Polymer 54 (2013) 4493–4500

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

New poly(arylene ether sulfone)s based on 4,4′-[*trans*-1,4-cyclohexanediylbis(methylene)] bisphenol

Bin Zhang, S. Richard Turner*

Department of Chemistry, Macromolecules and Interfaces Institute (MII), Virginia Tech, Blacksburg, VA 24061-0344, USA

A R T I C L E I N F O

Article history:
Received 15 April 2013
Received in revised form
8 June 2013
Accepted 11 June 2013
Available online 19 June 2013

Keywords:
Poly(ether sulfone)s
sub-T_g relaxations
trans-1,4-cyclohexylene rings

A B S T R A C T

Incorporation of 4,4′-dihydroxy-*p*-terphenyl (DHTP) and a new bisphenol comonomer, 4,4′-[*trans*-1,4-cyclohexanediylbis(methylene)] bisphenol (CMB), into a dichlorodiphenyl sulfone (DCDPS) based poly(ether sulfone) resulted in a synergistic effect with an order of magnitude increase observed in the strain at break when compared to the structural analogs. Polysulfones with the CMB monomer and other bisphenol comonomers such as 4,4′-dihydroxy-*p*-biphenyl (DHBP) and bisphenol-A (BisA) were also synthesized and characterized for comparison and this enhancement was not seen in these polymers. The cyclohexylene containing monomer and polymers were analyzed by 1d ^{1}H NMR and 2d H–H correlation spectroscopy (COSY) confirming that the cyclohexylene units in all the polymers were in the *trans*-configuration. DMA results suggested that the significant strain at failure enhancement was related to the strong intensity in both the β and γ-relaxations of the polysulfone containing CMB and DHTP monomers.

1. Introduction

Poly(arylene ether sulfone)s (PAESs) are important commercial polymers and have been extensively studied due to their excellent thermal and mechanical properties [1,2]. PAESs are commonly synthesized through aromatic nucleophilic substitution of dichlorodiphenyl sulfone (DCDPS) and various bisphenols in presence of base. There has been a continuous interest in developing new PAESs based on new monomers to obtain new properties or to enhance existing properties.

In this paper, we describe new PAES polymer systems with *trans*-1,4-cyclohexylene units incorporated into the backbone based on a new bisphenol monomer 4,4′-[*trans*-1,4-cyclohexanediylbis(methylene)] bisphenol (CMB) (Scheme 1). Polymers with 1,4-cyclohexylene ring units in the backbone are of great interest from both a fundamental and a practical point of view. The most explored areas of cyclohexylene containing polymers are polyesters, polycarbonates, and polyketones [3–11]. Yee and coworkers comprehensively studied the properties of cyclohexylene containing polyketones, polycarbonates and polyester-polycarbonates [5–9]. It was generally found that the incorporation of the cyclohexylene units in the backbone enhanced the local chain motion and showed enhanced craze resistance behavior. Poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) is an important commercial polyester. The cyclohexylene units in PCT impart a high melting point and significant toughness [12]. Credico and coworkers [10] did a systematic study on the dynamic mechanical behavior of a group of cyclohexylene containing polyesters with different *cis*/*trans* ratios. A series of relaxations were observed and attributed to the flexible methylene groups and cyclohexylene groups.

To the best of our knowledge, little research has been done on cyclohexylene containing polysulfones. We have recently reported a series of PAESs synthesized from *trans*-1,4-cyclohexylene ring-containing acid chloride monomers [13]. In this paper we report new PAESs that contain cyclohexylene ring units in the backbone based on the CMB monomer. The configurations of the cyclohexylene rings in the polymer backbones were carefully monitored to ensure the all *trans*-configurations were obtained. This feature provided a simplified polymer system to study the relaxation behaviors without the configuration complication in a *cis*/*trans* mixture as a result of the starting materials or the isomerization side reactions [4,5,10].

2. Experimental

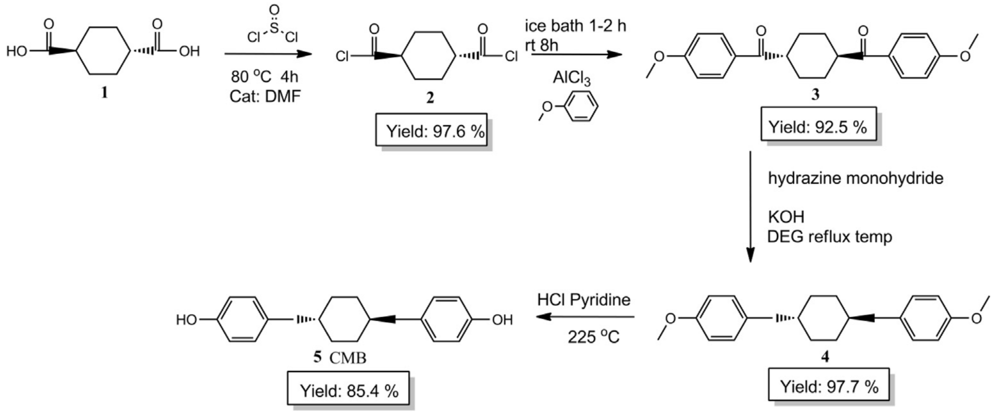
2.1. Materials

All chemicals were purchased from Aldrich with the exception of *trans*-1,4-cyclohexane dicarboxylic acid (CHDA) which was

---

* Corresponding author. Tel.: +1 540 231 4552; fax: +1 540 231 3971.
E-mail address: srturner@vt.edu (S.R. Turner).

0032-3861/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2013.06.018



Scheme 1. Synthesis scheme of 4,4′-[*trans*-1,4-cyclohexanediylbis(methylene)] bisphenol (CMB).

provided by Eastman Chemical Company. Radel® R sample was provided by Solvay Advanced Polymers L.L.C. All reagents were used without further purification.

2.2. Instrumentation

Size Exclusion Chromatography (SEC) was used to determine molecular weights and molecular weight distributions. With a flow rate of 0.500 ml/min, data were obtained in N-methyl-2-pyrrolidone (NMP) solvent 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. A Viscotek refractive index detector and a viscometer were used for molecular weight determination. Polystyrene standards were utilized to construct a universal molecular weight calibration curve.

