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Radical polymerization of methacryloyl isocyanate containing 1-adamantanol

Der-Jang Liaw*, Chih-Hung Tsai

Department of Chemical Engineering, National Taiwan University of Science
and Technology, Taipei, Taiwan 106, Republic of China

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Summary

Radical polymerization of the methacryloyl isocyanate containing 1-adamantanol (Ad-MAI) with AIBN in different solvents at 60°C was investigated. It is observed that polymerization is slower in polar solvents than in nonpolar ones. The rate of polymerization for Ad-MAI was found to be slower than those of Adph-MAI and MMA both in photopolymerization and in thermal polymerization. Copolymerization of Ad-MAI (M_1) with styrene (M_2) in benzene was studied at 60°C. The monomer reactivity ratio was calculated to be r_1=1.53 and r_2=0.76 according to the method of Fineman-Ross. The prominent glass transition temperature for poly(Ad-MAI) was observed at 142°C from global TSC spectrum.

Introduction

Adamantane is a rigid ring system comprised of three-fused chair conformation cyclohexane rings. It has the same structure as a diamond lattice (1). Its excellent thermal stability, bulkiness and tetrahedral geometry lead to improve physical properties such as higher Tg and good solubility.

Matsumoto et al. (2) reported that the introduction of the bulkyl adamantyl groups increases its polymerization rate compared with other methacrylate such as methyl methacrylate and cyclohexyl methacrylate, because of a decrease in the bimolecular termination rate between polymeric radicals.

Methacryloyl isocyanate (MAI) can react with alcohols or primary amines (3, 4). Although Ad-MAI is similar to adamantyl methacrylate, their differences in several properties such as solubility, melting point, and rate of polymerization are also interesting due to the amide group in Ad-MAI.

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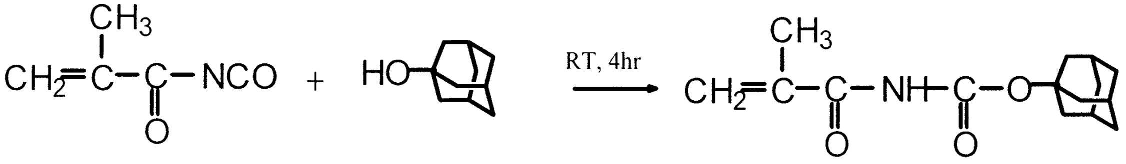
* Corresponding author
Tel.: 886-2-27335050 or 886-2-27376638; Fax: 886-2-27376644 or 886-2-23781441
e-mail: liaw@ch.ntust.edu.tw



MAI 1-Adamantanol Ad-MAI

Scheme I Synthesis of Ad-MAI

Experimental

Reagents

Methacryloyl isocyanate (MAI) (Nippon Paint Co.) was preparated from methacrylamide and oxalyl chloride, and purified by distillation under reduced pressure (52 ~ 53 °C / 39mmHg). 1-Adamantanol (ACROS) was used without further purification. The solvents were purified according to standards methods. AIBN was purified by recrystallization from methanol.

Monomer preparation (Scheme I)

1-Adamantanol (15.2g, 0.10 mol) and ethyl acetate (50 ml) were charged into a flask (150 ml). The mixture was stirred at room temperature under argon. MAI (12.1 g, 0.11 mol) was added by dropping funnel in a period of 30 mins. After completion of the addition, the mixture was stirred at room temperature for 4 hr. The product was purified by recrystallization from ethyl acetate and dried in vacuum at room temperature. Yield : 85%, mp:153~155°C.

IR and NMR spectroscopics and elemental analysis confirmed the structure. The monomer was soluble in methanol, ethyl ether, chloroform, benzene, toluene, pyridine, 1,4 dioxane, tetrahydrofuran (THF), dimethylformamide (DMF), dimethylsulfoxide (DMSO) and 1-methyl pyrrolidone (NMP) but insoluble in n-pentane and water.

IR (KBr) ν/cm^{-1}: ν_{NH}(3256), $\nu_{\mathrm{C=O}}$(1739, 1675), $\nu_{\mathrm{C=C}}$ (1629). ^{1}H NMR (Figure 1, 400 MHz, DMSO-d_6), ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 167.66, 150.24, 139.57, 122.75, 80.79, 41.37, 36.10, 30.74, 18.85. Elemental analysis: ($C_{15}H_{21}O_3N$) Calculated. C: 68.42%. H: 8.04%, N: 5.32%. Found. C: 68.32%, H: 8.03%, N: 5.37%. These results agree satisfactorily with the proposed structure.

In comparison with the rate of polymerization of Ad-MAI, methacryloyl isocyanate containing 4-(1-adamantyl) phenol (Adph-MAI) was synthesized by the corresponding 4-(1-adamantyl) phenol with MAI.

