Polymer 50 (2009) 1144–1149

Contents lists available at ScienceDirect

Polymer

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

Synthesis and characterization of cyclohexyl-containing poly(ether ketone sulfone)s

Keiichi Osano[a], Sudipto Das[b], S. Richard Turner[a,*]

[a] Department of Chemistry, Macromolecules and Interfaces Institute (MII), Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA
[b] Department of Chemical Engineering, Macromolecules and Interfaces Institute (MII), Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

ARTICLE INFO

Article history:
Received 16 October 2008
Received in revised form
7 January 2009
Accepted 10 January 2009
Available online 15 January 2009

Keywords:
Polysulfones
Polyketones
1,4-Cyclohexyl

ABSTRACT

A series of poly(ether ketone sulfone)s were synthesized from 1,4-di(fluorobenzoyl)cyclohexane, difluorodiphenylsulfone and bisphenol A. These polymers were characterized by NMR, IR, SEC, DSC, TGA, tensile tests and DMA. The results from NMR, IR, and SEC indicated that essentially no side reactions, such as cross-linking, associated with enolate chemistry take place during the polymerizations although cis/trans stereochemistry inversion was observed. Comparison of the T_gs of the polymers with 1,4-cyclohexyl units to those of the terephthaloyl analogs suggested that the trans-1,4-cyclohexyl imparts slightly higher T_g than the terephthaloyl control. Tensile tests and DMA revealed that polymers with 1,4-cyclohexyl have essentially the same storage moduli as the corresponding aromatic analogs despite the inherent flexibility of the cyclohexyl unit. DMA also showed that the cyclohexyl unit imparts a larger magnitude of sub-T_g motion than terephthaloyl unit while maintaining high modulus.

1. Introduction

Poly(arylene ether ketone)s and poly(arylene ether sulfone)s, or simply polyketones and polysulfones, are widely known as high T_g engineering thermoplastics with excellent hydrolytic and thermal stabilities [1,2]. Although there are several synthetic methods for these polymers, they are mainly synthesized in solution by the nucleophilic aromatic substitution (S_NAr) between bisphenols and aromatic dihalides, which requires high reaction temperatures (typically $>150\,^\circ C$) in the presence of weak bases such as K_2CO_3 and Na_2CO_3 [1,2]. A large number of polysulfones and polyketones have been reported and several amorphous polysulfones and semi-crystalline polyketones are commercially available today [1,2]. There remains, however, some structural modifications of these polymer classes that have not been explored. Previously, our research group has reported polysulfones with biphenyl and terphenyl segments in search of novel high performance materials [3]. Another intriguing and unexplored modification is to incorporate cyclohexyl groups. Cyclohexyl groups have been incorporated into a wide variety of polyesters and poly(ester carbonate)s to impart desirable physical properties [4–13]. Polyesters based on 1,4-cyclohexanedimethanol (CHDM) are perhaps the most well known examples of polymers containing 1,4-cyclohexyl groups in the backbone. The incorporation of CHDM into a polymer backbone is known to enhance impact performance and can have a major influence on crystallization rate [12]. Many examples of polyesters containing CHDM are commercial products [12]. Although incorporation of such aliphatic groups into polysulfones and polyketones would probably lower the thermal stabilities of the polymers, the fundamental structure-property relationships of such cyclohexyl-containing polyketones and polysulfones are of interest. We recently prepared 1,4-di(4-fluorobenzoyl)cyclohexane (**3**) conveniently in two steps from commercially available 1,4-cyclohexanedicarboxylic acid (CHDA, **1**). This monomer can be incorporated into either polyketones or polysulfones by the common S_NAr route. To the best of our knowledge, very little work has been reported to investigate the effects of the 1,4-cyclohexyl unit on the mechanical and thermal properties of polysulfones and polyketones. In this paper, we report the synthesis and characterization of bisphenol A (BPA)-based poly(ether ketone sulfone)s containing 1,4-cyclohexyl groups. We compare the properties of these 1,4-cyclohexyl-containing polymers with analogous polymers containing terephthaloyl groups. Bisphenol A was chosen as the bisphenol for our first investigation because its structure imparts high solubility to the polymers, which allows for important solution characterizations such as NMR and SEC.

---

* 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 © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.01.025

2. Experimental

2.1. General

All chemicals were purchased from Aldrich and used as received with an exception of trans-1,4-CHDA which was a gift from Eastman Chemical Company.

