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Melt-Phase Synthesis and Properties of Triptycene-Containing Copolyesters

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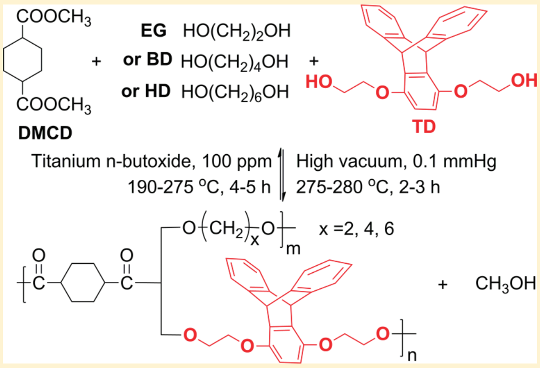
Supporting Information

ABSTRACT: A new triptycene diol (TD), triptycene-1,4-hydroquinone-bis(2-hydroxyethyl) ether, was synthesized and was used to prepare a series of copolyesters with dimethyl 1,4-cyclohexanedicarboxylate (1,4-DMCD) by melt polycondensation. Straight chain aliphatic spacers, including ethylene glycol (EG), 1,4-butanediol (BD), and 1,6-hexanediol (HD), were used as codiols with TD to explore the effects of straight chain flexible spacers on copolyester properties. A concomitant series of non-triptycene copolyesters based on hydroquinone bis(2-hydroxyethyl) ether (HBE), bis[4-(2-hydroxyethoxy)phenyl] sulfone (BHPS), 1,1-bis[4-(2-hydroxyethoxy)phenyl]cyclohexane (BHPC), or 1,1-bis(2-hydroxyethoxy)phenyl-3,3,5-trimethylcyclohexane (BHPT) were prepared for comparison. The results demonstrated that the triptycene-containing polyesters in this study have higher thermal stability and higher glass transition temperatures (T_g's) than the corresponding non-triptycene analogues. For triptycene-containing copolyesters, the mechanical properties were found to be dependent on the types and compositions of comonomer diols. A 1,4-butanediol-based triptycene copolyester was observed to have a significant increase in T_g and modulus while maintaining high elongation at ambient temperature (23 °C). However, all the studied 1,4-butanediol-based copolyesters were brittle and had comparable modulus values at low temperatures (−25 or −40 °C).



INTRODUCTION

Material scientists have been pursuing the enhancement of mechanical properties to produce high performance polymers for a wide range of applications. Incorporation of rigid structures into a polymer backbone to enhance properties has been studied extensively by many researchers.[1−3] Polymers containing such rigid building blocks usually show not only increased T_g but also decreased ductility. For example, adamantyl building blocks usually raise the T_g but also lower the ductility of a polymer by reducing the flexibility of the polymer backbone and intermolecular chain entanglements.[4−7] A variety of bisphenol derivatives are also well-known to produce high-T_g polymers.[8−10] However, a recent report from Swager and Thomas et al.[11] shows that incorporation of triptycene, a rigid aromatic cyclic structure, gives an increase in both modulus and ductility even at a low temperature of −30 °C when incorporated into certain polyester backbones. The authors hypothesized that neighboring chains can lie in a V-shaped cleft of the triptycene units and that this provides a mechanism for molecular interlocking and is the origin of these normally divergent mechanical properties.[11] Unlike common intermolecular interactions, such as hydrogen bonding and ionic interactions, this "mechanical interlocking" is a novel concept, and it is not known if this interaction is operative in other polymer structures.

Previous work on triptycene containing polyesters in the late 1960s from DuPont and Eastman Kodak resulted in polymers with significantly enhanced glass transition temperatures and increased brittleness as evidenced by the reported brittle nature of cast films.[12,13] Both of these early reports were based on incorporation of a triptycene monomer with a 9,10 functionality for polymerization into the various polymer backbones studied. In contrast, the Swager and Thomas work is based on the use of 1,4-hydroquinone triptycene structure which significantly changes the monomer structure and polymer backbone structure. Also, in the recent work a long aliphatic spacer was found to be necessary to bring this proposed mechanical interlocking mechanism into operation. The combination of decanediol and the 1,4-hydroquinone triptycene units in the polyester chain led to these unusual properties.

Our goal is to explore the properties of a series of copolyesters that incorporate the 1,4-hydroquinone triptycene group via a new primary diol triptycene derivative which permits the facile melt-phase preparation of copolyesters. We are interested in raising the T_g values of aliphatic polyesters based on 1,4-cyclohexane dicarboxylic acid (via 1,4-DMCD) without negatively impacting the mechanical properties of these materials. In this research the number of methylene groups in the aliphatic codiol was varied from two to six (ethylene diol to hexane diol), and selected thermal and mechanical properties of the resulting

