



# Preparation, Characterization, and Properties of New Generation of Polyesters Containing Bulky Groups

Shahram Mehdipour-Ataei<sup>\*1</sup> and Leila Akbarian-Feizi<sup>2</sup>

(1) Iran Polymer and Petrochemical Institute, P.O. Box: 14965/115, Tehran, Iran

(2) Department of Chemistry, Islamic Azad University, Doroud, Iran

Received 12 June 2007; accepted 6 October 2007

## ABSTRACT

**N**ucleophilic substitution reaction of two moles of benzoic acid with terephthaloyl chloride in the presence of triethylamine hydrochloride yielded terephthalic acid bis-(carboxydiphenyl methyl)ester (TBE) as a new monomer for the preparation of polyesters. This diester-diacid (TBE) was converted to its acid chloride derivative, terephthalic acid bis-(chlorocarbonyldiphenyl methyl)ester (TBECI), using thionyl chloride. Polymerization reactions of TBECI with different aromatic diols including hydroquinone, 1,5-dihydroxy naphthalene, phenolphthalein, 1,4-dihydroxy anthraquinone, 1,8-dihydroxy anthraquinone, and bisphenol A in the presence of triethylamine hydrochloride using high temperature solution polycondensation method resulted in different polyesters. All the polymers were characterized and their physical and thermal properties such as thermal behaviour, thermal stability, solution viscosity, and solubility behaviour were studied. Polymers showed good thermal stability while the presence of bulky groups improved their solubility.

## Key Words:

polycondensation;  
polyesters;  
thermal properties;  
synthesis;  
bulky group.

## INTRODUCTION

One of the distinct areas within polymer science is that of high temperature or thermally stable materials. It has been recognized as a special area within polymer chemistry for nearly 50 years. The most important classes of these polymers are polyimides, polyamides, polyarylates, and their copoly-

mers [1,2]. They show high thermal and oxidative stability, good chemical resistance, and excellent mechanical properties. Because of these properties, they are of major commercial and industrial importance. However, the poor solubility and high softening or melting temperature caused by high stiffness

(\*) To whom correspondence to be addressed.  
E-mail: [s.mehdipour@ippi.ac.ir](mailto:s.mehdipour@ippi.ac.ir)

and intermolecular bonding lead to difficult processability of these polymers [3,4].

Polyarylates are one of the most important types of heat-resistant polymers that are used as high performance engineering plastics. They are aromatic polyesters consisting of aromatic diols and aromatic dicarboxylic acids. The primary commercial polyarylates available today are the copolyesters based on 2,2-bis-(4-hydroxyphenyl)propane (bisphenol A) and a mixture of isophthalic and terephthalic acids.

Polyesters are now widely used for textile fibres, technical fibres, films, and bottles because of their good mechanical properties, thermal stability, and low production cost. Their demand has been estimated to be about 35 million tons in 2006 and is expected to grow annually by 9% [5-7]. There is still a need for the polyarylates having high  $T_g$  while retaining good solubility in organic solvents, thereby keeping the feasible processability.

Therefore, the main significant synthetic efforts in this area have been focused on improving their processability and solubility through the design and synthesis of new monomers to obtain polymers with improved solubility while maintaining thermal stability [8-11].

Here we wish to express the preparation of new generation of thermally stable polyesters containing bulky groups with improved solubility. In fact, our strategy is the incorporation of pendant bulky groups along the polymer backbone, which results in a polymer matrix increasing the solubility characteristics without affecting the thermal and mechanical properties to great extent. In this way, a diacid (TBE) was synthesized via nucleophilic substitution reaction of benzoic acid with terephthaloyl chloride. TBE was converted to its acid chloride derivative and it was subsequently polycondensed with different diols to prepare related polyesters with built-in ester units and bulky phenyl groups to induce specific property to the final polymers including high thermal stability and improved solubility.