^{1}H and ^{13}C NMR spectra were obtained by a Varian Inova 400 (400 MHz) spectrometer at room temperature with chemical shifts relative to tetramethylsilane (TMS). Differential Scanning Calorimetry (DSC) data were obtained from a Perkin Elmer Pyris1. Samples were run under nitrogen with a flow rate of 20 ml/min and a heating rate of 10 °C/min. The second heating cycle was used to determine T_gs. Thermogravimetric analysis (TGA) was carried out by a TA Instruments TGA2950 from 25 °C to 800 °C under nitrogen at a heating rate of 10 °C/min. Size Exclusion Chromatography (SEC) were recorded 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. 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. Elemental analysis was done by Atlantic Microlab, Inc (Norcross, Georgia). Tensile tests were performed on an Instron Model 4400 Universal Testing System with Series IX software. Samples (10 mm gauge length and 2.91 mm width) were cut by a standard bench-top die from compression-molded films (0.5 mm thickness). A Seiko DMS 210 with an attached autocooler was used in tension mode. Dynamic mechanical spectra of samples were recorded at a heating rate of 2 °C/min while they were deformed (10 μm amplitude) in the tension mode at a frequency of 1 Hz under nitrogen. A Zess Polarizing Optical Microscopy (POM) and a LEO 1550 Field Emission Scanning Electron Microscopy (SEM) with 5 kV accelerating voltage were used to investigate the presence of any crystallinity in solution-cast films. These films were cast from chlorobenzene on glass plates. The solvent was evaporated over 72 h at ambient condition and then in a vacuum oven overnight.

2.2. Synthesis of monomers

2.2.1. Preparation of trans-1,4-di(4-fluorobenzoyl)cyclohexane (*3a*)

Compound **3a** was prepared by Friedel–Craft acylation of fluorobenzene with 1,4-cyclohexanedicarbonyl chloride [14] (**2a**) (Scheme 1). 27.5 g (0.206 mol) $AlCl_3$ was placed in a flask containing 100 ml fluorobenzene and a magnetic stirring bar. This mixture was cooled under argon in an ice-water bath. To this mixture, 19.5 g (0.0933 mol) of **2a** dissolved in 50 ml fluorobenzene was added dropwise through a dropper. After the addition, the ice-water bath was removed and the mixture was stirred at room temperature for 8 h. The mixture was then poured into crushed ice to terminate the reaction and stirred overnight. The aqueous phase was decanted by the use of a separatory funnel. Fluorobenzene was evaporated on a rotary evaporator and the mixture was dried under high vacuum at 40 °C for 5 h. The white crude product was recrystallized from DMAc twice. The white crystalline solid was dried under high vacuum at 80 °C overnight to give 18.55 g of **3a**. Yield: 61%. mp: 210 °C. ^{1}H NMR ($CDCl_3$, ppm): δ7.97 (m, 4H), 7.15 (m, 4H), 3.29 (m, 2H), 2.01 (m, 4H), 1.64 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ201.8, 164.7, 132.6, 131.1, 116.0, 45.0, 28.8. Elemental Analysis: calculated C, 73.16; H, 5.53. found: C, 72.93; H, 5.45.

2.2.2. Preparation of a cis/trans (60/40) mixture of 1,4-di(4-fluorobenzoyl)cyclohexane (*3b*)

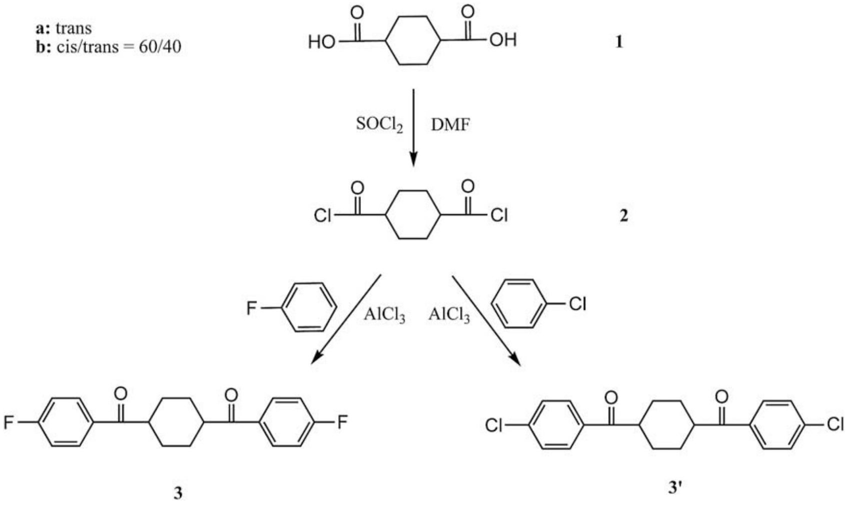
Compound **3b** was prepared from 18.5 g (0.0885 mol) of **2b** using the same procedure as above except that toluene was used as a recrystallization solvent. 21.3 g of **3b** was obtained. Yield: 73%. mp: 156 °C. ^{1}H NMR ($CDCl_3$, ppm): δ7.97 (m, 4H), 7.92 (m, 6H), 7.15 (m, 4H), 7.14 (m, 6H), 3.40 (m, 3H), 3.29 (m, 2H), 2.01 (m, 4H), 1.95 (m, 6H), 1.77 (m, 6H), 1.64 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ201.5, 166.8, 164.3, 132.6, 132.3, 130.8, 130.7, 115.8, 115.5, 44.7, 42.7, 28.6, 26.1. Elemental Analysis: calculated C, 73.16; H, 5.53. found: C, 72.98; H, 5.43.

