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Synthesis and Characterization of New Polyesters Derived from Diphenols and Aromatic Diacids Chlorides

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Summary

A series of aromatic polyesters, were synthesized under phase transfer conditions. The copolymers were obtained in an essentially quantitative yield. These polyesters were soluble in chloroform and readily form clear, colorless films from solution. The optimum conditions of polymerization were obtained via interfacial polymerization at room temperature and with a reaction time of 4 h in chloroform. All polymers were characterized by FTIR, GPC, viscosity, water contact angle, water absorption, TGA, DSC, X-ray, and NMR. The structures of the polymers were confirmed by NMR and FTIR spectroscopy. The prepared polyesters showed excellent thermal stability as measured by TGA (10% wt. loss) is moderate and ranges from 438 to 473 °C in argon, glass transition temperatures are between 147 and 215 °C, water contact angles for these polymers ranged were from 74° to 90°, Inherent viscosity values range obtained from 0.35 to 1.3 dL.g-1and Mw values range from 30.5 to 159 x 10^3.

Introduction

Aromatic polyesters (polyarilates) containing the 6F moiety were first reported by Korshan et al. on polymers condensed from bisphenol AF and phthalic acids [1]. The benefits of inclusion of 6F moiety in polymer backbones can be summarized as follows: increased T_g, improved solubility, decreased water absorption, increase thermal stability, lower dielectric constant, decrease color, decrease crystallinity. Polyarylates are aromatic polyesters consisting of aromatic diols and aromatic dicarboxylic acids. Numerous efforts have been made to clarify the structure-property relationships in polyesters. Some polyarylates are commercially available as high-performance engineering plastics [2, 3]. Polyesters are one route to get polymers with high molecular weight (this preparation has been previously carried out by means of solid state polymerization). Accordingly, starting materials are heated to a temperature higher than the glass transition temperature (T_g), but lower than the onset of the melting temperature (T_m) [4]. Aromatic polyesters are referred to as high performance materials due to their excellent thermal and mechanical properties. In recent years, much attention has been paid to fluorine-containing aromatic polyesters because of their unique properties compared to their non-fluorinated analogues, for example their solubility in common organic solvents [5, 6]. Different kinds of polyesters have been synthesized over the past decades from various types of diacid chlorides and diols; thermally stable polyesters, derived from isophthalic and terephthalic diacids with bisphenol-A, have been commercialized [7]. However, polyesters are generally difficult to process because of their limited solubility in organic solvents and their high melting temperature or high glass-transition temperature due to their rigid structures [8]. In this study, six novel thin-film membranes were produced by interfacial polymerization of an aqueous solution of a homologous series of bisphenols and an organic solution (diacid chloride). In this paper we worked with bisphenols dissolved in NaOH/H_2O and diacids chlorides in chloroform.

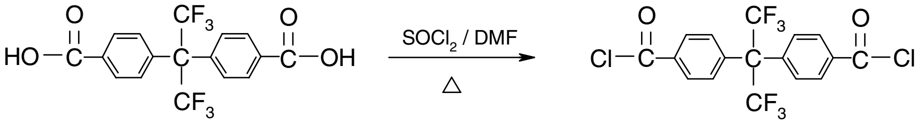
Experimental

Materials

The 2,2-bis(4-carboxyphenyl)hexafluoroisopropylidene, bisphenol O and bisphenol AF were kindly supplied by Central Glass, Japan. 4,4-Oxybis(benzoic acid), diphenic acid, bisphenol A, thionyl chloride and sodium hydroxide were obtained from Aldrich. Benzyl triethyl ammonium chloride, sodium bisulfite, methanol and chloroform were obtained from J. T. Baker.