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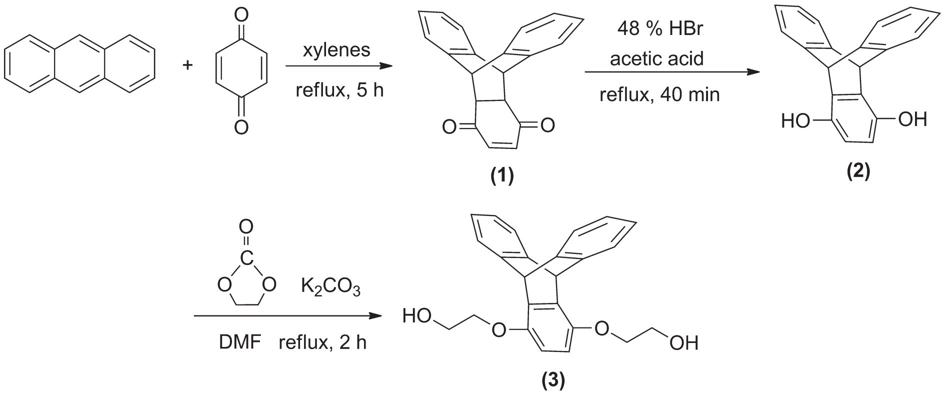
Scheme 1. Synthesis of Triptycene-1,4-hydroquinone-bis(2-hydroxyethyl) Ether (3)



copolyesters were studied. Furthermore, the incorporation of other bulky hydroxyethoxylated bisphenol derivatives into identical polyester backbones was investigated, and the mechanical properties, without the triptycene architecture, of these polyesters were compared to those of corresponding triptycene polyesters.

EXPERIMENTAL SECTION

Materials. Anthracene (97%) was purchased from Aldrich and recrystallized from xylene. Ethylene glycol (≥99%), 1,4-butanediol (99%), 1,6-hexanediol (99%), *p*-benzoquinone, hydroquinone bis(2-hydroxyethyl) ether (98%), and 4,4′-cyclohexylidenebisphenol (98%) were purchased from Aldrich and used as received. Dimethyl 1,4-cyclohexanedicarboxylate (1,4-DMCD) (cis/trans = 3/1) and 1,1-bis(hydroxyphenyl)-3,3,5-trimethylcyclohexane were donated by Eastman Chemical Co. and Hi-Bis GmbH, respectively. Titanium(IV) *n*-butoxide (>98%) was purchased from Alfa Aesar, and the titanium catalyst solution was prepared by mixing titanium *n*-butoxide with dry *n*-butanol in a dry bottle under nitrogen at a concentration of 0.06 g/mL based on Ti.

Instrumentation. All measurements were performed in Virginia Tech (Blacksburg, VA) except for the elemental analysis, which was done by Atlantic Microlab, Inc. (Norcross, GA). NMR spectra were determined at 25 °C at 400 MHz with an INOVA spectrometer. Molecular weights of the synthesized polymers were determined using size exclusion chromatography (SEC) with a refractive index (RI) detector and viscometer DP detector and using a polystyrene standard. SEC measurements were performed at 30 °C in chloroform with a sample concentration 5.00 mg/mL at a flow rate of 1.00 mL/min. Thermogravimetric analysis (TGA) was conducted under nitrogen from 25 to 600 °C at a heating rate of 10 °C/min using a TGA Q500 of TA Instruments. Differential scanning calorimetry (DSC) was conducted using a DSC Q2000 of TA Instruments. DSC data were obtained from −20 to 300 °C at heating/cooling rates of 20 °C/min under nitrogen circulation. The glass transition temperature was determined from analysis of the second heating cycle. Dynamic mechanical analysis (DMA) of samples was conducted using a DMA Q800 of TA Instruments at a heating rate of 5 °C/min from −150 to 100 °C while they were deformed (10 μm amplitude) in the tension mode at a frequency of 1 Hz under nitrogen. Tensile measurements at room temperature were performed on an Instron Model 4400 Universal Testing System equipped with a 1KN load cell. Tensile measurements at low temperatures (−25 or −40 °C) were performed on an Instron 5800R and Thermotron Testing System equipped with a load capacity of 1KN. The film samples were prepared using a PHI Model GS 21-J-C-7 compression molding press at 70 °C above T_g for 15 min. After the film samples were cooled down in ambient air, they were stored in a desiccator at ambient temperature. The molecular weights of the prepared film samples were unchanged from the original samples before compression molding. The film samples were dried in vacuum 24 h and then were cut to a dog bone shape at 40 × 4 × 0.3 mm (length × width × thickness) for tensile tests. The samples were tested at a rate of 15 mm/min using an initial grip-to-grip separation of 15 mm. Young's modulus was calculated from the linear part of the initial slope. All reported tensile data were averaged from at least three independent measurements, and a standard deviation was also reported. An X-ray diffractometer was used to determine if any crystallinity existed within the cast films. For this experiment, the original films or stretched films were fixed on the platform and the X-ray diffraction was observed from the surface of films by use of the reflection mode.

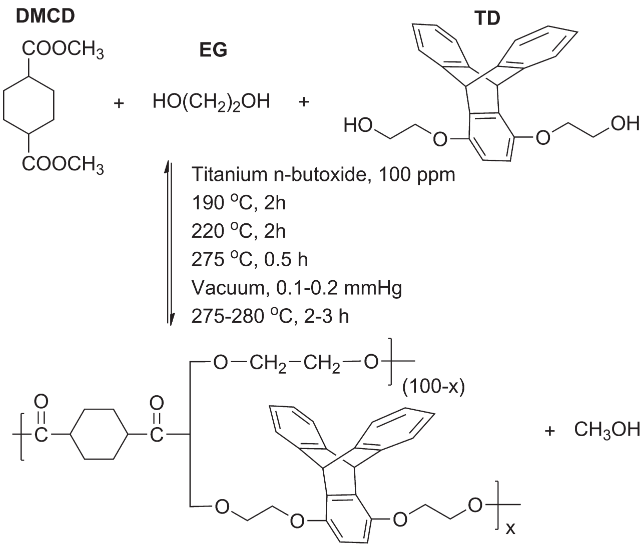
Synthesis of Triptycene-1,4-quinone (1) and Triptycene-1,4-hydroquinone (2). Triptycene 1,4-quinone (**1**) and triptycene-1,4-hydroquinone (**2**) were prepared according to the published literature.[14,15] The detailed procedures are described in the Supporting Information.