2.2.3. Preparation of trans-1,4-di(4-chlorobenzoyl)cyclohexane (*3′a*)

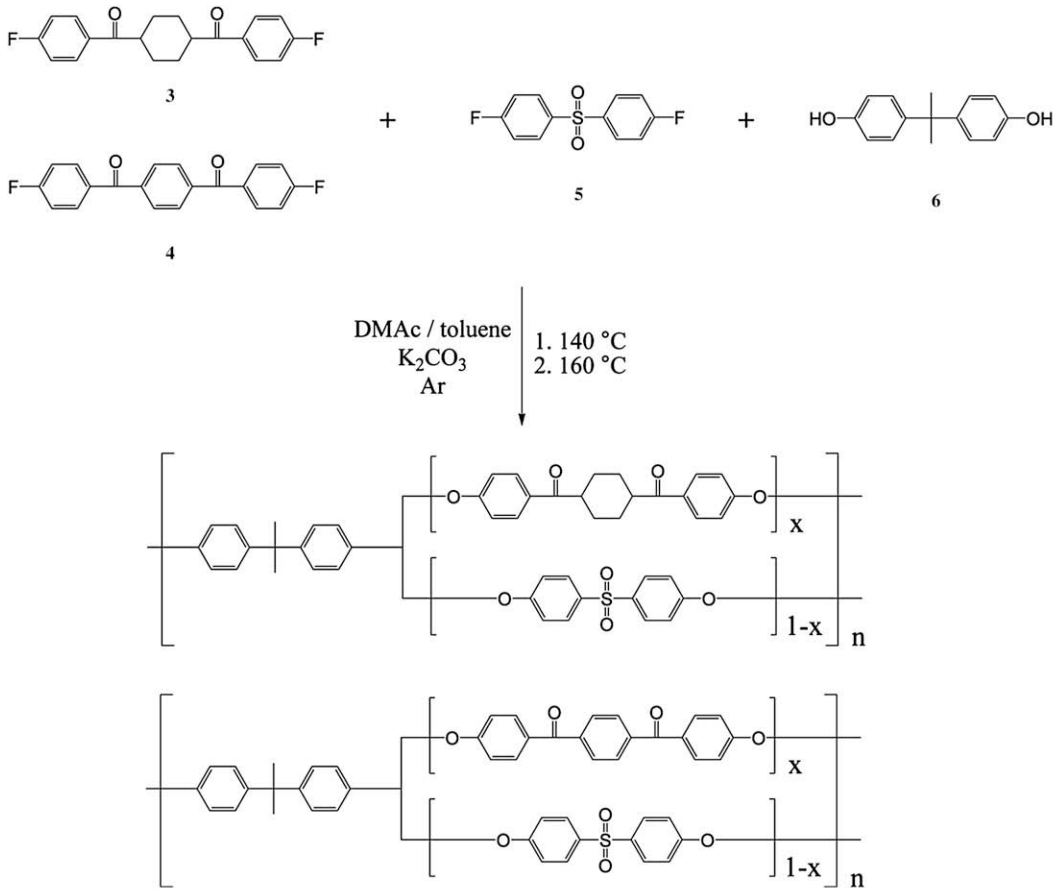
Compound **3′a** was prepared from 20.0 g of **2a** using the same procedure as **3a** except that chlorobenzene was used in Friedel–Crafts acylation. 11.20 g of **3′a** was obtained. Yield: 32%. mp: 230.6 °C. ^{1}H NMR ($CDCl_3$, ppm): δ7.87 (m, 4H), 7.42 (m, 4H), 3.25 (m, 2H), 2.01 (m, 4H), 1.64 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ201.9, 139.5, 134.2, 129.6, 129.0, 44.8, 28.5. Elemental Analysis: calculated C, 66.49; H, 5.02. found: C, 66.42; H, 5.03.

