Synthesis and Characterization of Novel Optically Active Polyesters with High Thermal Stability

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ABSTRACT: A new optically active diacid (DA) was prepared by nucleophilic substitution reaction of R-(−)-mandelic acid with terephthaloyl chloride in the presence of potassium hydroxide. This DA named terephthalic acid bis(carboxyphenylmethyl) ester was used as a monomer for the preparation of related optically active polyesters. Polycondensation of DA with different aromatic diols, including hydroquinone, 1,5-dihydroxy naphthalene, 1,4-dihydroxy anthraquinone, 1,8-dihydroxy anthraquinone, 2,4-dihydroxy benzophenone, and bisphenol A, in the presence of 4-toluenesulfonyl chloride using high temperature solution method led to preparation of different polyesters. The prepared monomer and all the polymers were characterized by conventional methods. Thermal and physical properties of the polyesters, including thermal stability, thermal behavior, solution viscosity, and solubility behavior, in addition to optical activity were studied. The optically active polyesters showed high thermal stability, whereas the presence of bulky groups improved their solubility. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2146–2153, 2011

Key words: high temperature materials; polyesters; thermal properties

INTRODUCTION

High temperature stable or thermally stable materials are one of the interesting areas within polymer science. It has been known as a particular area within polymer chemistry for nearly 60 years.[1] The most important classes of these polymers are polyimides, polyamides, polyarylates, and their copolymers. They are of major commercial and industrial importance because of their high thermal and oxidative stability, good chemical resistance, and excellent mechanical properties. High stiffness and intermolecular bonding lead to poor solubility and high softening or melting temperature and, therefore, difficult processability of these polymers.[2–5]

Polyarylates as one of the most important types of heat-resistant polymers are used as high-performance engineering plastics. They are aromatic polyesters consisting of aromatic diols and aromatic dicarboxylic acids. Polyesters are now widely used for textile fibers, technical fibers, films, and bottles because of their good mechanical properties, thermal stability, and low production cost.[6–9]

Therefore, a great deal of attention has been paid to different synthetic methods in this area for improving their processability and solubility through the design and synthesis of new and specific monomers to obtain polymers with improved solubility while maintaining thermal stability.[10–16]

On the other hand, certain properties could be imparted to the polymers by structural modification. One example in this field is the preparation of optically active polymers. The present synthetic optically active polymers have become of enormous attention because of their chiral structure, which may contribute an important position in the molecular arrangement and assembly that is critical for optoelectronics supramolecular structure.[17–19]

Here, we wish to express the preparation of new generation of optically active, thermally stable polyesters containing bulky groups with improved solubility. In this way, an optically active diacid (DA) with built-in ester units was synthesized via nucleophilic substitution reaction of R-(−)-mandelic acid with terephthaloyl chloride (TPC). Different diols were reacted with DA using 4-toluenesulfonyl chloride (p-TsCl) to prepare related optically active polyesters with high thermal stability and improved solubility.

EXPERIMENTAL

Materials

All the chemicals were purchased either from Merck (Darmstadt, Germany) or Aldrich Co. (St. Louis, MO). p-TsCl and R-(−)-mandelic acid were obtained from Merck Chemical Co. and used without further purification. TPC and all diols were purified by
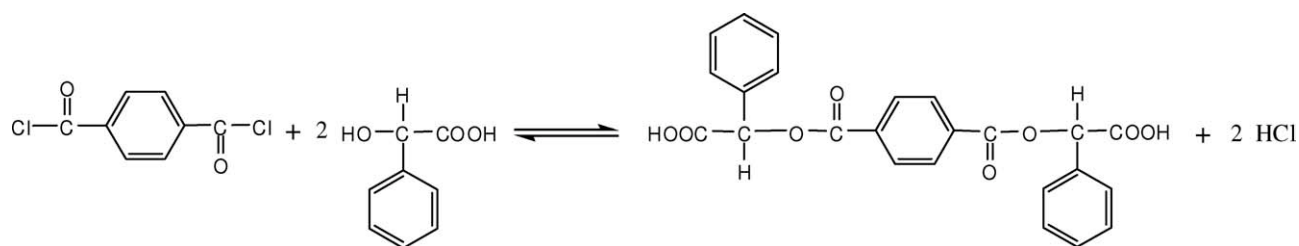
Scheme 1 Preparation of DA.

sublimation under reduced pressure. N,N-Dimethylformamide (DMF), toluene, and dimethylsulfoxide (DMSO) were purified by distillation over calcium hydride under reduced pressure.