FT-IR data were obtained on an M2004 FTIR spectrometer from MIDAC Corporation from 4000 cm^{-1} to 650 cm^{-1} with a 4 cm^{-1} resolution. ^1H and ^{13}C NMR spectra were obtained by a JEOL 500 (500 MHz) spectrometer at room temperature with chemical shifts relative to tetramethylsilane (TMS). High Resolution Mass Spectra (HRMS) were obtained from an Agilent liquid chromatography/mass spectrometry (LC/MS) mass spectrometer with a time of flight (TOF) analyzer. Elemental analysis was done by Atlantic Microlab, Inc (Norcross, Georgia). Oxygen contents in the elemental analysis were calculated by difference.

T_gs and T_ms were determined by Differential Scanning Calorimetry (DSC). Data were obtained by using a TA Instruments™ Q2000. Nitrogen was used as the carrying gas with a sample flow rate of 20 ml/min and a heating rate of 10 °C/min. T_gs were determined in the second heating cycle after the samples were quenched at nominally 100 °C/min in the cooling cycles. Thermogravimetric analysis (TGA) was carried out by a TA Instruments™ Q10 from 25 °C to 600 °C under nitrogen at a heating rate of 10 °C/min. Dynamic mechanical analysis (DMA) was performed on a TA Instruments™ Q800 in nitrogen atmosphere from −150 °C to 200 °C with a rate of 2 °C/min. The DMA parameters were Mode: Multi-Freq-Strain Tension Film; Amplitude: 10 μm; Preload force: 0.01 N. The tensile properties were obtained on an Instron Model 4400 Universal Testing System with a rate of 2 mm/min at room temperature. The results were the average of at least five samples.

2.3. Monomer synthesis

2.3.1. Synthesis of trans-1,4-cyclohexane dicarbonyl dichloride (compound 2 in Scheme 1)

With a Teflon coated magnetic stir bar, a condenser, and an argon inlet, a pre-dried 250 ml three-necked round bottom flask was charged with 16.00 g (93.02 mmol) of CHDA, 120 ml of thionyl chloride and 0.1 ml of N,N-dimethylformamide (DMF). After heated at 80 °C under argon for 4 h, excess thionyl chloride was removed under vacuum at 80 °C. A white crystalline product was obtained and dried in vacuum oven (−80 kPa, 80 kPa below atmospheric pressure) at room temperature for 12 h. The product was used directly in the next step without any further purification. Yield 97.6%. No melting point was observed due to the thermal instability of this compound. ^1H NMR ($CDCl_3$, ppm): δ2.73 (m, 2H), δ2.30 (m, 4H), δ1.58 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ188.4, 50.6, 30.0.

2.3.2. Synthesis of trans-1,4-cyclohexanediylbis[(4-methoxyphenyl) methanone (compound 3 in Scheme 1)

A 250 ml one-necked round bottom flask was charged with 8.000 g (38.28 mmol) *trans*-1,4-cyclohexane dicarbonyl dichloride and 100 ml anisole as the solvent and the reactant. The flask was equipped with a Teflon coated magnetic stir bar and a condenser. After a homogenous solution was obtained at room temperature, the system was placed in an ice bath and cooled to 0 °C. 12.76 g (95.69 mmol) of aluminum chloride was then slowly added to the solution with vigorous stirring. The reaction mixture was kept at 0 °C for 2 h followed by another 8 h at room temperature. Then 400 ml deionized water was added to the reaction mixture which was a light orange suspension. The mixture was vigorously stirred at room temperature for 1 h then filtered. The white solid product obtained by filtration was added to 200 ml methanol and stirred at room temperature for another 3 h to remove residual anisole. The suspension was filtered again to obtain the final product as a white solid which was thoroughly dried in vacuum oven (−80 kPa) at 80 °C for 12 h. Yield: 92.5%. m.p.: 157.1 °C. Elemental analysis: Found: C, 74.75; H, 6.90; O, 18.35. Calc. for $C_{22}H_{24}O_4$: C, 74.98; H, 6.86; O, 18.16%. ^1H NMR ($CDCl_3$, ppm): δ7.95 (d, 4H), δ6.95 (d, 4H), δ3.87 (s, 6H), δ3.31 (m, 2H), δ2.03 (m, 4H), δ1.69 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ202.0, 163.5, 130.6, 129.1, 113.9, 55.6, 44.6, 28.9.

2.3.3. Synthesis of trans-1,4-bis(4-methoxybenzyl)cyclohexane (compound 4 in Scheme 1)

To a 250 ml two-necked round bottom flask equipped with an argon inlet, a Teflon coated magnetic stir bar, and a condenser, 15.00 g (42.61 mmol) of compound 3, 19.18 g (38.35 mmol) of hydrazine monohydrate, 21.48 g (38.35 mmol) of potassium hydroxide and 100 ml of diethylene glycol were added. Under argon atmosphere, the mixture was heated to 250 °C in a high temperature silicon oil bath with stirring. The reaction mixture was held at this temperature for 24 h then the system was cooled to room temperature and 300 ml deionized water was added. The aqueous solution was extracted with 100 ml chloroform three times. The chloroform solutions were combined and chloroform was removed by rotary evaporation to obtain a light yellow solid. The solid was extracted in a Soxhlet extractor for 8 h with 400 ml methanol to remove soluble side products followed by drying at 80 °C in vacuum oven (−80 kPa) for 12 h. Yield: 97.7%. m.p.: 134.6 °C. Elemental analysis: Found: C, 81.39; H, 8.81; O, 9.80. Calc. for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70; O, 9.86%. ^{1}H NMR ($CDCl_3$, ppm): δ7.02 (d, 4H), δ6.80 (d, 4H), δ3.77 (s, 6H), δ2.39 (d, 4H), δ1.67 (m, 4H), δ1.40 (m, 2H), δ0.89 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ157.7, 133.5, 130.0, 113.5, 55.3, 43.1, 40.1, 33.0.

