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

Chien-Ting Lin a, Shiao-Wei Kuo b,1, Chih-Feng Huang a, Feng-Chih Chang a,∗

a Institute of Applied Chemistry, National Chiao Tung University, Hsin Chu 300, Taiwan
b Department of Materials and Optoelectronic Science, Center for Nanoscience and Nanotechnology, National Sun Yat-sen University, Kaohsiung 800, Taiwan

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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 $T_g$ ($\geq 250$ °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) tricyclocdecane 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 tricyclohexyl group of TCM will raise $T_g$ and reduce the moisture absorptions of PMMA-co-PMAAM-co-PTCM terpolymers,
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-PMMA-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 (tricyclic-decan-8-one) was purchased from TCI chemical company. Methacryloxy chloride, sodium borohydride and tricyclic-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 \( \text{H}_2\text{O} \) (50 mL) and ether (100 mL), the solution was transferred to a separating funnel, washed thoroughly with 5 wt% sodium quaternary ammonium salt, the solution was transferred to a separating funnel, washed thoroughly with 5 wt% sodium hydroxide solution, diluted 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, tricyclic), 1.92 (3H, methyl), 5.51 and 6.06 (2H, C=CH\(_2\)).

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 methacryloxy 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, diluted 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 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\(^3\) A) 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 Bruker 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-
these terpolymers show a single glass transition temperature, indicating that these terpolymers are mostly in short blocks and homogeneous in the range 10–30 nm [4]. Therefore, the incorporation of MAAM and TCM monomers into PMMA main chain can be considered as random. In poly(MMA-co-MAAM-co-Sty) terpolymers, the styrene units play a role as an inert diluent segment on the PMMA polymer chain to reduce the strength of MAAM self-associative hydrogen bonding [4]. Unlike styrene, the TCM unit is able to interact with MAAM effectively through inter-associative hydrogen bonding as MMA to raise \( T_g \), and the hydrogen-bonded rigid tricyclodecyl group of TCM also can raise \( T_g \).

In Fig. 1(a) and (b), at constant 90 and 85 mol% of MMA, the increase of TCM content results in \( T_g \) decrease, implying that hydrogen bonding interaction between MMA and MAAM is the main reason of high \( T_g \) of the copolymer. In Fig. 1(c) at a constant 80 mol% of MMA, the \( T_g \) of the composition of 80-16-4 is slightly higher than that of 80-20-0. Moreover, in Fig. 1(d) and (e) at constant 70 and 60 mol% of MMA, the \( T_g \) of the compositions of 70-24-6 and 60-32-8 are comparable to those of 60-40-0 and 70-30-0, indicating that small amount of TCM replacing for MAAM does not cause \( T_g \) reduction of the terpolymer. Small amount TCM replacing MAAM with decreasing proton donor for this hydrogen bonding in terpolymer system does not cause \( T_g \) decrease of the terpolymer because of the rigid and tied tricyclodecyl group of TCM. However, excess replacement of TCM for MAAM results in \( T_g \) decrease due to lower content of proton donor in the terpolymer system.

