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Synthesis and properties of aliphatic spirodilactam diphenol containing polyesters

Emilio Bucio*, John W. Fitch, Sreenu R. Venumbaka, Patrick E. Cassidy*

Shell Center for Polymer Science and Technology and Institute for Environmental and Industrial Science, Texas State University, San Marcos, TX 78666, USA

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Abstract

A series of aromatic polyesters containing 1,6-diazaspiro[4,4]-nonane-2,7-dione were synthesized under phase-transfer conditions. The copolymers were obtained in essentially quantitative yield, theses were soluble in common organic solvents, and would readily form clear, colorless films from solution. The optimum conditions of polymerization, was obtained via polycondensation at room temperature and reaction time of 4 h in chloroform. All polymers were characterized by FTIR, GPC, viscosity, water contact angle, water absorption, TGA, DSC and TMA. The prepared polyesters showed excellent thermal stability, as measured by TGA (10 wt% loss), are only moderate due to the alicyclic component and range from 365 to 401 °C in air; however, glass transition temperatures are quite high (245–309 °C). The inherent viscosities of these solutions ranged from 0.77 to 1.40 dl g^{-1}, depending on the polyester structure. The structures of the polyesters were confirmed by FTIR spectroscopy.

Keywords: Polyester; Synthesis; Interfacial polymerization

1. Introduction

Numerous efforts have been made to clarify the structure property relationships in polyarylates, some of these polymers having been commercialized as high-performance engineering plastics. A number of halogen-containing aromatic polyesters have been studied with respect to the effect of chemical structure on thermal properties; however, studies on fluorine-containing polyarylates are few [1,2].

A significant amount of research has been conducted aimed at incorporating the hexafluoroisopropylidene group (HFIP) via a bis-aromatic diacid (6FDAC). This approach has yielded solution or melt processable material from previously intractable polymers, many of which are good candidates for use as a gas separation membranes, seals, coatings and other high temperature applications [3].

The benefits of inclusion of the 6FDAC moiety in polymer backbone can be summarized as follows: increased T_g, improved solubility, decreased water absorption, increased thermal stability, lower dielectric constant, decreased color and decreased crystallinity [4].

Polyesters are important class of high performance and engineering polymers, which find use in a number of diverse applications [5–7]. 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 acids with bisphenol-A have been commercialized [8]. 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 by virtue of their rigid structures. Therefore, development of polyesters for use at high temperature with improved solubility is an important goal.

One of the approaches to improve solubility of the polymers without extreme loss of their high thermal stability is the introduction of polar and flexible groups into the polymer backbone [9–13]. The incorporation of bulky pendent groups can also provide beneficial effect for solubility because this approach produces a separation of

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* Corresponding authors. Address: Instituto de Ciencias Nucleares-UNAM, Ciudad Universitaria, 04510 Mexico, DF, Mexico. Tel.: +52 512 245 3632; fax: +52 512 245 1892.

E-mail addresses: ebucio@nuclecu.unam.mx (E. Bucio), pcassidy@txstate.edu (P.E. Cassidy).

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chains and lowering the chain packing with a gain of free volumes.

2. Experimental

2.1. Materials

The 2,2-bis(4-carboxyphenyl)hexafluoroisopropylidene was kindly supplied by Central Glass, Japan. 4,4-Oxybis (benzoic acid), diphenic acid, isophthaloyl dichloride, terephthaloyl chloride, thionyl chloride and sodium hydroxide were obtained from Aldrich. Benzyl triethyl ammonium chloride, sodium bisulfite, methanol and chloroform were obtained from Baker, and the 1,6-diazaspiro[4,4]-nonane-2,7-dione (SDL) was obtained from Shell Oil Company.