Instruments

Infrared analyses were performed on a Bruker-IFS 48 Fourier transform infrared (FTIR) spectrometer (Ettlingen, Germany) in the range of 400–4000 cm^{-1}. The ^{1}H-nuclear magnetic resonance (NMR) spectra were recorded in DMSO-d_6 solution using a Bruker Avance DPX 400 MHz. The mass spectrum was recorded on a Shimadzu GCMS-QP 1100-EX (Tokyo, Japan). Elemental analyses were performed by a CHN-O-Rapid Heraeus elemental analyzer (Wellesley, MA). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 (London, UK) from 25°C to 300°C and 25–600°C, respectively. Inherent viscosities were measured at a concentration of 0.5 g/dL in DMF at 30°C by using Ubbelohde viscometer. The weight-average molecular weight (M_w) was determined by gel permeation chromatography (GPC). GPC was performed on a Waters 150-C instrument using Styragel columns and a differential refractometer detector. The molecular weight calibration was carried out using polystyrene standards. Calibration and measurements were made at a flow rate of 1 mL/min, and DMF was used as solvent. A Jasco polarimeter was used for the measuring of specific rotations of the polymers. Mechanical tensile testing was determined from stress–strain curves with an ADAMEL testing instrument MTS 10/M equipped with a chamber. Stress–strain curves were obtained at a
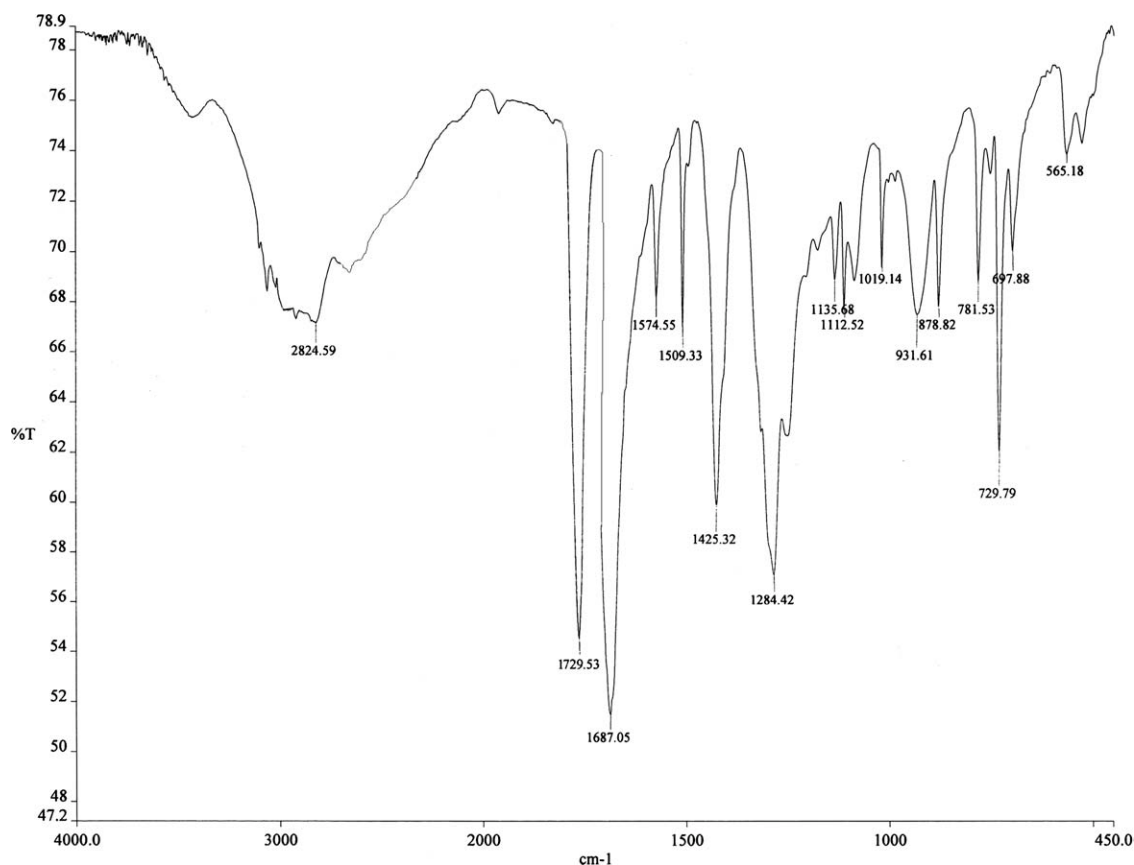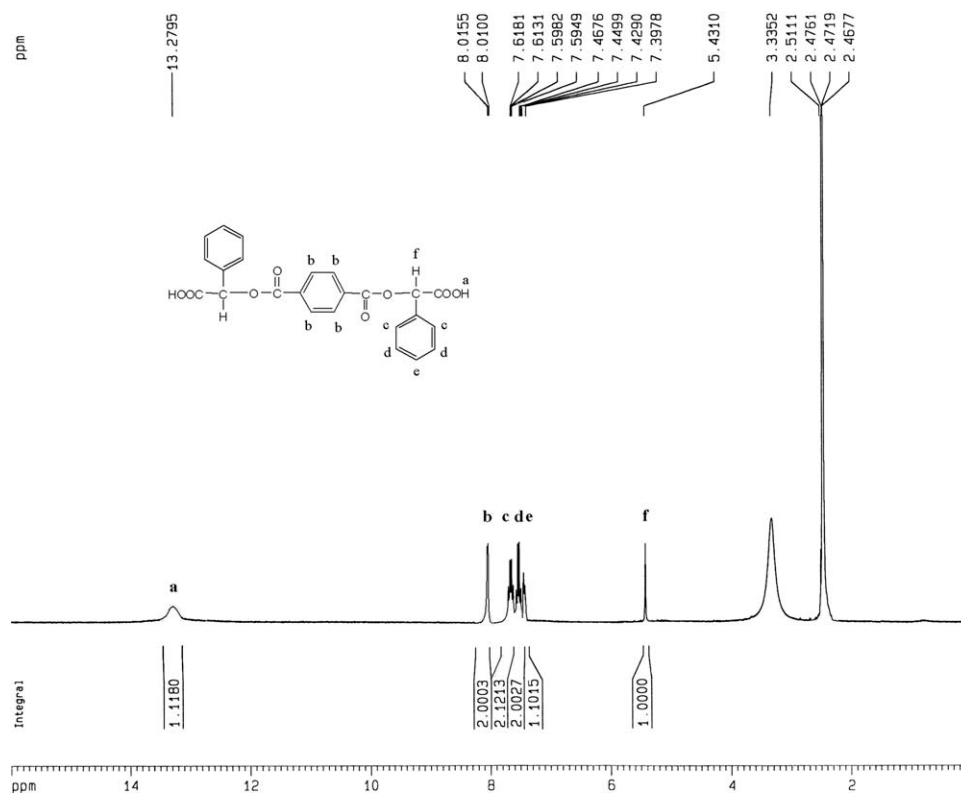

Figure 1 FTIR spectrum of DA.