2.3.4. Synthesis of 4,4′-[trans-1,4-cyclohexanediylbis(methylene)] bisphenol (CMB, compound 5 in Scheme 1)

15.00 g (46.30 mmol) of compound 4 and 53.47 g (46.30 mmol) of pyridine hydrochloric acid were added to a 250 ml two-necked round bottom flask equipped with an argon inlet, a Teflon coated magnetic stir bar, and a condenser. Under argon atmosphere, the system was heated in a high temperature silicon oil bath to 225 °C and allowed to react at this temperature for 12 h with stirring. Then the reaction mixture was cooled to room temperature and 200 ml water was added. The suspension was vigorously stirred at room temperature for 12 h then filtered to obtain the crude product with a beige color. Crystals with a light beige color were obtained after recrystallization with methanol with a yield of 85.4%. m.p.: 232.0 °C. Elemental analysis: Found: C, 80.35; H, 8.24; O, 10.66. Calc. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16; O, 10.80%. ^{1}H NMR (DMSO-d6, ppm): *δ*9.08 (s, 2H), *δ*6.89 (d, 4H), *δ*6.63 (d, 4H), *δ*2.30 (d, 4H), *δ*1.58 (m, 4H), *δ*1.32 (m, 2H), *δ*0.83 (m, 4H). ^{13}C NMR (DMSO-d6, ppm): δ155.7, 131.3, 130.3, 115.4, 42.9, 40.1, 32.9. HRMS (m/z): Found: 296.1776. Calcd for $C_{20}H_{24}O_2$: 296.1785. Diff: 2.80 ppm.

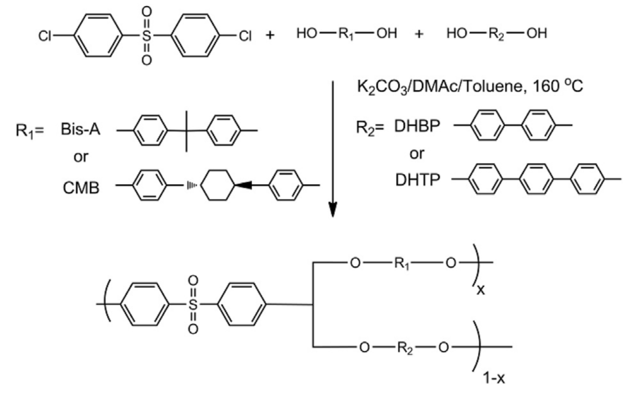
2.3.5. Synthesis of 4,4′-dihydroxy-p-terphenyl (DHTP)

4,4′-Dihydroxy-*p*-terphenyl (DHTP) was synthesized according to a previously published procedure [14]. ^{1}H NMR (DMSO-d6 ppm): δ7.56 (s, 4H), δ7.46 (d, 4H), δ6.80 (d, 4H). ^{13}C NMR (DMSO-d6 ppm): δ157.1, 138.1, 130.5, 127.5, 126.3, 115.8.

2.4. Polymer synthesis

2.4.1. Synthesis of 4,4′-[trans-1,4-cyclohexanediylbis(methylene)] bisphenol based polysulfone homopolymer and random copolymers

trans-1,4-Cyclohexylene ring-containing poly(arylene ether sulfone)s based on CMB, 4,4′-dihydroxy-*p*-biphenyl (DHBP), and DHTP were synthesized by nucleophilic aromatic substitution with DCDPS as shown in Scheme 2. The polymers based on bisphenol-A (BisA), DHTP, and DCDPS were synthesized in a similar fashion with different starting materials. We defined a homopolymer as a polymer from DCDPS with a single bisphenol and a copolymer as the one with two bisphenols. The synthesis of the random PAES copolymer based on 0.5 molar equivalent of CMB, 0.5 molar equivalent of DHBP, and 1 molar equivalent of DCDPS is described here as an example. All the other homopolymer and copolymers were synthesized via a similar technique. To a 100 ml round bottom flask equipped with a mechanical stirrer, an argon inlet and a Dean–Stark trap, 3.875 g (13.50 mmol) of DCDPS, 2.000 g (6.75 mmol) of CMB, 1.256 g (6.75 mmol) of DHBP, 4.842 g (35.09 mol) of K_2CO_3, 60 ml of N,N-dimethylacetamide (DMAc), and 30 ml of toluene were added. Under the protection of argon, the reaction was allowed to dehydrate at 140 °C for 3 h by azeotropic distillation. Then the temperature was slowly increased to 160 °C over 2 h to remove toluene. After 20 h at 160 °C the reaction mixture was cooled to room temperature. The solution was precipitated in a 5 weight percent HCl aqueous solution. The polymer product was obtained after filtration and subsequently washed three times with 200 ml deionized water and three times with 200 ml methanol. The polymer sample was obtained as a white solid and was dried thoroughly at 120 °C for 12 h in vacuum oven (−80 kPa). Yield: 92.4%. ^{1}H NMR ($CDCl_3$, ppm): δ7.86 (m), δ7.58 (m, 3.90), δ7.11 (m), δ7.06 (m), δ7.98 (m), δ6.92 (m), δ2.47 (d, 4.00), δ1.70 (m), δ1.46 (m), δ0.93 (m). In the proton NMR, the integration area ratio between the protons with chemical shift of δ7.58 and δ2.47 was used to determine the actual monomer percentage in the polymer sample.



Scheme 2. Synthesis of 4,4′-[*trans*-1,4-cyclohexanediylbis(methylene)] bisphenol based homopolymer ($x = 1$, R_1 = CMB) and random copolymers.

2.4.2. Synthesis of high molecular weight 4,4′-dihydroxy-p-biphenyl (DHBP) based polysulfone as a property control

The DHBP based PAES was synthesized with comparable high molecular weight to the commercial Radel® R sample. Both the Radel® R sample and the lab-synthesized high molecular weight DHBP based PAES sample were used as controls in the thermal and mechanical property evaluations. The high molecular weight DHBP based PAES sample was synthesized in the same way as described in the polymer synthesis paragraph above but with a stoichiometry imbalance to control the molecular weight based on the Carothers equation.

2.5. Polymer film preparation

Film samples were obtained by solution casting. The solid polymer sample was dissolved at room temperature in chloroform, DMAc, or NMP to offer a homogeneous solution with a concentration of 10% wt. The polymer solution was filtered through a 45 μm micro glass fiber filter and then was cast on a leveled glass substrate with a syringe, dried at 80 °C for 12 h, and subsequently dried at 120 °C under vacuum (−80 kPa) for 12 h. After drying, the tough film was separated from the glass substrate. Dog bone samples for the mechanical property evaluation were prepared from the polymer films by a dog bone puncher on a Teflon substrate. The dimensions on the tested area were 4.0 mm in width and about 20 mm in length. The thickness of the samples was in the range of 60–100 μm. All the soluble polymers formed transparent tough films with no color or a light yellow color.