2.2. Measurements

Water absorption measurement was done gravimetrically; the films were immersed in water at room temperature for 24 h and then weighed. Sessile drop water contact angles were measured at ambient temperature using a Tantec CAM-Micro instrument. Thermogravimetric analysis (TGA) measurements were obtained using a Rheometric Scientific Model TGA 1000M instrument. Differential Scanning Calorimetry (DSC) results were obtained using a Rheometric Scientific Model DSC Plus instrument. Gel Permeation Chromatography (GPC) was performed at 25 °C in tetrahydrofuran using Styragel HR5E and HR4E columns after calibration with standard polystyrene samples, Thermo Mechanical Analysis (TMA) measured in NASA for obtained T_g.

2.3. Synthesis of diacid chloride

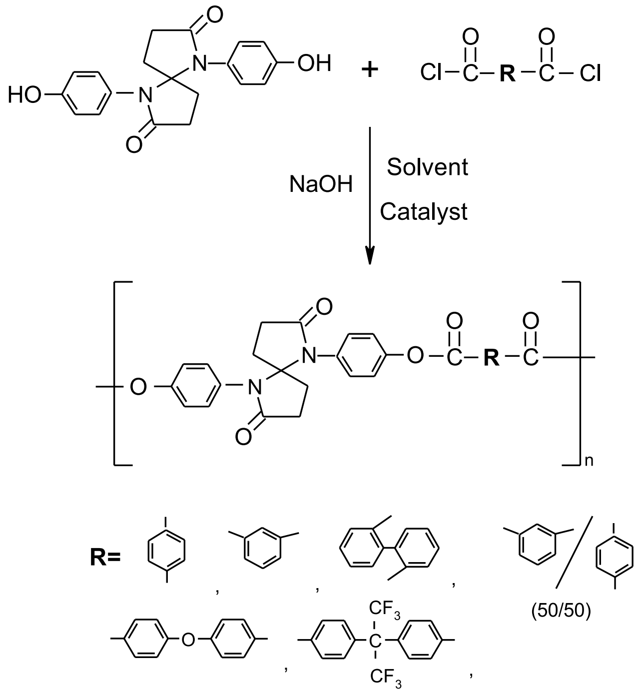
A 300 ml, round-bottomed flask was charged with 10 g of 4,4′-oxybis(benzoic acid), 60 ml of thionyl chloride, and three drops of *N*,*N*-dimethylformamide (DMF) as reaction catalyst. The reaction mixture was heated to 60–65 °C with stirring for 2 h. The resulted clear yellow solution was cooled, and excess thionyl chloride was removed from the product by vacuum distillation [4]. 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 to yield oxydibenzoyl chloride (80% yield, mp 94 °C); hexafluorodiacid chloride (6FDAC) (85% yield, mp 102 °C) and diphenic acid chloride (89% yield, mp 103 °C) were prepared like ODAC. Isophthaloyl chloride and terephthaloyl chloride used as received from Aldrich.

2.4. Polymer synthesis

In a 100 ml three-neck, round-bottomed flask equipped with a mechanical stirrer were placed 4.4 mmol of 1,6-diazaspiro[4,4]-nonane-2,7-dione (SDL), 8.8 mmol of NaOH (8.8 ml 1 M), and 10 ml of H_2O and the mixture was stirred until the SDL had dissolved. A solution of 4.4 mmol of diacid (6FDAC, DPAC, ODAC, etc.), 0.2 g of benzyl triethyl ammonium chloride, and 0.02 g of sodium bisulfite(anti-oxidant) in 20 ml of chloroform, were added to the SDL solution, and 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 dried in vacuo. The polymer was redissolved in chloroform, reprecipitated into methanol, filtered, and dried in vacuum at 60 °C overnight. After filtration the polymer was dried in vacuo for 15 h. The polymers were characterized by thermogravimetry analysis, differential scanning calorimetry, thermo mechanical analysis, infrared spectroscopy, solution (inherent) viscosity, water absorption (gravimetrically), and water contact angle.