## EXPERIMENTAL

### Materials

All the chemicals were purchased either from Merck

or Aldrich Chemical Co. Terephthaloyl chloride (TPC) and all diols were purified by sublimation under reduced pressure. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and dimethylsulphoxide (DMSO) were purified by distillation over calcium hydride under reduced pressure. The other materials were used as received.

### Instruments

Infrared analyses were performed on a Bruker-IFS 48 FTIR spectrometer (Ettlingen, Germany) in the range of 400-4000  $\text{cm}^{-1}$  after 32 scans. The  $^1\text{H}$  NMR spectra were recorded in DMSO- $d_6$  solution using a Bruker Avance DPX 400 MHz (GmbH, Germany). The mass spectrum was recorded on a Shimadzu GC-MS-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 25-300°C and 25-600°C, respectively. Glass transition temperature ( $T_g$ ) was taken as the midpoint of the change in slope of the baseline in DSC curve after second scan. Inherent viscosities were measured at a concentration of 0.5 g/dL in DMF at 30°C by using an 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.

### Monomer Synthesis

#### *Synthesis of Terephthalic Acid Bis-(carboxydiphenyl methyl)ester (TBE)*

A 250-mL, three-necked, round bottom flask equipped with a magnetic stirrer, nitrogen gas inlet tube, condenser, and dropping funnel was charged with 12.05 g (0.051 mol) of the benzoic acid and 25 mL of 1,2-dichlorobenzene. The mixture was stirred and 0.40 g of triethylamine hydrochloride was added. Then, 4.57 g (0.0225 mol) of terephthaloyl chloride was dissolved in 25 mL of 1,2-dichloroben-

zene and it was added into the flask slowly. The mixture was heated slowly to 180°C and remained at that temperature for about 10 h. During this time, the reaction progress was followed by HCl evolution. The mixture was cooled and the product was precipitated by pouring the flask content into hexane. Then it was filtered and washed with hot water. (Yield 75%) mp > 300°C. [IR (KBr):  $\nu$  3200-3400, 1710, 1683, 1423-1570, and 1285  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  13.30 (s, 2H, OH), 8.07 (d, 4H, phenyl), 7.98 (d, 8H, phenyl), 7.26 (m, 8H, phenyl), 7.12 (d, 4H, phenyl); mass spectrum: 586 m/z.

#### Synthesis of Terephthalic Acid Bis-(chlorocarbonyldiphenyl methyl)ester (TBCEl)

TBE (0.014 mol) was refluxed in the presence of thionyl chloride (80 mL) and two drops of dry DMF for 4 h. Then the excess of thionyl chloride was removed from the mixture by distillation. The crude product was recrystallized from ether and vacuum dried at 60°C. (Yield 97%). [IR (KBr):  $\nu$  3101, 3055, 1792, 1728, 1408, 1198, and 854  $\text{cm}^{-1}$ .

#### Polyesters Synthesis

A typical synthesis of polyesters (TBE-HQ) was carried out as follows:

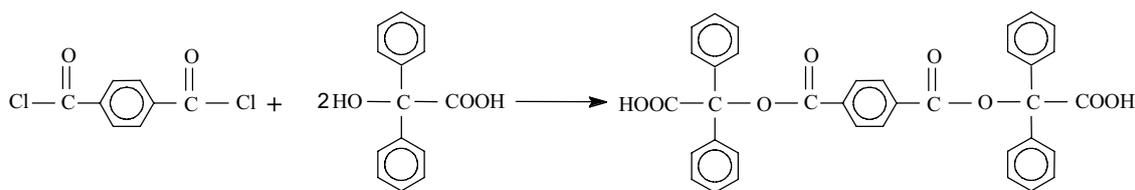
In a round-bottom flask equipped with a stirrer, nitrogen inlet tube, HCl outlet tube, and condenser was placed 6 mmol (0.661 g) of HQ, 0.1 g of triethylamine hydrochloride, and 12 mL of 1,2-dichlorobenzene. The mixture was heated to 180°C under nitrogen flow and a solution of 6 mmol (3.738 g) diacid chloride (TBCEl) in 12 mL of dichlorobenzene was added dropwise through a funnel. The mixture was heated until the evolution of HCl after a period of about 5 h ceased. After cooling, the polymer was precipitated in hexane and washed with methanol and water successively. The other polyesters were synthesized using the same procedure.

