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.

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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*-meth-acrylamide-*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$_2$O (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 dropwise to the reaction mixture
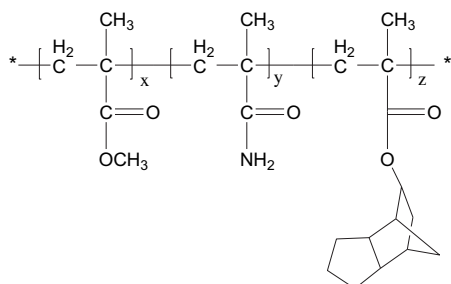
over a period of 0.5 h while maintaining the temperature of the reaction mixture at 0–4 °C and the reaction mixture was stirred for 24 h at room temperature. After removing the formed solid quaternary ammonium salt, the solution was transferred to a separating funnel, washed thoroughly with 5 wt% sodium 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$_2$).

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-

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

Table 1
Poly(MMA-co-MAAM-co-TCM) terpolymers synthesized in this study.

Polymer	Monomer feed (mol%)			Polymer composition (mol%)			Mw (g/mol.)	T_g(°C)
	MMA	MAAM	TCM	MMA	MAAM	TCM		
100-0-0	100	0	0	100	0	0	57,000	105
90-10-0	90	10	0	92.6	7.4	0	29,500	114
90-8-2[a]	90	8	2	95.3	4.1	0.6	34,700	118
90-6-4	90	6	4	94.0	4.7	1.3	34,000	109
90-4-6	90	4	6	92.0	5.2	2.8	38,400	96
90-2-8	90	2	8	91.5	4.8	3.7	29,300	97
85-15-0	85	15	0	88.9	11.1	0	23,600	120
85-12-3	85	12	3	88.3	11.6	0.1	25,900	119
85-9-6	85	9	6	87.8	9.1	3.1	31,700	115
85-6-9	85	6	9	90.3	4.3	5.4	26,400	118
85-3-12	85	3	12	89.1	3.0	7.9	25,100	84
80-20-0	80	20	0	86.2	13.8	0	35,600	133
80-16-4	80	16	4	88.3	11.4	0.3	34,300	142
80-12-8	80	12	8	88.1	9.1	2.8	26,600	117
80-8-12	80	8	12	81.3	9.5	9.2	22,800	101
80-4-16	80	4	16	81.8	6.5	11.7	30,200	103
70-30-0	70	30	0	80.3	19.7	0	28,300	140
70-24-6	70	24	6	81.4	16.1	2.5	32,200	138
70-18-12	70	18	12	82.6	9.7	7.7	29,800	130
70-12-18	70	12	18	81.3	6.3	12.4	20,800	114
70-6-24	70	6	24	79.1	6.5	14.4	28,100	110
60-40-0	60	40	0	72.4	27.6	0	29,500	170
60-32-8	60	32	8	72.1	26.7	1.2	34,600	163
60-24-16	60	24	16	75.4	20.2	4.4	23,800	147
60-16-24	60	16	24	75.2	11.5	13.3	29,900	130
60-8-32	60	8	32	66.2	6.3	27.5	20,700	132

[a] 90-8-2 is defined by the monomer feed, which means 90 mol% of MMA, 8 mol% of MAAM and 2 mol% of TCM content in poly(MMA-co-MAAM-co-TCM) terpoymers. The other samples are also defined in the same way.

(MMA-co-MAAM-co-TCM) terpolymers. The reactivity ratios (r) of (MMA + MAAM) and TCM in the terpolymers were estimated by graphical method of Kelen–Tudos method [12]:

