Synthesis and Properties of Cyclic Diester Based Aliphatic Copolyesters

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ABSTRACT: Melt polycondensation was used to prepare a systematic series of random and amorphous copolyesters using the following cycloaliphatic diesters: dimethyl-1,4-cyclohexane dicarboxylate (DMCD), dimethyl bicyclo[2.2.1]heptane-1,4-dicarboxylate (DMCD-1), dimethyl bicyclo[2.2.2]octane-1,4-dicarboxylate (DMCD-2), dimethyl bicyclo[3.2.2]nonane-1,5-dicarboxylate (DMCD-3), 1,4-dimethoxycarbonyl-1,4-dimethylcyclohexane (DMCD-M) and the aliphatic diols: ethylene glycol (EG) and 1,4-cyclohexane dimethanol (CHDM). The polymer compositions were determined by nuclear magnetic resonance (NMR) and the molecular weights were determined using size exclusion chromatography (SEC). The polyesters were characterized by dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The copolyester based on DMCD-2 was observed to have a higher glass transition temperature (T_g up to 115 °C) than the other copolyesters of this study. For poly[x(DMCD-2)y(DMCD) 30(EG)70(CHDM)], T_g increases linearly with increase of DMCD-2 mole content. DMA showed that all of the cycloaliphatic copolyesters have secondary relaxations, resulting from the conformational transitions of the cyclohexylene rings. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 2162–2169, 2010

KEYWORDS: amorphous; cycloaliphatic diesters; glass transition; polycondensation; polyesters

INTRODUCTION Aliphatic polyesters were among the first, if not the first, intentionally prepared synthetic polymers in the pioneering work of Carothers.[1] They were abandoned as useful polymers for fibers because of their low T_gs and melting points. The inclusion of aromatic terephthaloyl groups from dimethyl terephthalate by Whinfield and Dickson[2] led to acceptable T_gs and melting points for fiber applications and resulted in the huge commercial success of poly(ethylene terephthalate) (PET). However, aromatic group containing polyesters have some drawbacks. Because of the UV light absorption of the aromatic groups, these polyesters do not exhibit good stability in outdoor applications. In addition, biomedical applications of aromatic group containing polyesters are limited because of toxicity concerns about the aromatic degradation products of these polymers. Therefore there has been a significant effort in recent years on the polymerization chemistry and properties of all aliphatic polyesters.[3] All aliphatic polyesters have been shown to possess excellent UV stability as they do not contain any functional groups that absorb UV light, which enhances the photostability and renders them much more readily stabilizable for outdoor applications.[4–6] However, they often have low T_gs that limit their applications. In fact, many of these polymers have T_g below room temperature. Introduction of alicyclic units to the main chain of the polymer can improve solubility and impart enhanced glass transition temperatures due to the rigidity of the alicyclic structures.[7] Moreover, polymers having different isomers of alicyclic structures in a main chain have difficulty crystallizing and are, therefore, amorphous and transparent. Thus, such materials have potential applications in many fields due to their environmental resistance and potential low toxicity.

Cyclohexyl groups have been incorporated into a wide variety of polyesters to impart desirable physical properties.[8–10] 1,4-Cyclohexane dicarboxylic acid (CHDA) is an important monomer for raising the T_g in all aliphatic polyesters and has found wide applications as a monomer in coating resins. The all cyclic polyester poly(cyclohexylene dimethylene cyclohexane dicarboxylate) (PCCD) based on CHDA and 1,4-cyclohexane dimethanol (CHDM) has a T_g of only around 40–70 °C and has some apparent applications in situations where UV stability is required.[8,11] Higher T_g all aliphatic polyesters could have important applications in UV protective cap layers for extruded sheet products, as stable substrates for flexible displays and solar cells, and as substrates for microfluidic devices where the optical properties of the substrate are important.

Although there are numerous reports about the properties of various cyclic diol containing polyesters,[12] there are few reports of all aliphatic copolyesters based on a systematic variation of the cyclic diacid. To the best of our knowledge, there are no suitable all aliphatic diacid or diester monomers that can, when incorporated into a polyester backbone,

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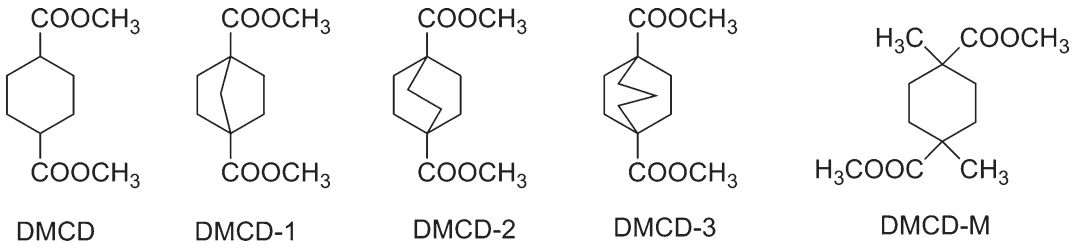


SCHEME 1 Structures and abbreviations of cyclic diesters

achieve the T_g necessary to achieve the applications described above. The research described in this study is directed at a systematic incorporation of several alicyclic diesters into an all aliphatic polyester backbone with the goal to synthesize high T_g all aliphatic polyesters to provide a useful combination of optical transparency, thermal stability, weatherability, and surface chemistry attributes.