Synthesis of Triptycene-1,4-hydroquinone-bis(2-hydroxyethyl) Ether (3). Synthesis of (**3**) is shown in Scheme 1. A 500 mL two-necked flask charged with 30 g (0.105 mol) triptycene-1,4-hydroquinone (**2**) and 1.45 g of K_2CO_3 (0.0105 mol) in 250 mL of *N,N*-dimethylformamide (DMF) was heated to reflux temperature (165 °C) under argon; 18.46 g (0.210 mol) of ethylene carbonate in 100 mL of DMF was added into the flask drop by drop (about 1 h). After that, the reaction mixture was stirred at reflux temperature for another 2 h and then cooled to room temperature. A fine precipitate was obtained by pouring the reaction mixture into 800 mL of deionized water. The solid was filtered and washed completely with deionized water. A fine white solid was obtained after recrystallization from methanol and drying under vacuum oven overnight. Yield: 89%, mp 238−239.3 °C. ^{1}H NMR (400 MHz; DMSO-d_6) δ ppm: 3.74−3.77 (m, 4H, CH_2OH), 3.92−3.96 (m, 4H, ArO−CH_2), 4.94−4.97 (t, 2H, O−*H*), 5.95 (s, 2H, Ar−C*H*), 6.64 (s, 2H, Ar−*H*), 6.97−6.70 (m, 4H, Ar−*H*), 7.15−7.17 (d, 4H, Ar−*H*). ^{13}C NMR (DMSO-d_6, 100 MHz) δ ppm: 46.81, 60.21, 72.11, 112.09, 124.13, 125.25, 135.71, 145.93, 148.64. Elemental analysis calculated: C, 76.99; H, 5.92. Found: C, 77.03; H, 5.89.

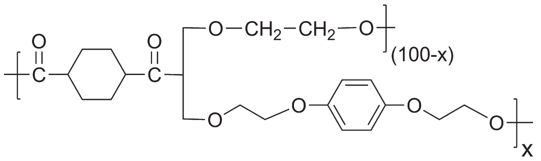
Abbreviation of Polyesters. The polymer nomenclature used in this article is based on a polyester containing 100 mol % of diester and 100 mol % of diol. For example, the polymer designated by poly[100(DMCD)75(EG)25(TD)] means that this targeted polymer contains 100 mol % DMCD as the diester units and 75 mol % EG and 25 mol % TD as the diol units. The letters stand for various monomers' abbreviation and the numbers indicate targeted mol % of monomers, respectively.

Melt-Phase Polymerization. The triptycene diol (TD) (**3**) and the comonomer EG were copolymerized with DMCD by melt polycondensation reaction. The detailed procedure in Scheme 2, which is similar to a published method,[9] is as follows (for poly[100(DMCD)75(EG)25(TD)]): 10 g (0.05 mol) of DMCD consisting of a *trans/cis*

Scheme 2. Synthesis of Poly[100(DMCD)(100−*x*)(EG)*x*(TD)]



Scheme 3. Structures of Non-Triptycene Poly[100(DMCD)(100−*x*)(EG)*x*(HBE)]



(1/3 molar ratio) mixture, 4.66 g (0.075 mol) of EG (100% excess), and 4.68 g (0.0125 mol) of TD were charged to a two-necked 50 mL reaction vessel equipped with a mechanical stirrer, nitrogen inlet, and condenser. The reactor was placed in a Belmont metal bath with a temperature controller. Titanium *n*-butoxide catalyst (100 ppm with respect to the targeted polyester) was added via a syringe under nitrogen. A multistep temperature procedure was used for the reaction; i.e., the reaction mixture was heated and stirred at 190 °C for 2 h, 220 °C for 2 h, and 275 °C for 0.5 h. Methanol was collected in a receiving flask. At the end, high vacuum (0.1−0.2 mmHg) was applied to drive the reaction to high conversion for an additional 2 h. Then the vacuum was discontinued, and nitrogen was passed through the system. The polymer was allowed to cool to room temperature and was removed from the reaction flask. The polymer was dissolved in chloroform and precipitated into methanol. The solid precipitate was obtained by vacuum filtration and was dried under vacuum at 30−60 °C overnight to yield 12.7 g (92%) of dry copolyester. The same procedure was employed to prepare poly[100(DMCD)(100−*x*)(EG)*x*(TD)].

Synthesis of Poly[100(DMCD)(100−*x*)(EG)*x*(HBE)] for Comparative Purposes. Non-triptycene analogues also were synthesized for comparison. Hydroquinone bis(2-hydroxyethyl) ether (HBE) was used as a corresponding diol shown in Scheme 3. The experimental procedures are the same as described above.

Synthesis of Poly[100(DMCD)75(BD or HD)25(TD or HBE)]. Copolyesters were prepared by the above-mentioned procedure except that the contents of straight-chain alkanediol and TD (or HBE) were fixed at 75 and 25 mol %, respectively. 1,2-Ethanediol was replaced by 1,4-butanediol or 1,6-hexanediol, which was used in 30 mol % excess.