$$\theta = r_1\varepsilon - \frac{r_2(1-\varepsilon)}{\gamma} \qquad (1)$$

where 1 stands for (MMA + MAAM) and 2 for TCM. θ, ε, and γ are mathematical functions of G and F are defined in Table 2. On plotting θ versus ε, a linear plot was obtained. The intercepts at $\varepsilon = 0$ and $\varepsilon = 1$ gave $-r_2/\gamma$ and r_1, respectively. The values obtained for r_1 and r_2 were $r_1 = 3.08$ and $r_2 = 3.42$. The same methodology can be employed to determine the reactivity ratios of (MMA + TCM) and MAAM, and the value r_1 for (MMA + TCM) and r_2 for MAAM are 1.29 and 0.19, respectively. The reactivity ratio of the copolymer has been calculated previously (PMMA-co-PMAAM: $r_{PMMA} = 1.38$, $r_{PMAAM} = 0.24$) [4]. As a result, the reactivities of these monomers in poly(MMA-co-MAAM-co-TCM) copolymer system follow the order MMA > MAAM > TCM. Furthermore, the molecular weights of copolymers are independent of increasing the contents of TCM and MAAM. This result indicates that the polarity difference between TCM and MAAM or MMA is relatively less than styrene and MAAM or MMA [2,4], and does not make copolymerization difficult as styrene.

3.2. Thermal analyses

Fig. 1 display the DSC thermograms of poly(MMA-co-MAAM-co-TCM) terpolymers and summarized results are listed in Table 1. All

Table 2
Kelen–Tudos parameters for (MMA + MAAM) and for TCM.

X	Y	G	F	ε	θ
$=\dfrac{M_1}{M_2}$	$=\dfrac{\Theta_1}{\Theta_2}$	$=\dfrac{X(Y-1)}{Y}$	$=\dfrac{X^2}{Y}$	$=\dfrac{F}{\gamma + F}$	$=\dfrac{G}{\gamma + F}$

M_1 is the mole fraction of (MMA + MAAM) and M_2 is the mole fraction of TCM in feed; Θ_1 and Θ_2 are their respective experimental mole fraction in the terpolymer.