The alicyclic monomers studied include bridgehead–bridgehead bicyclo[2.2.l]heptyl (DMCD-1), bicyclo[2.2.2]octyl (DMCD-2), bicyclo[3.2.2]nonyl (DMCD-3) diesters, as well as the nonbridged model 1,4-dimethoxycarbonyl-1,4-dimethylcyclohexane (DMCD-M). The structures and abbreviations of all cycloaliphatic diesters in this article are listed in Scheme 1. In this study, we synthesized random copolyesters containing these cycloalkanes groups in the backbone and investigated the effect of cycloalkanes groups on the properties of the copolyesters. The polyesters based on DMCD-2 stood out in terms of enhanced T_g versus the other bicyclic structures. Colorless and transparent films could be readily obtained by compression molding or by solvent casting, and the properties were studied and compared to the other bicyclic diester based polyesters.

EXPERIMENTAL

Materials

All reagents were used without further purification. Ethylene glycol (EG $\geq$ 99%), CHDM (99%), 1-bromo-2-chloroethane (98%), hexamethyl phosphoramide (HMPA) (99%), butyllithium (2.5M solution in hexane), iodomethane (99%), norbornylene (99%), and potassium permanganate (ACS reagent) were purchased from the Aldrich Chemical Co. *N,N*-diisopropylamine (99%) was purchased from Sigma Chemical Co. Titanium(IV) butoxide (98%) was purchased from Alfa Aesar Chemical Co. DMCD (*cis*/*trans* = 3/1) was donated by Eastman Chemical Co.

Measurements

The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained by a Varian Inova 400 (400 MHz) spectrometer at room temperature with internally referenced to tetramethylsilane (TMS). ^{1}H NMR spectra were used to determine the final polyester compositions. Size exclusion chromatography (SEC) was run in chloroform at 30 °C on a Waters Alliance model 2690 chromatograph equipped with a Waters HR 0.5 + HR 2 + HR 3 + HR 4 styragel column set. Monodispersed polystyrene standards were utilized to construct a universal molecular weight calibration curve. A Viscotek refractive index detector and a viscometer were used for the molecular weight determination. Differential scanning calorimetry (DSC) data were obtained from a PerkinElmer Pyris1. Samples were run from −20 to 200 °C at a heating/cooling rate of 20 °C/min under nitrogen. The glass transition temperature (T_g) was taken from the midpoint in the second heating cycle DSC traces. Thermogravimetric analysis (TGA) was obtained at a heating rate of 10 °C/min on a TA Instrument TGA 2950 from room temperature to 600 °C under nitrogen. Tensile tests were performed on an Instron Model 4400 Universal Testing System with Series IX software. Samples were run at a constant cross-head speed of 15 mm/min using an initial grip-to-grip separation of 10 mm. All reported tensile data represented an average of at least three independent measurements. A TA Instrument Q1000 dynamic mechanical analysis (DMA) was used to acquire storage modulus, loss modulus, and tan delta for films, which were deformed (10 micrometer amplitude) in the tension mode at a frequency of 1 Hz using a temperature ramp rate of 3 °C/min under nitrogen. For compression molding, the sample was sandwiched between two pieces of 3 mm thick aluminum plate and was centered in a mold of desired thickness. The samples were heated 40 °C above their T_g and a pressure of about 500 PSI was applied. The pressure was released after 15 min and these films were then utilized for various thermal and mechanical analyses.

Synthesis of Dimethyl bicyclo[2.2.1]heptane-1, 4-dicarboxylate (DMCD-1)

A modification of the improved synthesis of Della[13] was used. Acetone, instead of water, was used as the solvent for the synthesis of *cis*-1,3-cyclopentane dicarboxylic acid, yield: 83.3%, mp: 116.2–117 °C. The diacid and a large excess of methanol containing concentrated sulfuric acid were reacted under reflux for 22 h to produce the corresponding dimethylesters. Vacuum distillation (73–76 °C/0.4–0.5 mmHg) gave the pure *cis*-dimethyl cyclopentane-1,3-dicarboxylate (*cis*-DMCP), yield: 74%. The bisenolate of the cyclopentane diester in the presence of lithium diisopropylamide (LDA) solution was treated with a solution of 1-bromo-2-chloroethane in THF. Workup involved the same procedure as above and afforded a yellow solid, which upon sublimation (60–65 °C/0.2 mmHg) gave the bicyclic diester DMCD-1 (56%) as colorless crystals. mp: 57.2–58 °C ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 3.66 (s, 6H, COOCH_3), 2.01 (d, 4H, J = 6.4 Hz, CH_2CH$_2$), 1.89 (s, 2H, CCH_2C), 1.66 (d, 4H, J = 7.2 Hz, CH$_2$CH_2); ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 175.35

(COOCH$_3$), 52.54 (CCOOCH$_3$), 51.64 (COOCH$_3$), 44.92 (CCH$_2$C), 32.92 (CH$_2$$CH_2$).

Synthesis of Dimethyl bicyclo[2.2.2]octane-1,4-dicarboxylate (DMCD-2)

DMCD-2 was prepared by a published literature procedure.[14] The workup method was modified to improve the purity of the product. This modification involved vacuum distillation (130 °C/ 0.1–0.2 mmHg) and recrystallization from hexanes. Finally a white crystalline solid was obtained, yield: 38.5%, mp: 98.8–99.1 °C (literature 92.8 °C). The structure was confirmed by NMR measurement. NMR data were as follows: ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 3.61 (s, 3H, OCH_3), 1.75 (s, 6H, CH_2); ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 177.77 (COOCH$_3$), 51.66 (COOCH$_3$), 38.57 (CCOOCH$_3$), 27.69 (CH$_2$).

Synthesis of Dimethyl bicyclo[3.2.2]nonane-1,5-dicarboxylate (DMCD-3)

DMCD-3 was synthesized following a literature procedure.[15] The Dieckmann condensation of dimethylmalonate obtained white solid product dimethyl succinylsuccinate in 72% yield.[16] m.p.126–127 °C. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 12.12 (s, 2H, COH), 3.79 (s, 6H, COOCH_3), 3.18 (s, 4H, CH_2CCOOCH$_3$); ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 171.93 (COOCH$_3$), 168.82 (COH), 93.42 (CCOOCH$_3$), 52.10 (COOCH$_3$), 28.77 (CH$_2$).