Synthesis of Poly[100(DMCD)75(BD)25(BHPS or BHPC or BHPT)]. The other non-triptycene analogues (depicted in Scheme 4) with the same compositions were synthesized for comparative purposes. The same experimental procedures were applied.

■ RESULTS AND DISCUSSION

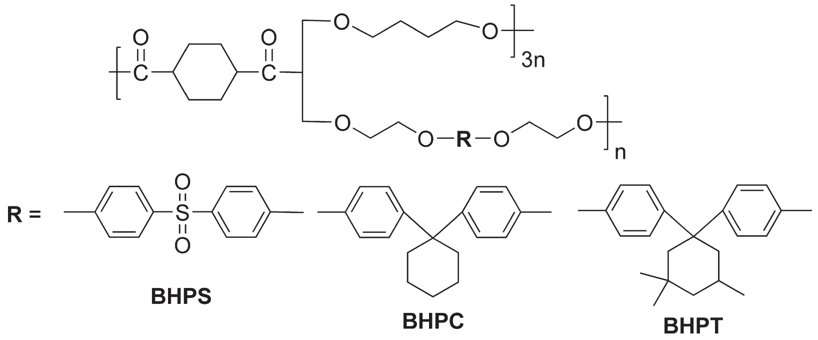
Selection of Monomers. The synthetic route to triptycene-1,4-hydroquione-bis(2-hydroxyethyl) ether (**3**) is shown in Scheme 1. Anthracene was reacted with quinone across the 9,10-position to yield triptycene-1,4-quinone (**1**).[14,15] When treated with HBr in glacial acetic acid, triptycene-1,4-quinone (**1**) gives triptycene-1,4-hydroquinone (**2**) with high yield.[14] This bisphenol can be readily and inexpensively converted to the primary alcohol triptycene-1,4-hydroquione-bis(2-hydroxyethyl) ether (**3**) in high yield by reaction of the phenol OH group with ethylene carbonate.[9] To the best of our knowledge, (**3**) has not been reported in the literature and is a new monomer. Triptycene (**3**) with primary alcohol groups is required for polyesters in diol−diester polycondensations because it is well know that the direct melt polycondensation of bisphenols is a low yield reaction.[9] 1,1-Bis[4-(2-hydroxyethoxy)phenyl]cyclohexane (BHPC) was obtained in much higher yield than the literature.[16] 1,4-DMCD (cis/trans ratio of 3 to 1) as the diacid unit was used in this study to provide amorphous polyesters with improved solubility, while maintaining the linear 1,4-enchainment mode. Thus, the introduction of cyclohexane units to the main chain of the polyesters does not significantly decrease the mechanical properties due to the rigidity of the alicyclic structure.

Copolyester Composition by ^{1}H NMR Spectroscopic Analysis. Figure 1 shows the ^{1}H NMR spectra of a representative copolyester based on DMCD, EG, and TD with a targeted molar ratio of 100:75:25. The diols within the copolyester chains are assumed to react in a random fashion. In brief, peak "a", "a′", "b", and "c" are assigned to the protons of the triptycene group. Peaks "d" and "e" are the methylene group adjacent to the oxygen at the TD unit. Peak "f" is assigned to the methylene group adjacent to the oxygen at the EG unit (single peak), and the cis/trans ratio of DMCD was determined by comparing the α-hydrogens on the cis and trans isomers. Some isomerization of DMCD from cis to trans occurred during polymerization (final mole ratio of cis/trans = 1/1). These broad peaks "h" come from the protons on carbons in the rings. The peak area ratio of "f" to "e" give 74% EG and 26% TD. The ^{1}H NMR spectrum of each of these polymers showed good agreement of its actual composition with the targeted composition.

Thermal Property Analysis of Copolyesters Poly[100(DMCD)(100−*x*)(EG)*x*(TD)]. All polymers became highly viscous when the polymerization proceeded to high conversion, which typically took about 6 h. Some of the copolyesters started to take on a yellow color due to the titanium catalyst. The semiaromatic copolyester samples were soluble in common chlorinated solvents, such as dichloromethane and chloroform, as expected from the amorphous polyester structure. In order to minimize the effect of physical aging of the respective polyesters on thermal and mechanical properties, all polyester film samples were run as soon as possible (in 24 h) after they were made by compression molding. The thermal properties, the molecular weights and tensile properties at ambient temperature (23 °C) are summarized in Table 1.

An examination of Table 1 shows that most of the copolyesters displayed high molecular weights as well as PDIs of 2.5−3.1,

Scheme 4. Structures of Poly[100(DMCD)75(BD)25(BHPS or BHPC or BHPT)]



