

Cross-linked Polyamides Prepared through Direct Bulk Michael Addition and Polycondensation from 1,6-Hexanediamine and Methyl Acrylate

Sheng-Qing Yang, Jin-Nan Zhao, Jing-Bo Zhao*, Zhi-Yuan Zhang, and Jun-Ying Zhang*

Key Laboratory of Carbon Fiber and Functional Polymers (Beijing University of Chemical Technology), Ministry of Education; College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Electronic Supplementary Information

Abstract Cross-linked polyamides (cPAs) were prepared through direct bulk Michael addition and subsequent polycondensation. Several mixed hexanediamine multi-esters (HDAMEs) were generated through the Michael addition of 1,6-hexanediamine (HDA) and methyl acrylate (MA) at 50 °C with different HDA/MA molar ratios. Melt polycondensation of HDAMEs then proceeded at 150 or 170 °C in flasks to obtain viscous fluids, and curing was continued in tetrafluoroethylene molds to obtain cPA films. The Michael addition was monitored on the basis of FTIR and ESI-MS spectra. The cPA films were characterized by DSC, TGA, dynamic mechanical analysis, and tensile test. These directly prepared cPAs exhibited T_g of 1–39 °C, tensile strength of up to 45 MPa, and strain at break from 18% to 40%. The cPAs with high tensile strength and good toughness were successfully synthesized through the direct bulk Michael addition from HDA and MA followed with polycondensation.

Keywords Michael addition; Polycondensation; Mechanical properties

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INTRODUCTION

Polyamides (PAs) are widely used in daily life because of their excellent mechanical properties. Based on their molecular structures, PAs are typically classified as either linear or cross-linked (cPAs). Linear PAs, such as PA6 and PA66, play a valuable role in early commercial PA products.^[1,2] These PAs are used mainly as engineering plastics and fibers. Recently, cPAs have also become important materials used for composites, adhesives, oil-resistant coatings, and separation membranes due to their high performance.

At present, two major methods are used to synthesize cPAs. (1) Synthesis of H₂N-terminated or other functionalized PA prepolymers followed by crosslinking. H₂N-terminated linear or branched PAs were synthesized through ring-opening polymerization of caprolactam or melt polycondensation of diacids with multi-amines (compounds having multiple amine groups). Other functionalized linear PAs were synthesized by introducing maleimide, azide, allyl, or cinnamoyl functional groups. Crosslinking of the H₂N-terminated or other functionalized PA prepolymers was conducted with caprolactam-

capped polyisocyanate,^[3] terephthaloyl bis(ϵ -caprolactam),^[4] epoxy resins,^[5] multi-thiols,^[6] and irradiation or heat.^[7–9] (2) Synthesis through solution polycondensation of diacid or polyacid chlorides with multi-amines.^[10,11]

Different from aromatic cPAs, aliphatic cPAs contain flexible backbones. The monomers used in the synthesis of aliphatic cPAs usually show higher reactivity than those in aromatic cPAs. Aliphatic cPAs are commonly easier to be prepared than the aromatic analogues. Irregular and less stiff structure of aliphatic cPAs endows them with tailored thermal properties, low solubility, good adhesion, and compatibility with inorganic fillers.^[6] These characters make aliphatic cPAs suitable to be used as adhesives, coatings, composites, and cPA-ceramic membranes for the separation of aromatic/aliphatic hydrocarbon mixtures.^[12]

Michael ene-amine addition is an efficient reaction to form C–N bonds. It is commonly used to prepare dendrimers in solution systems through several and complex reaction steps. The obtained dendrimers are suitable for the high value applications such as coatings, drug and gene delivery, and nanotechnology.^[13,14] Melt polycondensation is usually used in the synthesis of polyesters, polyamides, and segmented copolymers constructed with PA hard segments (HSs) and polyester or polyether soft segments.^[15] PA HSs can increase intermolecular interactions largely, and improve the mechanical properties of polymers efficiently.

* Corresponding authors, E-mail: zhaojb@mail.buct.edu.cn (J.B.Z.)

E-mail: zhangjy@mail.buct.edu.cn (J.Y.Z.)

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Trimellitic acid and pyromellitic acid are typical aromatic tricarboxylic acid and tetracarboxylic acid, respectively. Their reactivity is usually lower than that of aliphatic analogues. The methyl or ethyl esters of trimellitic acid or pyromellitic acid can react with diamines (DAs) to form aromatic cPAs. However, their esters are commonly expensive. Aliphatic tricarboxylic or tetracarboxylic acids are extremely rare. Citric acid is an example of aliphatic tricarboxylic acids. Melt polycondensation of tributyl citrate with 1,6-hexanediamine (HDA) could afford partially crosslinked poly(hexamethylene succinimide-co-citramide)s.^[16,17]

In our previous work, we synthesized a hexanediamine tetraester (HDATeE) through Michael addition of HDA and methyl acrylate (MA) at a 1/4 HDA/MA molar ratio. Melt polycondensation of the HDATeE with different DAs was conducted, and a series of cPAs with excellent mechanical properties were obtained.^[18] We found that at such a HDA/MA ratio, the HDATeE formed was not a single compound but a mixture of hexanediamine mono-ester (HDAMoE), hexanediamine di-ester (HDADE), hexanediamine tri-ester (HDATrE), and HDATeE. Except HDATeE, HDAMoE, HDADE, and HDATrE contained ester groups and reactive amino groups, *i.e.*, H₂N— or HN= groups. These amino groups might also react with ester groups in the curing process of HDATeE with different DAs.