Dimethyl succinylsuccinate was treated with sodium hydride in dry DME and then reacted with 1,3-dibromopropane to obtain white product 1,5-biscarbmethoxybicyclo[3.2.2]nonane-6,8-dione. Yield: 26%, m.p. 125–126 °C. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 3.77 (s, 6H, COOCH_3), 3.39 (s, 1H, CH_2CO), 3.35 (s, 1H, CH_2CO), 2.78 (s, 1H, CH_2CO), 2.73 (s, 1H, CH_2CO), 2.45–2.52 (m, 2H, CH_2CH$_2$CH_2), 1.92–1.99 (m, 2H, CH_2CH$_2$CH_2), 1.75–1.82 (m, 2H, CH$_2$CH_2CH$_2$).

The thiane was prepared from the diketone using the literature procedure[16] in 83% yield. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 3.64 (s, 6H, COOCH_3), 3.57 (s, 1H, CH_2CS), 3.54 (s, 1H, CH_2CS), 3.40–3.36 (m, 4H, SCH_2CH$_2$S), 3.26–3.21 (m, 4H, SCH$_2$CH_2S), 2.96 (s, 1H, CH_2CS), 2.93 (s, 1H, CH_2CS), 2.56–2.53 (m, 2H, CH_2CH$_2$CH_2), 1.89–1.86 (m, 4H, CH_2CH_2CH$_2$); ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 174.05 (COOCH$_3$), 70.20 (CSCH$_2$), 55.97 (COOCH$_3$), 55.07 (CCOOCH$_3$), 52.24 (CH$_2$CS), 40.89 (SCH$_2$CH$_2$S), 40.75 (SCH$_2$$CH_2$S), 37.19 ($CH_2CH_2$$CH_2$), 22.01 (CH$_2$$CH_2CH_2$).

Desulfurization of the thioketal by Raney nickel slurry occurred in ethanol, which was refluxed for 3 days. The product was purified by distillation under high vacuum (110 °C/0.08 mmHg) to give colorless solid DMCD-3. Yield: 70%, m.p. 34–35 °C. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 3.63 (s, 6H, COOCH_3), 1.94–1.67 (m, 14H, CH_2CH_2). ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 178.81 (COOCH$_3$), 51.87 (COOCH$_3$), 42.68 (CCOOCH$_3$), 37.38 (CH$_2$CH$_2$$CH_2$), 27.95 ($CH_2$$CH_2$), 21.36 (CH$_2$$CH_2CH_2$).

Synthesis of 1,4-Dimethoxycarbonyl-1,4-dimethylcyclohexane (DMCD-M)

DMCD-M was prepared from the DMCD by following a procedure described by Weagley et al.[17] for the dialkylation of 1,3-dimethoxycarbonylcyclopentane. Vacuum distillation (90–100 °C/0.2 mmHg) gave the product as a colorless oil (liquid and solid mixture, *cis-* and *trans*-product), yield, 88%. Recrystallization from hexane gave a white crystalline solid (*trans*-product), yield, 51%. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 3.63 (s, 6H, COOCH_3), 2.07 (d, 4H, $J = 10$ Hz, CH_2CH$_2$), 1.20 (d, 4H, $J = 10$ Hz, CH$_2$CH_2), 1.13 (s, 6H, CCH_3); ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 177.87 (COOCH$_3$), 51.89 (COOCH$_3$), 42.92 (CCH$_3$), 33.05 (CH$_2$$CH_2$), 27.51 (C$CH_3$). mp: 94.5–95.3 °C, MS (*m/z*): calcd for $C_{12}H_{20}O_4$, 228.14; found, 229.6 $[M+H]^+$.

Abbreviation of Polyesters

The polymer nomenclature used in this manuscript is based on a polyester containing 100 mol % of diester and 100 mol % of diol. For example, the polymer designated by poly[50(DMCD-2)50(DMCD)30(EG)70(CHDM)] means this targeted polymer containing 50 mol % DMCD-2 and 50 mol % DMCD as the diester units and 30 mol % EG and 70 mol % CHDM as the diol units. The letters, stand for various monomers' abbreviation and the numbers indicate targeted mol % of monomers, respectively.

Preparation of Catalyst Solution

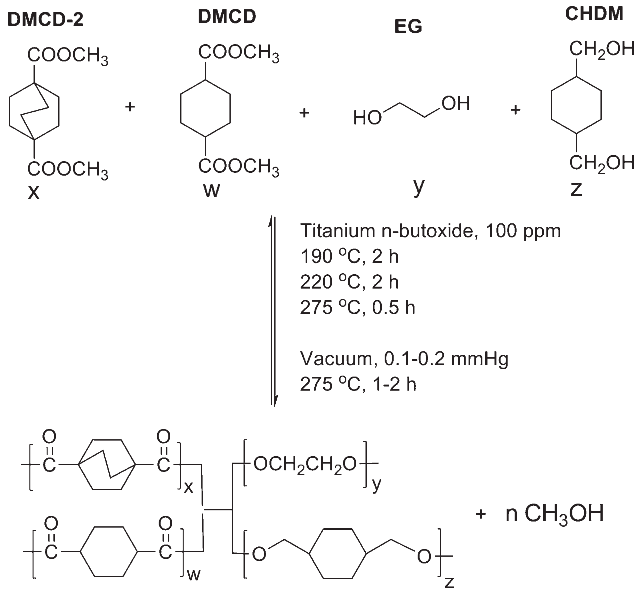
The Ti catalyst solution was obtained by mixing titanium *n*-butoxide with *n*-BuOH in a dry bottle under nitrogen at a concentration of 0.06 g/mL based on Ti.