IR (KBr) ν/cm^{-1}: ν_{NH}(3292), $\nu_{\mathrm{C=O}}$(1760, 1692), $\nu_{\mathrm{C=C}}$ (1629). Mp.:174~176°C. ^{1}H NMR (400 MHz, DMSO-d_6), 5.31, 5.68 (s, 2H, vinylic), 6.83, 7.10 (d, 4H, aromatic), 909 (s, 1H, N-H), ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 169.51, 155.21, 141.51, 140.07, 125.64, 124.20, 119.69, 114.83, 43.16, 36.46, 35.17, 28.54, 18.89. Elemental analysis: ($C_{21}H_{25}O_3N$) Calculated. C: 74.31%, H: 7.42%, N: 4.13%. Found. C: 74.12%, H: 7.51%, N: 4.12%.

Polymerization

The rate of polymerization in various solvents at 60°C was determined with a gravimetric method. The gas from an ampoule that contained the monomer, solvent and

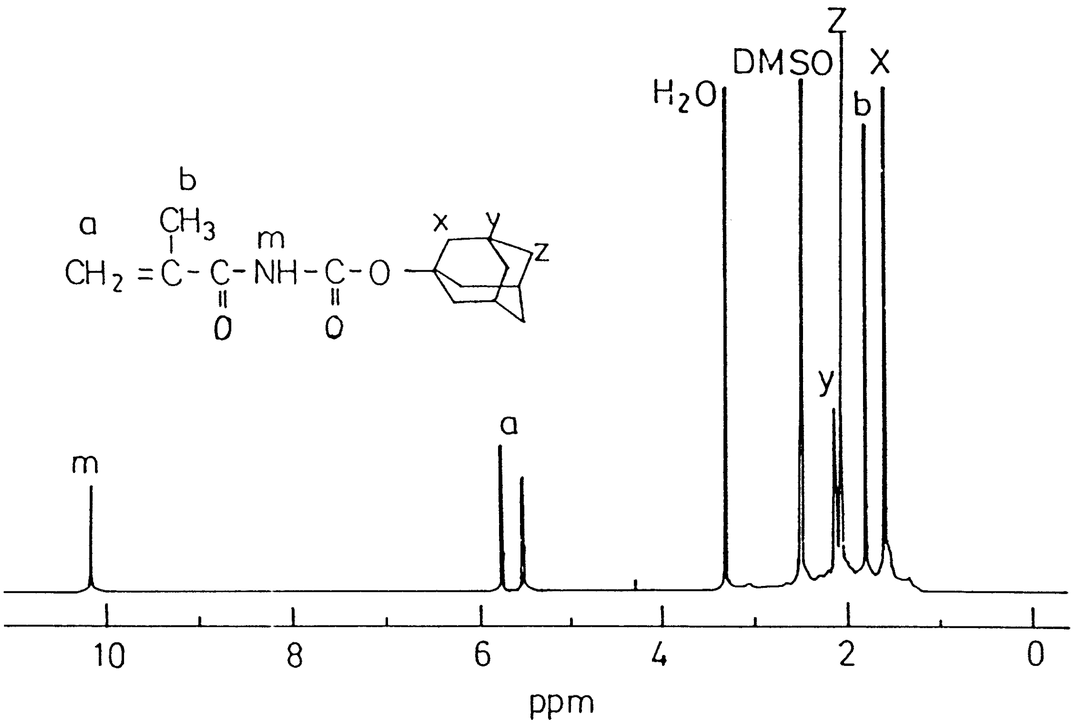


Fig.1. 400 MHz ^{1}H NMR spectrum taken in DMSO-d_6 at 25℃ for Ad-MAI

AIBN was removed several times by freeze-pump-thaw cycle and the ampoule was sealed. The polymer was precipitated in ethyl ether. Purification of polymer was carried out by reprecipitation from THF solution into ethyl ether, dried under vacuum at 60°C and weighted. The rate of photopolymerization at 30±0.01°C was measured in a vacuum sealed dilatometer. Copolymerization parameters were calculated by the Fineman-Ross method (5).

Characterization and measurements

^{1}H NMR spectra were recorded on a Bruker EM-360L ^{1}H NMR spectrometer at 400 MHz in DMSO-d_6. IR spectra were recorded on a JASCO IR-700 spectrometer on KBr pellets. Thermogravimetric analysis (TG) was performed on a Du Pont 2200 instrument at a heating rate of 10°C min^{-1}. The glass transition temperature was determined by the global TSC (Thermally Stimulated Current) spectrum.