2.2.4. Synthesis of 1,4-di(4-fluorobenzoyl)benzene (*4*)

Compound **4** was prepared from terephthaloyl chloride as described by Zhao and Carreira [15]. The ^{1}H and ^{13}C NMR spectra of this compound matched those reported in their paper.



Scheme 1. Synthesis of 1,4-di(4-fluorobenzoyl)cyclohexane (**3**) and 1,4-di(4-chlorobenzoyl)cyclohexane (**3′**).



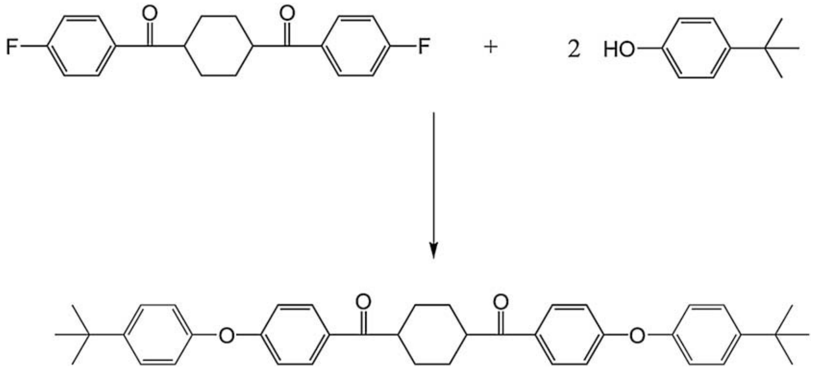
Scheme 2. Synthesis of poly(ether ketone sulfone)s.

2.3. Synthesis of polymers

In this paper, we give polymer samples descriptive names. For a polymer made from 100% **3a** and 0% 4,4′-difluorodiphenylsulfone (DFDPS, **5**), for example, the name is P-C100S0. The letters, C and S, stand for cyclohexyl and sulfone and the numbers indicate mol% of cyclohexyl and sulfone units, respectively. For samples made from the cis/trans mixture (**3b**), the first letter used is P′ (e.g. P′-C100S0). For terephthaloyl-containing controls, we use the letter T in place of C (e.g. P-T100S0).

2.3.1. Synthesis of cyclohexyl-containing poly(ether ketone sulfone)s

Polymers were synthesized from **3**, **5**, and BPA (**6**) (Scheme 2). The detailed procedure for P-C100S0 is as follows. 2.885 g (0.01264 mol) of **6**, 4.149 g (0.01264 mol) of **3a**, 3.50 g (0.0253 mol) of K_2CO_3, 30 ml of DMAc and 15 ml of toluene were added to a flask equipped with a mechanical stirrer and argon inlet. Water was removed by azeotropic distillation at 140 °C for 3 h. Then toluene was distilled out by increasing the temperature to 160 °C. The polymerization was allowed to continue until a highly viscous



Scheme 3. Model reaction for cis–trans inversion of 1,4-cyclohexyl unit.

Table 1
Molecular weights of soluble poly(ether ketone sulfone)s by SEC.

ID	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)
P-C25S75	4.0×10^4	6.1×10^4	1.5
P-C50S50	3.6×10^4	5.3×10^4	1.5
P-C75S25	3.0×10^4	4.5×10^4	1.5
P'-C25S75	5.2×10^4	7.3×10^4	1.4
P'-C50S50	3.1×10^4	5.8×10^4	1.9
P'-C75S25	4.3×10^4	7.9×10^4	1.8
P-T25S75	3.8×10^4	6.5×10^4	1.7
P-T50S50	2.7×10^4	4.9×10^4	1.8
P-T75S25	3.4×10^4	5.4×10^4	1.6
P-T100S0	2.3×10^4	4.6×10^4	2.0

Table 2
Thermal properties and cis/trans ratios of BPA-based poly(ether ketone sulfone)s.

ID	Final c/t	mol% **3a**	mol% **3b**	mol% **4**	mol% **5**	T_g (°C)	T_m (°C)	T_d[a] (°C)
P-C25S75	15/85	25	0	0	75	185	–	450
P-C50S50	14/86	50	0	0	50	178	216	445
P-C75S25	18/82	75	0	0	25	176	–	440
P-C100S0	–	100	0	0	0	173	–	437
P'-C25S75	17/83	0	25	0	75	180	–	416
P'-C50S50	18/82	0	50	0	50	174	–	436
P'-C75S25	17/83	0	75	0	25	169	–	399
P'-C100S0	–	0	100	0	0	178	–	390
P-T25S75	–	0	0	25	75	181	–	486
P-T50S50	–	0	0	50	50	172	–	497
P-T75S25	–	0	0	75	25	166	–	496
P-T100S0	–	0	0	100	0	164	205	504

[a] 5% weight loss under nitrogen.

mixture was obtained (3–5 h). The mixture was transferred into a beaker containing 800 ml dilute aqueous HCl and allowed to stand overnight. The water was decanted and the white solid was washed with hot water to remove any trapped salts and was dried under high vacuum at 130 °C overnight to give 6.3 g of a white polymer. The same procedure was employed to prepare other polymer samples.