Polycondensation of DMCD-2, EG, and CHDM

The detailed procedure is as follows: 3.62 g (16 mmol) DMCD-2, 1.10 g (17.6 mmol) of EG (120% excess), 1.15 g (8 mmol) CHDM, and 0.05 mL (100 ppm) of a titanium *n*-butoxide solution (0.06 g/mL in butanol) was added to a 50 mL single-necked, round-bottom glass flask. The reaction flask was immersed into a molten Belmont metal bath that was preheated to 190 °C. A multistep temperature procedure was used for the reaction, i.e. the reaction mixture was stirred at 190 °C for 2 h, 220 °C for 2 h. Then the temperature was increased to 275 °C and held for 30 min. The pressure then was gradually reduced and the temperature was raised to 275 °C. The final stage involved applying a high vacuum (up to 0.1 mmHg) for an additional 2 h at 275 °C and the highly viscous copolyester was obtained. Some copolyesters started to take on yellow color due to the titanium catalyst and the long reaction time. The vacuum was stopped and nitrogen was bled into the flask. The polymer was cooled to room temperature, dissolved in chloroform, and precipitated into methanol. The solid precipitate was obtained by vacuum filtration and dried at 60 °C *in vacuo* overnight. The same procedure was employed to prepare poly[w(DMCD)x(DMCD-2)y(EG)z(CHDM)] (where w and x, y, and z add up to 100, respectively) (Scheme 2).

Synthesis of All Aliphatic Polyester Poly[50(DMCD-M)50(DMCD)30(EG)70(CHDM)]

Copolyester was prepared by the same procedure as the above copolymer except that DMCD-M was used in place of DMCD-1.



SCHEME 2 Synthesis of poly[x(DMCD-2)w(DMCD)y(EG)z(CHDM)].

Synthesis of All Aliphatic Polyester Poly[50(DMCD-3)50(DMCD)30(EG)70(CHDM)]

Copolyester was synthesized by the same procedure as the above copolymer except that DMCD-3 was used instead of DMCD-1.

Synthesis of All Aliphatic Polyester Poly[50(DMCD-M)50(DMCD)30(EG)70(CHDM)]

Copolyester was prepared by the same procedure as the above copolymers except that DMCD-M was used in place of DMCD-3.

Hydrolytic Degradation

For hydrolytic degradation tests, the polyester films, which were obtained by casting from $CHCl_3$ solution (10% w/v), were placed into a 20 mL phosphate buffer saline (PBS) solution (pH 7.4) in a shaking air bath at 37 °C. The films were removed from the buffer solution after selected time intervals, washed with distilled water three times, and dried under vacuum at room temperature to constant weight. The extent of hydrolytic degradation was characterized by the weight loss percent, which was calculated from the mass difference between before and after hydrolytic degradation divided by the initial sample weight.

RESULTS AND DISCUSSION

Selection and Synthesis of Diester Monomers

Functionally bridgehead-substituted bicycloalkanes, such as DMCD-2, have been known for many years and polymers containing DMCD-2 possess interesting physical properties. Although liquid crystal copolyesters (rod-like) containing the bicyclo[2.2.2]octane ring were reported several decades ago,[18] prior literature did not describe its use in amorphous copolyesters.[18–20] Amorphous DMCD-2-containing copolyesters with high T_g were initially synthesized in this study. A convenient one-pot preparation of DMCD-2 was followed[14] and pure product was obtained by modifying the workup procedure as detailed in the experimental section. It is known that structural factors, such as the rigidity and symmetry of units, can greatly affect the properties of polymers. Therefore we have examined the effect of other cyclic compounds whose structures closely resembled that of DMCD-2. The bicyclo[2.2.1]heptane ring derivative (DMCD-1) and bicyclo[3.2.2]nonane ring one (DMCD-3) are suited for this purpose. DMCD-1 has a rigid symmetrical structure of similar steric size to that of DMCD-2. A one-pot procedure, which includes alkylation and cyclization of the bisenolates of DMCP with 1,2-dihaloethane, was successfully applied to the synthesis of DMCD-1. DMCD-3 has a more asymmetric structure due to the extra carbon on the bridge. This bicyclo derivative was synthesized by well-documented procedures.[15,16] Synthesis of DMCD-M involves dialkylation of readily available cyclohexane diester DMCD using two equivalents of base followed by two equivalents of methyl iodide in one step.

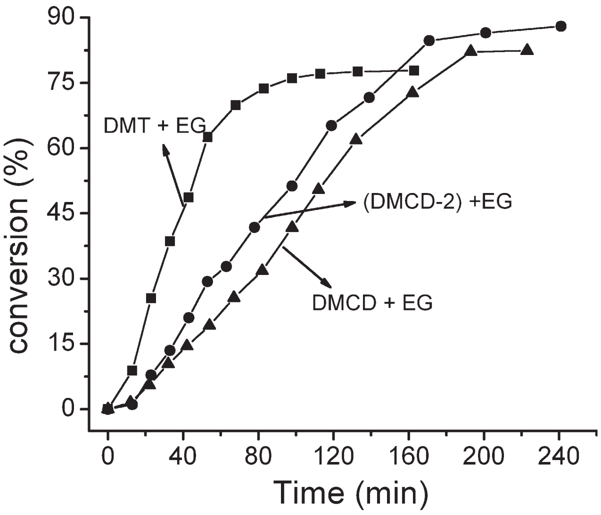


FIGURE 1 Kinetics of transesterification for different diesters--DMT, DMCD-2, or DMCD.