3.3. FTIR analyses

Fourier transform infrared spectroscopy is one of the most powerful tools for identifying and investigating hydrogen bonding in polymers. Fig. 2 displays FTIR spectra recorded at room temperature for pure PMAAM, PMMA and PTCM. Pure PMAAM exhibits two bands at 1650 and 1600 cm\(^{-1}\) corresponding to the amide I (C=O stretching vibrations) and amide II (N–H bending vibrations) bands. The carbonyl stretching bands of pure PMMA and pure PTCM are nearly overlapped at 1730 cm\(^{-1}\) and 1729 cm\(^{-1}\), corresponding to their respective free carbonyl groups. In our previous study [3], the absorption of the amide I group of the MAAM shifts to higher wavenumber and its intensity decreases upon increasing the MMA content in the PMMA-co-MAAM copolymers, implying that fraction of the self-associated hydrogen-bonded amide groups convert into inter-association through hydrogen bonding to carbonyl groups of MMA units. Fig. 3 displays FTIR spectra recorded at room temperature for these terpolymers. Similar phenomenon was also observed by incorporating the PS units in the poly(MMA-co-MAAM-co-Sty) copolymers [4]. Unlike polystyrene, the carbonyl group of TCM can also interact with NH\(_2\) group of MAAM through hydrogen bonding, and its absorption peaks of the free and hydrogen-bonded carbonyl stretching are essentially same as to those for the carbonyl group of MMA, splitting into two bands at 1730 and 1718 cm\(^{-1}\). Therefore, the carbonyl stretching bands located between 1620 and 1800 cm\(^{-1}\) are split into four major absorptions, 1660, 1680, 1718, and 1730 cm\(^{-1}\), corresponding to hydrogen-bonded carbonyl stretching of amide I, free carbonyl stretching of amide I, hydrogen-bonded carbonyl stretching of ester, and free carbonyl stretching of ester, respectively. These four peaks can be fitted well to the Gaussian function. Values of \( \sigma_{\text{HBr}}/\sigma_0 \) for MMA and 1.2 for MAAM are employed [13], and Table 3 summarizes the results from curve fitting of these spectra in terms of the fraction of free and hydrogen-bonded carbonyl of amide (MAAM) and ester (MMA and TCM). At constant 90 and 85 mol% of MMA, the increase of TCM content results in \( T_g \) decrease mainly due to reduce of the available proton donor MAAM.
and thus lower hydrogen bonding content. However, at constant 80, 70 and 60 mol% of MMA, the fractions of hydrogen-bonded carbonyl stretching of the composition of 80-16-4, 70-24-6 and 60-32-8 is comparable to that of 80-20-0, 70-30-0 and 60-40-0, respectively, indicating that small replacement of TCM for MAAM does not reduce the \( T_g \) of terpolymers. Decreasing small amount of hydrogen bond donor does not decrease the fraction of hydrogen-bonded carbonyl stretching of terpolymers substantially. However the fraction of hydrogen-bonded carbonyl stretching of terpolymers is decreased upon the excess addition of TCM units. Upon increasing the replacement of TCM for MAAM, the fraction of inter-associative hydrogen bonding between esters and amides decreases slowly but the fraction of self-associative hydrogen bonding in amide groups decreases sharply, indicating that the rigid bulky tricyclo-decyl group of TCM units actually plays a role of inert diluent segment to convert into inter-associative hydrogen bonding between ester groups and amide groups from self-associative hydrogen bonding in amide groups.

The fraction of inter-associative hydrogen bonding between polymer chains can affect the \( T_g \) and the miscibility of a binary polymer blend [15–17]. Upon increasing the fraction of inter-associative hydrogen bonding in a binary polymer blend, the \( T_g \) can be raised and the miscibility also can be enhanced [14,16]. Furthermore, the steric hindrance of bulky side group on hydrogen bonding interaction not only reduces the fraction but also weakens of hydrogen bond association [18,19]. To further understand the effect of bulky TCM units in details, three compositions of 85-15-0, 80-16-4 and 60-16-24 possess similar MAAM and similar \( \text{NH}_2 \) contents, implying that they have similar hydrogen-bonding donor

![Fig. 1. DSC scans of poly(MMA-co-MAAM-co-TCM) copolymers at MMA contents of (a) 90, (b) 85, (c) 80, (d) 70 and (e) 60 mol%.

![Fig. 2. IR spectra, displaying the range 1550–1800 cm\(^{-1}\), of pure PMMA, PMAAM, and PTCM.](image-url)
(NH₂) and similar hydrogen-bonding acceptor (carbonyl group) content. Fig. 4 displays DSC scans and IR spectra of these three compositions, and their curve fitting of the IR spectra and polymer composition are marked by bold face words in Tables 1 and 3. Compared with the composition of 85-15-0, the replacement of small amount of TCM for MMA at the composition of 80-16-4 results in increase the fraction of total hydrogen-bonded carbonyl stretching and the \( T_g \). The \( T_g \) increase can be attributed to the rigid bulky tricyclodecyl group of TCM units. However, comparing with the composition of 85-15-0, more TCM content of the composition 60-16-24 decreases the fraction of total associated hydrogen-bonded carbonyl groups and the value of \( T_g \), because of the bulky tricyclodecyl group obstructing hydrogen bond interaction, not only the inter-association between esters and amides but also the self-association of MAAM.