## RESULTS AND DISCUSSION

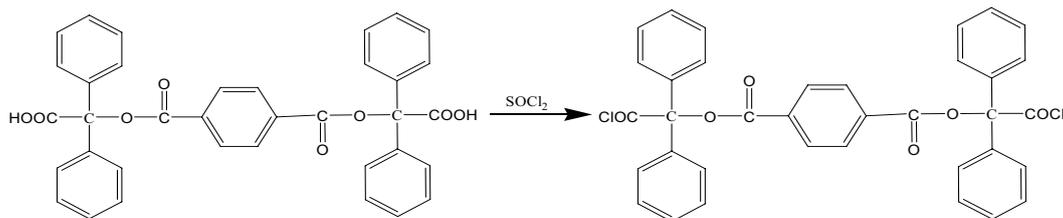
Polyarylates which have good thermal and mechanical properties belong to the class of high-performance engineering plastics and they are widely used in different industries [12-17]. However, polyarylates are generally difficult to process because of their limited solubility in organic solvents and their high melting or high glass transition temperatures by virtue of their rigid structures. There are some approaches to overcome such a problem. Generally, main approaches to obtain soluble and thermally stable polymers have involved the following modifications: (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 through copolymerization [18-25].

Preparation of new generation of thermally stable polyesters and improvement of their solubility were our main objectives in this study. Therefore, a new aromatic diacid (TBE) containing four bulky phenyl units was synthesized via the nucleophilic substitution reaction of two moles of benzilic acid with terephthaloyl chloride in the presence of triethylamine hydrochloride via high temperature solution polycondensation (Scheme I). The structure of TBE was fully characterized using FTIR,  $^1\text{H}$  NMR, and mass spectroscopy and the spectra are shown in Figures 1a, 1b and 2. In the FTIR spectrum, peaks at about 1730, 1686, and 1285  $\text{cm}^{-1}$  were related to the carbonyl of ester groups, carbonyl of acid groups, and ether units, respectively.

TBE was converted to terephthalic acid bis-(chlorocarbonyldiphenyl methyl)ester (TBCEl) by using  $\text{SOCl}_2$  and catalytic amount of dry DMF in order to activate the acidic groups toward nucleophilic attack (Scheme II). Disappearance of a broad band at 3200-3400  $\text{cm}^{-1}$  from the FTIR spectrum of



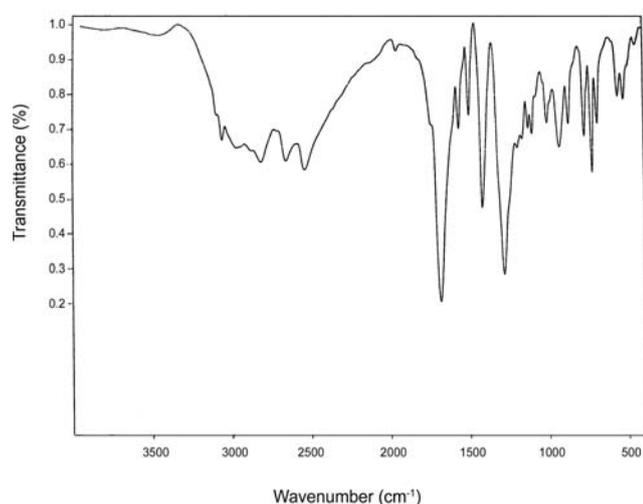
**Scheme I.** Synthesis of terephthalic acid bis-(carboxydiphenyl methyl)ester (TBE).



