkyl esters due to the absence of facile elimination at the side chain. Copolymerization of both monomers with St showed higher (poly(AdMMA)) and much higher (poly(AdPMA)) incorporation than MMA and AdMA. Incorporation of adamantyl monomers resulted in very large incremental increases in T_g with AdPMA being the most effective of any monomer reported to date.

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References and Notes

(1) *Adamantane: The Chemistry of Diamond Molecules;* Fort, R. F., Gassman, P. G., Eds. In *Studies in Organic Chemistry*; Dekker: New York, 1976; Vol. 5.
(2) Matsumoto, A.; Tanaka, S.; Otsu, T. Synthesis and Characterization of Poly(1-adamantyl methacrylate): Effects of the Adamantyl Group on Radical Polymerization Kinetics and Thermal Properties of the Polymer. *Macromolecules* **1991**, *24*, 4017.
(3) Grubb, T. L.; Mathias, L. J. Benzyl Ether Polymers: Crystallinity and Pendant Adamantyl Effects. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1743.
(4) Steter, H. Advances in the Chemistry of Organic Ring Systems with Adamantane Type Structures. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 286.
(5) Mathias, L. J.; Jensen, J. J.; Reichert, V. T.; Lewis, C. M.; Tullos, G. L.; Adamantane-Containing Polymers. In *Step-Growth Polymers for High-Performance Materials: New Synthetic Methods*; American Chemical Society: Washington, DC, 1996; p 197.
(6) Jensen, J. J.; Grimsley, M.; Mathias, L. J. Adamantyl-Substituted Phenolic Polymers. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 397.
(7) Avci, D.; Mathias, L. J.; Thigpen, K. Photopolymerization Studies of Alkyl and Aryl Ester Derivatives of Ethyl α-hydroxymethacrylate. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 3191.
(8) Mathias, L. J.; Tullos, G. L. Synthesis of Adamantyl and Benzoxazole Substituted Poly(*m*-phenylene)s via the Nickel Catalysed Coupling of Aryl Chlorides. *Polymer* **1996**, *37* (16), 3771.
(9) Novikov, S. S.; Khardin, A. P.; Radchenko, S. S.; Zlotin, S. G.; Orlinson, B. S. Synthesis and Polymerization of Unsaturated Adamantane Derivatives. *Izv. Akad. Nauk SSSR, Ser Khim.* **1977**, *12*, 2765.
(10) Novikov, S. S.; Khardin, A. P.; Radchenko, S. S.; Kargin, Y. N. Methacrylic Derivatives of Adamantane. Russian Patent, SU 490797 19751105.
(11) Liaw, D. J.; Tsai, C. H. Radical Polymerization of Methacryloyl Isocyanate Containing 1-Adamantanol. *Polym. Bull.* **1999**, *42*, 373.
(12) Aigami, K.; Inamoto, Y.; Takaishi, N.; Hattori, K.; Takatsuki, A.; Tamura, G. Biologically Active Polycycloalkanes. 1. Antiviral Adamantane Derivatives. *J. Med. Chem.* **1975**, *18*, 8 (7), 713.
(13) Tidewell, P. W.; Mortimer, G. A. An Improved Method of Calculating Copolymerization Reactivity Ratios. *J. Polym. Sci., Part A* **1965**, *3*, 369.
(14) Tidewell, P. W.; Mortimer, G. A. Science of Determining Copolymerization Reactivity Ratios. *Rev. Macromol. Chem.* **1970**, *5* (2), 135.
(15) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley and Sons: New York, 1989; p II/223 and V/78.
(16) *Polymer Physics*; Gedde, U. W., Ed.; Chapman and Hall: New York, 1995.
(17) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley and Sons: New York, 1989; p II/369.

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