Synthesis of diacid chloride

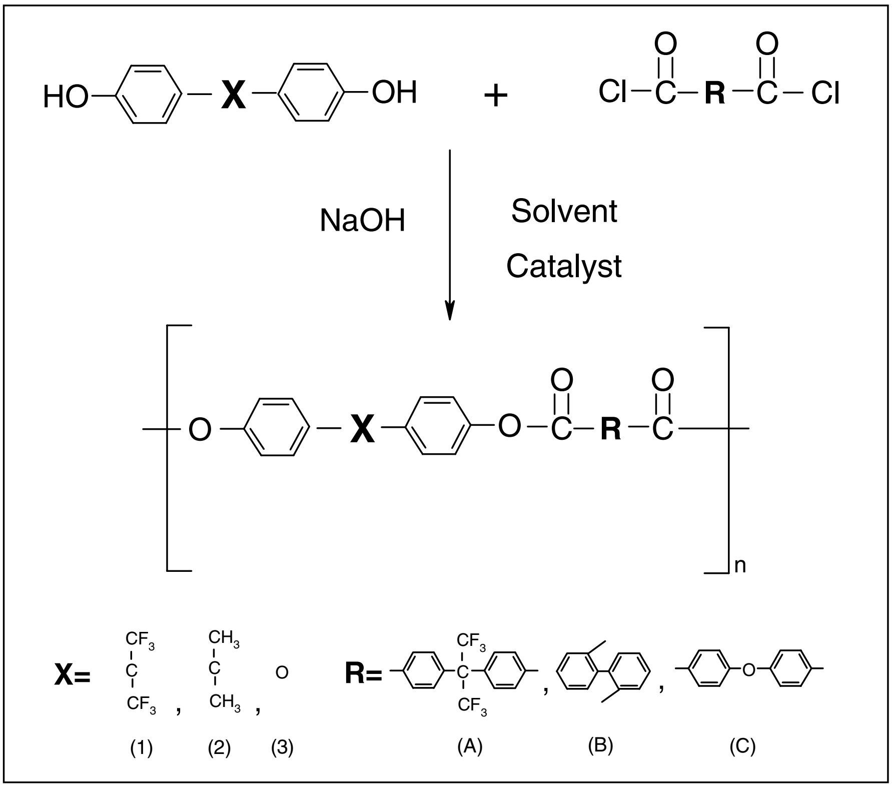
A 300 mL round-bottomed flask was charged with benzoic acid, thionyl chloride, and 3 drops of N,N-dimethylformamide used as a catalyst for the reaction. The reaction mixture was heated at 62 ± 2 °C with stirring for 2 hours. As a result, a clear yellow solution was formed, then it was cooled and the excess thionyl chloride was removed from the product by vacuum distillation. Hexane was added to the remaining viscous residue with heating. A solid white crystalline mass was formed and later dissolved in hexane at reflux reaction and the solution was vacuum filtered hot to yield a clear colorless filtrate which was cooled and filtered to obtain a diacid chloride (Scheme 1). To the remaining viscous residue were added 150 mL of hexane with heating. A solid white crystalline mass formed which was isolated and then dissolved in hexane at reflux and the solution was vacuum filtered hot to yield a clear colorless filtrate which was cooled and filtered.



Scheme 1. Preparation of 6-fluoro diacid chloride

Polymer Synthesis

Typical polyester polymerization: In a 100 mL three-neck round-bottomed flask equipped with a mechanical stirrer, 4.4 mmol of bisphenol, 8.8 mL 1M of NaOH, 10 mL of H_2O were placed. The mixture was stirred until the bisphenol dissolved. A solution of 4.4 mmol of diacid chloride, 0.2 g of benzyltriethylammonium chloride, and 0.02 g of sodium bisulfite in 20 mL of chloroform was added to the bisphenol solution. The resultant mixture was stirred vigorously for 4 h. The polymer was precipitated in methanol with rapid stirring and the white precipitate was collected by suction filtration and then vacuum dried. The polymer was redissolved in chloroform, reprecipitated into methanol, filtered, and vacuum dried (60 °C) overnight (Scheme 2).



Scheme 2. Route of synthesis of polyesters

Measurements

FTIR-ATR (attenuated total reflectance) spectra were taken using a Perkin-Elmer Paragon 500 spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT). The onset of glass transition temperature for every polymer was evaluated from the second scans of a DSC run at a 20 °C/min temperature ramp in a DSC 2010 calorimeter (TA Instruments, New Castle, DE). The decomposition temperatures in argon were determined from the thermogravimetric analysis carried out in a TGA Q50 (TA

Instruments, New Castle, DE). The contact angle of water droplets was measured using a Tantec CAM-Micro instrument. The average-molecular mass for every polymer was determined from Gel Permeation Chromatography (GPC) at 25 °C in chloroform using Styragel HR5E and HR4E columns after calibration with standard polystyrene samples. Water absorption measurement was done gravimetrically; the films were immersed in water at room temperature for 24 h and then weighed. X-ray spectroscopy data was obtained with a diffractometer Bruker-AXS D8-Advance. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were observed at 300 MHz, using a 300 MHz Varian Unity Inova Spectrometer.