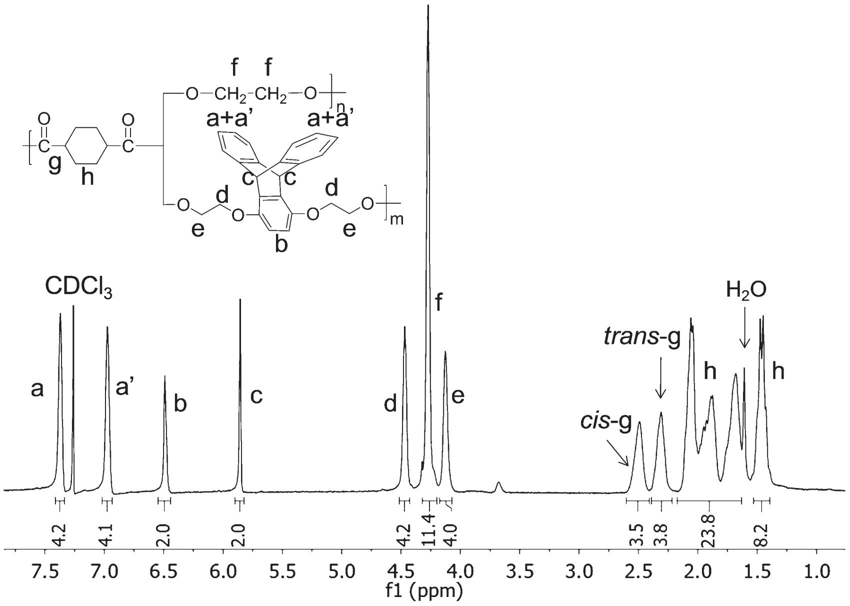


Figure 1. ^{1}H MNR spectra of poly[100(DMCD)(74)(EG)26(TD)].

which are typical for melt polymerization polyesters. The SEC trace of poly[100(DMCD)74(EG)26(TD)] by the refractive index detector is shown in Figure 2 as representative of these samples. The presence of small peaks, following the main sharp peak, suggests the presence of some cyclic oligomers in the polyester. Molecular weights of polyesters, containing DMCD, EG, and TD, decrease with decreasing EG content. However, T_g increases with increasing TD content. As shown in Table 1, the 5% weight loss (T_d) for all TD-containing polymers was higher than those of the corresponding non-TD analogues, as expected from the more highly aromatic structure of TD. For example, poly[100(DMCD)74(EG)26(TD)] showed a T_d at 384 °C, whereas poly[100(DMCD)74(EG)26(HBE)] displayed a T_d of 372 °C. These data indicate that copolyesters containing TD have marginally higher thermal stability than non-triptycene analogues. When the triptycene unit was incorporated into the polyester, the T_gs were remarkably increased when compared to those of the non-triptycene polyesters. From Table 1, the incorporation of 26 mol % HBE into the DMCD/EG backbone only raised the T_g 8 °C, whereas TD at the same incorporation level raised the T_g 54 °C. This is consistent with the bulky structure of TD. The data in Table 1 also show that, as expected, the T_g of triptycene copolyesters decreases when the carbon number of the linear aliphatic codiol increases to 4 (BD) and 6 (HD). Average molecular weights also decreased with the longer chain aliphatic diols because of their lower volatility than EG, making it more difficult to drive the conversion. The TD-containing polymers poly[100(DMCD)75(BD or HD)25(TD)] exhibited higher thermal stabilities than the corresponding non-triptycene analogues poly[100(DMCD)75(BD or HD)25(HBE)]. The absence of a melting peak in all DSC traces indicates that the copolyesters are amorphous, in contrast to the results reported by Swager and Thomas et al.[11] (their triptycene-containing polyesters were semicrystalline). It is difficult to obtain high molecular weight copolyesters with an incorporation level of 70 mol % or more TD due to the nonvolatility of TD.

Mechanical Property Analysis of Copolyesters Poly[100-(DMCD)75(EG or BD or HD)25(TD or HBE)]. Tensile data at ambient temperature revealed that poly[100(DMCD)74-(EG)26(TD)] has a higher modulus and yield stress than poly-[100(DMCD)74(EG)26(HBE)], which is a flexible material (Figure 3 and Table 1). But the low elongation to break of poly[100(DMCD)74(EG)26(TD)] indicated that this triptycene polyester is brittle under these same conditions. Unlike

Table 1. Characterization Results of Triptycene and Non-Triptycene Copolyesters

polyester composition (^{1}H NMR)	TGA T_d, 5% weight loss (°C)	SEC M_n (g/mol)	M_w/M_n	DSC T_g (°C)	tensile[a] stress at break (MPa)	tensile[a] strain at break (%)	modulus[a] (MPa)
100(DMCD)100(EG)	307	51 000	2.7	15	[b]	[b]	[b]
100(DMCD)74(EG)26(TD)	384	54 000	3.1	69	48 ± 4	4.5 ± 0.7	1475 ± 137
100(DMCD)49(EG)51(TD)	384	17 000	2.7	99	[c]	[c]	[c]
100(DMCD)26(EG)74(TD)	385	9 500	2.9	118	[c]	[c]	[c]
100(DMCD)74(EG)26(HBE)	372	43 000	3.1	23	6 ± 0.7	1920 ± 76	0.9 ± 0.1
100(DMCD)49(EG)51(HBE)	372	33 000	2.5	27	[b]	[b]	[b]
100(DMCD)26(EG)74(HBE)	372	106 000	2.6	31	[b]	[b]	[b]
100(DMCD)74(BD)26(TD)	375	25 500	2.2	44	32 ± 2	319 ± 14	1169 ± 21
100(DMCD)74(BD)26(HBE)	368	20 000	1.9	4	0.39 ± 0.03	737 ± 33	1.0 ± 0.2
100(DMCD)75(HD)25(TD)	370	24 000	2.0	25	11 ± 1	494 ± 47	50 ± 3
100(DMCD)65(HD)35(TD)	368	27 800	2.0	47	43 ± 3	10 ± 2	734 ± 27
100(DMCD)50(HD)50(TD)	360	24 300	2.5	77	[c]	[c]	[c]
100(DMCD)75(HD)25(HBE)	346	19 000	2.1	−6	0.24 ± 0.01	339 ± 32	1.4 ± 0.4
100(DMCD)74(BD)26(BHPS)	331	20 100	1.9	32	20 ± 2.0	433 ± 41	316 ± 30
100(DMCD)74(BD)26(BHPC)	359	20 400	2.0	26	15 ± 0.7	688 ± 27	4 ± 0.2
100(DMCD)75(BD)25(BHPT)	357	19 500	2.0	36	19 ± 0.7	249 ± 18	673 ± 46

[a] Tensile tests were done at 23 °C. [b] Tensile tests were not run. [c] Samples failed during preparation of dogbone specimens.