2.3.2. Synthesis of terephthaloyl-containing poly(ether ketone sulfone)s

Polymers were prepared by the same procedure as the cyclohexyl-containing polymers except that **4** was used in place of **3**.

2.3.3. Model reactions for cis–trans inversion

1.000 g (3.046 mmol) of **3a** and 0.915 g (6.092 mmol) of tert-butylphenol were exposed to the same condition as the polymerization procedure in DMAc (Scheme 3). After the reaction, the mixture was cooled to room temperature and filtered to remove inorganic salts. The solvent was evaporated under high vacuum at 80 °C overnight. The white solid was analyzed by ^{1}H NMR. The same experiment was performed on **3b** as well.

3. Results and discussion

An attempt to synthesize a high molecular weight polymer from BPA and **3′a**, which is a much more economical monomer than either **3a** or **3b** due to the lower cost of chlorobenzene than fluorobenzene, was unsuccessful apparently because of the much lower reactivity of the chloride than the analogous fluoride. The reaction mixture never became viscous after 72 h of reaction and even started to take on dark brown color due to the prolonged reaction time. The resultant product was, therefore, not investigated any further and we focus our attention on the polymers made from the fluoro monomers in this paper.

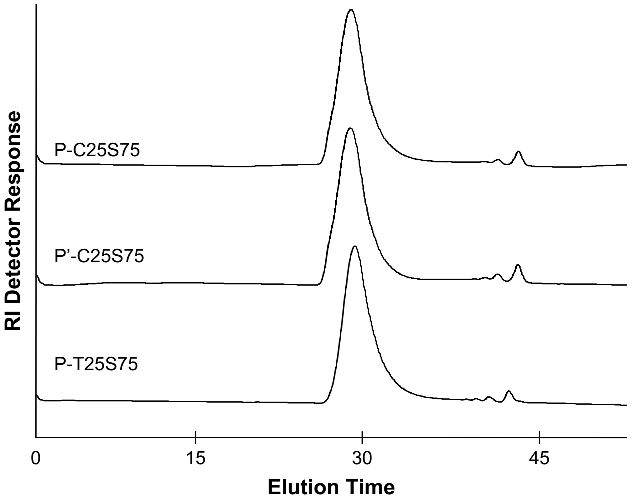


Fig. 1. SEC traces of P-C25S75, P′-C25S75 and P-T25S75.

All polymerizations utilizing the fluoro monomers (**3a**, **3b** and **4**) yielded highly viscous mixtures as the polymerization proceeded to high conversion, which typically took less than 5 h. The samples containing sulfone groups were soluble in common chlorinated solvents at room temperature, such as dichloromethane and chloroform, as expected from the highly kinked structure of sulfone. The molecular weights of the soluble polymers were determined by SEC and are summarized in Table 1. These samples displayed high molecular weights as well as PDIs of about 2 with unimodal traces, suggesting the absence of side reactions during polymerizations. The SEC traces of a few of these samples are shown in Fig. 1 as representatives of these samples. The ^{1}H NMR spectrum of each of these polymers showed that its composition was in good agreement with the initial monomer feed ratio. Also, the fact that none of these ^{1}H NMR spectra showed any vinyl peaks eliminated our concern that side reactions associated with enolate chemistry might happen. In contrast, the polymers with the highest percentage of cyclohexyl unit (P-C100S0 and P′-C100S0) were insoluble in any common organic solvent at room temperature and only soluble in hot (>100 °C) chlorinated and polar aprotic solvents whereas the corresponding terephthaloyl control, P-T100S0, was soluble in chlorinated solvents at room temperature. The solubility differences between the 1,4-cyclohexyl-containing polymers and the 1,4-phenyl-containing polymers were surprising. The IR spectra of the poorly soluble cyclohexyl-containing polymers did not show the presence of vinyl groups or any other difference that could lead to branching or ultimately cross-linked structure. It is possible that this difference in solubility results from the cyclohexyl polymer chains packing more tightly than the aromatic counterparts. Ridgway reported that an increase in T_m brought about by a partial replacement of adipic acid units in nylon 6,6 by CHDA was larger than that caused by terephthalic acid [16]. Although our polymers are not semi-crystalline, the cyclohexyl units may play a role in minimizing the interaction with solvents.