To verify the reaction of the ester groups with residual amino groups in the curing reaction, in this study, we synthesized several mixed hexanediamine multi-esters (HDAMEs) through bulk Michael addition of HDA and MA at different molar ratios. Melt polycondensation of the HDAMEs was followed to directly synthesize cPAs. The Michael addition was monitored by Fourier transform infrared spectroscopy (FTIR) and electrospray ionization mass spectrometry (ESI-MS). The obtained cPAs were characterized by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and tensile testing.

EXPERIMENTAL

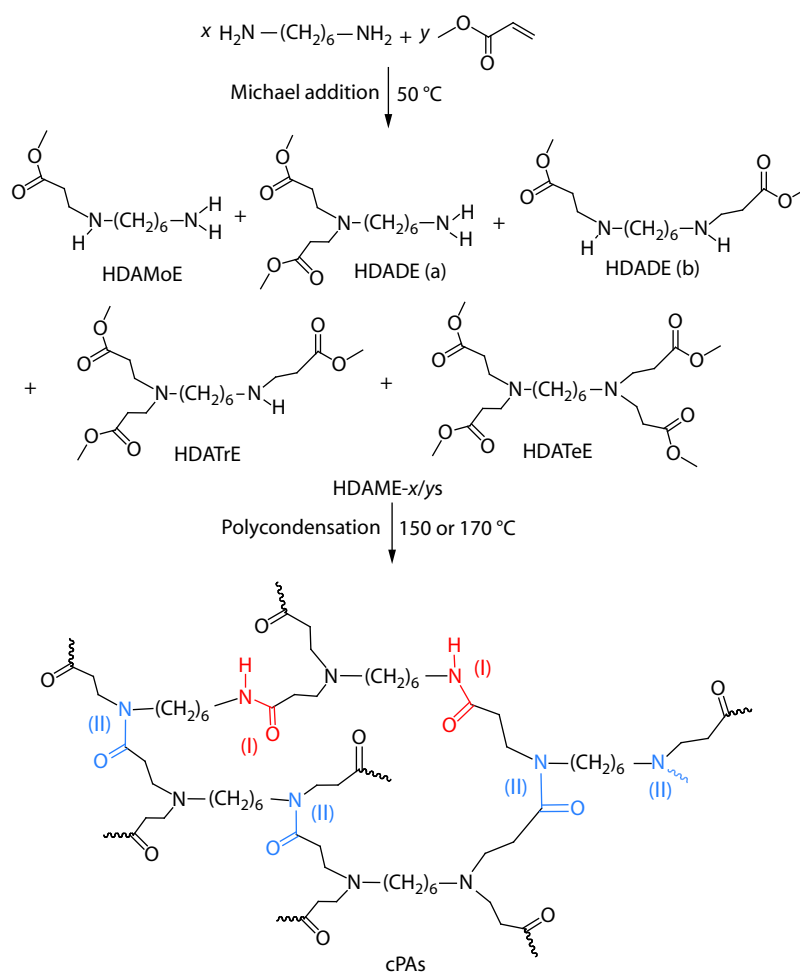
Materials

HDA and MA were obtained from Aladdin in Shanghai, China and used directly.

Synthesis of cPAs

cPA-*x/y*s were synthesized at different HDA/MA (*x/y*) molar ratios (Scheme 1) under similar reaction conditions. cPA-1/1.5 was synthesized as follows:

In a 100 mL 3-neck flask, 4.65 g (0.04 mol) of HDA and 5.17 g (0.06 mol) of MA were mechanically stirred and reacted at 50 °C for 3 h. The mixture was reacted further at



Scheme 1 cPAs prepared through direct bulk Michael addition and polycondensation from HDA and MA.

170 °C under nitrogen until a flowing viscous fluid was formed. The fluid was poured into Teflon molds of different shapes. The curing process was continued in a vacuum oven at 170 °C for 13 h to obtain solid films. A series of 40 mm × 6 mm × 1 mm rectangular or 20 mm × 4 mm × 1 mm dumbbell-shaped cPA-1/1.5 films were prepared.

Characterization

FTIR spectra were recorded on a NICOLET 60SXB FTIR spectrometer. ESI-MS spectra were recorded on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS spectrometer with methanol as the solvent. DSC was carried out using a TA Q200 differential scanning calorimeter in N₂ via a cooling (40 °C·min⁻¹)-heating (10 °C·min⁻¹) process. TGA was conducted on a TGA Q50 analyzer at a heating rate of 10 °C·min⁻¹ in N₂.

The mechanical properties of cPAs were recorded on a LLOYD LR30K tensile testing machine at a tensile speed of 5 mm·min⁻¹. Dumbbell samples (a central part 10 mm × 4 mm × 1 mm) were used in the tensile test. DMA was conducted with a DMTA V from -50 °C to 180 °C at a heating rate of 3 °C·min⁻¹ under nitrogen atmosphere. The imposed strain was 0.01%, and the frequency was 1 Hz. 40 mm × 6 mm × 1 mm rectangle films were used in DMA detection. The moisture content was detected by direct drying at 100 °C for 6 h.

RESULTS AND DISCUSSION

Synthesis of cPAs

cPAs were prepared through direct bulk Michael addition of HDA and MA followed by melt polycondensation (Scheme 1). Fig. 1 shows the monitoring FTIR spectra of the Michael addition at different *x/y*s. In the FTIR spectrum of MA, a weak band corresponding to —C=C— bonds appears at 1636 cm⁻¹. After 3 h Michael addition at 50 °C, this band became negligible in HDAME-*x/y*s. It means that at this moment, the Michael addition between —C=C— groups of MA and —NH₂ groups of HDA was nearly complete. A series of HDAMEs were obtained through the Michael reaction.