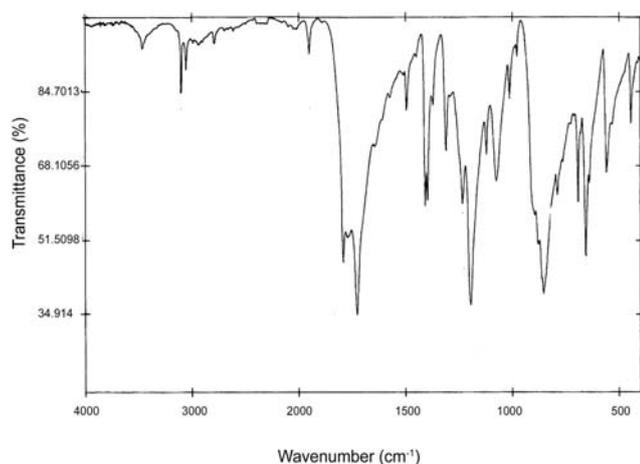
**Scheme II.** Synthesis of terephthalic acid bis-(chlorocarbonyldiphenyl methyl)ester (TBECI).

TBE and also presence of a band at  $1792\text{ cm}^{-1}$  in the spectrum of TBECI due to the generation of acid chloride were good evidence for confirmation of the structure of TBECI (Figure 1).

High temperature solution polycondensation of TBECI with six different diols including hydro-



(a)

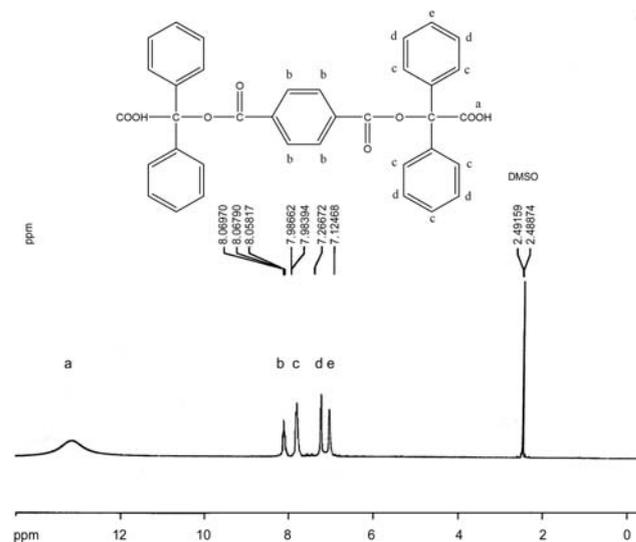


(b)

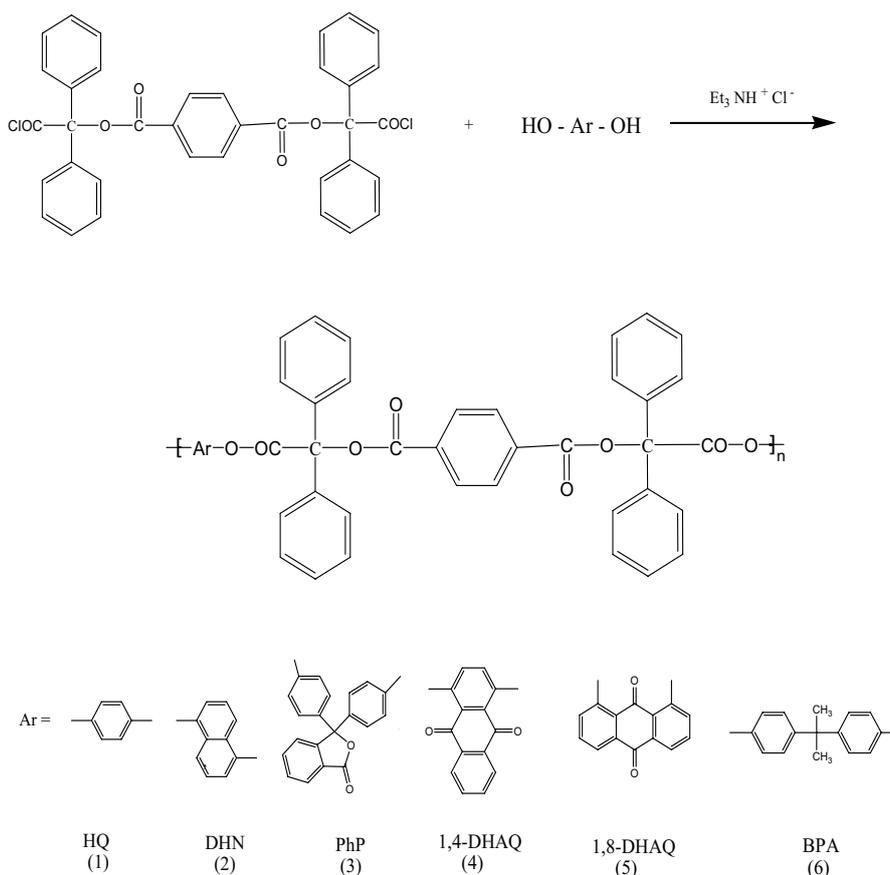
**Figure 1.** FTIR Spectra of: (a) TBE and (b) TBECI.