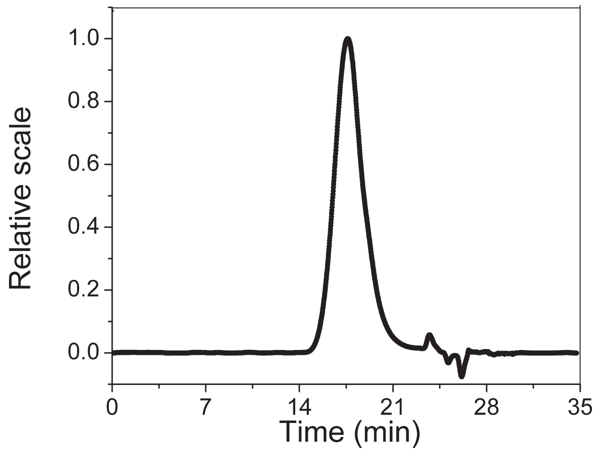


Figure 2. SEC trace of poly[100(DMCD)(74)(EG)26(TD)].

the polyesters in the paper of Swager and Thomas et al., which use long chain diols, this polyester poly[100(DMCD)74(EG)26(TD)] based on a short chain diol, EG, does not demonstrate ductile behavior.

Therefore, we replaced EG with a longer diol, BD, and kept the TD composition the same. A similar polymer was also prepared with a longer diol, HD, so that the effects of the length of aliphatic spacers could be elucidated. We observed significantly different properties with the longer straight chain diols BD and HD.[11] These characterization results are also summarized in Table 1. Tensile data revealed that poly[100(DMCD)74(BD)26(TD)] has a higher modulus and stress to yield than poly[100(DMCD)75(HD)25(TD)], which has more elastic-like properties. High elongation to break (319%) and high modulus (1.17 GPa) of poly[100(DMCD)74(BD)26(TD)] indicated that it is ductile and a relatively tough material. Therefore, BD is considered to possess a suitable chain length to demonstrate enhanced ductility and enhanced modulus of triptycene polyesters. A decrease of HD content in the triptycene copolyester from 75 to 65 mol % resulted in a brittle material with low elongation to break (10%) at ambient temperature. When the HD content was lowered to 50 mol %, poor films were obtained and tensile tests were not possible for this triptycene copolyester composition. The TD-containing polyesters poly[100(DMCD)75(BD or HD)25(TD)] also exhibited much higher modulus at 23 °C when compared to the HBE analogues poly[100(DMCD)75(BD or HD)25(HBE)], which are highly flexible with a modulus of about 1 MPa as shown in Table 1.

Mechanical Property Analysis of Copolyesters Containing BHPS, BHPC, or BHPT. Numerous bisphenol derivatives have been synthesized and incorporated into polymer backbones to increase the T_g for high-performance materials.[9,17] BHPS is commercially available; BHPC and BHPT were synthesized as described in the synthesis section. In this study, they were incorporated into identical polyester backbones by replacing the triptycene units with the respective bisphenol derivatives, BHPS, BHPC, or BHPT. The properties of their copolyesters are shown in Table 1. We can see that poly[100(DMCD)74(BD)26(TD)] still has the highest thermal stability and highest modulus among these copolyesters. These data thus confirmed that the incorporation of TD into the polyester backbone can increase T_g due to its rigid structure. The glassy solid BHPT possesses an amorphous and bulky structure due to the three pendent methyl groups. When the BHPT concentration was also fixed at 25 mol %, the modulus of the corresponding copolyester was significantly less than the 25 mol % TD copolyester. From the tensile test data of poly[100(DMCD)74(BD)26(BHPC)], we conclude that it has some elastic-like properties with a low modulus (only 4 MPa) since T_g is very close to the ambient temperature, at the temperature where the tensile measurements were run. The copolyester based on BHPS, poly[100(DMCD)74(BD)26(BHPS)], has a lower T_g and modulus and a higher elongation than the corresponding TD copolyester.