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 PMAAM 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_gs 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-PMAAM 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 $a_{HB}/a_F = 1.5$ for MMA and 1.2 for MAAM are employed [13], and Table 3 summaries 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
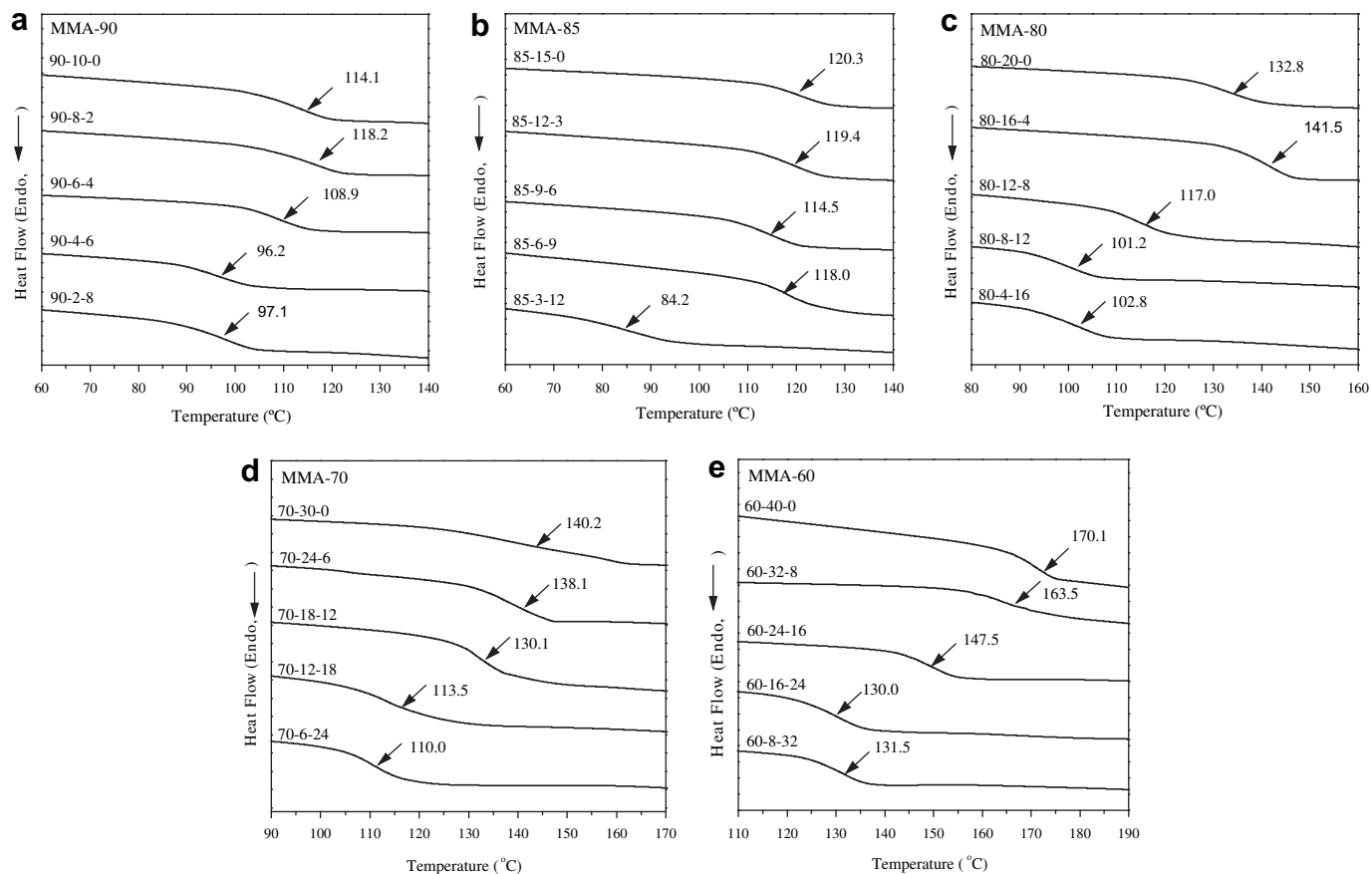
Fig. 1. DSC scans of poly(MMA-*co*-MAAM-*co*-TCM) copolymers at MMA contents of (a) 90, (b) 85, (c) 80, (d) 70 and (e) 60 mol%.
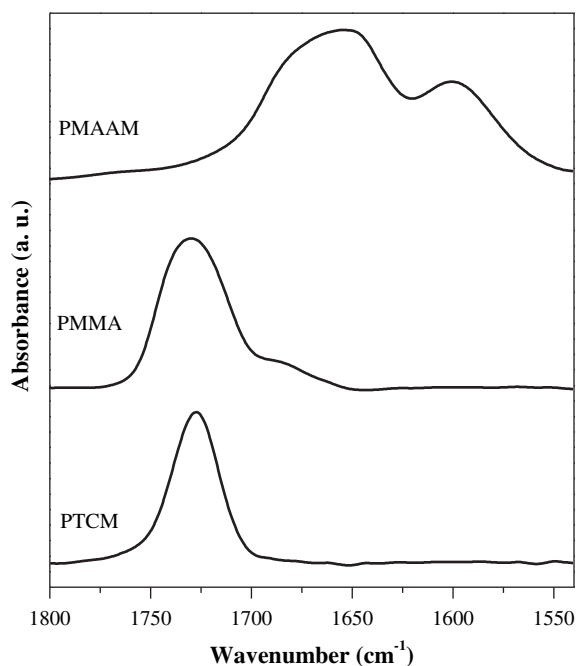

Fig. 2. IR spectra, displaying the range 1550–1800 cm^{-1}, of pure PMMA, PMAAM, and PTCM.