quinone, 1,5-dihydroxy naphthalene, phenolphthalein, 1,4-dihydroxy anthraquinone, 1,8-dihydroxy anthraquinone, and bisphenol A in the presence of triethylamine hydrochloride in dichlorobenzene resulted in new generation of aromatic and semi-aromatic polyesters containing bulky groups (Scheme III). Characterization of the polymers was achieved using FTIR,  $^1\text{H}$  NMR, and elemental analysis techniques and the results are shown in Table 1. A representative FTIR spectrum for TBE-HQ is shown in Figure 3 in which peaks at about  $3079$ ,  $1794$ ,  $1733$ , and  $1221\text{ cm}^{-1}$  were related to aromatic C-H bond, carbonyl of polyester units, carbonyl of ester groups, and ether units, respectively. Also other polyesters peaks in the range of  $1789$ - $1796\text{ cm}^{-1}$  were related to the carbonyl of polyester units.

The inherent viscosity of the polymers as a criterion for evaluation of molecular weights was measured in DMF at a concentration of  $0.5\text{ g.dL}^{-1}$  at  $30^\circ\text{C}$  and the weight average molecular weights ( $M_w$ ) determined by GPC were collected in Table 2. These



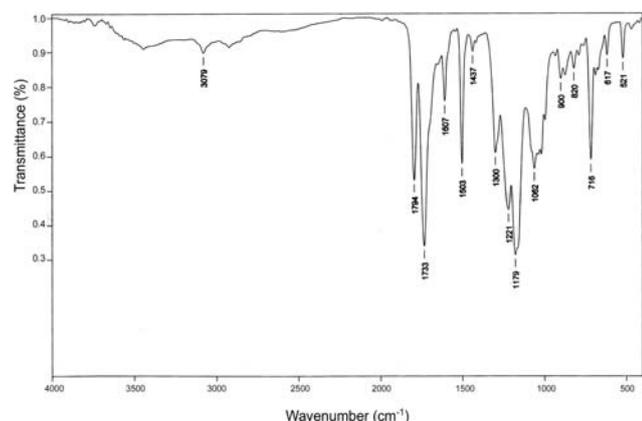
**Figure 2.**  $^1\text{H}$  NMR Spectrum of TBE.



**Scheme III.** Synthesis of polyesters.

results reveal that the polymers are of reasonable molecular weights.

The solubility of the polymers was measured in dipolar aprotic solvents including NMP, DMAc, DMF, DMSO and also *m*-cresol. The polymers showed solubility in the range of 2.0-2.9 g.dL<sup>-1</sup> which



**Figure 3.** FTIR Spectrum of TBE-HQ.

was mainly attributed to the bulky groups. Incorporation of phenyl groups disrupted the crystal packing, reduced intermolecular interactions and enhanced solubility of the resulting polyesters.