Figure 2 ^{1}H-NMR spectrum of DA.

stretching speed of 25 mm/min for samples cut into a dumbbell shape [ASTM D638].

Monomer synthesis: Synthesis of terephthalic acid bis(carboxyphenylmethyl) ester

1.5 g (26.78 mmol) of KOH, 10 mL of DMSO, 1.94 g (12.75 mmol) of R-(−)-mandelic acid, and 10 mL of dry toluene for azeotropic distillation were placed into a 100 mL, two-necked, round-bottomed flask equipped with a Dean-Stark trap, a condenser, a stirrer bar, and a nitrogen inlet tube. The mixture was heated at reflux for 4 h for removing the water from the reaction mixture. It was cooled to room temperature and then 1.24 g (6.107 mmol) of TPC was added to the mixture gradually. The mixture
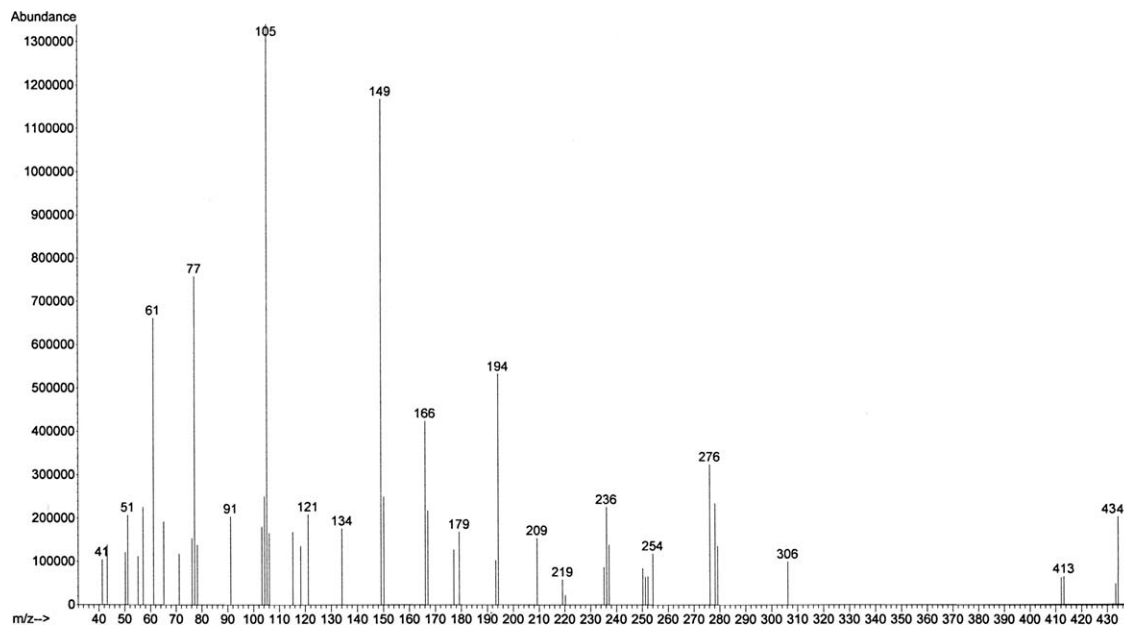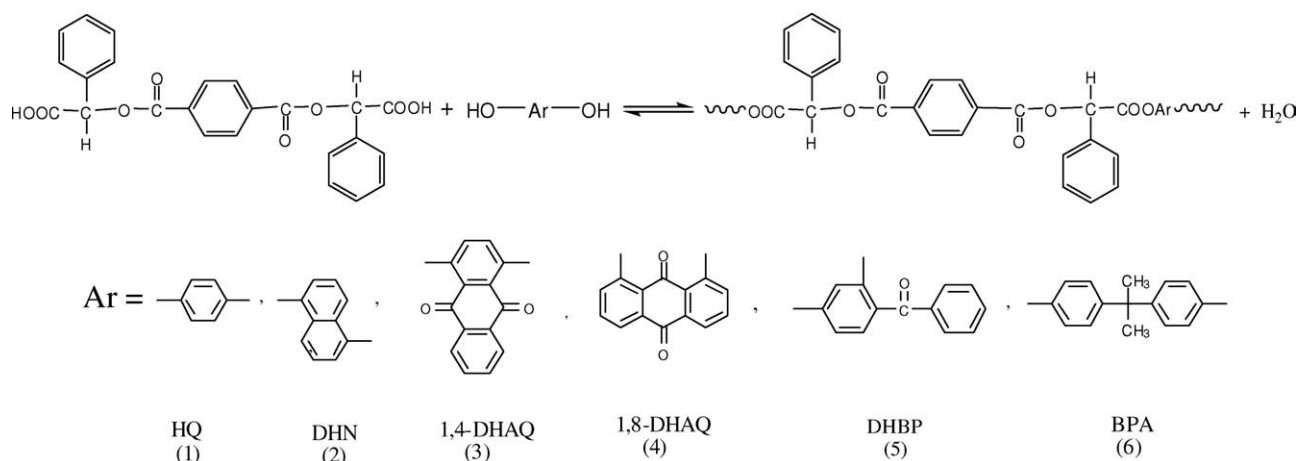

Figure 3 Mass spectroscopy of DA.