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-associated hydrogen bonding between esters and amides decreases slowly but the fraction of self-associated hydrogen bonding in MAAM 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 [14] 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 NH$_2$ contents, implying that they have similar hydrogen-bonding donor
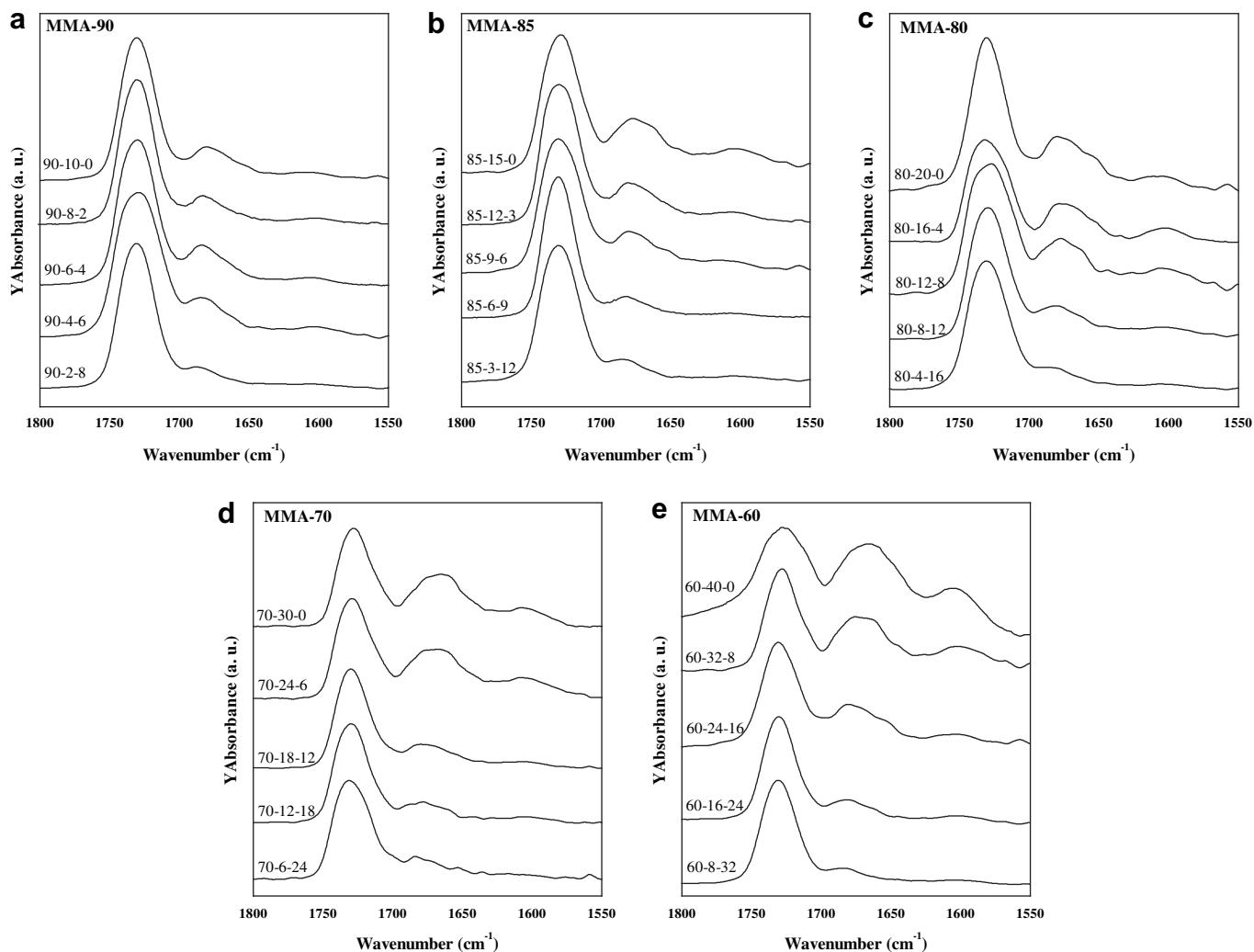
Fig. 3. IR spectra, displaying the range 1550–1800 cm^{-1} of poly(MMA-co-MAAM-co-TCM) copolymers at MMA contents of (a) 90, (b) 85, (c) 80, (d) 70 and (e) 60 mol%.