According to the DSC analysis the prepared polyesters showed glass transition temperature ( $T_g$ ) in the range of 159-188°C. TGA Analysis in air at a heating rate of 10°C.min<sup>-1</sup> was used for evaluation of thermal stability. The initial decomposition temperature ( $T_0$ ) was about 251-291°C. The 10% weight loss and the char yield of polyesters at 600°C were about 341-376°C and 36-53%, respectively and the maximum decomposition temperature of the polymers ( $T_{max}$ ) that was derived from the first derivative of TGA versus temperature was in the range of 338-408°C. Table 3 and a typical TGA curve are presented in Figure 4. The obtained data showed that, these polymers were high thermally stable polymers and more rigid ones were showed greater heat resistant. Incorporation of flexible groups from the diol moiety

**Table 1.** Characterization of polymers.

Polymer	Elemental analysis				H NMR (DMSO- $\delta$ -ppm)	FTIR (KBr-cm <sup>-1</sup> )
	Calculated		Found			
	C	H	C	H		
TBE-HQ	76.36	4.24	76.04	4.64	8.16 (d, 4H), 7.23-7.27 (m, 20H) 7.06 (d, 4H)	3079, 1794, 1733, 1503, 1221, 1179
TBE-DHN	77.75	4.22	78.00	4.05	8.18 (d, 4H), 7.75 (d, 2H) 7.52 (dd, 2H), 7.24-7.29 (m, 20H) 7.14 (d, 2H)	3068, 1791, 1742 1507, 1210, 1159
TBE-PhP	77.42	4.15	77.13	4.36	8.20 (d, 4H), 7.92 (d, 1H) 7.42 (dd, 1H), 7.33 (dd, 2H) 7.24-7.30 (m, 20H), 7.18 (d, 4H), 7.03 (d, 4H)	3075, 1789, 1738, 1505, 1212, 1173
TBE-1,4-DHAQ	75.95	3.80	75.68	3.98	8.17 (d, 4H), 7.83 (d, 2H) 7.58 (dd, 2H), 7.36 (d, 2H) 7.23-7.28 (m, 20H)	3083, 1790, 1741, 1596, 1195, 1163
TBE-1,8-DHAQ	75.95	3.80	75.72	3.97	8.15 (d, 4H), 7.64 (d, 2H) 7.55 (dd, 2H), 7.40 (d, 2H) 7.21-7.25 (m, 20H)	3081, 1792, 1744, 1593, 1192, 1160
TBE-BPA	78.66	4.88	78.42	5.01	8.13 (d, 4H), 7.18-7.22 (m, 20H), 7.11 (d, 4H), 7.04 (d, 4H) 1.68 (s, 6H)	3087, 2968, 1796, 1736, 1504, 1202 1169

decreased the thermal stability and increased the solubility of the polymers. Thus, TBE-HQ polyester with

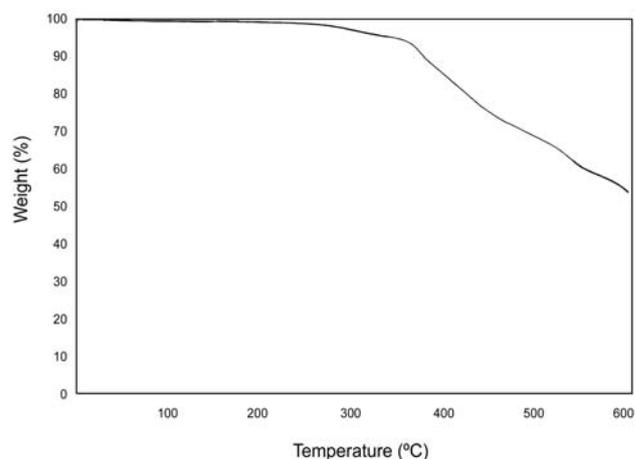
high rigid and symmetric structure showed the highest thermal stability and lowest solubility, while TBE-