3. Results and discussion

3.1. Synthesis of 4,4′-[trans-1,4-cyclohexanediylbis(methylene)] bisphenol (CMB) monomer

The CMB monomer was successfully synthesized in four steps with an overall yield of 77%. The key reaction step was the Wolff-Kishner-Huang reduction reaction [15] where a strong base

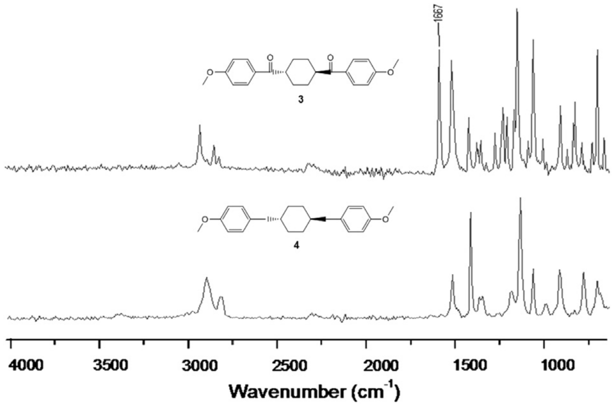


Fig. 1. FT-IR spectra monitoring the Wolff-Kishner-Huang reduction reaction.

(potassium hydroxide), a reducing agent (hydrazine monohydrate), and a high boiling point solvent (diethylene glycol) were used (shown in Scheme 1). The FT-IR spectra in Fig. 1 clearly showed the characteristic adsorption of the carbonyl group at 1667 cm^{-1} was eliminated which was indicative of the successful reduction of the carbonyl. The structures of compound 3 and 4 were confirmed by ^{1}H NMR and ^{13}C NMR. They also exhibited sharp melting points.

In the CMB monomer synthesis, *trans*-CHDA was used as the starting material. In Scheme 1, the configurations of the cyclohexylene rings were carefully monitored by NMR. For example, the 1d ^{1}H NMR of CMB is shown in Fig. 2 with the 2d H–H Correlation Spectroscopy (COSY) NMR shown in Fig. 3. The enlarged area in Fig. 2 showed the aliphatic ring protons where F protons were the cyclohexyl protons and D protons were the methylene protons between the phenyl rings and the cyclohexylene rings. Based on the H–H COSY NMR spectra, the only H–H correlation of D protons was with the F protons, which confirmed that the F protons were the cyclohexyl protons. Due to the fact that only one signal (broadened by multiple splitting) was observed for both D and F protons, the cyclohexylene ring in the CMB monomer remained in the *trans*-configuration. The cyclohexyl proton single peak (broadened by multiple splitting) was consistent with the raw material (*trans*-CHDA) NMR spectrum and agreed with the reference observation [4,16]. All the cyclohexylene ring-containing compounds and polymers showed the same proton NMR pattern which confirmed the *trans*-configurations. The CMB monomer structure and purity were further confirmed by ^{13}C NMR, HRMS and elemental analysis.

3.2. Polysulfone homopolymer and random copolymers based on 4,4′-[trans-1,4-cyclohexanediylbis(methylene)] bisphenol (CMB), 4,4′-dihydroxy-p-biphenyl (DHBP) and 4,4′-dihydroxy-p-terphenyl (DHTP)

3.2.1. Characterization of the cyclohexylene ring-containing polysulfones

The PAES homopolymer based on CMB as the only bisphenol and the random copolymers based on different ratios of CMB and DHBP (or DHTP) were all synthesized with high yield. In the random copolymer names, the numbers after the acronyms indicate the molar percentages of the phenol monomers. For example, CMB75DHBP25 is the random copolymer made with 75 M percent of CMB, 25 M percent of DHBP, and 100 M percent of DCDPS. The configurations of the cyclohexylene ring units in the polymers were monitored by ^{1}H NMR. The ^{1}H NMR of the homopolymer based on CMB is shown in Fig. 4 as an example. The aliphatic ring proton area in all the soluble polymer samples displayed the same pattern as shown in the CMB monomer in Fig. 2. Only one signal was observed for F (broadened by multiple splitting) and D protons which indicated the cyclohexylene ring units retained the *trans*-configuration and no isomerization reactions occurred during the polymerizations.

3.2.2. Homopolymer and random copolymers based on 4,4′-[trans-1,4-cyclohexanediylbis(methylene)] bisphenol (CMB) and 4,4′-dihydroxy-p-terphenyl (DHTP)

The compositions, molecular weights, thermal properties of CMB/DHTP polysulfone random copolymers are summarized in Table 1. The CMB50DHTP50 and CMB25DHTP75 polymer samples exhibited limited solubility in all common organic solvents including chloroform, dichloromethane, DMF, DMAc, and NMP, etc. even at 80 °C for the high boiling point solvents. Therefore molecular weight and monomer composition results were not obtained for these two samples. CMB75DHTP25 was soluble in DMAc and NMP.

Glass transition temperatures were observed to increase from 172 °C to 222 °C as the DHTP content increased from 0 to 75 M percent. These results are expected due to the rigidity of the DHTP units and the trends were similar to our previous work on DHTP containing polysulfones [14]. No melting points were observed in the CMB homopolymer and CMB/DHTP random copolymers. The polymers all showed excellent resistance to thermal decomposition. The decomposition temperatures (defined as 5% weight loss temperatures in nitrogen) were observed higher than 460 °C. The decomposition temperatures increased from 466 °C to 510 °C when DHTP content increased from 0 to 75 M percent. Similar high

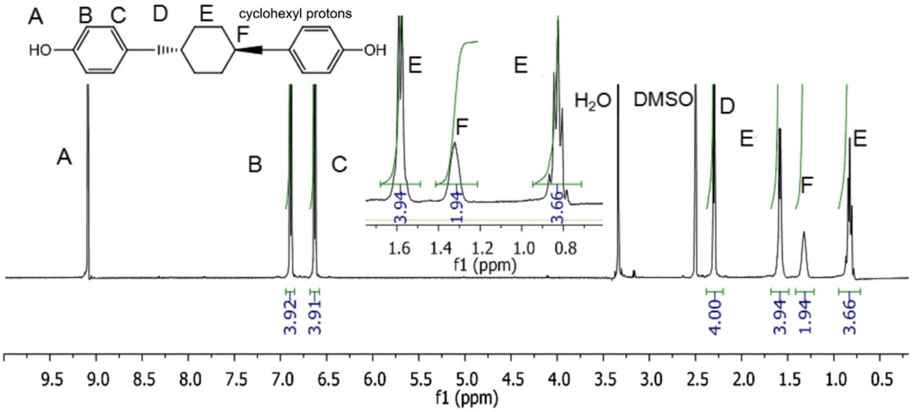


Fig. 2. 1d ^{1}H NMR spectrum of the CMB monomer.