The T_gs, T_ms, and T_ds of the cyclohexyl-containing polymers and of the corresponding terephthaloyl analogs as well as the cis/trans ratios of the cyclohexyl after the polymerizations are shown in Table 2. As can be seen, the cis/trans ratios of the cyclohexyl groups in the polymers changed after the polymerization reactions and very similar cis/trans ratios were observed for polymers made from **3a** and **3b**. The cis/trans ratios were determined by comparing the α-hydrogens on the cis and trans isomers. The ^{1}H NMR spectrum of P-C50S50 is shown in Fig. 2 as a representative of the cyclohexyl-containing polymers. In order to verify the cis–trans inversion in the polymerization reactions, a model study was carried out using

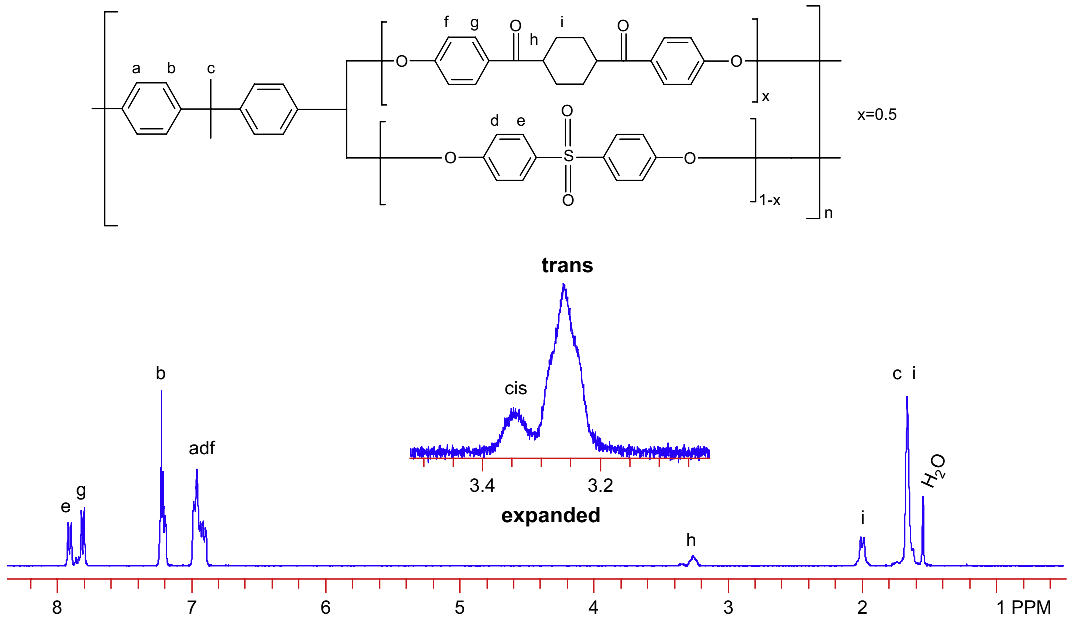


Fig. 2. ^{1}H NMR spectrum of P-C50S50 in d-chloroform.

the all-trans monomer (**3a**) and tert-butylphenol (Scheme 3). The product obtained showed a cis/trans ratio of 15/85. The same experiment performed using **3b** (cis/trans = 60/40) in place of **3a** displayed a cis/trans ratio of 14/86. These observations suggest that cis–trans inversion readily occurs in the polymerizations apparently due to the formation of enolate during the reaction and are consistent with the cis/trans ratios of the final polymers shown in Table 1. A cis/trans ratio of 15/85 has been observed in a CHDA-based polyamide [17] which was synthesized via high-temperature polycondensation.

The comparison of the cyclohexyl-containing polymers with the terephthaloyl-containing controls revealed that all the cyclohexyl-containing polymers had slightly higher T_gs than those of the controls despite the flexibility of the cyclohexyl units. These observations, however, are consistent with the results reported by Yee and Li [10] who compared trans-1,4-cyclohexyl-containing poly(ester carbonate)s to terephthalate-containing analogs and argued that trans-1,4-cyclohexyl unit imparts T_gs slightly higher than or equal to terephthalate because its spatial conformation is very similar to that of 1,4-phenylene linkage which makes the persistence lengths of the polymers essentially the same as those with terephthalate analogs. Yee also reported that poly(ester carbonate)s containing 1,4-cyclohexyl with a cis/trans ratio of 72/28 displayed T_gs remarkably lower than those of all-trans analogs and those of the terephthalate controls because of the much shorter persistent length of the cis isomer [10]. In our case, however, all polymers showed slightly higher T_gs than the corresponding terephthaloyl controls probably because our final polymers have low cis percentages and are essentially all trans.