From the above tensile curves for poly[100(DMCD)75(BD)25(BHPT)] (Figure 4), the copolyester based on BHPT is found to be a high modulus and ductile material with a yield point, although no necking was observed during the deformation. However, when compared to poly[100(DMCD)75(BD)25(BHPT)], the triptycene

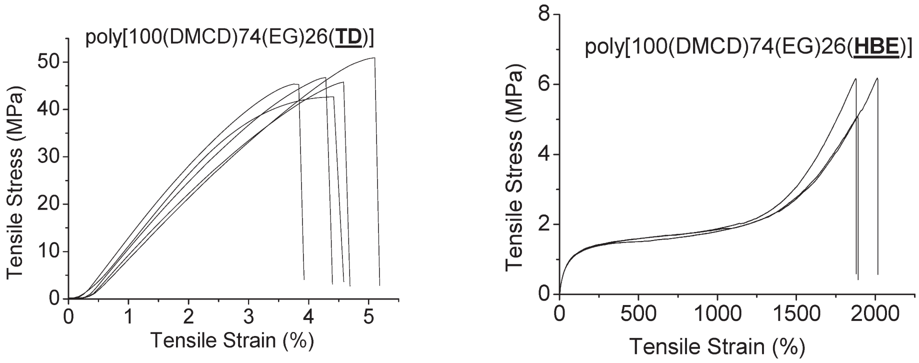


Figure 3. Tensile properties of poly[100(DMCD)74(EG)26(TD)] (left) and poly[100(DMCD)74(EG)26(HBE)] (right) at 23 °C.

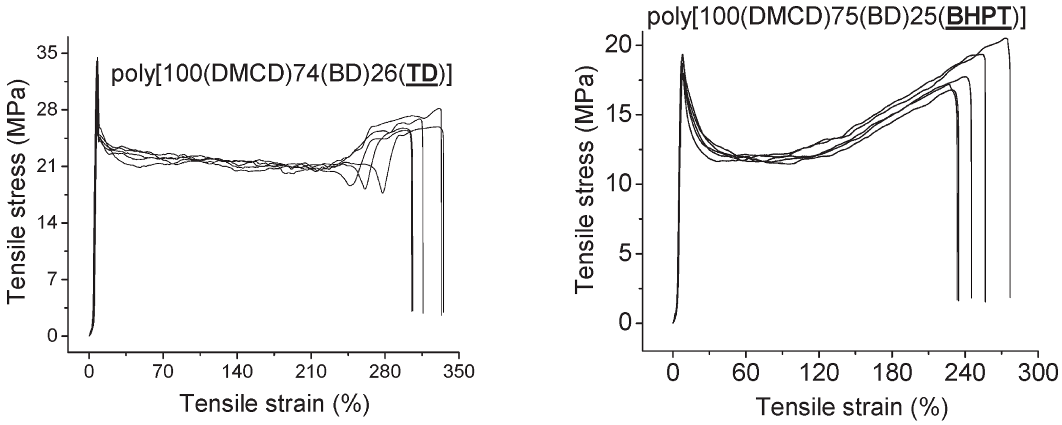


Figure 4. Ambient temperature tensile properties of poly[100(DMCD)74(BD)26(TD)] (left) and poly[100(DMCD)75(BD)25(BHPT)] (right).

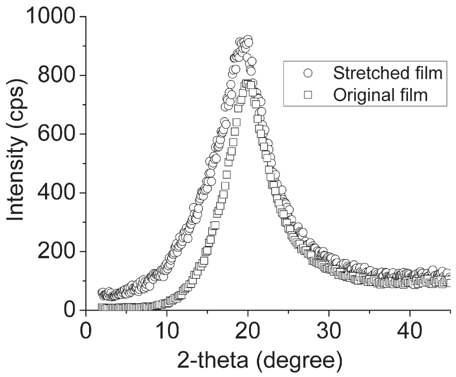


Figure 5. X-ray diffraction traces of poly(100(DMCD)74(BD)26(TD) films before and after stretching.

copolyester poly[100(DMCD)74(BD)26(TD)] exhibits the synergistic effect observed by Swager and Thomas et al. because both the elongation to break and modulus of the triptycene copolyester are improved. The distinct upward turn in both tensile curves in Figure 4 is due to strain hardening, which begins at a fairly high level of strain. Necking formation is also observed for poly(100(DMCD)74(BD)26(TD) and is similar to the observation of Swager and Thomas et al.[11] However, the polyesters of this study did not show crystallinity in contrast to Swager and Thomas et al.[11] In order to verify if crystallization is induced during the deformation, we obtained the X-ray diffraction of the elongated polymer film, which was maintained in the stretched condition during the measurement. Figure 5 shows the X-ray diffraction traces for both the original and stretched samples. No significant difference between these films is observed. The broad diffuse peaks (almost across 20°) indicate that both samples are amorphous.

In order to better compare the mechanical properties of triptycene polyesters to non-triptycene analogues in their glassy states, tensile measurements at low temperatures were carried out, and the results are shown in Table 2. The tensile properties of these non-triptycene polyesters were measured at −25 °C, except for the HBE-containing polyester, which was measured at −40 °C due to its low T_g.

All copolyesters in Table 2 exhibit comparable glassy modulus values and are brittle at temperatures well below their T_g's. Since the tensile elongation to break of the triptycene copolyester poly[100(DMCD)74(BD)26(TD)] is greatly decreased at −25 °C, this triptycene polyester does not behave differently in regards to ductility and modulus when compared to the other copolyesters of this study containing rigid and bulky units (BHPS, BHPC, and BHPT) measured at well below T_g. These data differ from the earlier results of Swager and Thomas et al.,[11] who observed ductile behavior for their triptycene-containing copolyesters at −30 °C.