The cyclic diesters of this study were found to readily participate in melt-phase polycondensation with little, if any, effect of

TABLE 1 Properties of Poly[w(DMCD)x(DMCD-2)y(EG)z(CHDM)]

Polyester Composition DMCD/(DMCD-2)/EG/CHDM w/x/y/z (^{1}H NMR)	TGA T_d 5% Weight Loss (°C)	SEC M_n (kg/mol)	SEC M_w (kg/mol)	T_g (°C)
0/100/100/0	363	47	65	75
0/100/75/25	382	37	55	92
0/100/50/50	378	29	45	102
0/100/31/69	372	26	43	115
31/69/31/69	370	30	46	83
50/50/29/71	367	31	52	70
77/23/28/72	360	30	51	52
100/0/29/71	355	28	48	40

TABLE 2 Properties of Various Copolyesters Based on Different Cyclic Diesters

Polyester Composition (^{1}H NMR)	SEC M_n (kg/mol)	SEC M_w (kg/mol)	T_g (°C)	Tensile Stress at Break (MPa)	Tensile Strain at Break (%)	Modulus (MPa)
DMCD/EG/CHDM 100/29/71	28	48	40	31 ± 6	394 ± 50	1363 ± 110
(DMCD-1)/DMCD/EG/CHDM 48/52/29/71	27	58	35	44 ± 3	361 ± 9	1330 ± 40
(DMCD-2)/DMCD/EG/CHDM 50/50/29/71	31	52	70	25 ± 8	114 ± 30	1815 ± 154
(DMCD-3)/DMCD/EG/CHDM 48/52/31/69	28	53	46	19 ± 2	392 ± 30	673 ± 30
(DMCD-M)/DMCD/EG/CHDM 49/51/29/71	24	36	36	52 ± 3	660 ± 37	1473 ± 36
DMT/DMCD/EG/CHDM 50/50/29/71	31	48	62	34 ± 3	86 ± 5	588 ± 18

the bulky cyclic units. For example, DMCD-2 was found to readily undergo polycondensation with EG, as shown in Figure 1. The rate of the transesterification and elimination of methanol was observed to be faster than DMCD but somewhat slower than dimethyl terephthalate (DMT).

Synthesis of Copolyesters and Their Composition by ^{1}H NMR

Melt transesterification is a preferred route to prepare polyesters and it requires high reaction temperatures, high vacuum, and proper catalysts.[7] All the polyesters examined in this study were prepared by melt-phase polymerization with the use of titanium tetrabutoxide as catalyst. The polymerization time was about 6 h and the temperature 190–275 °C. However, an attempt to synthesize a high molecular weight polyester from DMCD-2 and CHDM by melt polymerization was unsuccessful because of the low volatility of CHDM and the high melt viscosity of oligomers. As EG has higher volatility and can be removed easily under vacuum, it was used in excess to improve the molecular weights of polyesters in our study. Therefore, for this study we chose polymers containing both EG and CHDM diols to compare the properties of polyesters with various cyclic diesters. The copolyester samples were soluble in common chlorinated solvents at room temperature, such as dichloromethane and chloroform. The molecular weights of the soluble polymers were determined by SEC and are summarized in Tables 1 and 2. These samples displayed high molecular weights as well as PDIs close to 2 with a main peak followed by several small peaks, suggesting the presence of some oligomers during polymerizations. The SEC trace of one sample was shown in Figure 2 as a representative of these samples.

Figure 3 shows the ^{1}H NMR spectrum of representative copolyester based on DMCD-2, EG, and CHDM with targeted molar ratio 30/70 of EG/CHDM. The correlation between the various structural components and the observed NMR peaks were listed. Peak "a" is assigned to the methylene group adjacent to the oxygen at ethylene glycol unit (single peak), and peak "b" is the methylene group adjacent to the oxygen at CHDM unit (*cis*/*trans* = 30/70). The *cis*/*trans* ratios of CHDM were determined by comparing the α-hydrogens on the *cis* and *trans* isomers and they did not change during polymerization. These broad peaks "c" and "d" come from the protons on the cycloaliphatic rings. The polymer composition calculated from this ^{1}H NMR spectra based on the peak area ratio of "a" to "b" gave 29% EG and 71% CHDM (calculated copolyester composition values from peak areas are reported in Table 1–2). The ^{1}H NMR spectrum of each of these polymers showed that its actual composition was in good agreement with the targeted polymer composition.

Thermal Properties of Different Copolyesters

Initially, we synthesized copolyesters based on 100% DMCD-2 and different EG and CHDM contents and the results are summarized in Table 1. These results show that high molecular weight polyesters can be readily achieved with DMCD-2. Polyesters with 100% DMCD-2 were brittle, but the incorporation of DMCD was shown, as expected, to lower T_g and render the sample more flexible. Therefore, a second series of copolyesters were prepared by varying the diester content by adding DMCD and holding the CHDM/EG ratio constant at 70/30. The characterization results of poly[x(DMCD-2)w(DMCD)31(EG)69(CHDM)] are also shown in Table 1. The copolyesters were all amorphous as no melting transitions were observed by DSC. An inspection of the data shows that DMCD-2 is a very effective monomer for raising the T_g, when compared to DMT. For example, the copolyester based on 100% DMT, 30% EG, and 70% CHDM diol has a T_g of 85 °C, which is lower than the T_g of 115 °C for poly[100(DMCD-2)31(EG)69(CHDM)], indicating the rigid structure of bicyclo[2.2.2]octane group in the polyester main chain. A sharp decrease in T_g was observed when DMCD is added. The data were plotted in Figure 4 and exhibited a good linear

