International Journal of Natural and Engineering Sciences 2 (3): 75-78, 2008
ISSN: 1307-1149 www.nobel.gen.tr

Synthesis and Characterization of Novel Soluble Aromatic Polyesters with Pendant Cyano Groups

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Received: April 12, 2008
Accepted: July 21, 2008

Abstract

2, 6-Bis (4-carboxyphenoxy) benzonitrile was first synthesized by condensation of 2, 6-difluorobenzonitrile with p-Hydroxybenzoic acid in the presence of KOH and DMSO. And then the reaction of 2, 6-bis (4-carboxyphenoxy) benzonitrile with sulfur oxychloride yieded 2,6-bis (4-chloroformylphenoxy) benzonitrile (BClPOBN). A series of novel soluble aromatic polyesters with pendant cyano groups were prepared by polycondensation of different aromatic diphenols and 2,6-bis (4-chloroformylphenoxy) benzonitrile (BClPOBN) using 1,2-dichoroethane (DCE) as solvent and pyridine as the absorbent of HCl. The resulting polymers were characterized by different physico-chemical techniques, such as FT-IR, Thermogravimetric analysis (TGA), Wide angle X-ray diffraction (WAXD), and so on. All the polymers had the proposed structure and were amorphous. Thermogravimetric studies showed that the thermal decomposition temperatures (T_ds) at 5% weight loss of polymers were 391~406 *v* in N_2 atmosphere, indicating they had good thermal stabilities. The prepared polyesters exhibited good solubility in some common solvents, such as $CHCl_3$, ethylene dichloride (DCE), CH_2Cl_2, tetrahydrofuran (THF) as well as aprotic polar organic solvents such as N-methyl pyrrolidone (NMP), N, N-dimethylacetamide (DMAC) and N, N-dimethylformamide (DMF), and so on.

Key words: novel soluble aromatic polyesters with pendant cyano groups, polycondensayion, solubility

INTRODUCTION

Aromatic polyesters are a type of high-performance polymers with excellent thermal, physical and mechanical properties. But their poor solubility in organic solvents often restricts the use for many applications [1~2]. Thus, it appears very important that various structure changes are introduced in the polyesters' chain to obtain better solubility for processing [3~6]. Previously it has been found that introduction of groups with sp^3-hybridized atoms ($–CR_2$-), ether linkage, and pendant phenyl groups can improve the solubility of polyesters [7~9]. Due to strong polarity and easy reactivity of cyano group, better heat-resistant properties of the polymers would be received and many functional polymers could be prepared by the several reactions of cyano group if cyano group was incorporated into polymers' main chain as side groups. Moreover, these aromatic polymers containing pendant cyano groups would undergo crosslinking on being heated to elevated temperatures [10~11]. As a result of crosslinking, the glass transition temperatures (T_gs) of these polymers would increase and solvent-resistant films could be yielded. However, it appears that soluble aromatic polyesters with pendant cyano groups have not been reported in detail in the open literatures. In this article, we designed a series of novel soluble aromatic polyesters with pendant cyano groups as the following route: a new monomer 2, 6-bis (4-chloroformylphenoxy) benzonitrile (BClPOBN) was first prepared. Then a series of novel soluble aromatic polyesters with pendant cyano groups were synthesized by polycondensation of 2, 6-bis (4-chloroformylphenoxy) benzonitrile (BClPOBN) and different aromatic diphenols.

EXPERIMENTAL

Materials

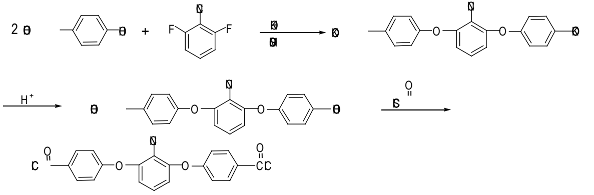
P-Hydroxybenzoic acid (Aldrich, Shanghai Wulian Chemical Factory, China), 2, 6-difluorobenzonitrile (Aldrich), N-methyl pyrrolidone (NMP, Aldrich), dimethyl sulphoxide (DMSO, Aldrich)) , N,N- dimethylacetamide (DMAC, Aldrich, Tianjin Damao Chemical Reagent Factory, China) and N,N -dimethylformamide (DMF, Aldrich, The First Chemical Reagent Factory of Tianjin, China) were used as received. 1, 2-Dichloroethane (DCE, Aldrich) and pyridine were dried with molecular sieves (type 4Å). The other fractions were collected and stored over sieves.