Scheme 2 Preparation of polyesters.

was stirred at room temperature for 60 h. Then, the reaction solution was poured into water and acidified with hydrochloric acid until pH 3 is reached. The slurry was stirred and then filtered. The crude solid was washed with hot water, successively. The obtained DA was dried in a vacuum oven at 120°C.

Polyester synthesis

A typical synthesis of polyesters was carried out as follows: A 50-mL, two-necked, round-bottomed flask equipped with a magnetic stirrer, a reflux condenser, a thermometer, oil bath, and dropping funnel was charged with 2.23 g (11.7 mmol) of p-TsCl, 1 mL of dry DMF, and 4 mL of pyridine. The mixture was stirred at room temperature for 30 min, and then 0.868 g (2 mmol) of DA was added to it. The mixture was stirred until a viscous solution appeared, and then it was heated at 80°C for 10 min. After this time, 2 mmol of diol dissolved in 5 mL of pyridine was added in small quantities into the flask over a period of 10 min. The mixture was heated to 120°C and remained at this temperature for about 2 h. After cooling, the polymer was precipitated in water and filtered. Then, it was washed with hot water and methanol several times. The product was dried in a vacuum oven at 80°C overnight.

RESULTS AND DISCUSSION

Monomer preparation and characterization

The main objective of this study was focused on the preparation of some optically active polyesters with good thermal stability and enhanced solubility. There are some approaches to maintain thermal stability of the polymers while increasing their solubility. The basic modifications include (a) introduction of a bulky substituent along the polymer backbone; (b) incorporation of flexible or kinked linkages in the backbone; and (c) the disruption of symmetry and regularity of the repeating unit.

In this way, a new DA was prepared via nucleophilic substitution reaction of R-(−)-mandelic acid with TPC. In this reaction, potassium hydroxide was applied to increase the nucleophilic character of OH group in mandelic acid, and also toluene was used for water removal by azeotropic distillation during the progress of reaction (Scheme 1). The DA with preformed ester units showed optical activity, which was as a result of intactness of chiral center in mandelic acid during the reaction with TPC. The structure of DA was fully characterized using FTIR, ^{1}H-NMR, and mass spectroscopy, and the spectra are shown in Figures 1–3. Yield of this reaction was about 78% (2.07 g), and the melting point of product was greater than 300°C. In the FTIR spectrum of the DA using KBr pellet technique, the following peaks
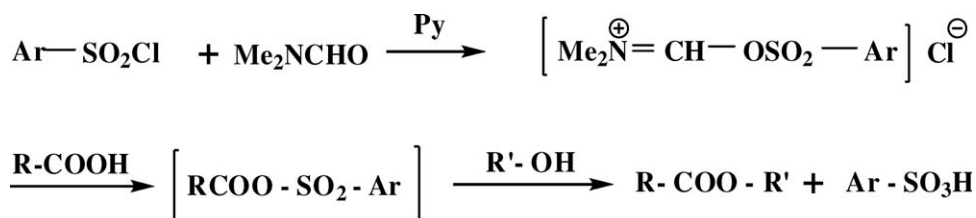
Scheme 3 Mechanism of direct esterification via Vilsmeier adduct.