Fig. 2 shows the ESI-MS spectra of the main components in HDAME-*x/y*s obtained through Michael addition at 50 °C for 3 h. The major components were HDAMoE, HDADE, HDATrE, and HDATeE. Their molecular weights calculated according to the structures (in Scheme 1) were 202, 288, 374, and 460

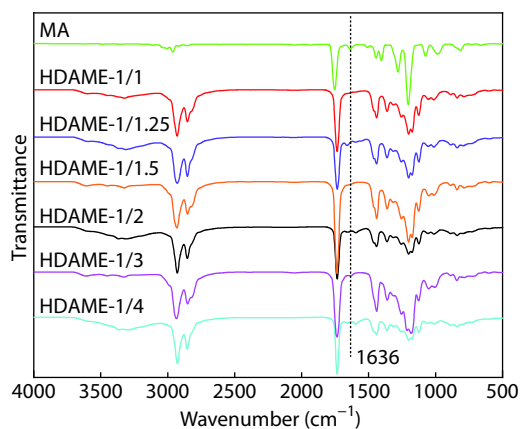


Fig. 1 FTIR spectra of HDAME-*x/y*s obtained through Michael addition at 50 °C for 3 h.

g·mol⁻¹, respectively. HDAMoE, HDADE, HDATrE, and HDATeE show *m/z* peaks at *M* + 1 or *M* - 1 in ESI-MS spectra, except in Figs. 2(e) and 2(f), where the peaks of HDAMoE appear at *M* - 14 with an —NH— lost. HDAME-*x/y*s synthesized at different *x/y*s contained similar components. HDAMoE, HDADE, HDATrE, and HDATeE were all present in different HDAME-*x/y*s although their contents vary. For each component, the same sensitivity in similar HDAME-*x/y*s might appear. An increase or decrease of *m/z* intensity might qualitatively reflect the increase or decrease of the content. In HDAME-1/1, HDAME-1/1.25, and HDAME-1/1.5, HDADE was the major component, and HDAMoE, HDATrE, and HDATeE were at relatively high levels (Figs. 2a–2c). In HDAME-1/2, HDADE, HDATrE, and HDATeE were the major components, and HDAMoE was the minor component (Fig. 2d). In HDAME-1/3, HDATrE was the major component, while HDAMoE, HDADE, and HDATeE were in lower contents. In HDAME-1/4, HDATrE and HDATeE were the major components, whereas HDAMoE and HDADE were the minor components but could still be observed (Figs. 2e and 2f).

cPA-*x/y*s were prepared by heating HDAME-*x/y*s in flasks at 170 °C and then curing in Teflon molds. As HDAME-1/1, HDAME-1/1.25, and HDAME-1/1.5 were synthesized at low MA amount, the components HDAMoE, HDADE, HDATrE, and HDATeE were at relatively high levels (Figs. 2a–2c). HDAMoE, HDADE, and HDATrE contained a sufficiently high amount of reactive —NH₂ or —HN— groups and ester groups, while HDATeE contained only ester groups. Crosslinking between the —NH₂ or —HN— groups and ester groups led to high level of curing with gel percentage up to 88% in cPA-*x/y*s (Table 1). HDAME-1/3 and HDAME-1/4 were synthesized at high MA amount. HDATrE and HDATeE components were primarily formed in their HDAME-*x/y*s, while HDAMoE and HDADE formed at a relatively low level. HDATrE contained a higher amount of ester groups compared to the —NH₂ or —HN— groups, and HDATeE contained only ester groups. Crosslinking between these ester groups and —NH₂ or —HN— groups led to a low level of curing with gel percentage at approximately 25% in cPA-*x/y*s, and some ester groups were left unreacted.

Fig. 3 shows FTIR spectra of the viscous fluids formed in bulk polycondensation at the end in flasks. Three characteristic bands were found corresponding to the ester $\nu_{C=O}$ (1738 cm⁻¹), amide $\nu_{C=O}$ (1649 cm⁻¹), and amide δ_{N-H} (1549 cm⁻¹). Polycondensation between the ester groups and —NH₂ or —HN— groups occurred at this period, and some amide groups were formed. Many unreacted ester groups were left because polycondensation was incomplete. As the HDA/MA molar ratios or *x/y*s used in cPA-*x/y* synthesis decreased from 1:1 to 1:4, few amide groups were formed, and a larger number of ester groups were left.

The reaction time for bulk polycondensation of HDAME-1/1, HDAME-1/1.25, and HDAME-1/1.5 in flask (Table 1) was shorter than that for the reported system (HDAME-1/4 reacted with HDA and isophoronediamine (IPDA) at a HDA/IPDA molar ratio of 5:5).^[18] HDAME-1/1, HDAME-1/1.25, and HDAME-1/1.5 showed obviously weaker bands for ester $\nu_{C=O}$ (1738 cm⁻¹) in their FTIR spectra (Figs. 3a–3c) than the reported system, which means that they polymerized faster than