As shown in Table 2, P-C50S50 and P-T100S0 exhibited melting transitions. However, these melting transitions were very small and only visible on the first heating cycle in DSC, suggesting that these two samples are not semi-crystalline polymers in a practical sense. In fact, P-T100S0 has been reported as an amorphous polymer in the literature [18,19]. All polymers in Table 1, except for the ones containing 75% or higher cyclohexyl (P-C75S25, P-C100S0, P′-C75S25 and P′-C100S0), were compression moldable at 230 °C. Compression molding on P-C75S25, P-C100S0, P′-C75S25 and P′-C100S0, however, gave inhomogeneous films. No melting transitions were observed for these samples by DSC. Nor was any crystallinity detected in their solvent-cast films by POM and SEM, suggesting that the inhomogeneity in these compression molded samples is likely the result of some thermal degradation during the compression molding process due to the large percentages of the cycloaliphatic groups. In fact, the PDI of P-C75S25 increased from 1.5 to 2.5 after the compression molding at 230 °C whereas no significant difference was observed for P-C50S50.

As shown in Table 2, the T_ds for the cyclohexyl-containing polymers were all lower than those of the corresponding terephthaloyl analogs as expected from the aliphatic structure. P-C25S75, for example, showed a T_d of 450 °C whereas its control, P-T25S75, displayed a T_d of 486 °C. The same trend was observed for all the other samples. However, the T_ds of P′ series were lower than those of P series. One possible explanation is that P and P′ series may have slightly different monomer sequences because of the difference in reactivity between the cis and trans isomers.

Tensile tests by Instron revealed that P-C50S50 has essentially the same modulus, yield stress, strain to yield and strain to failure as P-T50S50 (Fig. 3). This was further supported by a plot of storage modulus, E', versus temperature measured by DMA (Fig. 4a), which showed that the modulus of P-C50S50 is the same as or slightly

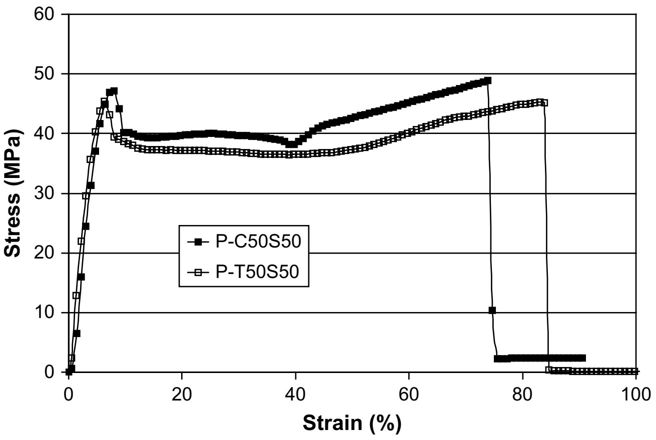


Fig. 3. Stress–strain properties of P-C50S50 and P-T50S50.

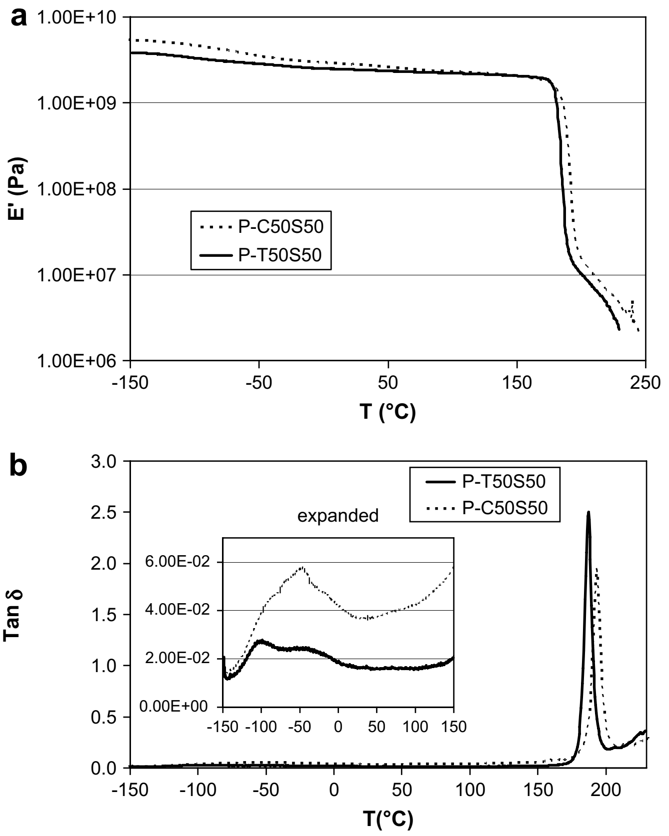


Fig. 4. a: E' versus temperature for P-C50S50 and P-T50S50 by DMA. b: Tan δ versus temperature for P-C50S50 and P-T50S50 by DMA.