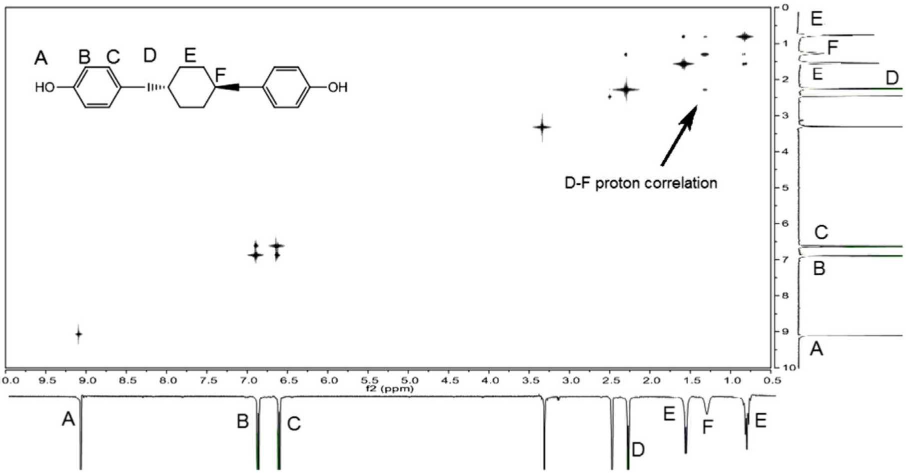


Fig. 3. 2d H–H COSY spectrum of the CMB monomer.

decomposition temperatures also have been reported in polymers with DHTP moiety [17].

Due to the solubility issues and the unknown molecular weights of the CMB50DHTP50 and CMB25DHTP75 samples, the structure analogs of CMB75DHTP25 were prepared to perform a mechanical property comparison. The structures are shown in Fig. 5. These polymers were all soluble in DMAc which allowed us to cast films from homogeneous 10 weight percent solutions. Transparent tough films with no color or a light yellow color were obtained. Mechanical properties were obtained from the dog bone samples made from the film samples. The compositions, molecular weights, and thermal properties of these random copolymers were summarized in Table 2. As shown in the table, the actual monomer compositions determined by ^{1}H NMR exhibited an excellent agreement with the monomer feed compositions. The cyclohexylene ring-containing polymers (CMB75DHBP25 and CMB75DHTP25) showed lower glass transition temperatures in the vicinity of 190 °C due to the flexibility provided by the *trans*-1,4-cyclohexylene ring units incorporated in the CMB monomer via low energy conformational changes. This result agreed very well with our recent results on a series of PAESs based on the *trans*-1,4-cyclohexylene ring-containing acid chloride monomers [13]. The CMB75DHTP25 sample showed slighter higher T_g than CMB75DHBP25 sample due to the backbone rigidity increase by replacing the biphenyl units with the terphenyl units. All three polymers showed excellent resistance to thermal decomposition with decomposition temperatures all higher than 470 °C. Comparable molecular weights were obtained with M_n higher than 35 kg/mol. Reasonable polycondensation Polydispersity Indexes (PDIs) were also obtained. They were slightly lower than the theoretical PDI value of 2.0 because of fractionation in the precipitation process. The SEC traces of the samples were all monomodal with no indication of branching. The comparable high molecular weights and comparable PDIs of these polymers ensured that the mechanical properties were not molecular weight dependent.

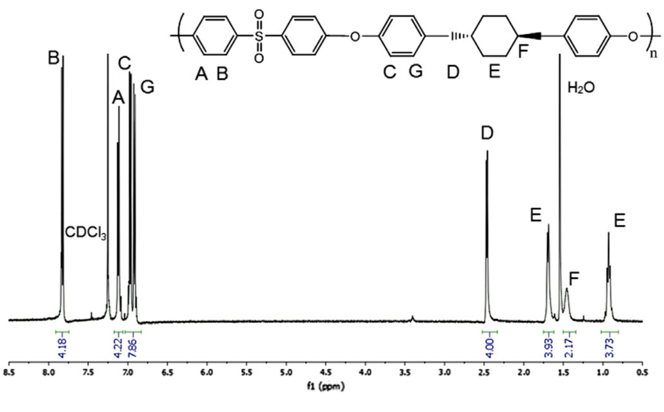


Fig. 4. 1d ^{1}H NMR of the CMB DCDPS homopolymer (CMB100).

The polymers shown in Fig. 5 shared structural similarity exhibiting similar glass transition temperatures and comparable high molecular weights. However mechanically, they showed significantly different behaviors which are shown in Table 3. When DHTP was copolymerized with BisA, the polymer exhibited brittle behavior where the polymer failed immediately after the yield point. When CMB was copolymerized with DHBP, slight improvement was observed over the BisA/DHTP polymer. A significant strain at failure enhancement, about 10-folds over the latter, was observed in CMB/DHTP copolymer. The moduli results of the materials shown in Table 3 indicated that the elongation enhancement was not obtained due to the loss of stiffness.

Tan δ curves obtained from DMA (Fig. 6) showed that the three copolymers had very different relaxation behaviors.

Two relaxations, β-relaxation and γ-relaxation, were observed in the low temperature DMA range of these polymers as shown in Fig. 6. The γ-relaxation in DMA at 1 Hz has been widely reported in cyclohexylene ring-containing polymers and non-cyclohexylene containing polysulfones at around −100 °C. Similar γ-relaxations were also observed in a series of PAESs based on *trans*-1,4-cyclohexylene ring-containing acid chlorides which we recently reported [13]. In a paper by McGrath and coworkers [18], the dynamic mechanical behavior of non-cyclohexylene containing polysulfones was reviewed. The origin of the γ-relaxation was concluded to be a combination of motions of aryl ether bonds and sulfone-water complexes. In the work reported by Yee and coworkers [6,8], Tomomi and coworkers [19], and Credico and coworkers [10], γ-relaxations were observed in DMA studies of cyclohexane ring-containing polycarbonates, polyesters, and poly(1,4-cyclohexylene dimethylene phthalate)-reinforced epoxy resins, respectively. The relaxation peak values were reported in the vicinity of −60 °C for these polymers. All the results listed above were reported for polymer samples containing *cis*/*trans*-mixed cyclohexylene rings. In relaxation studies on the all *trans*-configuration cyclohexylene ring incorporated into poly(butylene 1,4-

Table 1
Compositions, molecular weights, and thermal properties of the CMB/DHTP polysulfone random copolymers.