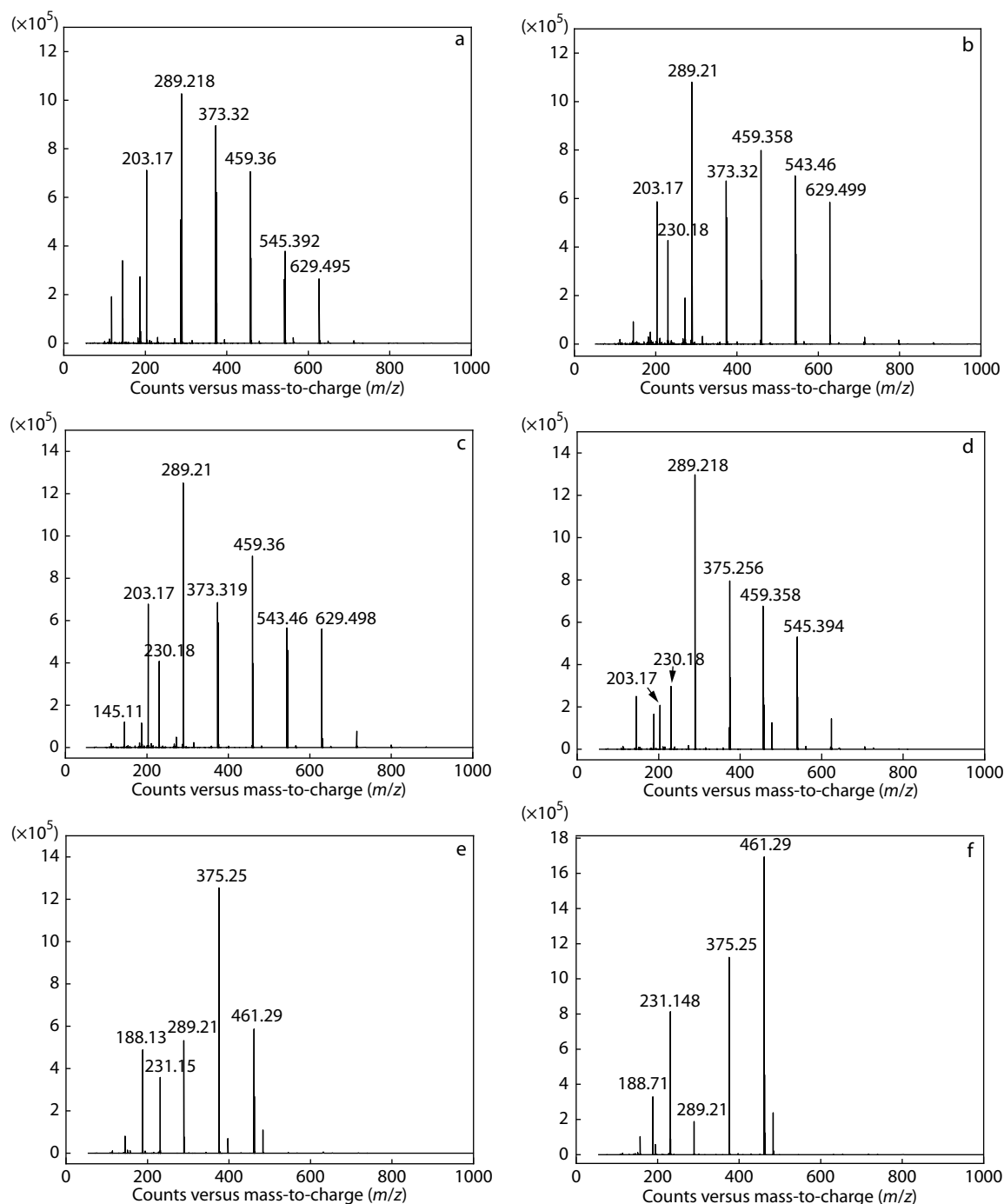


Fig. 2 ESI-MS spectra of main components in HDAME-*x*/ys obtained in Michael addition at 50 °C for 3 h: (a) HDAME-1/1, (b) HDAME-1/1.25, (c) HDAME-1/1.5, (d) HDAME-1/2, (e) HDAME-1/3, and (f) HDAME-1/4.

the reported system because they all contained sufficient ester and $-\text{NH}_2$ or $-\text{HN}-$ groups. The bulk polycondensation lasted for 1 h for HDAME-1/2, which was the same as that of the reported system. The band intensity of ester or amide $\nu_{\text{C=O}}$ shown in HDAME-1/2 FTIR spectrum (Fig. 3d) is similar to that of the reported system. Hence, HDAME-1/2 exhibited similar reactivity to the reported system. Bulk polycondensation time of HDAME-1/3 and HDAME-1/4 was longer than that of the reported system. However, weaker amide $\nu_{\text{C=O}}$

(1649 cm^{-1}) bands and stronger ester $\nu_{\text{C=O}}$ bands were found in their FTIR spectra (Figs. 3e and 3f). Bulk polycondensation of HDAME-1/3 and HDAME-1/4 was much evidently than the reported system because HDAME-1/3 and HDAME-1/4 lacked sufficient $-\text{NH}_2$ or $-\text{HN}-$ groups, while the reported system contained additional HDA and IPDA to react with ester groups.

Fig. 4 shows the FTIR spectra of solid cPA-*x*/y films. After curing at 170 °C for 13 h, the band at 1731 cm^{-1} correspond-

Table 1 Properties of cPA films obtained at 170 °C.

cPA-x/y	HDA/MA (x/y) (molar ratio)	Time ^a (h)	Moisture content ^b (%)	Gel percentage (%)	<i>T_g</i> (DSC) (°C)	DMA		
						<i>T_α</i> (°C)	<i>E'</i> (<i>T_α</i> + 40) (MPa)	<i>v_e</i> (mol·m ⁻³)
cPA-1/1	1:1	0.4	3.78	76	1	8	3.8	480
cPA-1/1.25	1:1.25	0.5	4.48	88	27	37	9.2	1053
cPA-1/1.5	1:1.5	0.7	4.31	88	39	25/50	11.7/8.3	1387/916
cPA-1/2	1:2	1	5.43	26	31	33/91	24.6/4.0	2844/395
cPA-1/3	1:3	2	5.86	25	32	31/55/91	14.8/6.4/3.4	1725/701/337
cPA-1/4	1:4	3	6.03	25	38	36/52/112	13.1/10.4/5.3	1508/1142/496

^a Bulk polymerization time in flasks; ^b Moisture content detected by direct drying at 100 °C for 6 h.