Results and Discussion

The polyarylates were prepared by the condensation (Scheme 2), diacid chloride with either bisphenol. Polymerization in chloroform with the use of benzyl triethyl ammonium chloride (catalyst) with sodium bisulfite (anti-oxidant), were conduced phase-transfer catalyst. All of the polyesters were soluble in solvents such as chloroform, toluene, tetrahydrofuran, and other aprotic solvents. These polymers could be cast readily from chloroform solution to form clear and colorless films. Optimal reaction time was 4h, which were the best conditions, because from 30 minutes to 2 hours obtained polymer with low molecular weight (soluble in methanol), at 4h obtained high molecular weight. The polyesters have been prepared in excellent yield from 93 to 98 %. X-ray diffraction patterns consisted of a diffuse halo, due to the amorphous regions in the polymers, with no evidence of any crystalline diffraction (Fig. 1).

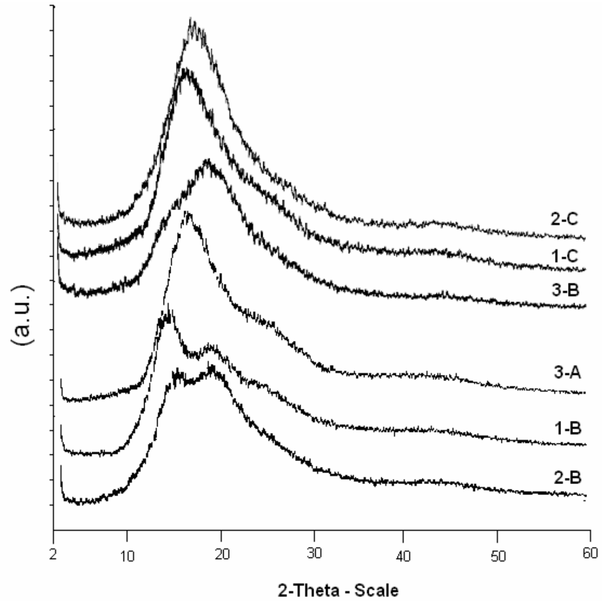


Figure 1. X-ray diffractograms of intensity Vs angle (2θ) for polyesters

Table 1. Chemical structure of the polyesters repeating units labeling the corresponding protons and carbons for NMR

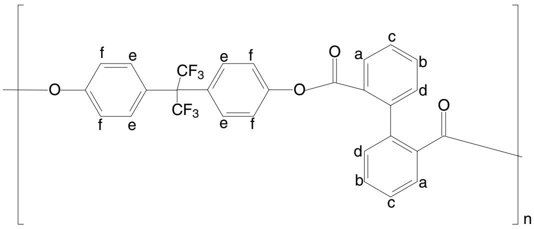
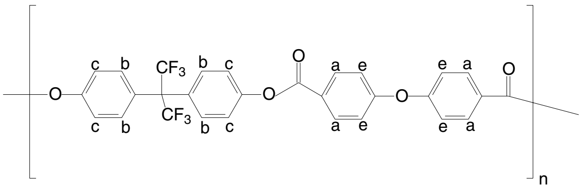
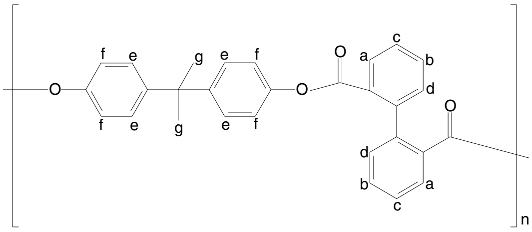
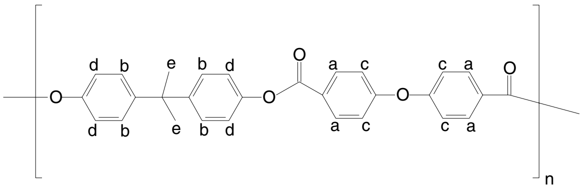
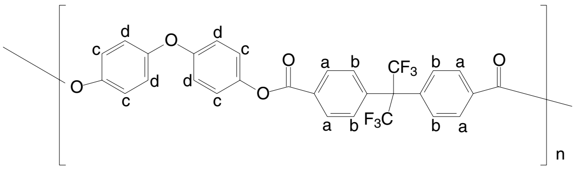
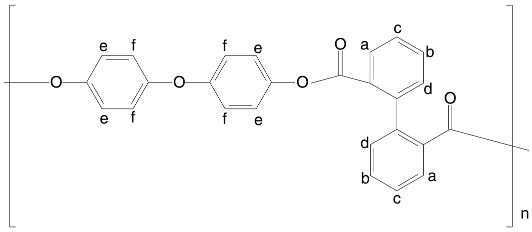
Code	Polyester
1-B	
1-C	
2-B	
2-C	
3-A	
3-B	