Polymer	CMB	DHTP	CMB	DHTP	T_g	T_d[c]	Molar mass		PDI
	mol[b] (%)	mol[b] (%)	mol[b] (%)	mol[b] (%)	(°C)	(°C)	(kg/mol)		
							M_n	M_w	
CMB100[a]	100	0	100	0	172	466	28.9	64.2	2.2
CMB75DHTP25	75.0	25.0	74.8	25.2	189	472	35.1	68.5	1.9
CMB50DHTP50	50.0	50.0	NA[d]	NA	207	490	NA[d]	NA	NA
CMB25DHTP75	25.0	75.0	NA	NA	222	510	NA	NA	NA

[a] The numbers indicate the percentage contents of the bisphenol monomers.
[b] The first two columns are the feed compositions of the monomers; the second two columns are the actual monomer percentages determined by ^{1}H NMR.
[c] The decomposition temperature is the 5% weight loss temperature in nitrogen.
[d] The polymers with 50 and 75 M percent of DHTP monomer were not soluble in SEC solvents.

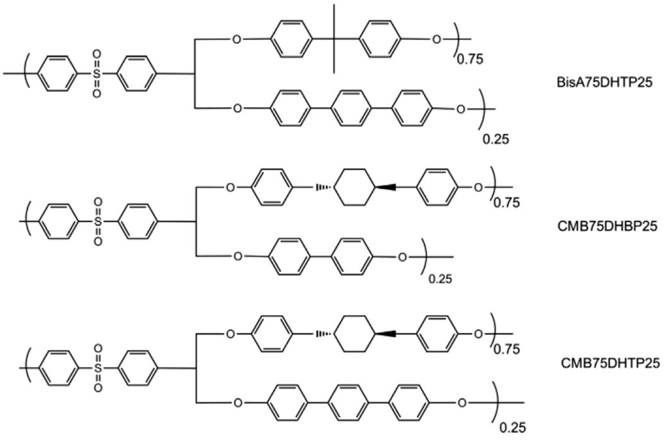


Fig. 5. Structures of CMB or DHTP containing random copolymers.

cyclohexanedicarboxylate) (PBCHD), enhanced γ-relaxations around −100 °C were observed which were attributed to the local motion of the methylene units enhanced by the less polar *trans*-enchained cyclohexylene units when compared to the *cis*-enchained units [10]

In the system shown in Figs. 5 and 6, all the DMA samples were dried at elevated temperature in vacuum which eliminated the formation of the sulfone-water complex suggested by McGrath. The γ-relaxation also only appeared in cyclohexylene ring-containing polymers (CMB75DHTP25 and CMB75DHBP25). Based on these facts and the *trans*-configuration of the cyclohexylene rings, we assigned the γ-relaxation to the motion of the methylene groups and the *trans*-cyclohexylene ring units, probably chair boat conformational transitions under DMA conditions. This assignment agreed with the γ-relaxation observation in PBCHD with all *trans*-configuration cyclohexylene rings. This assignment was also supported by the correlation of the γ-relaxation intensities and the cyclohexylene ring contents in the CMB/DHBP copolymer series shown later in this paper (Fig. 8).

The β-relaxation observed in the low temperature DMA Tan δ curve at around 50 °C has been reported in non-cyclohexylene containing polysulfones in the temperature range of 0 °C–60 °C with no clear conclusion on the origin [18]. Since it showed strong intensity in the BisA75DHTP25 sample, this β-relaxation was likely related to the sulfone units or the aromatic units in the polymers and not the cyclohexylene groups. This hypothesis was also suggested by the CMB/DHBP copolymers DMA study shown later in this paper (Fig. 8).

As shown in Fig. 6, the CMB containing copolymers (CMB75DHTP25 (squares) and CMB75DHBP25 (triangles)) exhibited strong γ-relaxation due to the incorporation of the *trans*-cyclohexylene units. In contrast, only β-relaxation which related with aromatic sulfone units was observed in the BisA75DHTP25 polymer (circles). The γ-relaxation was absent due to the absence of the cyclohexylene ring. The CMB75DHTP25 copolymer (squares) exhibited a strong intensity in both β-relaxation and γ-relaxation which is possibly contributive to the significant ultimate elongation enhancement. In the cases of BisA75DHTP25 copolymer (circles) and CMB75DHBP25 copolymer (triangles), significantly lowered intensities in γ-relaxation and β-relaxation were observed respectively.

3.2.3. Polysulfone homopolymer and random copolymers based on 4,4′-[trans-1,4-cyclohexanediylbis(methylene)] bisphenol (CMB) and 4,4′-dihydroxy-p-biphenyl (DHBP)

To further evaluate the DMA and mechanical behavior of *trans*-cyclohexylene ring-containing PAESs, copolymers based on CMB and DHBP were studied. The CMB/DHBP copolymers were prepared by the same synthetic method as used for the CMB/DHTP copolymers. However, unlike the CMB/DHTP system, the characterization of the CMB/DHBP system was not limited by solubility. The

Table 2
Compositions, molecular weights, and thermal properties of CMB or DHTP containing polysulfone random copolymers.

Polymer	M1	M2	M1	M2	T_g	T_d[c]	Molar mass		PDI
	mol[b] (%)	mol[b] (%)	mol[b] (%)	mol[b] (%)	(°C)	(°C)	(kg/mol)		
							M_n	M_w	
BisA75DHTP25[a]	75.0	25.0	75.2	24.8	207	515	38.2	66.2	1.7
CMB75DHBP25	75.0	25.0	74.4	25.6	186	474	39.9	72.7	1.8
CMB75DHTP25	75.0	25.0	74.8	25.2	189	472	35.1	68.5	1.9

[a] The numbers indicate the percentage contents of the bisphenol monomers.
[b] The first two columns are the feed compositions of the monomer 1 (M1) and monomer 2 (M2); the second two columns are the actual monomer percentages determined by ^{1}H NMR.
[c] The decomposition temperature is the 5% weight loss temperature in nitrogen.

