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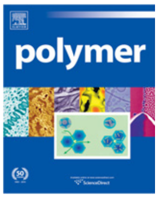

Glass transition temperature enhancement of PMMA through copolymerization with PMAAM and PTCM mediated by hydrogen bonding

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ABSTRACT

A series of poly(methyl methacrylate-*co*-methacrylamide-*co*-tricyclodecyl methacrylate) (PMMA-*co*-PMAAM-*co*-PTCM) copolymers possessing high glass transition temperatures and high transparency are prepared. By incorporating the aliphatic tricyclodecyl methacrylate moiety into the PMMA-*co*-PMAA main chain results in high glass transition temperature and high transparency of PMMA-based polymeric material. The TCM content affects the fraction of hydrogen bonding in these terpolymers, small content of TCM does not sacrifice the fraction of hydrogen-bonded association in and does not cause T_g decrease. The extent of free amide group plays the major role in dictating moisture absorption of terpolymers. The incorporation of TCM significantly reduces the moisture absorption of terpolymers due to its hydrophobic and bulky tricyclodecyl group. In addition, the TCM plays the role of inert diluent to convert portion of the strong self-associated hydrogen bonded amide groups into inter-associated hydrogen bonding between carbonyl groups of ester units and MAAM.

1. Introduction

Polymers possessing high glass transition temperatures are attractive for polymer industry because of strong economic rewards that may arise from their potential applications. For instance, poly(methyl methacrylate) (PMMA) is a polymeric material possessing many excellent properties, such as light weight, high light transmittance, chemical resistance, colorlessness, and good insulation. The glass transition temperature of PMMA is relatively low at ca. 105 °C, which limits its applications in the optical-electronic industry such as optical glasses, polymer waveguide, and optical fiber. Different approaches have been assayed to enhance T_g of non-aromatic polymers while maintain their high transmittance in near UV region through copolymerization with different cycloaliphatic monomers. Santos et al. [1] reported that higher content of methacrylated-b-cyclodextrin copolymerized with poly(hydroxyethyl methacrylate) results in higher T_g due to the increase of crosslinking density caused by the methacrylated-b-cyclodextrin. In our previous studies [2–4], we developed a new approach to raise T_g of PMMA through strong inter-associative hydrogen bonding interactions by copolymerization with a strong proton donor methacrylamide. In PMMA-*co*-PMAAM copolymers, some of the self-associated hydrogen-bonded amide groups become inter-associated through hydrogen bonding to carbonyl groups of MMA units, to raised T_g of PMMA [3]. However, increasing moisture absorption of PMMA-*co*-PMAAM copolymers is unavoidable because MAAM is highly moisture absorptive. To reduce the moisture absorption, we offered another novel approach through copolymerization of MMA, MAAM, and styrene [2]. The hydrophobic styrene units play dual roles in the terpolymer: (1) as inert diluent segment to enhance inter-associative hydrogen bonding between MMA and MAAM by reducing the strong self-associative hydrogen bonding of MAAM, and (2) to reduce the moisture absorption due to its hydrophobic nature. However, it is well known that the aromatic group of styrene will cause poor transmittance in near UV region (250–380 nm).

In this study, we choose copolymerization of MMA, methacrylamide (MAAM), and tricyclodecyl methacrylate (TCM) for these reasons: (1) PMAAM is known to possess extremely high T_g (≈ 250 °C); (2) T_g of the copolymers are expected to be higher than the corresponding polymer blends because of compositional heterogeneities existed in hydrogen-bonded copolymers [5–7]; (3) the tricyclodecane-based polymers such as tricyclodecyl methacrylates and bis(hydroxymethyl) tricyclodecane have been reported suitable for optical applications and photo-curing industry with excellent transmittance in near UV region [8,9]; (4) the bulky and hydrophobic tricyclodecyl group of TCM will raise T_g and reduce the moisture absorptions of PMMA-*co*-PMAAM-*co*-PTCM terpolymers,

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similar to the styrene in poly(MMA-*co*-MAAM-*co*-Sty); (5) the TCM units will also play the role as inert diluent segment, similar to the styrene, but without absorption near UV region; (6) the carbonyl group of TCM is able to interact with MAAM effectively through inter-associative hydrogen bonding as MMA to raise T_g.

A series of random poly(methyl methacrylate-*co*-methacrylamide-*co*-tricyclodecyl methacrylate) (PMMA-*co*-PMAAM-*co*-PTCM) copolymers (Scheme 1) were prepared by free radical polymerization and then characterized by using DSC and FTIR. The incorporation of the bulky aliphatic TCM group is expected to maintain good transmittance near UV region of PMMA, while the hydrogen bonding interaction is able to tie up the bulk group inhibiting its free rotation and thus raises the copolymer T_g.

2. Experimental

2.1. Materials

Methyl methacrylate was purchased from Aldrich chemical company that was purified by distillation under nitrogen before polymerization. The radical initiator azobisisobutyronitrile (AIBN) was recrystallized from ethyl alcohol prior to use. 1,4-dioxane was distilled under vacuum and then used as the solvent for the copolymerization experiments performed in solution. Tricyclo [5.2.1.0^{2,6}]-decan-8-one (tricycle-decan-8-one) was purchased from TCI chemical company. Methacryloyl chloride, sodium borohydride and tricycle-decan-8-one were used as received without further purification.