Results and Discussion

Polymerization and polymer characterization

The homopolymer of Ad-MAI is a white solid and is soluble in THF, DMF, DMSO, pyridine and NMP. On the other hand, it is insoluble in ethyl ether, methanol, acetone, benzene, tetrachlorocarbon and water. The polymerization proceeded apparently homogeneous in tetrachlorocarbon, acetone and benzene, although the isolated poly(Ad-MAI) was no longer soluble in these solvents. (Monomer concentration is 0.2 M and the conversion is smaller than 10 %).

The thermal properties of poly(Ad-MAI) were determined by TGA, DSC and

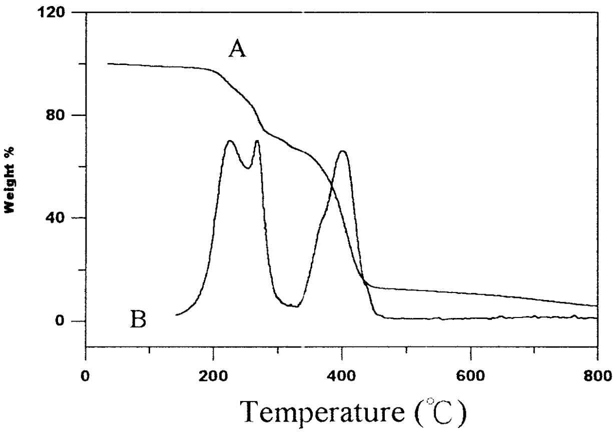


Fig.2. (A) TG and (B) DTG curves of poly(Ad-MAI) at a heating rate of 10℃/min under nitrogen.

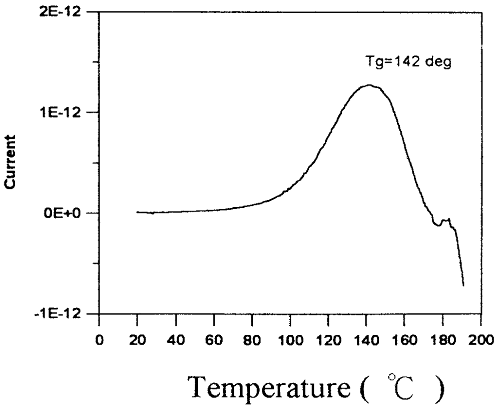


Fig.3. Global TSC spectrum for poly(Ad-MAI).

TSC. The thermogravimetric (TG) and DTG of poly(Ad-MAI) are shown in Figure 2. The polymer starts to decompose at 200°C. The residue at 500°C was less than 10% of the initial polymer weight.

The theraml property of the poly(Ad-MAI) was determined by DSC and TSC. Poly(Ad-MAI) showed no Tm in the DSC thermogram below its decomposition temperature. The global TSC spectrum of poly(Ad-MAI) taken at a heating rate of 10°C /min is shown in Figure 3. Prominent glass transition temperature (Tg) for poly(Ad-MAI) was observed at 142°C.

Copolymerization of Ad-MAI (M_1) with styrene (M_2)

Coplymerization of Ad-MAI (M_1) and styrene (M_2) with AIBN was carried out in benzene at 60°C. The copolymerization yield in each run was less than 10%. The copolymer composition was estimated from the carbon content by elemental analysis.

Figure 4 shows a Fineman-Ross plot used to determine the reactivity ratios for Ad-MAI (M_1) and styrene (M_2). The reactivity ratios, r_1 and r_2, for the monomer pair M_1 and M_2, can be determined from

$$F(f-1)/f=r_1(F^2/f)-r_2$$

where $f=d[M_1]/d[M_2]$, $F=[M_1]/[M_2]$.

The monomer reactivity ratios were determined by the Fineman-Ross method. (r_1=1.53 and r_2=0.76). These values reveal that Ad-MAI shows a higher reactivity than styrene irrespective of the kind of propagating ends. In addition, random copolymerization occurs between these different types of monomers. It is interesting to note that a rather opposite parameters (r_1=0.88 and r_2=1.24) (6) are reported for N-phenyl methacrylamide (M_1)/stryene (M_2) in polar solvent compared with Ad-MAI (M_1)/styrene (M_2) system in nonpolar solvent such as benzene. Otsu et al. (6, 7) reportd that the reactivity of N-phenyl methacrylamide (PMAM) is strongly affected by the hydrogen bonding between PMAM monomer and polar solvent, such as ethanol. The fact that $r_1 x r_2$=1.16 is greater than unity and poly(Ad-MAI) is insoluble in benzene, implied that the interaction through hydrogen bonding between polymer [poly(Ad-MAI)] and/or Ad-MAI monomer is significant.

Rate of polymerization

The rate of polymerization of Ad-MAI was investigated both in photopolymerization and in thermal polymerization (6, 7). In comparison the rate of polymerization of Ad-MAI, Adph-MAI hving a more bulky group was also studied. The rate of polymerization for Ad-MAI, Adph-MAI and MMA both in photopolymerization and in thermal polymerization is discernible in Table 1. The rate of thermal polymerization both for MMA and Adph-MAI is larger than that of Ad-MAI in benzene.