Synthesis of new Monomer: 2, 6-bis (4-chloroformylphenoxy) benzonitrile (BClPOBN)

To a 250ml, round-bottomed flask equipped with a mechanical stirrer, a thermometer, nitrogen inlet and out tubes, and a Dean-Stark trap, 72 mmol of p-Hydroxybenzoic acid, 144mmol of KOH, 70 ml of dimethyl sulphoxide (DMSO) and 55 ml of tolune were added. The reaction mixture was heated to 140~150*v* until no further water was azeotropically distilled from the reaction mixture, and then temperature was raised to 170 *v* to remove tolune. After being cooled to 40*v*, 30mmol of 2, 6-difluorobenzonitrile was added and the reaction mixture was heated to185~195*v* and stirred at this temperature for 8h. After cooling to room temperature, the reaction mixture was dissolved in water and hydrochloric acid was added, and then the product was precipitated. The solid product was washed with water and recrystallized from the mixture of ethyl alcohol and water three times to give 2, 6-bis (4-carboxyphenoxy) benzonitrile. Yield 85%; Purity 96%; m.p.311~312*v*;IR(KBr): 3429(OH),2235(CN),1695(C=O),1605,1578,1506(C=C)*v*1245*v*—O—*v*. Elemental Analysis calculated for $C_{21}H_{13}NO_6$; C, 67.2; H, 3.47; O, 25.6. Found: C, 67.3; H, 3.54; O, 25.7.

The reaction of 2, 6-bis (4-carboxyphenoxy) benzonitrile with sulfur oxychloride yieded 2, 6-bis (4-chloroformylphenoxy) benzonitrile (BClPOBN). The product was recrystallized from anhydrous hexane. Yield 96%; Purity 97%; m.p.140~142*v*; IR(KBr): 2232(CN),1774(C=O),1602,1574,1497(C=C)*v*1245 *v*—O—*v*. Elemental Analysis calculated for $C_{21}H_{11}NCl_2O_4$; C, 61.65; H, 2.70; O, 15.53; Cl, 17.23. Found: C, 61.59; H, 2.67; O, 15.46; Cl, 17.36.

2, 6-Bis (4-chloroformylphenoxy) benzonitrile (BClPOBN) was synthesized as shown in scheme 1.

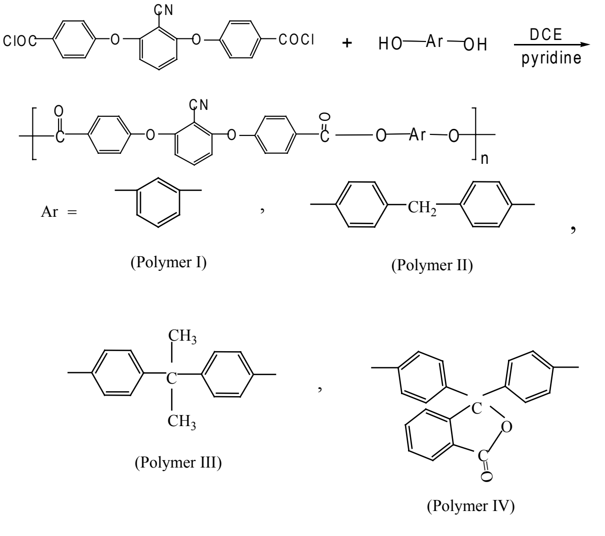


Scheme 1 Synthesis of BClPOBN

Polymer synthesis

To a 100ml, round-bottomed flask equipped with a mechanical stirrer, a thermometer, nitrogen inlet and out tubes. 0.01mol diphenols, 25ml of 1, 2-dichloroethane (DCE), and 1ml pyridine as the absorbent of HCl were added. Into the resulting suspension were added 0.01mol 2, 6-bis (4-chloroformylphenoxy) benzonitrile (BClPOBN). The reaction mixture was stirred at room temperature for 8 h and then warmed to 80 *v* over 2h. After the reaction is over, the products were precipitated from hexane, washed with water, and dried under vacuum to give the novel aromatic soluble polyesters with pendant cyano groups.

The novel soluble aromatic polyesters with pendant cyano groups were synthesized by polycondensation of 2, 6-bis (4-chloroformylphenoxy) benzonitrile (BClPOBN) and different aromatic diphenols as shown in scheme 2.