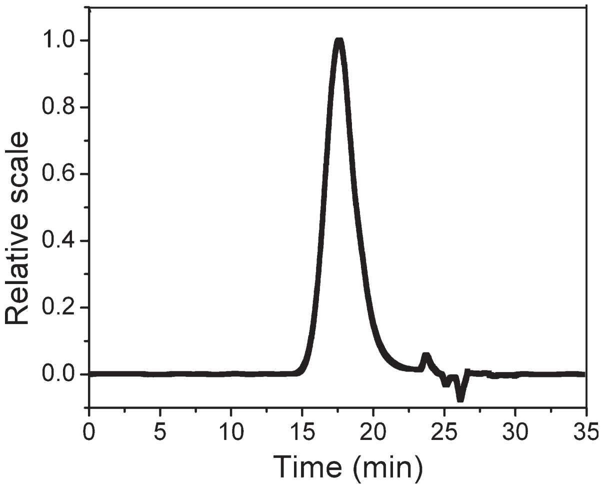


FIGURE 2 SEC trace of poly[100(DMCD-2)29(EG)71(CHDM)].

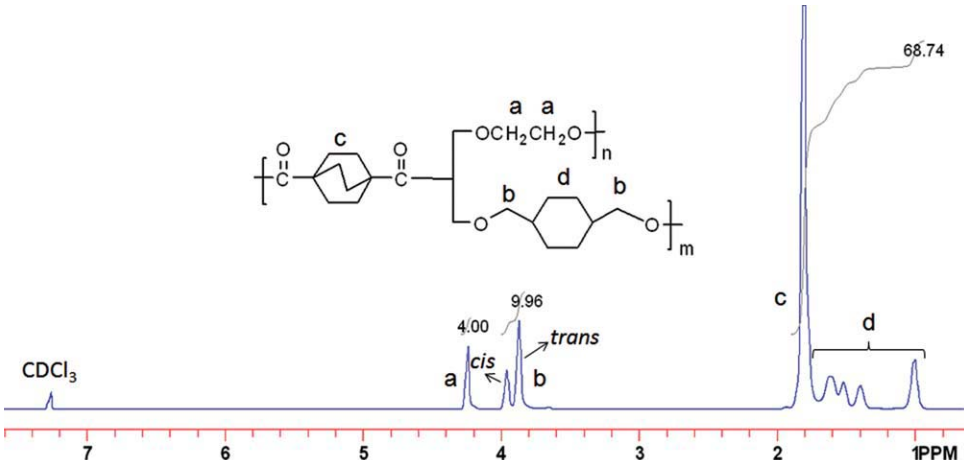


FIGURE 3 ^{1}H MNR spectra of poly[100(DMCD-2)29(EG)71(CHDM)]. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

relationship between T_g and DMCD-2 mole percent. All copolyesters have high molecular weights, up to 30 kg/mol, so we can assume that molecular weights have little effect on T_g. When bicyclo[2.2.2]octane units were incorporated into polyester at 50 mol %, molecular weights of the copolyester are highest among those five copolyesters with similar compositions of EG/CHDM.

Using the same type and content of diols, we also synthesized a semiaromatic polyester for comparative purpose, in which 50% DMCD was replaced by DMT. The corresponding results were shown in Table 2. We found that these two copolyesters have similar molecular weights. The copolyester based on 50% DMCD-2 has a higher T_g than one based on 50% DMT. Other cycloaliphatic copolyesters based on DMCD-1, DMCD-3, and DMCD-M were also synthesized. The properties of these cycloaliphatic copolyesters are shown in Table 2. High molecular weights were obtained for all copolyesters. The copolyester based on 50% DMCD-2 still has higher T_g than other copolyesters. As DMCD-1 is supposed to be rigid structure, it was surprising that the T_g of the copolyester based on 50% DMCD-1 was only 35 °C, similar to the T_g value of the copolyester based on DMCD. This is probably due to the inefficient chain packing of DMCD-1 structure. The related copolyester based on 50% DMCD-3 had a T_g of 46 °C, which was lower than 70 °C for the polyester based on 50% DMCD-2. This is most likely due to asymmetric structure of bicyclo[3.2.2]nonane because of the extra carbon on the bridge. Three dimensonal models in Figure 5 show that functional groups attached to the bridgehead carbons of the bicyclo[2.2.2]octane ring are arranged at 180° to one another, however, these same groups form an angle of approximately 150 and 120°, respectively in the bicyclo[3.2.2]nonane ring and the bicyclo[2.2.1]heptane ring. These 3-D structures were obtained from geometry optimization in the augmented MM3 force field contained in Scigress Explorer Ultra version 7.7.0.47.

The Tensile Mechanical Properties of Copolyesters

Tensile tests were conducted on compression molded films, which are optically clear. The results are summarized in Table 2 and the stress–stain curves are plotted in Figure 6. poly[50(DMCD-2)50(DMCD)29(EG)71(CHDM)] has the highest modulus (1815 MPa) and yield stress (96 MPa) among these six copolyesters due to the rigid structure of DMCD-2. It is interesting to note that even though the polyester based on 50% DMCD-2 has the lowest average strain to failure, 114%, it still exhibited high ductility. The high level of CHDM is the likely basis of the ductility.

The Secondary Relaxation of Copolyesters

Figure 7 showed the secondary relaxation of these copolyesters. The β relaxation peaks appeared at about −60 °C. This plot of tan δ versus temperature showed that the magnitude of these secondary relaxation peaks are similar due to the existence of the cyclohexyl units in backbones of all these copolyesters. The β relaxation, with small intensity, results from the chair-boat-chair conformational transition of the cyclohexylene ring. The presence of 50 mol % rigid diesters, such as DMCD-2 and DMCD-1, failed to depress the β relaxation intensity.