**Table 2.** Yield, viscosity, and molecular weight of the polymers.

Polymer	Yield (%)	Inherent <sup>a</sup> viscosity (dL/g)	M <sub>w</sub> <sup>b</sup>
TBE-HQ	93	0.42	33600
TBE-DHN	91	0.40	32700
TBE-PhP	87	0.38	32600
TBE-1,4-DHAQ	86	0.37	31500
TBE-1,8-DHAQ	89	0.39	33100
TBE-BPA	86	0.38	31900

(a) Measured at a concentration of 0.5 g/dL in DMF at 30°C.

(b) According to GPC measurement in g/mol.

**Figure 4.** TGA Curve of TBE-HQ.

**Table 3.** Thermal characteristic data.

Polymer	T <sub>g</sub> (°C)	T <sub>0</sub> (°C)	T <sub>10</sub> (°C)	T <sub>max</sub> (°C)	Char yield (%)
TBE-HQ	188	291	376	408	53
TBE-DHN	183	284	370	391	50
TBE-PhP	185	278	366	388	48
TBE-1,4-DHAQ	176	267	362	356	41
TBE-1,8-DHAQ	172	262	358	352	40
TBE-BPA	159	251	341	338	36

T<sub>g</sub>: glass transition temperature; T<sub>0</sub>: initial decomposition temperature; T<sub>10</sub>: temperature for 10% weight loss; T<sub>max</sub>: maximum decomposition temperature; char yield: weight of polymer remained at 600°C.

BPA with flexible unit showed the lowest thermal stability and highest solubility among the prepared polymers. Also the other polyesters were between two extremes.

Thus, incorporation of bulky groups and disruption of symmetry enhanced the solubility of the related polyesters while the presence of ester groups and phenylation of backbone improved the thermal stability of the polymers. In this way, polyesters with high thermal stability and improved solubility were obtained.

## CONCLUSION

Patterned polyesters were prepared via polycondensation reactions of a diacid containing ester groups with different diols. Therefore, a diacid (TBE) with pre-formed ester groups and bulky groups were synthesized by nucleophilic reaction of benzoic acid with terephthaloyl chloride. Polycondensation reactions of its acid chloride derivative (TBECl) with different diols via high temperature solution method yielded different polyesters. All the polymers were fully characterized and their physical and thermal properties were studied. Due to the introduction of ester units and pendant groups the obtained polymers showed agreeable balance of properties including good thermal stability and improved solubility.

## REFERENCES

- Cassidy P.E., *Thermally Stable Polymers*, Marcel & Dekker, New York, 1980.
- Yang H.H., *Aromatic High-Strength Fibers*, Wiley, New York, 1989.
- Frazer A.H., *High Temperature Resistant Polymers. Polymer Reviews*, **17**, Interscience, New York, 1968.
- Jeong H.J., Kakimoto M., Imai Y., Synthesis and characterization of novel aromatic polyamides from 3,4-bis(4-aminophenyl)-2,5-diphenylpyrrole and aromatic diacid chlorides, *J. Polym. Sci. Part A: Polym. Chem.*, **29**, 767-772, 1991.
- Mulliez L., *PTA and Polyester-Session 1, A Global Overview in Polyester & PET Chain*, Presented at Maack Business Service, Amsterdam, The Netherlands, 2005.
- Liou G.S., Yen H.J., Su Y.T., Lin H.Y., Synthesis and properties of wholly aromatic polymers bearing cardofluorene moieties, *J. Polym. Sci. Part A: Polym. Chem.*, **45**, 4352-4363, 2007.
- Hsiao S.H., Chiang H.W., Synthesis and properties of new fluorinated polyarylates derived from 1,1-bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane and aromatic diacid chlorides, *Eur. Polym. J.*, **40**, 1691-1697, 2004.
- Iijima T., Kunimi T., Oyama T., Tomoi M., Modification of cyanate ester resin by soluble polyarylates, *Polym. Int.*, **52**, 773-782, 2003.
- Mehdipour-Ataei S., Einollahy P., Novel diols containing ester and amide groups and resulting poly(ester amide ester)s, *J. Appl. Polym. Sci.*, **93**, 2699-2703, 2004.
- Mehdipour-Ataei S., Einollahy P., Synthesis, characterization and properties of novel poly(ester-amide-urethane)s, *Macromol. Symp.*, **214**, 339-