Table 3
Mechanical properties of CMB or DHTP containing polysulfone random copolymers.

Polymers	Modulus (MPa)	Yield stress (MPa)	Strain at yield (%)	Strain at failure (%)
BisA75DHTP25[a]	972 ± 161	40.8 ± 9.0	5.8 ± 0.7	6.4 ± 1.5
CMB75DHBP25	1132 ± 110	55.6 ± 5.7	6.6 ± 0.8	9.9 ± 3.8
CMB75DHTP25	1055 ± 67	52.4 ± 4.2	7.2 ± 0.5	118 ± 19

[a] The numbers indicate the percentage contents of the bisphenol monomers.

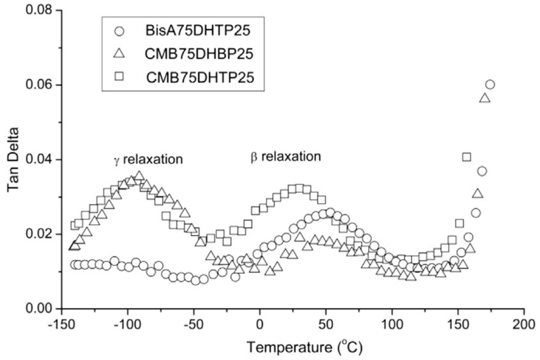


Fig. 6. The dynamic mechanical analysis results of BisA75DHTP25 (circles), CMB75DHBP25 (triangles), and CMB75DHTP25 (squares) copolymer.

good solubility of the polymers allowed the property comparisons to be performed with different phenol monomer contents. The compositions, molecular weights, and thermal properties are shown in Table 4. As shown in the table, the actual monomer percentages determined by ^{1}H NMR were very close to the monomer feed percentages. The SEC traces of the samples were all monomodal with no indication of branching. The homopolymer and random copolymers exhibited high molecular weights with number average molecular weights around 30 kg/mol and PDIs close to 2.0. The comparable high molecular weights of the new PAESs ensured that thermal properties and mechanical properties results were from structural and/or composition differences not molecular weight based effects. These polymer samples were readily soluble in chloroform, DMF, DMAc, NMP at room temperature but not in THF and methanol.

As expected, decreasing glass transition temperatures were observed in DSC with increasing CMB incorporation as shown in Table 4. The decreasing glass transition temperature was due to the enhanced flexibility in backbone from the incorporated cyclohexylene rings. This agreed with the previous conclusion based on the data in Table 2 and the previously published results [13]. No melting points were observed in the CMB homopolymer and CMB/DHBP random copolymers. All the polymer samples exhibited high resistance to thermal decomposition. In nitrogen, the thermal degradation temperatures at 5% weight loss were all observed around 450 °C.

Table 5
Mechanical properties of the CMB homopolymer and CMB/DHBP polysulfone random copolymers.

Polymers	Modulus (MPa)	Yield stress (MPa)	Strain at yield (%)	Strain at failure (%)
Radel® R[a]	1353 ± 92	62.3 ± 6.0	7.0 ± 1.0	8.1 ± 1.3
DHBP PAES[b]	1498 ± 140	82.3 ± 5.7	7.8 ± 0.7	7.9 ± 0.8
CMB100[c]	1157 ± 31	64.8 ± 3.5	8.2 ± 0.9	14.3 ± 6.0
CMB75DHBP25	1132 ± 110	55.6 ± 5.7	6.6 ± 0.8	9.9 ± 3.8
CMB50DHBP50	1130 ± 302	58.8 ± 4.8	10.4 ± 3.4	18.2 ± 4.0
CMB25DHBP75	1063 ± 51	50.2 ± 5.0	9.4 ± 5.7	21.1 ± 4.0

[a] Provided by Solvay Advanced Polymers L.L.C.
[b] Lab synthesized DHBP based PAES.
[c] The numbers indicate the percentage content of the bisphenol monomers.

The excellent solubility of the homopolymer and CMB/DHBP copolymer system allowed us to cast films from homogeneous 10 weight percent DMAc solution. Transparent tough films with no color or a light yellow color were obtained. Mechanical properties were obtained from dog bone samples made from the films. The film samples of Radel® R provided by Solvay Advanced Polymers L.L.C. and the lab synthesized DHBP based PAES with comparable high molecular weight were used as the mechanical property controls with the same solvent casting technique. As the tensile results show in Table 5, the CMB containing polymers exhibited slightly reduced moduli when compared to the controls, however, independent of the monomer percentages in the copolymer, all CMB containing polymers showed similar moduli values. Moderate strain at failure enhancement was observed for the CMB homopolymer and CMB/DHBP copolymers. The largest strain at failure value about 20% was observed in the CMB25DHBP75 sample.

Figs. 7 and 8 show the dynamic mechanical analysis data of the tan δ curves with relaxations in the decreasing temperature sequence of α, β, γ peaks. The relaxations shown in the high temperature region (Fig. 7) are the α-relaxations which correspond to the relaxations at the glass transition. With increasing CMB content, a shift of the α-relaxation peak value to the lower temperatures was observed. These results agreed well with the glass transition values obtained from the DSC measurements shown in Table 4. In the low temperature region, two series of relaxations, the β and γ-relaxations, were observed and are shown in Fig. 8.

Table 4
Compositions, molecular weights, and thermal properties of CMB homopolymer and CMB/DHBP polysulfone random copolymers.

Polymer	CMB	DHBP	CMB	DHBP	T_g	T_d[e]	Molar mass		PDI
	mol[d] (%)	mol[d] (%)	mol[d] (%)	mol[d] (%)	(°C)	(°C)	(kg/mol)		
							M_n	M_w	
Radel® R[a]	–	–	–	–	220	526	14.2	28.8	2.0
DHBP PAES[b]	–	–	–	–	227	565	21.6	37.4	1.7
CMB100[c]	100	0	100	0	172	466	28.9	64.2	2.2
CMB75DHBP25	75.0	25.0	74.4	25.6	186	474	39.9	72.7	1.8
CMB50DHBP50	50.0	50.0	49.7	50.3	199	453	40.3	84.6	2.1
CMB25DHBP75	25.0	75.0	24.1	75.9	214	442	34.7	68.2	2.0

[a] Provided by Solvay Advanced Polymers L.L.C.
[b] Lab synthesized DHBP based PAES.
[c] The numbers indicate the percentage content of the bisphenol monomers.
[d] The first two columns are the feed compositions of the monomers; the second two columns are the actual monomer percentages determined by ^{1}H NMR.
[e] The decomposition temperature is the 5% weight loss temperature in nitrogen.