TABLE I
Polymer Characterization Data

| Polymer	FTIR (KBr cm^{-1})	^{1}H-NMR (DMSO-d_6) (δ ppm)	Elemental analysis	
			Calc. C—H—O	Found C—H—O
DA-HQ	3069, 1730, 1689, 1499, 1266, 1222, 1175	8.03 (d, phenyl, 4H), 7.61 (dd, phenyl, 4H), 7.47 (dd, phenyl, 4H), 7.42 (t, phenyl, 2H), 7.08 (d, HQ, 4H), 5.43 (s, CH, 2H)	70.87, 3.94, 25.20	70.49, 4.10, 25.41
DA-DHN	3064, 1736, 1687, 1502, 1263, 1227, 1161	8.04 (d, phenyl, 4H), 7.77 (dd, DHN, 4H), 7.62 (dd, phenyl, 4H), 7.48 (dd, phenyl, 4H), 7.43 (t, phenyl, 2H), 7.37 (dd, DHN, 4H), 6.99 (dd, DHN, 4H), 5.44 (s, CH, 2H)	73.12, 3.94, 22.94	72.98, 3.80, 23.11
DA-1,4-DHAQ	3075, 1744, 1675, 1506, 1258, 1230, 1169	8.61 (dd, anthra, 2H), 8.11 (m, anthra, 2H), 8.03 (d, phenyl, 4H), 762 (dd, phenyl, 4H), 7.59 (d, anthra, 2H), 7.47 (dd, phenyl, 4H), 7.41 (t, phenyl, 2H), 5.44 (s, CH, 2H)	71.47, 3.45, 25.08	71.32, 3.62, 24.91
DA-1,8-DHAQ	3079, 1743, 1676, 1505, 1269, 1229, 1163	8.28 (dd, anthra, 2H), 8.17 (dd, anthra, 2H), 8.04 (d, phenyl, 4H),7.63 (dd, phenyl, 4H), 7.46 (dd, phenyl, 4H), 7.42 (t, phenyl, 2H), 7.31 (dd, anthra, 2H), 5.43 (s, CH, 2H)	71.47, 3.45, 25.08	71.29, 3.28, 25.21
DA-DHBP	3062, 1729, 1681, 1507, 1265, 1225, 1160	8.02 (d, phenyl, 4H),7.96 (s, benzo, 1H), 7.79 (dd, benzo, 2H), 7.74 (d, benzo, 1H), 7.67 (m, benzo, 1H), 7.60 (dd, phenyl, 4H), 7.58 (dd, benzo, 2H), 7.47 (dd, phenyl, 4H), 7.40 (t, phenyl, 2H), 7.24 (dd, benzo, 1H), 5.42 (s, CH, 2H)	72.55, 3.92, 23.53	72.33, 4.07, 23.64
DA-BPA	3061, 1727, 1672, 1501, 1261, 1221, 1158	8.02 (d, phenyl, 4H), 7.60 (dd, phenyl, 4H), 7.46 (dd, phenyl, 4H), 7.40 (t, phenyl, 2H), 7.24 (d, BPA, 4H), 6.91 (dd, BPA, 4H), 5.41 (s, CH, 2H), 1.58 (s, BPA, 6H)	74.76, 4.79, 20.45	74.54, 4.90, 20.61
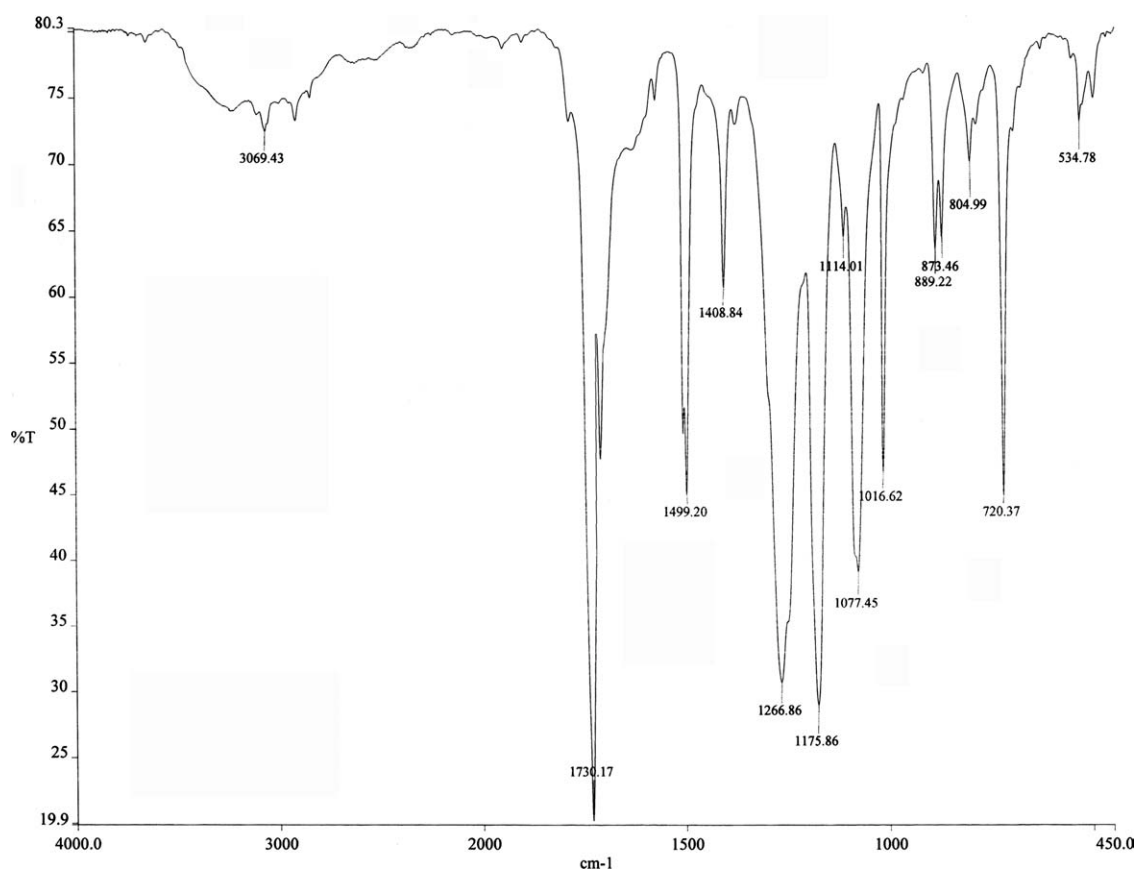
Figure 4 FTIR spectrum of DA-HQ polymer.
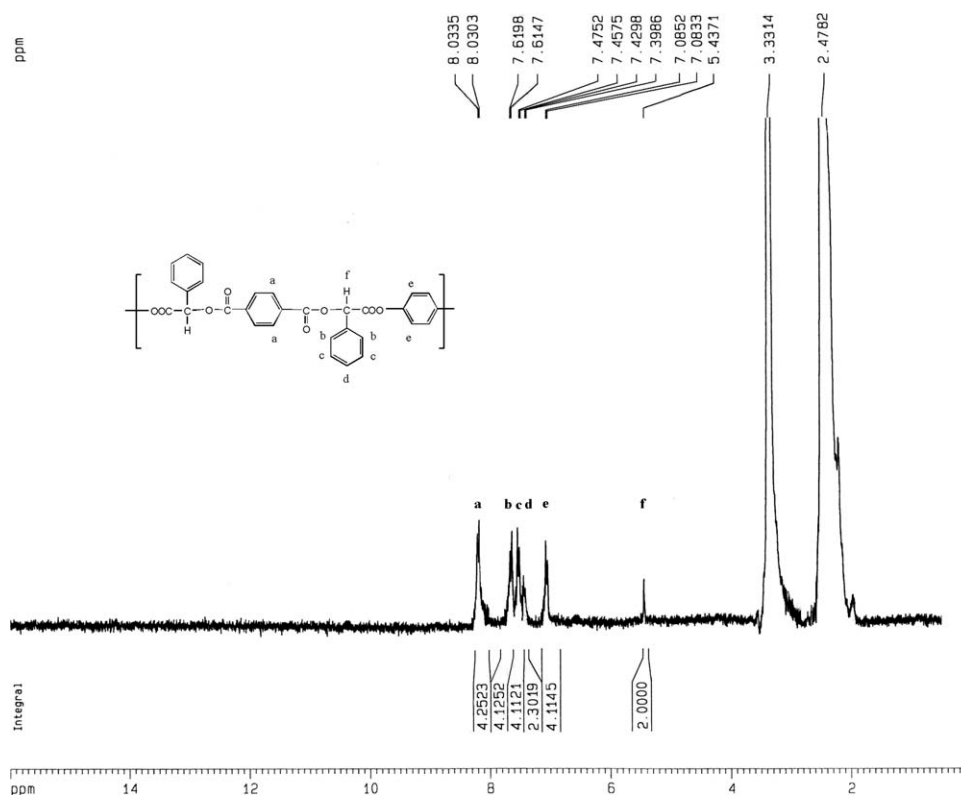
Figure 5 ^{1}H-NMR spectrum of DA-HQ polymer.