3.4. Moisture absorption analyses

PMAAM is highly moisture absorptive because its amide groups form hydrogen bonds with water. Especially the free NH₂ groups of MAAM that do not form inter-associative or self-associative hydrogen bonding, they can absorb moisture from the atmosphere. TCM has bulky aliphatic group to provide greater hydrophobic character, therefore, the moisture absorptive property of this terpolymer system is expected to be substantially reduced. Fig. 5 displays the moisture absorptions of these poly(MMA-co-MAAM-co-TCM) terpolymers. Compared with pure PMMA, the moisture absorption increases upon increasing the MAAM content in the PMMA-co-MAAM copolymer and decreases upon increasing the TCM content the terpolymers. Again, three compositions of 85-15-0, 80-16-4 and 60-16-24 are selected for comparison. The moisture absorptions for compositions of 85-15-0, 80-16-4 and 60-16-24 are 3.02, 1.57, and 2.73, respectively. Small extent replacement of TCM for MMA (80-16-4) slightly increases the fraction of hydrogen-bonded carbonyl compared to the composition of 85-15-0. The moisture absorption of the composition of 80-16-4 significantly lower than the composition of 85-15-0 due to hydrophobic character of the bulky aliphatic group in TCM. However, comparing with the composition of 85-15-0, more replacement of TCM for MMA in the composition 60-16-24 decreases the fraction of total hydrogen-bonded carbonyl groups, and the free N–H groups can form hydrogen bonding with water to increase the moisture absorption even though more bulky aliphatic groups is existed in the composition of 60-16-24.

3.5. Transparency

Ultraviolet technology is seeing an increase in demand with many industries needing the ability to use non-X-ray short wavelengths [20]. Key industries include lithography where writing
smaller traces is the key to staying viable. However, ultraviolet light is very energetic light. For a material to be considered UV transparent, there cannot be an atomic absorption resonance at the desired wavelength. Moreover, high absorption also results in another effect due to UV: damage. UV photons can have enough energy to ionize an atom or change its chemical structure. This process, known as solarization, results in a decreased transmission and a change in color of the substrate material. As use of this new

Table 3
Curve fitting of the IR spectra of the copolymers recorded at room temperature.

<table>
<thead>
<tr>
<th>PMMA-co-PMAA-co-PTCM Carbonyl in MMA and TCM</th>
<th>Amide I in MAAM</th>
<th>Total C=O</th>
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<tbody>
<tr>
<td>Free C=O (Ester)</td>
<td>H-bonded C=O (Ester)</td>
<td>Free Amide I (C=O)</td>
</tr>
<tr>
<td>r (cm⁻¹)</td>
<td>A⁺ (%)</td>
<td>r (cm⁻¹)</td>
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<tr>
<td>PMMA</td>
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<tr>
<td>90-10-0</td>
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<td>PMAA</td>
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</tr>
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</table>

a A⁺ and A⁻ are defined respectively by the mole fraction of free carbonyl group and the mole fraction of H-bonded carbonyl group of all esters which are including TCM and MMA.
b A⁺ and A⁻ are defined respectively by the mole fraction of free carbonyl group and the mole fraction of H-bonded carbonyl group of amides.
c A⁺ and A⁻ are defined respectively by the mole fraction of free carbonyl group and the mole fraction of H-bonded carbonyl group of all esters and amide, including TCM, MMA and MAAM.

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Fig. 4. DSC and IR spectra of poly(MMA-co-MAAM-co-TCM) at composition of 85-15-0, 80-16-4, and 60-16-24.
technology, there remains a continuing need for improved materials with higher UV transparency. Fig. 6 displays UV–vis transmittance spectrum of pure PMMA and the composition of 80-16-4. The UV–vis transmittance of the composition of 80-16-4 shows its transmittance with almost 100% at 350 nm and more than 80% at 300 nm, maintaining high transmittance at 300–350 nm of pure PMMA. This result implies that the incorporation of TCM does not reduce the good transparent characteristic of PMMA-based polymeric material.

4. Conclusions

We have prepared a series of poly(methyl methacrylate-co-methacrylamide-co-tricyclodecyl methacrylate) (PMMA-co-MAAM-co-PTCM) copolymers that have high glass transition temperatures and high transparency. By incorporating the aliphatic tricyclodecyl methacrylate moiety into the PMMA-co-MAAM main chain results in high glass transition temperature and high transparency of PMMA-based polymeric material. We found that 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. A selected composition, 80-16-4, exhibits lower moisture absorption (1.57 vs. 2.0 wt% for PMMA), higher \( T_g \) (142 °C vs. 105 °C for PMMA) and good transparency of PMMA-based polymeric material. This selected polymer composition has the potential to replace the pure PMMA in optical device applications.

References