(NH$_2$) 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 NH$_2$ 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-PMAAM 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

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

| PMMA-co-PMAAM-co-PTCM | Carbonyl in MMA and TCM | | | | Amide I in MAAM | | | | Total C=O | |
| | Free C=O (Ester) | | H-bonded C=O (Ester) | | Free Amide I (C=O) | | H-bonded Amide I (C=O) | | Free C=O | H-bonded C=O |
	ν (cm^{-1})	A_f^a (%)	ν (cm^{-1})	A_b^a (%)	ν (cm^{-1})	A_f^b (%)	ν (cm^{-1})	A_b^b (%)	A_f^c (%)	A_b^c (%)
PMMA	1730	100.0	–	–	–	–	–	–	–	–
90-10-0	1731	80.6	1720	19.4	1680	76.0	1658	24.0	80.3	19.7
90-8-2	1731	85.4	1720	14.5	1682	79.9	1659	20.0	85.2	14.8
90-6-4	1732	87.3	1719	12.7	1683	77.3	1660	22.7	86.9	13.1
90-4-6	1732	89.4	1718	10.6	1683	77.2	1660	22.8	88.8	11.2
90-2-8	1732	91.1	1719	8.9	1683	75.2	1660	24.8	90.4	9.6
85-15-0	1732	77.0	1719	23.0	1680	67.2	1660	32.8	76.0	24.0
85-12-3	1731	75.8	1720	24.2	1680	72.9	1660	27.1	75.5	24.5
85-9-6	1732	75.8	1720	24.2	1682	70.8	1660	29.2	75.4	24.6
85-6-9	1731	76.3	1720	23.7	1683	77.5	1660	22.5	76.4	23.6
85-3-12	1732	80.3	1720	19.7	1683	85.5	1660	14.5	80.4	19.6
80-20-0	1732	76.3	1718	23.7	1680	63.8	1658	36.3	74.6	25.4
80-16-4	1732	76.0	1718	24.0	1680	68.9	1659	31.1	75.2	24.8
80-12-8	1733	79.0	1718	21.0	1682	80.1	1659	19.9	79.1	20.9
80-8-12	1732	80.6	1718	19.4	1683	79.8	1660	20.2	80.5	19.5
80-4-16	1732	84.1	1718	15.9	1683	78.8	1660	21.2	83.8	16.2
70-30-0	1732	65.5	1718	34.5	1681	53.9	1659	46.1	61.1	38.9
70-24-6	1732	66.8	1718	33.2	1682	57.3	1659	42.7	63.7	36.3
70-18-12	1733	72.4	1718	27.6	1681	66.2	1659	33.8	70.7	29.3
70-12-18	1733	78.0	1719	22.0	1683	70.4	1660	29.6	76.5	23.5
70-6-24	1733	82.2	1719	17.8	1682	71.1	1660	28.9	80.4	19.6
60-40-0	1732	52.0	1718	48.0	1680	45.2	1661	54.8	50.1	49.9
60-32-8	1730	56.0	1718	44.0	1680	58.0	1661	42.0	56.6	43.4
60-24-16	1733	65.0	1719	35.0	1680	65.2	1661	34.8	65.0	35.0
60-16-24	1733	79.6	1720	20.4	1681	75.1	1660	24.9	79.1	20.8
60-8-32	1733	81.4	1720	18.6	1682	80.1	1660	19.9	81.3	18.7
PMAAM	–	–	–	–	1677	29.2	1652	70.8	–	–

[a] A_f and A_b 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_f and A_b are defined respectively by the mole fraction of free carbonyl group and the mole fraction of H-bonded carbonyl group of amides.
[c] A_f and A_b 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.