were observed: 3150–3240 (O-H, acid), 3066 (C-H, aromatic), 2970, 2824 (C-H, aliphatic), 1729 (C=O, ester), 1687 (C=O, acid), and 1284 cm^{-1} (C-O, ester). Also, peaks at about 13.27 (s, 2H, COOH), 8.01 (d, 4H, phenyl), 7.59 (dd, 4H, phenyl), 7.45 (dd, 4H, phenyl), 7.39 (t, 2H, phenyl), and 5.43 (s, 2H, C-H) ppm in ^{1}H-NMR spectrum of DA were assigned using DMSO-d_6 as solvent. Molecular ion peak (m/e) = 434 was observed in the mass spectrum of the DA.

Presence of two peaks at about 1729 and 1687 cm^{-1} in the FTIR spectrum of the DA confirmed the prepared structure. They were related to the carbonyl of ester groups and carbonyl of acid groups, respectively. Disappearance of proton of OH groups in ^{1}H-NMR spectrum of DA at about 5.9 ppm was another confirmation for the prepared structure. Also, existence of molecular ion peak in the mass spectrum of DA at m/e = 434 proved the structure.

Polymer preparation and characterization

Solution polycondensation of DA with different diols, including hydroquinone (HQ), 1,5-dihydroxy naphthalene, 1,4-dihydroxy anthraquinone, 1,8-dihydroxy anthraquinone, 2,4-dihydroxy benzophenone, and bisphenol A, in the presence of p-TsCl using high-temperature solution method in DMF and pyridine resulted in preparation of optically active polyesters in high yields (Scheme 2). In the direct polycondensation reaction of DA with diols, a Vilsmeier adduct derived from p-TsCl/DMF/Pyridine was used as condensing agent to prepare polyesters with improved molecular weights.[20–22] The mechanism is shown in Scheme 3. In this mechanism, p-TsCl reacted with DMF to form a Vilsmeier adduct that activated dicarboxylic acid to produce the mixed anhydride, which subsequently gave the related polyester on alcoholysis with the diols.

The polymers were characterized by FTIR, ^{1}H-NMR, and elemental analysis techniques, and the

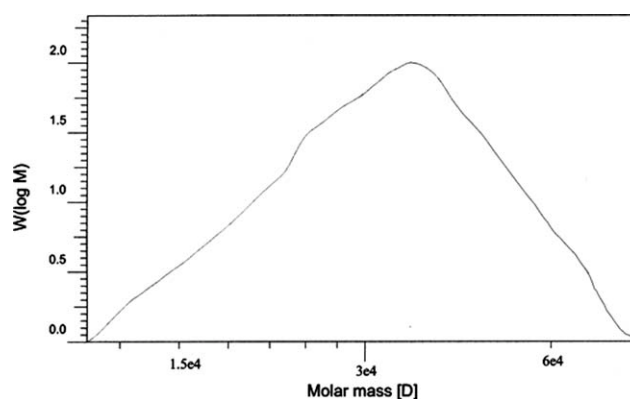**Figure 6** GPC chromatogram of DA-HQ polymer.

TABLE II
Yeild, Viscosity, and Molecular Weight of the Polymers

Polymer	Yield (%)	Inherent viscosity[a] (dL/g)	M_w[b]	M_n	PDI
DA-HQ	89	0.49	34,500	28,050	1.23
DA-DHN	88	0.47	33,480	24.260	1.38
DA-1,4-DHAQ	85	0.43	33,100	23,000	1.44
DA-1,8-DHAQ	86	0.41	32,500	21,530	1.51
DA-DHBP	81	0.39	29,900	19,420	1.54
DA-BPA	83	0.40	30,050	22,770	1.32

[a] Measured at a concentration of 0.5 g/dL in DMF at 30°C.
[b] According to GPC measurment in g/mol.
PDI, polydispersity index.