Table 2. Results of Nuclear Magnetic Resonance and Infrared

Sample	*^{1}H NMR (δ in ppm)*	*^{13}C NMR (δ in ppm)*	FTIR (cm^{-1})
1-B	6.89 (d, 4H, H_f); 7.28 (d, 4H, H_e); 7.32 (d, 2H, H_d); 7.50 (t, 2H, H_c); 7.62 (t, 2H, H_b); 8.19 (d, 2H, H_a).	63.9 [m, $(\Phi)_2$-C-$(CF_3)_2$]; 121.3 (aromatic); 123.9 (c, CF_3); 127.7; 128.3; 130.4; 130.7; 131.3; 132.5; 143.5; 151.0 (aromatic); 164.9 (C=O)	1738 -C=O 1210 –O-C=C 1600 –C=C
1-C	7.18 (d, 4H, H_d); 7.28 (d, 4H, H_c); 7.53 (d, 4H, H_b); 8.25 (d, 4H, H_a).	64.1 [m, $(\Phi)_2$-C-$(CF_3)_2$]; 118.9; 121.6 (aromatic); 124.1 (CF_3); 124.8; 130.7; 131.5; 132.7; 151.3; 160.7 (aromatic); 164.0 (C=O)	1735 -C=O 1211 –O-C=C 1591 –C=C
2-B	1.56 (s, 6H, CH_3); 6.75 (d, 4H, H_f); 7.08 (d, 4H, H_e); 7.29 (d, 2H, H_d); 7.45 (t, 2H, H_c); 7.57 (t, 3H, H_b); 8.16 (d, 2H, H_a).	30.8 (C-CH3); 42.3 (-C-); 120.7; 127.4; 127.6; 128.7; 130.3; 130.6; 132.0; 143.5; 147.6; 148.4 (aromatic); 165.4 (C=O)	1728 -C=O 1234 –O-C=C 1596 >C=C
2-C	1.72 (s, 6H, CH_3); 7.13 (d, 4H, H_d); 7.16 (d, 4H, H_c); 7.31 (d, 4H, H_b); 8.23 (d, 4H, H_a).	30.9 (C-CH_3); 42.5 [m,$(\Phi)_2$-C-$(CH_3)_2$]; 118.8; 121.0; 125.2; 127.9; 132.5; 148.0; 148.0; 160.5 (aromatic); 164.4 (C=O)	1737 -C=O 1609 –O-C=C 1241 –C=C
3-A	7.10 (d,4H, H_d); 7.20 (d,4H, H_c); 7.57 (d,4H, H_b); 8.24 (d,4H, H_a).	64.8 [m, $(\Phi)_2$-C-$(CF_3)_2$]; 119.7; 122.8 (aromatic); 123.7 (c, CF_3); 130.1;130.4; 138.2; 146.2, 154.9 (aromatic); 164.3 (C=O)	1738 -C=O 1210 –O-C=C 1600 –C=C
3-B	6.81 (d, 4H, H_f); 6.87 (d, 4H, H_e); 7.32 (d, 2H H_d); 7.47 (t, 2H, H_c); 7.59 (t, 2H, H_b); 8.16 (d, 2H, H_a).	119.3; 122.5; 127.5; 128.7; 130.3; 130.5, 132.1; 143.4; 146.0; 154.5 (aromatic); 165.5 (C=O)	1726 -C=O 1232 –O-C=C 1595 –C=C

^{1}H and ^{13}C NMR results of the polyesters and the peak assignments correspond to the structures with the different CH groups presented in Table 1. The ratios of the peak areas are in agreement with the expected molecular formula. Table 2 shows all the protons associated with the CH groups as a further proof for the structures. Infrared spectra indicated the presence of C=O between 1738 to 1726 cm^{-1}, O-C=C 1210 to 1236 cm^{-1}, and C=C 1609 to 1595 cm^{-1}, this information confirmed the presence of a polyarylate.

The molecular weights of the polyesters were characterized by their inherent viscosities in solution and by GPC determinations. Inherent viscosity values for polymers range from 0.35 to 1.30 dL.g^{-1}and Mw values range from 30.5 x 10^{-3} to 159 x 10^{-3} g.mol^{-1} with polydispersity values between 1.2 and 2.6 for polymers 1-C, 2-B, 2-C, 3-A and 3-B, whereas for polyester 1-B the polydispersity was 8.8 (Table 3), this is evidence that the polymers were indeed of high molecular weight.