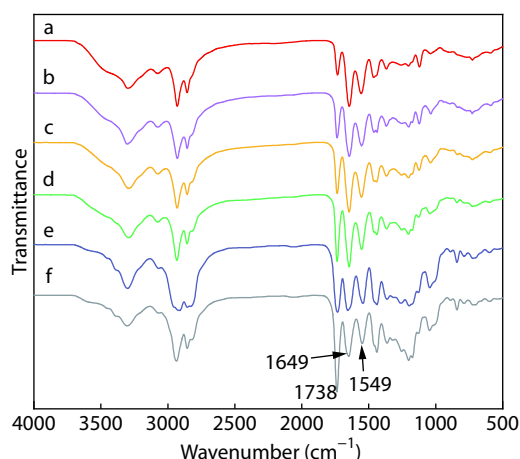


Fig. 3 FTIR spectra of viscous fluids formed in bulk polycondensation in flasks: (a) HDAME-1/1, (b) HDAME-1/1.25, (c) HDAME-1/1.5, (d) HDAME-1/2, (e) HDAME-1/3, and (f) HDAME-1/4.

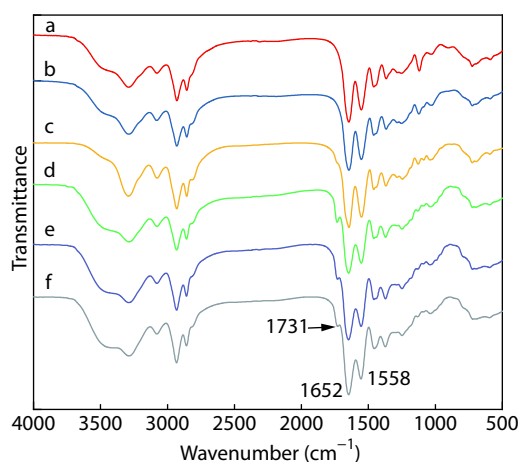


Fig. 4 FTIR spectra of cPA-x/ys: (a) cPA-1/1, (b) cPA-1/1.25, (c) cPA-1/1.5, (d) cPA-1/2, (e) cPA-1/3, and (f) cPA-1/4.

ing to $-\text{COOCH}_3$ disappeared in the FTIR spectra of cPA-1/1 and cPA-1/1.25, while a very weak shoulder peak related to $-\text{COOCH}_3$ groups remained for cPA-1/1.5. Nearly all the original $-\text{COOCH}_3$ groups were transformed into amide groups. A high level of crosslinking was achieved in cPA-1/1, cPA-1/1.25, and cPA-1/1.5 because their HDAME-x/ys contained sufficiently high amount of $-\text{NH}_2$ or $-\text{HN}-$ groups and ester groups. In the FTIR spectra of cPA-1/2, cPA-1/3, and cPA-1/4, an obvious shoulder peak related to $-\text{COOCH}_3$ groups remained because their HDAME-x/ys were synthesized at low

x/ys. The obtained HDAME-x/ys contained $-\text{COOCH}_3$ groups at a level equal to or higher than that of the $-\text{NH}_2$ or $-\text{HN}-$ groups. Thus, cPA-1/2, cPA-1/3, and cPA-1/4 with a low level of gel percentage were prepared (Table 1), and some $-\text{COOCH}_3$ groups were left as terminal groups after the curing reaction.

In the FTIR spectrum of cPA-5/5 (HDAME-1/4 polymerized with HDA and IPDA at a HDA/IPDA molar ratio of 5:5 and cured at 170 °C),^[18] at shorter curing time (9 h), the ester $\nu_{\text{C=O}}$ band disappeared completely. It means that the curing of cPA-1/2, cPA-1/3, and cPA-1/4 was slower than that of the reported cPA-5/5, because cPA-1/2, cPA-1/3, and cPA-1/4 lacked sufficient $-\text{NH}_2$ or $-\text{HN}-$ groups.

DSC Characterization

DSC was performed to obtain the glass transition temperature (T_g) and thermal features of cPAs. T_g of the cPAs prepared at 170 °C was at 1–39 °C (Fig. 5, Table 1). cPA-1/1 (170 °C), which exhibited the lowest T_g of 1 °C, was prepared at an x/y of 1/1. HDAD was the major component of HDAME-1/1, and HDAMoE was at a higher level than other HDAMEs (Fig. 2). HDAMoE contained an ester group, a secondary amine $-\text{HN}-$ group, and a primary amine $\text{H}_2\text{N}-$ group. In the curing process, the reaction between the $\text{H}_2\text{N}-$ group and an ester group formed a 2-branched amide linkage (Scheme 1, linkage I, in red), while the $-\text{HN}-$ group that reacted with an ester group formed a 3-branched amide linkage (Scheme 1, linkage II, in blue). The 3-branched amide linkages (II) benefited cross-linking, whereas the 2-branched amide linkages (I) were linear amide units and helpless to cross-linking. HDAD possessed two possible structures: HDAD (a) and HDAD (b). HDAD (a) contained two ester groups and one $\text{H}_2\text{N}-$ group, while HDAD (b) contained two

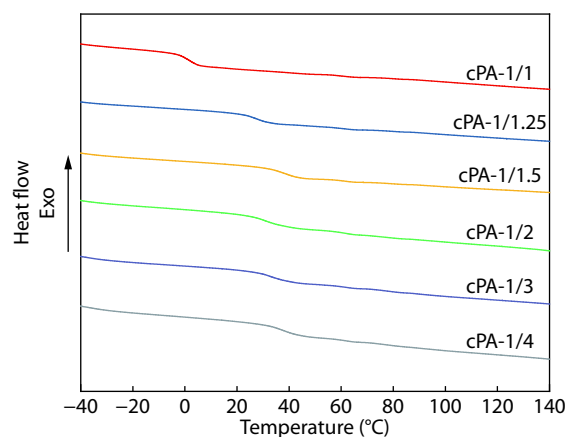


Fig. 5 Heating DSC scans of cPAs obtained at 170 °C (10 °C·min⁻¹).