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
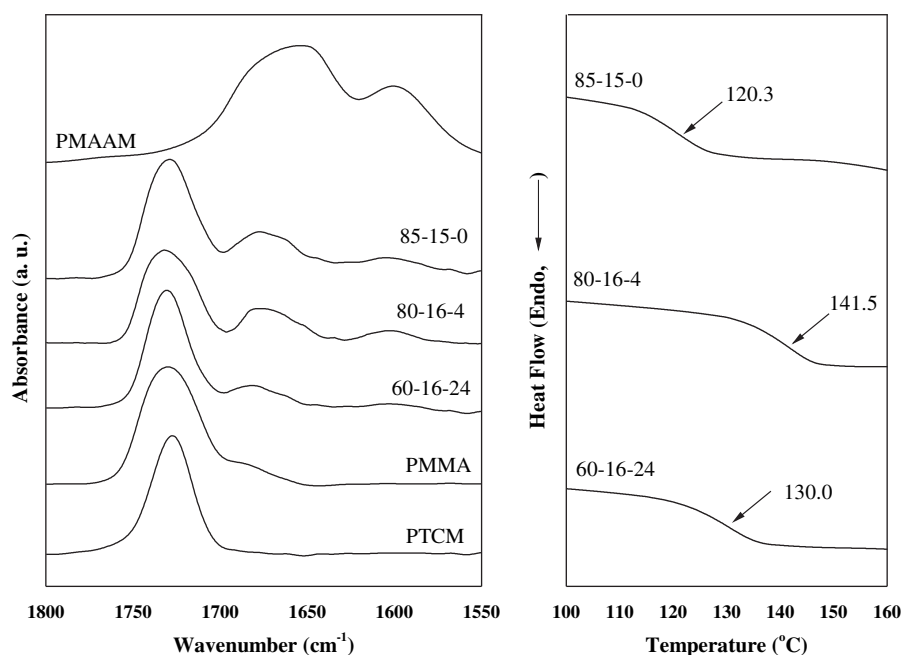

Fig. 4. DSC and IR spectra of poly(MMA-co-MAAM-co-TCM) at composition of 85-15-0, 80-16-4, and 60-16-24.
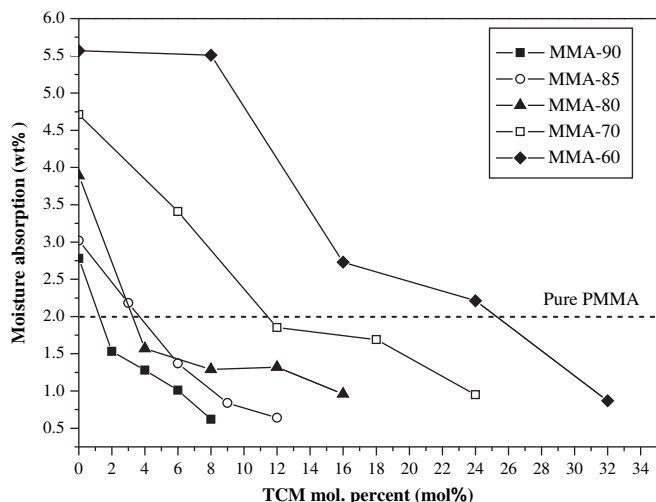
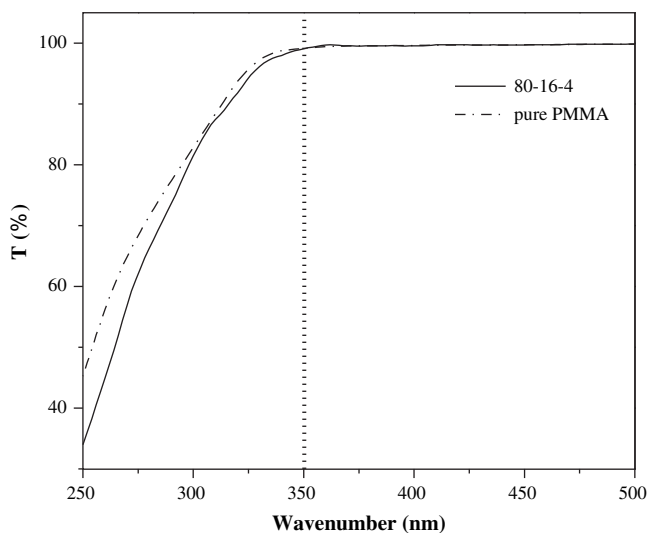**Fig. 5.** Moisture absorption of poly(MMA-*co*-MAAM-*co*-TCM) terpolymers.

Fig. 6. The UV–vis transmittance spectrum of poly(MMA-*co*-MAAM-*co*-TCM) composition of 80-16-4 and pure PMMA.

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*-PMAAM-*co*-PTCM) copolymers that have high glass transition temperatures and high transparency. 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. 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.

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