Scheme 2 Synthesis of novel aromatic polyesters

Characterization

Elemental analysis was performed with Perkin-Elmer Model 2400 CHN analyzer. The inherent viscosities (η_{inh}) of polymers were measured in a 0.1wt% NMP solution at 30*v*. The FT-IR spectra of the polymers in KBr pellets (2%) were recorded using a Nicolet FT-IR (510P) spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a Perkn-Emler 7 Series thermal analysis system with an increasing rate of 10*v*/min, N_2 atmosphere at the flow rate of 40ml/min, scanning scope ranging from 50 to 750*v*, and sample weight of 5.0~7.0mg.Wide angle X-ray diffraction (WAXD) was measured with a Rigaku D/MAX-*v*A X-ray diffractometer, using CuKa radiation, at 30KV and 20mA.The diffractogramas were recorded at room temperature over the rang of $2\theta=10$~40º.

RESULTS AND DISCUSSION

New monomer synthesis

2, 6-Bis (4-chloroformylphenoxy) benzonitrile (BClPOBN) was synthesized as shown in scheme 1. 2, 6-bis (4-carboxyphenoxy) benzonitrile was first synthesized by condensation of 2, 6-difluorobenzonitrile with p-Hydroxybenzoic acid in the presence of KOH and DMSO, and toluene was used for the azeotropic removal of water. Then the reaction of 2, 6-bis (4-carboxyphenoxy) benzonitrile with sulfur oxychloride yieded 2, 6-bis (4-chloroformylphenoxy) benzonitrile (BClPOBN), and a little DMF was added to improve the rate of production. The chemical structure of BClPOBN was confirmed by FT-IR and elemental analysis.

NOVEL POLYESTER SYNTHESIS

Scheme 2 outlines the synthesis of novel soluble aromatic polyesters with pendant cyano groups by polycondensation. Firstly, Inherent viscosities (η_{inh}) of polymers are affected by the purity of monomers. Thus, the monomers (BClPOBN and diphenols) must be puritied by recrystallizing many times before polycondensation. Secondly, the molar ratios of monomers (BClPOBN and diphenols) affect also the inherent viscosities (η_{inh}) of polymers. According to the modified Carothers equation [12], i.e., $X_n= (1+r)/ (1-r)$, where X_n is the number-average degree of polymerization and r is the molar ratio of BClPOBN to diphenols, the η_{inh} values of polymers are highest when the molar ratio of BClPOBN to diphenols is near to 1:1. In addition, pyridine which is added to the reaction mixture as the absorbent of HCl is benefit to obtain higher-weight-molecular polymers.

The FT-IR and elemental analysis

The chemical structures of the prepared polyesters were confirmed by FT-IR and elemental analysis. The results are as follows:

Polymer I: IR (cm^{-1}): 2231(CN); 1739(C=O, ester); 1261(C-O-C, ester); 1242(Ar-O-Ar). Calculated(found)elemental Analysis for $(C_{27}H_{15}NO_6)_n$, %: C, 72.16(72.14); H, 3.34(3.33); N, 3.12(3.10).

Polymer II: IR (cm^{-1}): 2232(CN); 1738(C=O, ester); 12621(C-O-C, ester); 1241(Ar-O-Ar). Calculated(found)el emental Analysis for $(C_{34}H_{21}NO_6)_n$, %: C, 75.70(75.66); H, 3.90(3.89); N, 2.60(2.58).

Polymer III: IR (cm^{-1}): 2231(CN); 1740(C=O, ester); 1259(C-O-C, ester); 1243(Ar-O-Ar); 2971($-CH_3$). Calculated(found) elemental Analysis for $(C_{36}H_{25}NO_6)_n$, %: C, 76.19(76.16); H, 4.41(4.39); N, 2.50(2.48).

Polymer IV: IR (cm^{-1}): 2233(CN); 1737(C=O, ester); 1774(C=O); 1259(C-O-C, ester); 1241(Ar-O-Ar). Calculated(found)elemental Analysis for $(C_{41}H_{23}NO_7)_n$, %: C, 76.76(76.71); H, 3.59(3.56); N, 2.18(2.17).

The elemental analysis values, i.e., C, H, and N content of polymers I-IV are in close agreement with theoretical values confirming the proposed structure. The FT-IR spectra of polymers show that All the spectra have a stretching vibration for the C=O group in the ester linkage, a stretching vibration for CN group, a stretching vibration for ester C-O-C , and a stretching vibration for the ether group asymmetrical vibration of Ar—O—Ar, indicating that the prepared polyesters have the proposed structure.

The WAXD analysis

The analysis of WAXD shows, all the polymers are amorphous. This might be attributed to the flexible units (meta-phenylene units,etc) and cyano pendant groups which can't make the polymers match the crystalline structure. The curves of polymer I, II, III and IV is shown in Figure 1.