DMA spectra of triptycene and various non-triptycene polyesters are presented in Figure 6. The plots of storage modulus versus temperature indicate that all polyesters possess an expected glassy storage modulus (above 1 GPa) except for the HBE-containing polyester. The α peaks in the tan δ curves,

Table 2. Tensile Properties of Various Copolyesters at −25 or −40 °C

various copolyesters with similar compositions (T_g)[a]	tensile stress at break/yield (MPa)	tensile strain at break (%)	modulus (MPa)
DMCD/BD/BHPS (32) 100/74/26	46 ± 6 (break)	6 ± 1	1406 ± 96
DMCD/BD/BHPC(26) 100/74/26	50 ± 3 (yield)	19 ± 2	1448 ± 65
DMCD/BD/BHPT(36) 100/75/25	51 ± 4 (yield)	10 ± 1	1526 ± 82
DMCD/BD/TD(44) 100/74/26	69 ± 3 (break)	8 ± 0.4	1688 ± 61
DMCD/BD/HBE(4) 100/74/26	37 ± 4 (break)	24 ± 5	952 ± 66

[a] T_g values are shown in parentheses. The tensile tests of poly(DMCD/BD/HBE) was run at −40 °C.

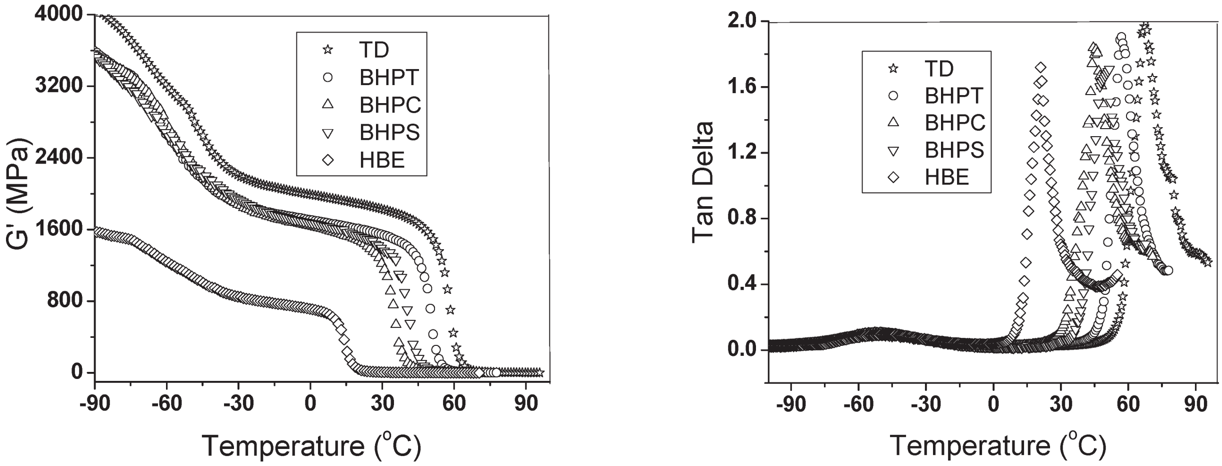


Figure 6. DMA of poly[100(DMCD)75(BD)25(TD/BHPT/BHPC/BHPS/HBE)].

accompanied by a sharp decrease in modulus, correspond to the T_g's of the respective polyesters. The triptycene polyester displays the highest glassy storage modulus (above 1.8 GPa) and T_g (66 °C from tan δ), together with the widest glassy plateau well past room temperature among these polyesters, while the HBE-containing polyester shows the lowest glassy DMA modulus of 0.7 GPa and T_g of 21 °C. The tan δ T_g was about 20 °C higher than the DSC T_g as expected. All copolyesters exhibit the existence of a secondary relaxation tan δ peak from −57 to −51 °C with about the same intensity. The conformational changes of the cyclohexyl units in the polyester backbones are the origin of sub-T_g loss peak. It is of interest to note that other cyclohexyl group-containing polyesters, such as the poly(1,4-cyclohexylenedimethylene terephthalate) (PCT), were confirmed by Yee et al.[18] to have a weak transition in this region as well.

CONCLUSION

In summary, we have described the melt-phase synthesis of triptycene-containing polyesters using a new primary triptycene diol, and we have also characterized some of the properties of these new materials. All TD-containing polymers in this study have higher thermal stability by TGA and higher T_g's than the corresponding non-triptycene analogues. The T_g of TD-containing polymers increased with increasing TD content. The results from tensile tests revealed that poly[100(DMCD)74(EG)26(TD)] is rigid but brittle at ambient temperature. However, the copolyester poly[100(DMCD)74(BD)26(TD)] was found to simultaneously possess high modulus and excellent ductility at ambient temperature. It indicates that its short flexible spacer (butane unit) in combination with triptycene units can also promote an improved ambient temperature modulus and enhanced ductility. However, our results do not confirm the synergistic effect observed by Swager and Thomas et al. since the triptycene copolyester does not show enhanced ductility when compared to other copolyesters containing rigid and bulky units (BHPS, BHPC, and BHPT) at −25 °C. These polyesters, including triptycene polyesters, are brittle and display similar modulus values at temperatures well below their DMA (tan δ) T_g's. Poly[100(DMCD)74(BD)26(TD)] in this study differs from the triptycene-containing copolyesters of Swager and Thomas et al.,[11] which still exhibited ductile behavior at −30 °C.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthetic procedures for triptycene 1,4-quinone (**1**), triptycene-1,4-hydroquinone (**2**), BHPC and BHPT, the synthetic scheme of poly[100(DMCD)75(BD or HD)25(TD or HBE)]. This material is available free of charge via the Internet at http://pubs.acs.org.

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