Hydrolytic Degradation of the Polyesters

Hydrolytic degradation of the polyesters in PBS solution was studied on solvent cast polyester films. The degradation was followed by mass loss during the experiments. The weight loss of the polyester based on DMCD-3 in the hydrolytic tests is the highest among these samples (Fig. 8). The

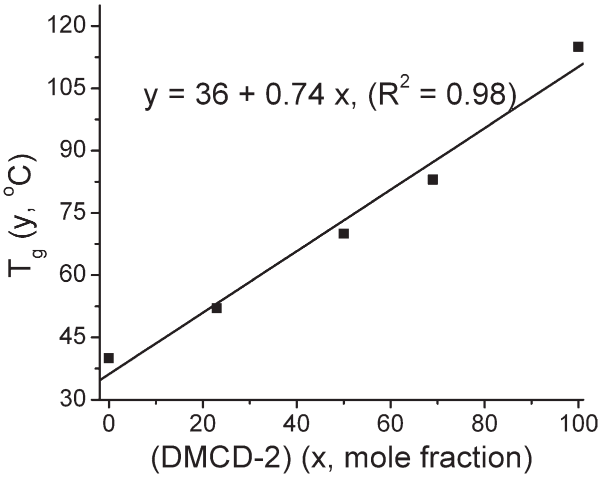


FIGURE 4 T_g versus DMCD-2 content of poly[w(DMCD)x(DMCD-2)30(EG)70(CHDM)].

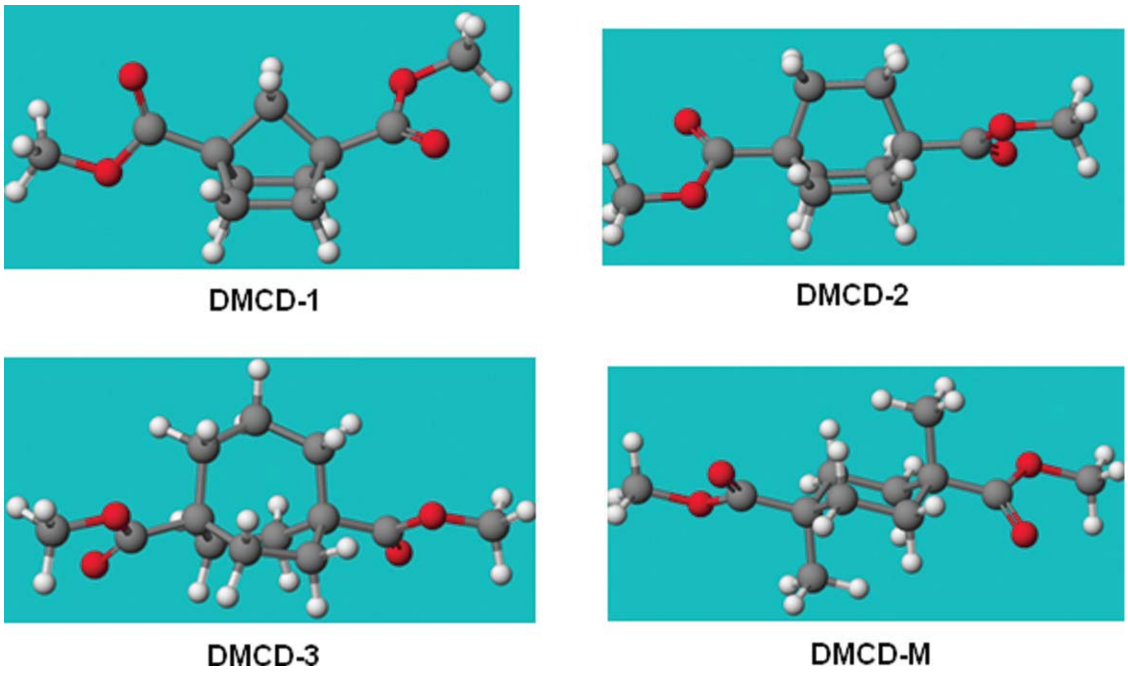


FIGURE 5 3-D models of DMCD-1, DMCD-2, DMCD-3, and DMCD-M.