Table 3. Selected Physical Properties of Polyesters

Sample	**Inh viscosity ($CHCl_3$, dL g^{-1})**	**Mn (x10^{-3})**	**Mw (x10^{-3})**	**PD**	**Yield (%)**
1-B	0.91	17.9	159.0	8.8	91
1-C	1.30	27.8	66.7	2.4	98
2-B	0.83	56.5	151.0	2.6	93
2-C	0.71	24.0	30.5	1.2	96
3-A	1.20	64.0	155.6	2.4	98
3-B	0.35	23.8	62.9	2.6	96

Table 4. Thermal Properties and water absorption of Polyesters

Sample	**T_g (2nd heating)* (°C)**	**TGA (°C) (10%wt loss)***	**% Char Yield (800 °C)**	**Water absorption**	**Water Contact Angle (°)**
1-B	162	448	29.1	0.18	76 ± 2
1-C	210	467	41.4	0.13	90 ± 2
2-B	160	440	19.6	0.49	74 ± 1
2-C	169	461	27.1	nil	79 ± 1
3-A	215	473	10.0	0.18	88 ± 2
3-B	147	438	42.4	0.14	75 ± 1

* measured at 10 °C/min in Ar

Glass transition temperature (T_g) could be clearly determined by DSC thermograms, values were between 147 and 215 °C, confirmed amorphous material. Table 4 summarizes the onset of the glass transition values. The values of the T_g´s decrease with the presence of fluorine atom (1-B, 3-B) content of the polymer. However, the different T_g between these polymers may be affected to some extent by the differences in molecular weight. The thermal stability data for the polyesters (10% wt loss) are as expected and range from 438 °C to 473 °C, these temperatures indicated good stability. All of them exhibit a great stability at least from TGA determinations in argon (see Table 4).

Water absorption in the polymers was extremely low, and constant weights were observed within 24 h for films immersed in water at ambient temperature: 1-B, 0.18%; 1-C, 0.13%; 2-B, 0.49%; 2-C, nil; 3-A, 0.18%; 3-B, 0.14% (Table 4). Low water absorption is requisite for materials used in electronic applications. Water contact angles for these polymers ranged from 75° to 90° (Table 4) confirmed hydrophobic materials (confirmed low water absorption).

Conclusions

A homologous series of six polyesters were prepared from different bisphenols and some aromatic diacids chlorides. The polyarylates were readily soluble in polar solvents and could be cast into amorphous readily formed tough films, clear, colorless film; syntheses proved ordinary with excellent yields. Water contact angles and water absorption data were as expected and not particularly notable. Solution viscosities and Mw indicated high molecular weight; FTIR and NMR confirmed chemist structure of polyester in all polymers. X-ray diffraction and DSC showed amorphous materials. These polyarylates presented moderately high thermal stability, can be considered as candidates of high-performance polymeric materials for applications as gas separation membranes and dielectric layers.

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References

1. Korshak V., Vinogradoba S., and Pankratov V. (1964). Dokl. Akad Nauk, SSSR 156: 880
2. Sheng-Huei H., Hsien-Wei Ch (2004) Eur Polym J 40: 1691
3. Bucio E., Fitch J. W., Venumbaka S. R. and Cassidy P. E. (2005) Polymer 46: 3791
4. Vouyiouka S.N., Karakatsani E.K., Papaspyrides C.D. (2005) Prog. Polym. Sci. 30: 10
5. E-Joon Ch., Hill D., Ki-Yup K. (1997) Polymer 38: 3669
6. Seung-Yeop K., Min-Oh Y., Juhn R., Dong-Young K., Jae-Jin K. (1997) Journal of Membrane Science.132: 183
7. Duboisa P., Krishnanb M., Narayan R. Polymer (1999) 40:3091
8. Bahman T., Hamid Y., Gholam K. (2004) Eur Polym J 40, 1651
9. Kane K., E. Wells L. A., Cassidy, P. E. (1991) High Performance Polymers 3: 191
10. Gharbi S., Andreolety J. P., Gandini A. (2000) Eur Polym J 36: 463
11. Cassidy P. E., Aminabhavi T. M., Farley (1989) Macromol. Chem. Phys. 29: 365
12. Tullos G. L., Cassidy P. E., St.Clair A. K. S. (1991) Macromolecules 24: 6059