- 350, 2004.
- Lee D.L., Wang D.C., Chiu W.Y., Synthesis of flexible polyarylate by interfacial polycondensation, *J. Polym. Res.*, **1**, 1-6, 1999.
  - Maiti S., Das S., Synthesis and properties of a new polyesterimide, *Angew Makromol. Chem.*, **86**, 181-191, 1980.
  - Maiti S., Das S., Synthesis and properties of polyesterimides and their isomers, *J. Appl. Polym. Sci.*, **26**, 957-978, 1981.
  - Douli S.K., Pal D., Maiti S., Synthesis of a novel polyesterimide, *J. Appl. Polym. Sci.*, **30**, 3867-3878, 1985.
  - Maresca L.M., Matzner M., Process for preparing polyarylates, *US Patent 4,386,186*, 1983.
  - Li C.H., Chen C.C., Chen K.M., Chang T.C., Studies on the synthesis and properties of soluble homo- and copolyester-imide derived from imide-diacid, *J. Appl. Polym. Sci.*, **55**, 747-752, 1995.
  - Yang C.P., Liou G.S., Chen R.S., Yang C.Y., Synthesis and properties of new organo-soluble and strictly alternating aromatic poly(ester-imide)s from 3,3-bis[4-(trimellitimidophenoxy)phenyl] phthalide and bisphenols, *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 1090-1099, 2000.
  - Tan L.S., Venkatasubramanian N., Aromatic polyamides containing keto-benzocyclobutene pendants, *J. Polym. Sci. Part A: Polym. Chem.*, **34**, 3539-3549, 1996.
  - Kang S.J., Hong S.I., Park C.R., Preparation and properties of a new aromatic polyamide with an ethoxycarbonyl pendant group: Poly(4,4-diamino-2-ethoxycarbonyl-benzanilide terephthalamide), *J. Polym. Sci. Part A: Polym. Chem.*, **38**, 936-942, 2000.
  - Liaw D.J., Liaw B.Y., Yu C.W., Synthesis and characterization of new soluble cardo polyamide-imides containing cyclododecyl groups, *J. Polym. Sci. Part A: Polym. Chem.*, **38**, 2787-2793, 2000.
  - Nishikubo T., Kameyama A., Nakajika T., Kishi K., Synthesis of new photoresponsive polyamides containing norbornadiene residues in the main chain, *Polym. J.*, **24**, 1165-1168, 1992.
  - Melissaris A.P., Mikroyannidis J.A., New crosslinkable polyimides, polyamides and polyureas derived from 2,4,6-tris(4-aminophenoxy)-s-triazine, *Eur. Polym. J.*, **25**, 455-460, 1989.
  - Yang C.P., Hsiao S.H., Yang C.C., Synthesis and properties of aromatic polyamides derived from 2,6-bis(4-aminophenoxy)naphthalene and various aromatic dicarboxylic acids, *J. Polym. Sci. Part A: Polym. Chem.*, **35**, 2147-2156, 1997.
  - Liaw D.J., Wang K.L., Synthesis and characterization of fluorine-containing polyamides derived from 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane by direct polycondensation, *J. Polym. Sci. Part A: Polym. Chem.*, **34**, 1209-1217, 1996.
  - Liaw D.J., Chang F.C., Leung M.K., Chou M.Y., Muellen K., Molecular architecture of novel organosoluble polyimides, *Macromolecules*, **38**, 4024-4029, 2005.