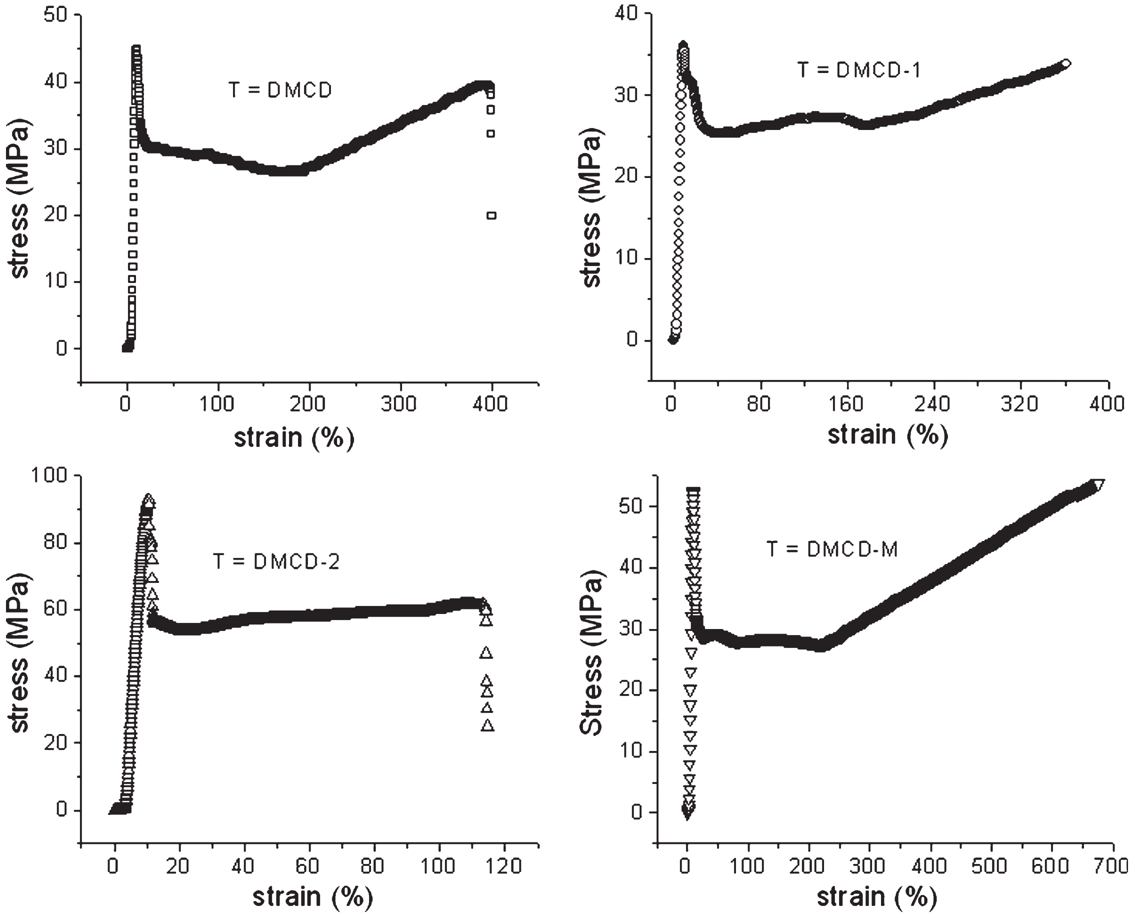


FIGURE 6 Tensile properties of poly[50(T)50(DMCD)29(EG)71(CHDM)] at RT.

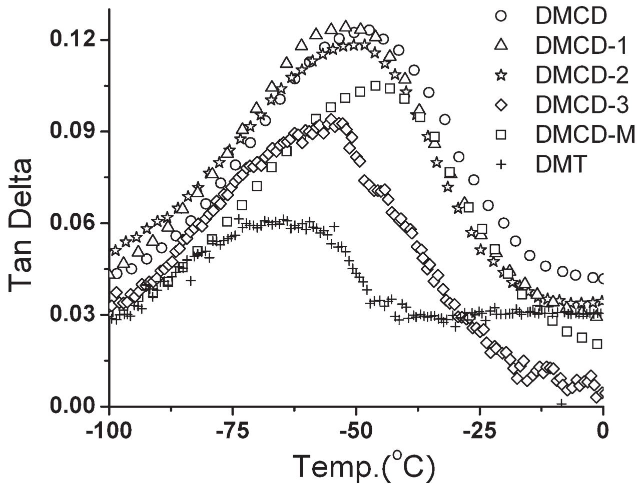


FIGURE 7 Tan delta versus temperature of poly[50(T)50(DMCD)29(EG)71(CHDM)].

incorporation of the bulky and somewhat bent monomer DMCD-3 may open up the structure and increase free volume, which could facilitate the diffusion of water molecules and attack at the ester bond and hence accelerate the hydrolytic degradation. Aromatic polyesters are well known to undergo very slow hydrolytic degradation and this was confirmed since the polyesters based on DMCD, DMCD-1, DMCD-2, or DMCD-M have faster hydrolytic degradation rate than the DMT containing polyester in this study.

CONCLUSIONS

In summary, we have described the synthesis of various cycloaliphatic polyesters with different compositions and characterized some of the properties. Amorphous DMCD-2-containing copolyesters were found to exhibit significantly higher T_gs (up to 115 °C) than any of the other alicyclic polyesters and the terephthalate analog in this study. For copolyesters based on DMCD-2, T_g increases linearly with increase of DMCD-2 mole percent. Poly[50(DMCD-2)50(DMCD)29(EG)71(CHDM)] was also found to possess highest T_g and the highest modulus among these six copolyesters containing DMCD due to the rigid units of DMCD-2 in the backbone. DMA showed that these cycloaliphatic copolyesters have similar secondary relaxations, which result from the conformational transition of cyclohexylene rings in the backbone. The polyester based on DMCD-3 in the hydrolytic tests undergoes the fastest hydrolytic degradation among these samples.

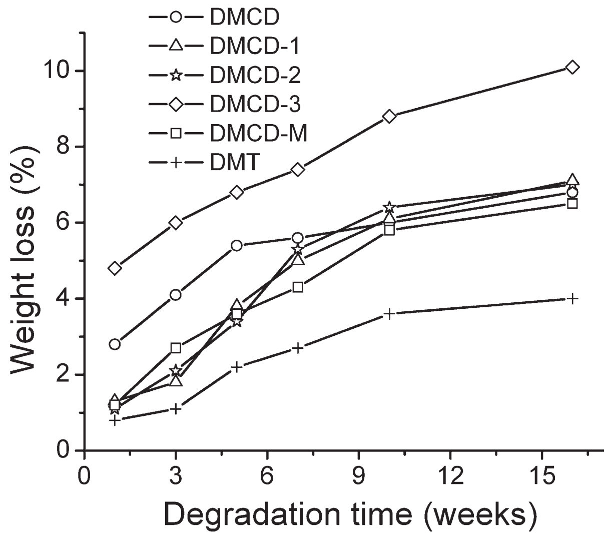


FIGURE 8 Weight loss of polyesters versus hydrolysis time in PBS (pH 7.4, 37 °C).

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