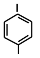
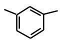
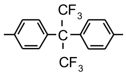
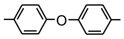
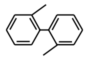
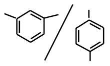
3. Results and discussion

Table 1 shows the results of polymerizations (Scheme 1) in chloroform for 4 h with the use of benzyl triethyl ammonium chloride (catalyst) with sodium bisulfite(anti-oxidant), which were the best conditions arrived at after the investigation of several options, i.e. different solvents (toluene, 1,1,2-trichloroethane, chloroform), different



Scheme 1. Interfacial polymerization.

Table 1
Selected physical properties of polyesters

R	Inh ($CHCl_3$, dl g^{-1})	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	PD	Water contact angle ($\pm 2°$)	Water absorption
	0.95	11	35	3.2	66	5.9
	0.85	2.6	21	8.0	68	9.0
	0.95	13.5	61	4.5	79	4.0
	1.40	14.3	27	2.0	72	6.8
	0.77	12.5	124	9.8	72	4.6
 (50/50)	0.90	74	166	2.3	64	8.6

catalysts (tetra butyl ammonium bromide, triethyl ammonium chloride with sodium bisulfite and triethyl ammonium bromide) and different reaction times (1, 2, 4, and 10 h). Clearly, yields were excellent; solutions viscosities were all quite good and water contact angles in the range of 64–79° with the fluorinated material being highest, as expected.

Infrared spectra indicated presence of an aromatic ring 3070 cm^{-1}, C=O 1740 cm^{-1}, C=C 1600 cm^{-1}, CH_3 2964 cm^{-1}, aromatic 3070 cm^{-1}, N 3480 cm^{-1}. This information confirmed at the presence of a polyarylate.

Water absorptions ranged from 4 to 9%. Lowest water absorption by SDL/6FDAC at 4%, and the highest by SDL/isophthaloyl dichloride 9.0% (Table 1). Incorporation of 6F decreases water absorption, as expected. The benefits of inclusion of the 6F moiety in SDL/6FDAC, decrease crystallinity and water absorption.

Thermogravimetric analysis in argon indicated initial decomposition at 360–400 °C and in air at 320–360 °C (Table 2). Presence of 6F increase thermal stability, 407 and 401 °C (10 wt% loss) in argon and air, respectively.

Differential scanning calorimetry indicated amorphous polymer; and the glass transition could not be observed from room temperature to 300 °C at 10 °C min^{-1}, in first heating was possible to see T_g, but in second heating disappeared, because T_g is close to decomposition.

Thermo mechanical analysis indicate T_g from 245 to 309 °C, in this case was not possible to see glass transition in SDL/6FDAC, some times is impossible to see T_g in polyester systems.

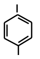
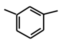
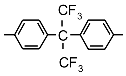
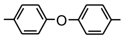
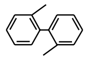
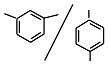
Inherent viscosities ranged between 0.77 and 1.40 dl g^{-1}; and films were readily solvent cast which were tough, clear and colorless.

M_w values range from 21,000 to 166,000 with polydispersity values between 2 and 9.8.

4. Conclusions

An homologous series of six polyesters was prepared from a 1,6-diazaspiro[4,4]-nonane-2,7-dione and several aromatic diacid chlorides: hexafluoro diacid chloride, oxybisbenzoic chloride, biphenyl diacid chloride,

Table 2
Thermal properties of polyesters

R	TGA (°C) (10 wt% loss)[a]		% Char yield (800 °C)		T_g (°C)
	Argon	Air	Argon	Air	
	398	367	44	4	309
	390	368	42	3	284
	407	401	44	3	–
	377	365	42	1	286
	396	400	32	3	245
 (50/50)	400	368	49	8	292

[a] Measured at 20 °C min^{-1}.

isophthaloyl chloride and terepthaloyl chloride. After some experimentation with reaction times, solvents and catalysts, the syntheses proved to be ordinary with excellent yields and solution viscosities, water contact angles, water absorption and thermal data were as expected and not particularly notable. However, there was no indication of crystallinity and glass transition temperature could not be detected by DSC, but was possible by TMA.

All the polymers synthesized were soluble in common organic solvents and readily formed tough, clear, colorless films, and good thermal stability.

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