ester groups and two $-\text{HN}-$ groups. The reaction of the $\text{H}_2\text{N}-$ group in HDADE (a) with an ester group also led to a linear amide linkage (I), and the reaction of the $-\text{HN}-$ groups in HDADE (b) with ester groups produced 3-branched amide linkages (II). HDAME-1/1 contained a relatively high amount of HDAMoE and HDADE, which let cPA-1/1 form many flexible linear amide linkages (I). Thus, cPA-1/1 with the lowest T_g was prepared. HDAME-1/1.25 and HDAME-1/1.5 also contained relatively high amount of HDAMoE and HDADE. From cPA-1/1 to cPA-1/1.5, with the decrease of x/y s or increase in the amount of MA used, the amount of HDAMoE decreased, causing the decrease of linear amide linkages (I) and increase of 3-branched or cross-linking amide linkages (II). Thus, T_g increased. In HDAME-1/2, HDADE, HDATrE, and HDATeE were the major components, while HDAMoE was the minor component (Fig. 2d), so T_g of cPA-1/2 was measured as 31 °C. HDAME-1/3 and HDAME-1/4 contained a higher amount of HDATrE or HDATeE and HDATeE than that of HDAMoE and HDADE. Therefore, mainly 3-branched amide linkages (II) were formed in cPA-1/3 and cPA-1/4, which led to a relatively high T_g observed. However, the crosslinking was incomplete because of the excessive ester groups in HDAME-1/3 and HDAME-1/4. cPA-1/1, cPA-1/1.25, cPA-1/2, and cPA-1/3 showed T_g lower than that of cPA-1/0 reported in literature,^[18] whereas cPA-1/1.5 and cPA-1/4 exhibited T_g similar to that of cPA-1/0. They were all prepared merely from flexible HDAMEs and HDA. Above cPAs exhibited T_g lower than the values reported in literature for other cPAs because the latter contained stiff isophorone amide units.

Compared to the cPAs prepared at 170 °C, those prepared at 150 °C showed lower T_g (Fig. S1 and Table S1 in the electronic supplementary information, ESI) because lower curing extent was reached at 150 °C. They showed amorphous characteristics due to their irregular and crosslinking structures.

Dynamic Mechanical Analysis

DMA detection can provide useful information on the storage modulus (E'), glass transition, and crosslinking density (v_e) of polymers. Fig. 6 gives the E' and $\tan \delta$ curves versus temperature. cPA-1/1 was in the glassy state with E' above 600 MPa below -5 °C (Fig. 6, Table 1), while other cPAs, including cPA-1/1.25, cPA-1/1.5, cPA-1/2, cPA-1/3, and cPA-1/4, were in a glassy state with E' above 760 MPa below 17 °C. cPA-1/1 showed

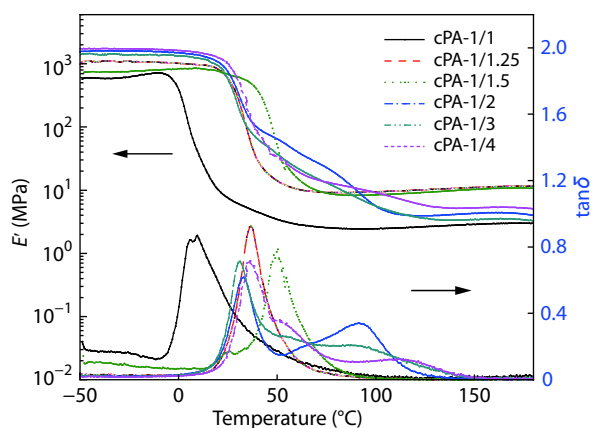


Fig. 6 Relationship between E' or $\tan \delta$ of cPAs (prepared at 170 °C) and temperature.

one $\tan \delta$ peak (T_a) at 8 °C, which may correspond to the mixed state of linear amide linkages (I) with a lower level of 3-branched amide linkages (II) (m-State LC). cPA-1/1.25 showed one T_a at 37 °C, which may correspond to the mixed state of linear amide linkages (I) with a higher level of 3-branched amide linkages (II) (m-State HC). cPA-1/1.5 showed two T_a peaks: a weak T_{a1} corresponding to m-State LC and a strong T_{a2} corresponding to m-State HC. cPA-1/2 also showed two T_a peaks: a sharp T_{a1} corresponding to m-State LC and a wide T_{a2} peak corresponding to neat 3-branched amide linkages (II). cPA-1/3 and cPA-1/4 showed three T_a peaks: a large T_{a1} peak corresponding to m-State LC, a shoulder T_{a2} peak corresponding to m-State HC, and a weak T_{a3} peak corresponding to neat 3-branched amide linkages (II). As the x/y ratio decreased, T_a peaks shifted to higher temperature, and additional 3-branched amide linkages (II) were formed because a large amount of HDATrE and HDATeE was formed in HDAMEs during the Michael addition. cPA-1/1 and cPA-1/1.25 showed one T_a peak similar to that of cPA-1/0 reported in literature because they all contained a higher amount of linear amide linkages (I).^[18] Other cPAs from cPA-1/1.5 to cPA-1/4 showed two or three T_a peaks. More 3-branched amide linkages (II) introduced made their stiffness increased and their $\tan \delta$ curves similar to the cPAs containing isophorone amide units.^[18]