Thermogravimetric analysis (TGA) of polymers

The thermal stabilities of the polymers were investigated by TG.A. Thermogravimetric analysis (TGA) was carried out on a Perkn-Emler 7 Series thermal analysis system with an increasing rate of 10*v*/min,N_2 atmosphere at the flow rate of 40ml/min,scanning scope ranging from 50 to 750*v*.The thermal decomposition temperatures (T_ds) at 5% weight loss of the polymers are also listed in Table 1. The thermal decomposition temperatures (T_ds) of the polymers show the polymers prepared are thermally stable from 391 *v* to 406 *v*, indicating that the novel polymers have good thermal stabilities used as novel polyester materials.

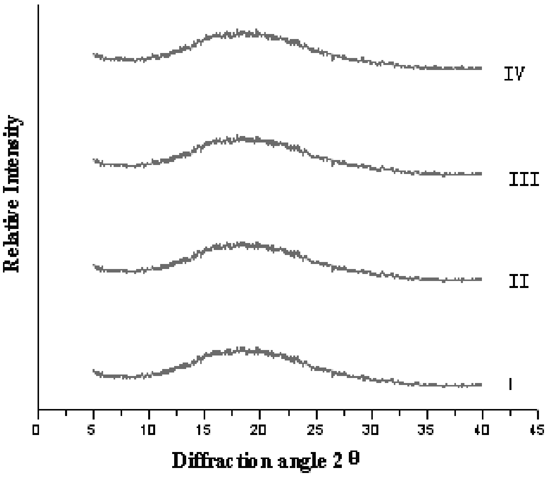


Figure.1 the WAXD curves of polymer I, II, III and IV

Table 1 the TGA of polymers

Polymer	I	II	III	IV
T_d (*v*)	391	397	406	403

T_d (*v*)*v*Temperatures at 5% weight loss

The solubility and inherent viscosities (η_{inh}) of polymers

The solubility behavior of the polymers prepared in this study was determined for powdery samples in excess solvents at room temperature for 24 h and the results are listed in Table 2. It is shown that all the polymers are soluble in some common solvents, such as $CHCl_3$, ethylene dichloride (DCE), CH_2Cl_2, tetrahydrofuran (THF) as well as aprotic polar organic solvents such as N-methyl pyrrolidone (NMP), N, N-dimethylacetamide (DMAC) and N, N-dimethylformamide (DMF), and so on, the good solubility of polymers might be attributed to flexible units (meta-phenylene units,etc) and cyano pendant groups. In addition, the good solubility of polymers indicates they have much potential for solvent processing and application. Inherent viscosities of the polymers are also given in Table 2. Inherent viscosities (η_{inh}) (0.61~0.68 dl/g) reveal that high molecular weight polymers are obtained in the given reaction medium. Thus, the polycondensation route is appropriate.

Table 2 the η_{inh} and solubility of polymers

Polymer	NMP	DMAC	DMF	$CHCl_3$	DCE	THF	C_2H_5OH	η_{inh}(dl/g)
Polymer I	+	+	+	+	+	+	-	0.63
Polymer II	+	+	+	+	+	+	-	0.68
Polymer III	+	+	+	+	+	+	-	0.67
Polymer IV	+	+	+	+	+	+	-	0.61

+: soluble; -: insoluble

CONCLUSIONS

The conclusions that can be drawn from the present study are as follows:

(1) A new monomer 2, 6-bis (4-chloroformylphenoxy) benzonitrile (BClPOBN) was first prepared. Then a series of novel soluble aromatic polyesters with pendant cyano groups were synthesized by polycondensation of 2, 6-bis (4-chloroformylphenoxy) benzonitrile (BClPOBN) and different aromatic diphenols.

(2) Thermogravimetric studies showed that the thermal decomposition temperatures (T_ds) at 5% weight loss of polymers were 391~406 *v* in N_2 atmosphere, indicating they had good thermal stabilities used as novel polyester materials.

(3) The prepared polyesters exhibited good solubility in some common solvents, such as $CHCl_3$, ethylene dichloride (DCE), CH_2Cl_2, tetrahydrofuran (THF) as well as aprotic polar organic solvents such as N-methyl pyrrolidone (NMP), N, N-dimethylacetamide (DMAC) and N, N-dimethylformamide (DMF), and so on, indicating they have much potential for solvent processing and application. Inherent viscosities (η_{inh}) (0.61~0.68 dl/g) reveal that high molecular weight polymers are obtained in the given reaction medium. Thus, the polycondensation route is appropriate.

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