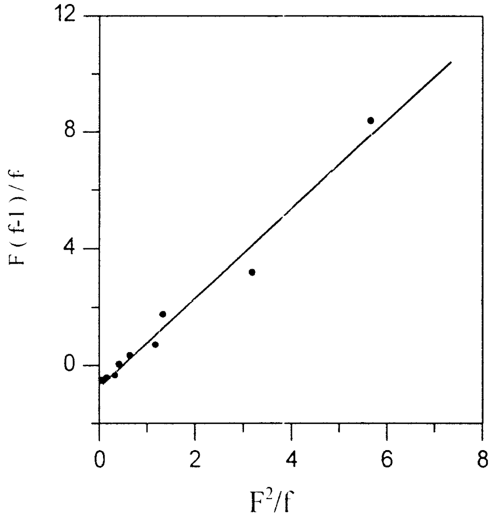


Fig.4. Determination of reactivity ratios for the copolymerization of Ad-MAI with styrene by method of Fineman-Ross.

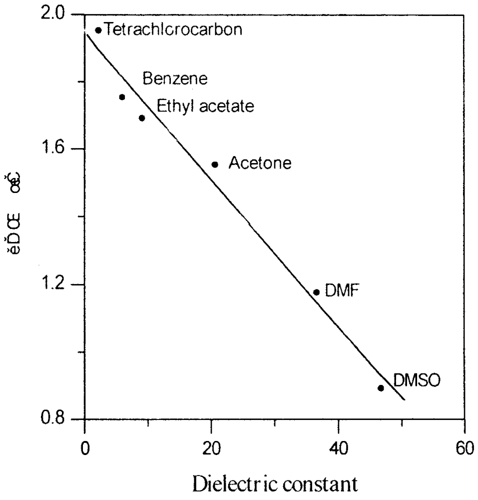


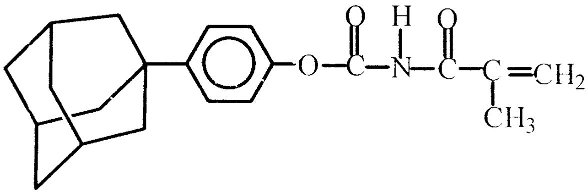
Fig.5. Relationship between rate of polymerization (R_p) for Ad-MAI and the dielectric constant of various solvents.

Table 1. Rate of polymerization of various monomers

Monomer	Photo-polymerization[a] $Rp / 10^{-8}\ mol{\cdot}L^{-1}{\cdot}s^{-1}$	Thermo-polymerization[b] $Rp / 10^{-7}\ mol{\cdot}L^{-1}{\cdot}s^{-1}$
Ad-MAI	6.3	1.8
Adph-MAI	13.1	5.6
MMA	11.3	6.2

a Solvent : DMF, [monomer] = 0.2 M,
[1,1'-Azobis (cyclohexanecarbonitrile)] = 6 × 10^{-3}M,
Temperature = 30 ℃, by dilatometer method
b Solvent: benzene, [monomer] = 0.2 M,
[AIBN] = 2 × 10^{-3}M , Temperature = 60 ℃, by gravimetric method

c Adph-MAI :



The rate of Adph-MAI or MMA was about thrice of Ad-MAI. In photopolymerization, found that polymer side chain with adamantyl group shows remarkably higher rate of polymerization than MMA in benzene. However, we did not find such behavior on Ad-MAI and Adph-MAI. It may be due to the stronger interaction between solvents and amide group of Ad-MAI than that between solvents and ester group of adamantyl methacrylate. Compared with the rates of polymerization of Ad-MAI and Adph-MAI, we found that Adph-MAI having bulkier group have higher rate of polymerization than Ad-MAI. This fact was in accord with Matsumoto results (2).

Solvent effect on the rate of polymerization

Rates of polymerization (Rp) of Ad-MAI in various solvents were determined at 60°C. As shown in Figure 5, the solvents significantly affect the rate of polymerization. It is observed that polymerization is slower in polar solvents than in nonpolar ones. A similar phenomenon was observed in the polymerization of mono-methacrylic esters containing bisphenol-S (10). Liaw et al. (10) reported that the enhanced rate of polymerization in non-polar solvents is ascribed to the large rate constant (kp) for propagation. The polymer chain interacts with its solvent. A polar solvent readily interacts with the polymer chain, thus probably resulting decreasing k_p. Since the rate of polymerization is proportional to k_p, the dielectric constant may be used as a rough measure of such interaction. Figure 5 shows a plot of log R_p against the dielectric constant of solvents. This result indicates that less polar solvents for the polymerization of Ad-MAI give a larger R_p values.

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