After the maximal T_a ($T_{a,\max}$) peak, E' gradually dropped to a low value of 3–11 MPa and entered a rubbery plateau. Crosslinking density (v_e) is an important parameter to describe the crosslinking features of cured materials. v_e can be calculated according to the Eq. (1):^[19]

$$E' = 3v_eRT \quad (1)$$

where E' represents the storage modulus at $T_a + 40$ °C, and R and T represent the ideal gas constant and absolute temperature at $T_a + 40$ °C, respectively. cPA-1/1 showed v_e with a low value of 480 mol·m⁻³ (Table 1) because it contained extremely highly flexible linear amide linkages (I). cPA-1/1.25 showed high v_e (1053 mol·m⁻³) because it contained a large number of 3-branched amide linkages (II). cPA-1/1.5 showed two v_e s of 1387 and 916 mol·m⁻³. An increase in the level of 3-branched amide linkages (II) made the crosslinking in cPA-1/1.25 and cPA-1/1.5 nearly completed. Thus, the v_e s of cPA-1/1.25 and cPA-1/1.5 were high. cPA-1/2, cPA-1/3, and cPA-1/4 showed two or three v_e s which correspond to different T_a s, and their v_e s at the highest T_a were only 395, 337, and 496 mol·m⁻³, respectively. In their Michael addition, the HDAMEs contained an extremely high amount of HDATrE and HDATeE and an extremely low number of $-\text{HN}-$ or $\text{H}_2\text{N}-$ groups to make the crosslinking incomplete, and some ester groups were left as terminal groups. Thus, their v_e at the highest T_a was relatively low.

TGA Characterization

Fig. 7 presents the TGA and DTGA curves of the cPAs prepared at 170 °C. Table 2 shows their initial decomposition temperature (T_i) and decomposition peaks (T_{p1} and T_{p2}). An extremely weak decomposition peak was observed between 100 and 200 °C due to the emission of CH_3OH during further condensation between residual $-\text{HN}-$ or $-\text{NH}_2$ groups with $-\text{COOCH}_3$ groups. cPAs exhibited a T_i above 180 °C. cPA-1/1, cPA-1/1.25, and cPA-1/1.5 with high x/y ratios showed relatively high T_i probably because of their high crosslinking. cPA-1/2, cPA-1/3, and cPA-1/4 with low x/y ratios showed relatively low T_i due

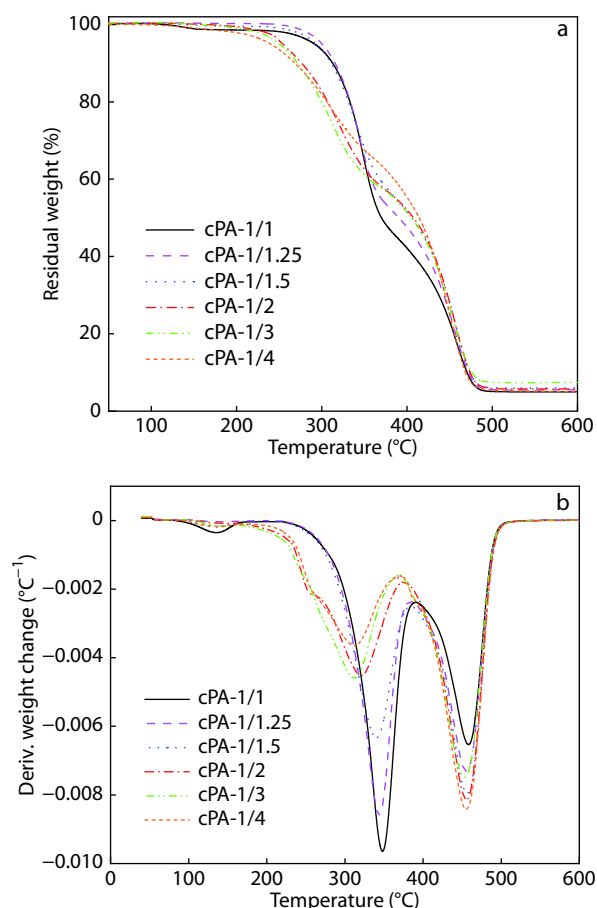


Fig. 7 (a) TGA and (b) DTGA curves of cPAs prepared at 170 °C (10 °C·min⁻¹, N₂).

Table 2 TGA (10 °C·min⁻¹, N₂) and tensile testing data of cPAs prepared at 170 °C.

cPA-x/y	T_i (°C)	T_{p1} (°C)	T_{p2} (°C)	End mass (%)	Tensile strength (MPa)	Strain at break (%)
cPA-1/1	250	348	459	5.0	5	18
cPA-1/1.25	247	343	456	5.5	27	38
cPA-1/1.5	241	339	455	6.0	45	21
cPA-1/2	194	320	455	5.7	21	40
cPA-1/3	180	313	452	7.4	38	21
cPA-1/4	208	313	454	6.0	38	25

to their low crosslinking. These cPAs showed T_i lower than that of cPA-1/0 prepared from HDAME-1/4 and HDA,^[18] because the latter contained relatively high amount of thermally stable linear amide linkages (I) and cross-linked sufficiently. The decomposition peak (T_{p1}) at 200–370 °C corresponds to the cleavage of linear amide linkages (I) or 3-branched amide linkages (II), while the decomposition peak (T_{p2}) at 370–500 °C corresponds to C—C or C—H cleavages. From cPA-1/1 to cPA-1/4, the area of T_{p1} peak decreases as the x/y ratio decreases. The reason may be that although the cPAs with low x/y's formed a relatively high amount of HDATrE and HDATeE in their Michael addition, an extremely low amount of linear amide linkages (I) and 3-branched amide linkages (II) in them led to the appearance of small T_{p1} areas. cPAs were thermally stable below their T_i .