TABLE III
Thermal Characteristic Data

Polymer	T_g (°C)	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	Char yield (%)
DA-HQ	186	290	395	465	55
DA-DHN	178	277	355	460	52
DA-1,4-DHAQ	172	268	342	447	47
DA-1,8-DHAQ	169	253	337	435	45
DA-DHBP	162	246	331	410	39
DA-BPA	155	240	326	400	35

T_g, glass-transition temperature; T_0, initial decomposition temperature; T_{10}, temperature for 10% weigth loss; T_{max}, maximum decomposition temperature; char yield: weigth of polymer remain at 600°C.

results are tabulated in Table I, and the FTIR and ^{1}H-NMR results of DA-HQ polymer are shown in Figures 4 and 5, respectively. Formation of polyesters from related DA was confirmed by absence of O-H acidic peaks at 3150–3240 cm^{−1} in the FTIR and absence of O-H acidic peaks at 13.27 ppm in the ^{1}H-NMR spectra of the polymers.

Polymer properties

Polyesters showed reasonable molecular weights according to the GPC and inherent viscosity measurements. The weight-average molecular weight (M_w) of the polymers based on the GPC method was in the range of 29,900–34,500, and the number-average molecular weight (M_n) was about 19,420–28,050. Accordingly, the polydispersity index of polymers was in the range of 1.23–1.51. The typical GPC chromatogram of DA-HQ polymer is shown in Figure 6. Also, the inherent viscosity of the polymers in DMF at a concentration of 0.5 g/dL at 30°C was about 0.39–0.49 dL/g. The results are given in Table II.

The polymers showed good solubility in dipolar aprotic solvents, including N-methyl-2-pyrrolidone,

N,N-dimethyl acetamide, DMF, DMSO, and m-cresol. The solubility of the polymers was in the range of 1.80–2.65 g/dL, which was mostly related to the presence of bulky phenyl groups in the backbone originated from the structure of DA. From diol point of view, bisphenol A- and 2,4-dihydroxy benzophenone-based polyesters showed highest solubility among the polyesters, which was related to the presence of flexible alkyl groups and meta-catenation of structure, respectively. Consequently, reduction of interchain interactions led to penetration of solvent molecules and improving of the solubility.

Thermal behavior and stability of the polyesters were investigated using DSC and TGA methods in air at a heating rate of 10°C/min. The glass-transition temperature (T_g) of the polymers, which was measured based on the DSC method (the midpoint of the change in slop of the baseline) was in the range of 155–186°C. Also, thermal stability of the polymers was evaluated by TGA method as decreasing weight of polymers versus increase in the temperature. No remarkable weight loss was observed for the polymers below 240°C. The initial weight loss, temperature for 10% weight loss, and char yield of polymers at 600°C were in the
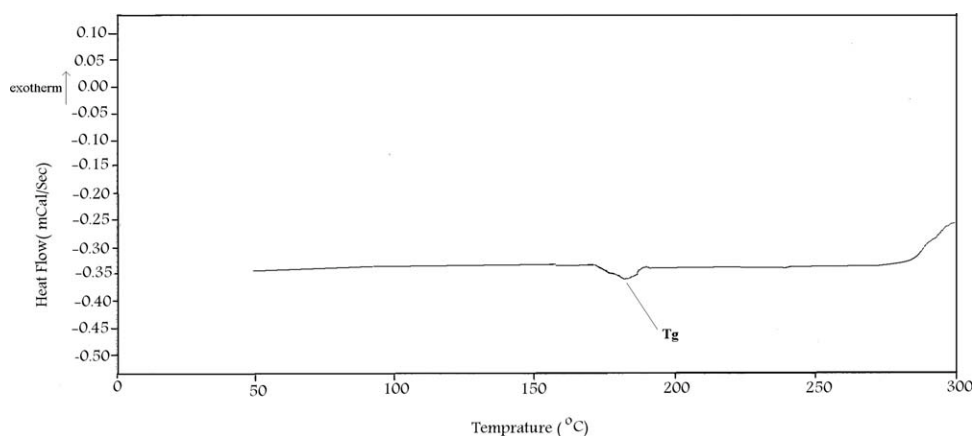

Figure 7 DSC curve of DA-HQ.

range of 240–290°C, 326–395°C, and 35–55%, respectively. These data (Table III) revealed high thermal stability of these polyesters, which mainly resulted from contribution of DA moiety (aromaticity and symmetry of structure and avoidance of weak linkages) into the polymer backbone. Among the different diols used to prepare polyesters, the HQ-based polyesters showed highest thermal stability because of the more symmetric and less bulky structure, which resulted in more close packing of the polymer chains. The representative DSC and TGA curves of DA-HQ are shown in Figures 7 and 8, respectively.

Films for mechanical properties were prepared by dissolution of the polymer (5% w/v) in *N,N*-dimethyl acetamide followed by casting solution on a glass substrate by doctor blading. The solvent exclusion was achieved via heating the polymer with a temperature programming procedure. According to the obtained stress–strain curves, the maximum stress was in the range of 4–11 MPa, and the maximum strain was about 19–25%.