higher than that of P-T50S50 at all temperatures investigated. It has also been reported in the literature that no significant change in modulus was observed upon partial substitutions of terephthalate units in PETs by CHDA [5]. Interestingly, a plot of tan δ versus temperature (Fig. 4b) showed that the magnitude of the secondary relaxation for P-C50S50 is larger than that for P-T50S50, meaning that the cyclohexyl units lead to a higher magnitude of sub-T_g motion than the terephthaloyl units apparently due to the flexibility of the cyclohexyl units while maintaining the high modulus.

4. Conclusions

In summary, we have described the synthesis of 1,4-cyclohexyl-containing poly(ether ketone sulfone)s and characterized some of the properties. Despite the relatively low thermal stability of cyclohexyl, it was successfully incorporated into poly(ether ketone sulfone)s by S_NAr without any detrimental side reactions. In spite of its flexibility, the 1,4-cyclohexyl was found to impart slightly higher T_g than the terephthaloyl analog. The results from tensile testing and DMA revealed that the cyclohexyl units lead to essentially the same stress–strain properties as the terephthaloyl control. Also significant was that the cyclohexyl groups lead to a larger magnitude of sub-T_g relaxation than the terephthaloyl control apparently due to their flexibility, suggesting that an incorporation of this cyclohexyl-containing monomer into poly(ether ketone sulfone)s may be a way of improving the impact strength without a loss of modulus. We are currently working to prepare semi-crystalline poly(ether ketone sulfone)s with 1,4-cyclohexyl units in the backbone. Such polymeric materials could possess enhanced chemical resistance and could lead to new biaxially orientable high T_g films.

Acknowledgements

We are grateful to Dr. Timothy Long's group for allowing our group to use their SEC, TGA, and DSC. We would also like to thank Eastman Chemical Company for donating CHDA to us. We would also like to acknowledge Dr. Garth Wilkes for analyzing the morphology of our samples by POM and SEM.

References

[1] Cotter RJ. Engineering plastics: a handbook of polyarylethers. Amsterdam: Gordon and Breach Publishers; 1995.
[2] Devaux J, Carlier V, Bourgeois Y. In: Olabisi O, editor. Handbook of thermoplastics. New York: Marcel Dekker, Inc.; 1997. p. 951.
[3] Mao M, Das S, Turner SR. Polymer 2007;48(21):6241.
[4] Jeong YG, Jo WH, Lee SC. Macromolecules 2003;36(11):4051.
[5] Sanchez-Arrieta N, Martinez de Ilarduya A, Alla A, Munoz-Guerra S. Eur Polym J 2005;41(7):1493.
[6] Johnson AH, Wegner J, Soucek MD. Eur Polym J 2004;40(12):2773.
[7] Lee S-S, Yee AF. Macromolecules 2003;36(18):6791.
[8] Iijima T, Hamakawa S, Tomoi M. Polym Int 2000;49(8):871.
[9] Polk MB, Bota KB, Akubuiro EC, Phingbodhipakkiya M. Macromolecules 1981;14(6):1626.
[10] Li X, Yee AF. Macromolecules 2003;36(25):9421.
[11] Li X, Yee AF. Macromolecules 2004;37(19):7231.
[12] Turner SR. J Polym Sci Part A Polym Chem 2004;42(23):5847.
[13] Brenner AR, Voit BI, Massa DJ, Turner SR. Macromol Symp 1996;102:47.
[14] Dang TD, Dalton MJ, Venkatasubramanian N, Johnson JA, Cerbus CA, Feld WA. J Polym Sci Part A Polym Chem 2004;42(23):6134.
[15] Zhao W, Carreira EM. Org Lett 2006;8(1):99.
[16] Ridgway JS. J Polym Sci Part A-1 Polym Chem 1970;8(11):3089.
[17] Vanhaecht B, Teerenstra MN, Suwier DR, Willem R, Biesemans M, Koning CE. J Polym Sci Part A Polym Chem 2001;39(6):833.
[18] Herold F, Schneller A. Adv Mater 1992;4(3):143.
[19] Walker KA, Markoski LJ, Moore JS. Macromolecules 1993;26(14):3713.