Tensile Testing

Fig. 8 shows stress-strain curves of the cPAs prepared at 170 °C. Table 2 lists their tensile strength and strain at break. Tables 1 and 2 show that cPAs with high T_g and v_e exhibited good tensile strength. cPA-1/1 showed the lowest tensile strength of 5 MPa. The reason may be that HDAME-1/1 formed in the Michael addition contained a higher amount of HDAMoE than other HDAMEs, and a larger number of —NH₂ groups in HDAME-1/1 led to more flexible linear amide linkages (I) formed in cPA-1/1. Thus, cPA-1/1 with low T_g , v_e , and tensile strength was prepared. From cPA-1/1 to cPA-1/1.25 and cPA-1/1.5, as the x/y ratio decreases or the MA used in the Michael addition increases, T_g , v_e (for cPA-1/1.5, v_e corresponding to T_{q1}), and tensile strength increased because a larger number of 3-branched amide linkages (II) or crosslinking sites were formed. cPA-1/1.5 exhibited the highest tensile strength of 45 MPa with good toughness or relatively high strain at break (21%). cPA-1/1.5 also showed higher tensile strength and better toughness than those of cPA-1/0 (tensile strength: 41 MPa, strain at break: 11%) prepared via bulk polycondensation of the previously synthesized HDAME-1/4 with HDA.^[18] In HDAME-1/1.5, HDADe was the major component and HDAMoE was at a relatively high level (Fig. 2). Thus, a relatively high amount of linear amide linkages (I) were formed. Linear amide linkages benefited the intermolecular interaction or hydrogen bonding in cPAs. Sufficiently high crosslinking and hydrogen bonds caused HDAME-1/1.5 to show the highest tensile strength. In HDAME-1/2, HDADe remained at the highest level, and HDATrE and HDATeE were also at a high level. However, the content of HDAMoE was quite small. Although cPA-1/2 formed a relatively high level of 3-branched amide linkages (II), a low level of linear amide linkages (I) reduced the intermolecular interaction or hydrogen bonding, and thereby caused cPA-1/2 to show moderate tensile strength of 21 MPa. In HDAME-1/3 and HDAME-1/4, HDATrE or HDATrE and HDATeE were the major components. Meanwhile, a certain amount of HDAMoE and HDADe remained. These factors endowed cPA-1/3 and cPA-1/4 with a relatively high T_g and high initial v_e (the v_e corresponds to T_{q1}). Thus, cPA-1/3 and cPA-1/4 with excellent tensile strength of 38 MPa and good toughness or strain at break above 21% were prepared. cPA-1/3 and cPA-1/4 showed slightly lower tensile strength and obviously higher strain at break than those of the

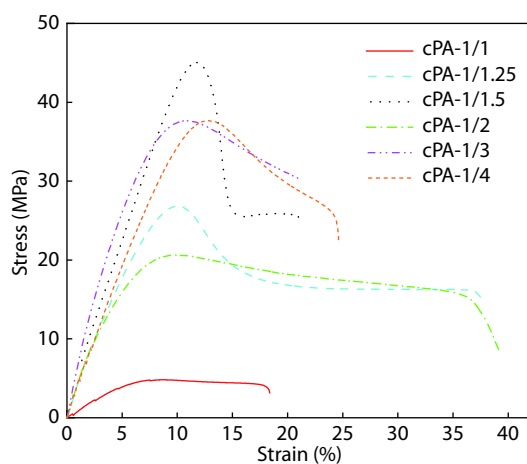


Fig. 8 Stress-strain curves of cPAs prepared at 170 °C.

cPA-1/0 reported in literature.^[18]

Similar cPA films were also prepared at 150 °C curing temperature. These films showed lower T_g and tensile strength than those of cPAs prepared at 170 °C (see Figs. S1 and S2 and Table S1 in ESI). The reason is that the lower curing temperature led to a decrease in crosslinking and caused the decrease of T_g and tensile strength.

Finally, the moisture content of cPA films was also characterized. cPA films showed moisture content ranging from 3.78% to 6.03% (Table 1). cPAs prepared at low x/y s exhibited high moisture content probably because of their high amount of loose 3-branched amide linkages (II) which benefited the absorption of moisture.

CONCLUSIONS

The bulk Michael addition of HDA and MA was studied at different HDA/MA molar ratios. The mixed hexanediamine multi-esters formed (*i.e.*, HDAMEs) consisted mainly of hexanediamine mono-ester, hexanediamine di-ester, hexanediamine tri-ester, and hexanediamine tetra-ester (*i.e.*, HDAMoE, HDADE, HDATrE, and HDATeE). HDAMoE, HDADE, and HDATrE contained reactive $-HN-$ or $-NH_2$ groups and $-COOCH_3$ ester groups, while HDATeE contained only ester groups. The reaction of the $-NH_2$ or $-HN-$ groups with $-COOCH_3$ groups formed linear amide linkages (I) and 3-branched amide linkages (II) in the curing reaction. At the higher HDA/MA (x/y) molar ratios, a relatively high level of linear amide linkages (I) was formed in the cPAs. As the x/y ratios decreased, the amount of 3-branched amide linkages (II) increased, and T_g , v_e , and tensile strength also increased. Intermolecular interaction or hydrogen bonds formed from linear amide linkages (I) and crosslinking caused by 3-branched amide linkages (II) played important roles in the thermal and mechanical properties of cPAs. High temperature favors the crosslinking. The reaction between $-COOCH_3$ and $-HN-$ or $-NH_2$ groups in HDAMEs produced cPAs effectively. cPAs with high tensile strength of up to 45 MPa and good toughness or strain at break above 18% were synthesized successfully. The direct bulk Michael addition of HDA and MA followed by polycondensation provides a valuable method for synthesizing cPAs with excellent mechanical properties.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2332-y>.

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