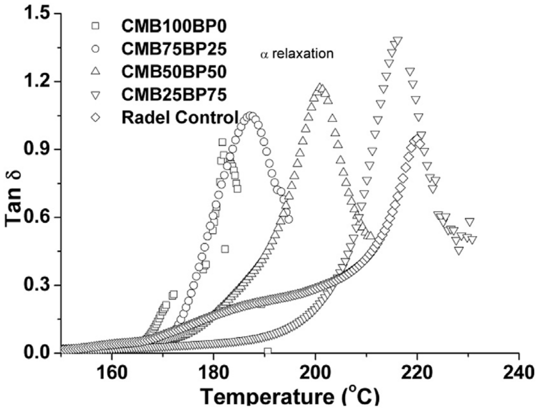


Fig. 7. Dynamic mechanical analysis results of the CMB/DHBP copolymers in the high temperature region.

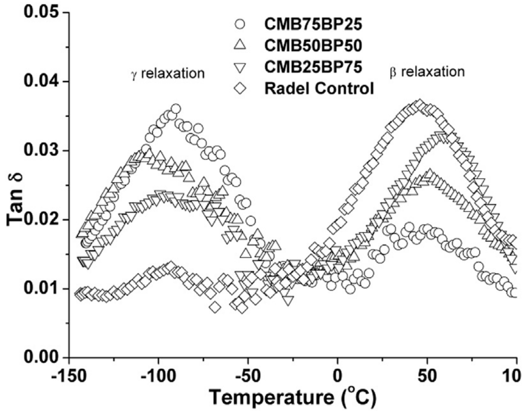


Fig. 8. Dynamic mechanical analysis results of the CMB/DHBP copolymers in the low temperature region.

As shown in Fig. 8, with increasing CMB content, the intensity of the γ-relaxations at around −100 °C was observed to significantly increase. In the CMB/DHTP copolymers, the γ-relaxation was assigned to be the motion of the methylene groups and the *trans*-cyclohexylene ring units, probably chair boat conformational transitions. In the CMB/DHBP system, this clear trend of increase in intensities of the γ-relaxation peak values with increasing *trans*-cyclohexylene content strongly supported this assignment. A decrease in the intensity of β-relaxation with increasing *trans*-cyclohexylene content was also observed in the CMB/DHBP copolymers as shown in Fig. 8. This result indicated that the β-relaxation was likely related to aromatic units or sulfone units but not the cyclohexylene group as stated in the CMB/DHTP system discussion.

4. Conclusions

In this paper, we prepared 1,4-*trans*-cyclohexylene ring-containing poly(arylene ether sulfone)s based on a new CMB bisphenol monomer with 4,4′-*trans*-1,4-cyclohexanediylbis(-methylene) unit. The monomer and the polymers were carefully characterized. The mechanical properties and relaxation characteristics were studied. A ten-fold elongation to break enhancement was observed in the CMB75DHTP25 polymer, which may be a result of the strong sub-T_g β-relaxation and γ-relaxation. In the CMB/DHBP copolymers, moderate strain at failure improvements with reduced moduli were observed. The sub-T_g relaxations were assigned based on the previous studies and the DMA study of the CMB/DHBP and CMB/DHTP systems. The β-relaxation was assigned to the sulfone units or the aromatic units in the polymers. The γ-relaxation was assigned to the combination motion of the cyclohexylene ring and the methylene groups.

Acknowledgments

This research was sponsored by the Army Research Laboratory and was accomplished under Cooperative Agreement Number W911NF-06-2-0014. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing official policies, either expressed or implied, of the Army Research Laboratory or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation hereon. We acknowledge the assistance of the Department of Chemistry and the Macromolecules and Interfaces Institute at Virginia Tech. We are grateful to Solvay Advanced Polymers L.L.C. and Eastman Chemical Company for supplying chemicals. We appreciate the assistance of Professor Long's, Professor Riffle's, and Professor McGrath's groups at Virginia Tech.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.06.018.

References

[1] Robeson LM, Farnham AG, McGrath JE. Appl Polym Symp 1975;26:373–85. Polym. Polycondensat.
[2] Rose JB. Polymer 1974;15:456.
[3] Rao YQ, Greener J, Avila-Orta CA, Hsiao BS, Blanton TN. Polymer 2008;49(10):2507–14.
[4] Osano K, Das S, Turner SR. Polymer 2009;50(5):1144–9.
[5] Li X, Yee AF. Macromolecules 2003;36(25):9421–9.
[6] Li X, Yee AF. Macromolecules 2003;36(25):9411–20.
[7] Li X, Yee AF. Macromolecules 2004;37(19):7231–9.
[8] Liu J, Yee AF. Macromolecules 1998;31(22):7865–70.
[9] Liu J, Yee AF. Macromolecules 2000;33(4):1338–44.
[10] Berti C, Celli A, Marchese P, Marianucci E, Barbiroli G, Di Credico F. Macromol Chem Phys 2008;209(13):1333–44.
[11] Berti C, Celli A, Marchese P, Marianucci E, Sullalti S, Barbiroli G. Macromol Chem Phys 2010;211(14):1559–71.
[12] Scheirs J, Long TE. Modern polyesters: chemistry and technology of polyesters and copolyesters. 1st ed. Wiley; 2003.
[13] Zhang B, Turner SR. J Polym Sci Part A Polym Chem 2011;49(20):4316–24.
[14] Mao M, Das S, Turner SR. Polymer 2007;48(21):6241–5.
[15] Huang M. J Am Chem Soc 1946;68:2487–8.
[16] Supporting materials.
[17] Salunke AK, Madhra MK, Sharma M, Banerjee S. J Polym Sci Part A Polym Chem 2002;40(1):55–69.
[18] Robeson LM, Farnham AG, McGrath JE. Midl Macromol Monogr 1978;4:405–25. Mol. Basis Transitions Relaxations.
[19] Lijima T, Ohnishi K, Fukuda W, Tomoi M. Polym Int 1998;45(4):403–13.