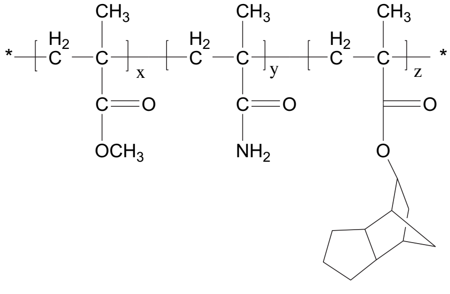
2.2. Synthesis

2.2.1. Synthesis of tricyclodecyl alcohol (reduction of tricyclodecyl ketone) [10]

Tricyclo [5.2.1.0^{2,6}]-decan-8-one (0.01 mol) and 50 mL ethanol were placed in a 100-mL round-bottom flask equipped with a magnetic stirrer. After stirring the reaction mixture for 5 min at room temperature, sodium borohydride ($NaBH_4$, 0.05 mol) was added and the reaction mixture was stirred for 15 h at room temperature. After adding H_2O (50 mL) and ether (100 mL), the solution was transferred to a separating funnel, washed thoroughly with 5 wt% sodium hydroxide solution, dilute hydrochloric acid, and water, and then dried over anhydrous magnesium sulfate. On evaporation of the solvent, oil tricyclodecyl alcohol was obtained. ^{1}H NMR ($CDCl_3$, ppm): 0.6–2.6 (17H, tricyclodecyl), 3.7 and 4.2 (1H, endo and exo).

2.2.2. Synthesis of tricyclodecyl methacrylate [11(a)]

Tricyclodecyl alcohol (0.05 mol), 4-dimethylamino pyridine (DMAP, 0.05 mol) and 50 mL dried THF were fed in a 250-mL round-bottom flask equipped with a magnetic stirrer, dropping funnel and thermometer. The reaction mixture was cooled to 0–4 °C using an ice and salt mixture. Then, 0.06 mol of methacryloyl chloride in dried THF (20 mL) was added dropwisely to the reaction mixture over a period of 0.5 h while maintaining the temperature of the reaction mixture at 0–4 °C and the reaction mixture was stirred for 24 h at room temperature. After removing the formed solid quaternary ammonium salt, the solution was transferred to a separating funnel, washed thoroughly with 5 wt% sodium hydroxide solution, dilute hydrochloric acid, and water, and then dried over anhydrous magnesium sulfate. On evaporation of the solvent, oily tricyclodecyl methacrylate was obtained. It was purified by distillation under vacuum: b.p. = 139–140 °C/3 torr (296 °C/760 torr [11(b)]). ^{1}H NMR ($CDCl_3$, ppm): 0.8–2.4 (17H, tricyclodecyl), 1.92 (3H, methyl), 5.51 and 6.06 (2H, $C{=}CH_2$).



Scheme 1. Chemical structure of PMMA-*co*-PMAAM-*co*-PTCM.

2.2.3. Synthesis of poly(methyl methacrylate-co-methacrylamide-co-tricyclodecyl methacrylate) copolymers

The solution copolymerization of methyl methacrylate, methacrylamide and tricyclodecyl methacrylate was carried out in 1,4-dioxane at 80 °C under a nitrogen atmosphere in a glass reaction flask equipped with a condenser. AIBN (1 wt% based on monomers) was employed as the initiator. The mixture was stirred for ca. 24 h before being poured into excess isopropyl alcohol vigorous agitation to precipitate the product. The crude copolymer product was purified by redissolving it in 1,4-dioxane and then adding this solution dropwisely into a large excess of isopropyl alcohol. This procedure was repeated several times and then the residual solvent of the final product was removed under vacuum at 70 °C for 1 day to yield pure white poly(methyl methacrylate-*co*-methacrylamide-*co*-tricyclodecyl methacrylate). The chemical composition of the copolymer was determined by the use of elemental analysis and ^{1}H NMR spectroscopy.

2.3. Characterizations

The elementary analyses (EA) of N, C, and H atoms in the polymers were determined by an auto elementary analysis equipment using helium as the carrier gas. The glass transition temperature of the copolymer was determined using a Du-Pont DSC-9000 DSC system. The sample was kept at 200 °C for 1 min and then cooled quickly to 30 °C from the melt of the first scan. The value of T_g was obtained as the inflection point of the jump heat capacity at a scan rate of 20 °C/min within the temperature range of 30–250 °C. All measurements were conducted under a nitrogen atmosphere. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) using a Waters 510 HPLC-equipped with a 410 Differential Refractometer and three Ultrastyragel columns (100, 500, and 10^3 Å) connected in series using THF as eluent at a flow rate of 0.4 mL/min. The molecular weight calibration curve was obtained using polystyrene standard. Infrared spectra of the copolymer films were determined by using the conventional NaCl disk method. The 1,4-dioxane solution containing the blend was cast onto a NaCl disk. The film used in this study was thin enough to obey the Beer–Lambert law. FTIR measurements were performed on a Nicolet Avatar 320 FTIR spectrophotometer; 32 scans were collected at a spectral resolution of 1 cm^{-1} ^{1}H NMR spectra of these copolymers were recorded on a Brucker ARX300 spectrometer using $CDCl_3$ as the solvent.

3. Results and discussion

3.1. Copolymer analyses

Table 1 lists all monomer feed ratios, copolymer compositions, molecular weights and glass transition temperatures of poly(MMA-*co*-MAAM-*co*-TCM) terpolymers. For convenience, we use monomer feeds to define the specimen codes. For example, 90-8-2 means 90 mol% of MMA, 8 mol% of MAAM and 2 mol% of TCM in poly-