The monomer and polymers showed optical activity that was attributed to the intactness of the chiral center of R-(−)-mandelic acid during the course of monomer and polymer preparation. Accordingly, the $[\alpha]_D^{25}$ for R-(−)-mandelic acid and resulting DA was −6.5 and −5.8 at a concentration of 1 g/dL in DMF respectively, whereas polymers showed −3.0 to −3.7 for $[\alpha]_D^{25}$ at a concentration of 0.1 g/dL in DMF (Table IV).

It is worth to mention that various optically active polyesters with different structures have been prepared using direct method, indirect method, and also microwave-assisted polymerization. Almost similar properties, including optical activity and high thermal stability, have been reported, which make them suitable candidate for optical resolution of racemic mixtures.[23–25]
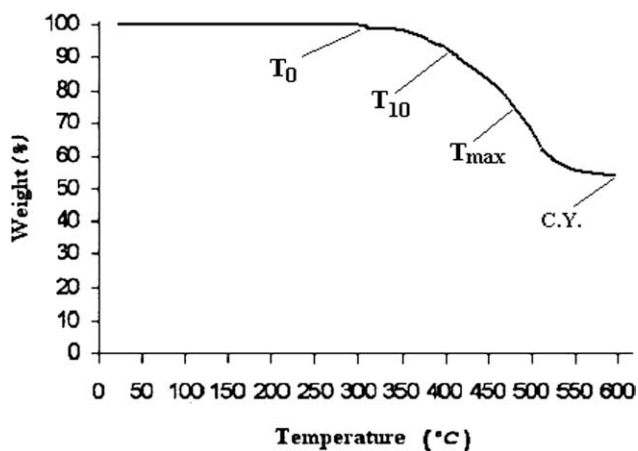
TABLE IV
Optical Activity Data[a]

Polymer	DA-HQ	DA-DHN	DA-1,4-DHAQ	DA-1,8-DHAQ	DA-DHBP	DA-BPA
$[\alpha]_D^{25}$	−3.7	−3.0	−3.3	−3.5	−3.1	−3.4

[a] Measured at a concentration of 0.1 g/dL in DMF.

CONCLUSIONS

New types of optically active polyesters with high thermal stability and improved solubility were prepared using polycondensation reactions of different diols with a prepared optically active DA. Introduction of bulky phenyl units was the main basis for enhancing solubility while aromatization and avoidance of weak linkages were reasons for maintaining thermal stability of the polyesters. Possessing of optical activity was another specific property of these polymers that will extend their potential applications such as preparation of stationary phase for packing of chromatographic columns for resolution of optically active mixtures.

References

1. Cassidy, P. E. Thermally Stable Polymers; Dekker: New York, 1980.
2. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. Plenum Press: New York, 1990.
3. Ghosh, M. K.; Mittal, K. L.; Polyimides: Fundamentals and Applications; Marcel Dekker: New York, 1996.
4. King, F. A.; King, J. J. Engineering Thermoplastics; Marcel Dekker: New York, 1995.
5. Kricheldorf, H. R. Adv Polym Sci 1999, 141, 83.
6. Peng, G.; Li, Q.; Yang, Y.; Wang, H.; Li, W. 2008, 19, 1629.
7. Maiti, S.; Das, S. J Appl Polym Sci 1981, 26, 957.
8. Maiti, S.; Das, S. Angew Makromol Chem 1980, 86, 181.
9. Lienert, K. Adv Polym Sci 1999, 141, 45.
10. Kakali, F.; Kallitsis, J.; Pakula, T.; Wegner, G. Macromolecules 1998, 31, 6190.
11. Higashi, F.; Kim, J. H.; Ong, C. H. J Polym Sci Part A: Polym Chem 1999, 37, 621.
12. Watanabe, S.; Kobayashi, A.; Kakimoto, M.; Imai, Y. J Polym Sci Part A: Polym Chem 1994, 32, 909.
13. Wang, H.; Shen, Z.; Cheng, S. Z. D.; Harris, F. W. Polym Prepr 1999, 40, 88.
14. Mehdipour-Ataei, S.; Amirshaghaghi, A.; Bahri-Laleh, N. Eur Polym J 2006, 42, 2646.
15. Mehdipour-Ataei, S.; Zigheimat, F. Des Mono Polym 2007, 10, 145.
16. Mehdipour-Ataei, S.; Akbarian-Feizi, L. Iran Polym J 2007, 16, 607.
17. Singfield, K. L.; Brown, G. R. Macromolecules 1995, 28, 1290.
18. Muller, M.; Zentel, R. Macromolecules 1996, 29, 1609.
19. Simitzis, J.; Zoumpoulakis, L.; Soulis, S. Polym Int 2002, 51, 297.
20. Higashi, F.; Tobe, A. Macromol Chem Phys 2001, 202, 745.
21. Higashi, F.; Ong, C. H.; Okada, Y. J Polym Sci Part A: Polym Chem 1999, 37, 3625.
22. Higashi, F.; Akiyama, N.; Takahashi, I.; Koyama, T. J Polym Sci Part A: Polym Chem 1984, 22, 1653.
23. Mallakpour, S.; Kolahdoozan, M. Iran Polym J 2006, 15, 307.
24. Mallakpour, S.; Seyedjamali, H. Amino Acids 2008, 34, 531.
25. D'Hondt, C. G.; Lenz, R. W. J Polym Sci Part A: Polym Chem 1978, 16, 261.

Figure 8 TGA curve of DA-HQ.