Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Shirish J. Naik[a][b]; Bhimrao D. Sarwade[a]; Prakash P. Wadgaonkar[a]; Sudhakar S. Mahajan[a]
[a] Division of Polymer Chemistry, National Chemical laboratory, Pune, India [b] Thermax Limited, Pune

To cite this Article Naik, Shirish J. , Sarwade, Bhimrao D. , Wadgaonkar, Prakash P. and Mahajan, Sudhakar S.(1995) 'Copolyesters Containing Oxyethylene Linkages: Synthesis and Characterization', Journal of Macromolecular Science, Part A, 32: 1, 1071 — 1076

To link to this Article: DOI: 10.1080/10601329508019147

URL: http://dx.doi.org/10.1080/10601329508019147

MACROMOLECULAR REPORTS, A32(SUPPL. 7), 1071-1076 (1995)

COPOLYESTERS CONTAINING OXYETHYLENE LINKAGES: SYNTHESIS AND CHARACTERIZATION*

Shirish J. Naik[**], **Bhimrao D. Sarwade, Prakash P. Wadgaonkar and Sudhakar S. Mahajan**[+]

Division of Polymer Chemistry,
National Chemical laboratory,
Pune 411 008, India.

ABSTRACT

Oxyethylene-containing copolyesters were synthesized from bisphenol-A (BPA) and diacyl chlorides containing oxyethylene linkages, isophthaloyl chloride (IPC), and terephthaloyl chloride (TPC) by interfacial polycondensation. All the copolyesters were obtained in almost quantitative yields and showed film forming properties. The copolyesters were amorphous/semicrystalline and were soluble in common organic solvents. Copolyesters showed similar pattern of decomposition with no weight loss below 380°C in nitrogen.

INTRODUCTION

Aromatic polyesters (polyarylates) belong to a category of engineering thermoplastics which have been dormant for some time but are presently witnessing renewed commercial interest. Generally, they are derived from bisphenol-A and aromatic dicarboxylic acids such as terephthalic/isophthalic acids. However, these polymers have problems in processing due to high softening temperature by virtue of their rigid structure. Many attempts have been made in the past to modify aromatic polyesters for improving the processability (1-9).

The objective of the present work was to synthesize and characterize copolyesters containing flexibilizing oxyethylene linkages and to study the effect of their incorporation on the thermal properties of the resulting copolyesters. The copolyesters were synthesized from bisphenol-A and diacyl chlorides containing oxyethylene linkages, isophthaloyl chloride and terephthaloyl chloride by interfacial polymerization.

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* NCL Commn.NO: 6237

** Present Address : Thermax Limited, 97-E General Block, Pune-411 026.

+ To whom all correspondence should be addressed.

EXPERIMENTAL

Materials: Bis [2-(4-carboxy phenoxy) ethyl] ether (4-OEDA) and bis [2-(3-carboxy phenoxy) ethyl] ether (3-OEDA) were synthesized according to the method reported elsewhere (10). BPA (Aldrich) was purified by recrystallization from toluene. Terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were recrystallized from dry n-hexane. The phase transfer catalyst benzyltriethylammonium chloride (BTEAC), (Aldrich) was used as received. All solvents were distilled prior to use.

Synthesis of bis[2-(4-chlorocarbonyl phenoxy) ethyl] ether (4-OEDAC)

Bis [2-(4-carboxy phenoxy) ethyl] ether (3.46 g, 0.01 mol), thionyl chloride (24.0 g, 0.02 mol) and one drop of pyridine was refluxed for 4 h. The excess of thionyl chloride was removed under reduced pressure. The crude diacyl chloride was recrystallized from petroleum ether-benzene mixture to give bis [2-(4-chlorocarbonyl phenoxy) ethyl] ether. Yield 3.4 g (95 %), mp 139°C.

^{1}H-NMR ($CDCl_3$) δ ppm: 3.80-4.00 (m, 4H, $-OCH_2$), 4.13-4.33 (m, 4H,CH_2), 6.84-7.08 (m, 4H, ArH), 7.90-8.20 (m, 4H, ArH).

Bis [2-(3-chlorocarbonyl phenoxy) ethyl] ether (3-OEDAC) was prepared by the similar procedure mentioned above. Yield 3.3 g, (92 %), mp 70°C.

^{1}H-NMR ($CDCl_3$) δ ppm: 3.38-4.00 (m, 4H, $-OCH_2$), 4.06-4.31 (m, 4H, CH_2O-), 7.00-7.78 (m, 8H, ArH).

Polymerization

Polyester PE-4 : In a 100 ml round bottom flask fitted with a high speed stirrer were placed 2.28 g (0.01 mol) of BPA and 20 ml of 1 M sodium hydroxide solution. A clear solution was obtained which was cooled to 5-10°C and 0.006 g of BTEAC was added in it. Then the mixture of TPC (1.015 g, 0.0005 mol), IPC (0.9135 g, 0.0045 mol) and 4-OEDAC (0.1915 g, 0.005 mol) in 20 ml dry methylene chloride was added with vigorous stirring (4000 rpm). The polymerization was continued further for 40 minutes at the same temperature and stirring speed. The polyester was isolated by adding methanol, filtered and dried in a vacuum oven at 80°C for 6 h. Yield 3.56 g (99%).

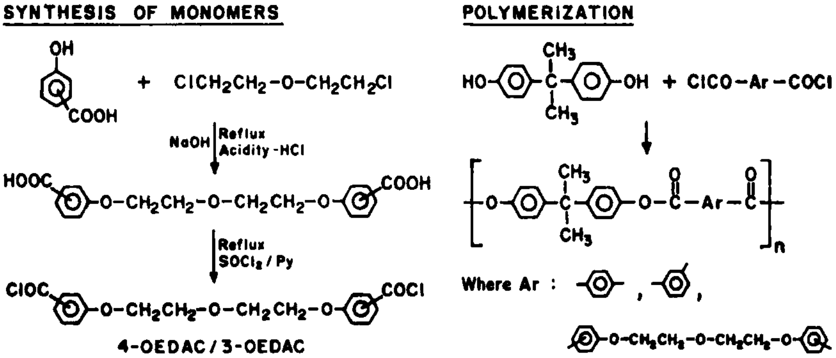
The same procedure was followed for the preparation of other polyesters (Table 1).

Measurements

The inherent viscosity measurements were made with 0.5 % (w/v) solution of polyester in chloroform at 30±0.1°C using an Ubbelohde suspended level viscometer. IR spectra were recorded on a Pye Unicam SP-3 300 spectrophotometer. Thermogravimetric analysis and differential thermal analysis were performed on Perkin-Elmer TGA-7 and Perkin-Elmer DSC-7 respectively at a heating rate of 10°C/min. The X-ray diffractograms were obtained with a Phillips X-ray unit (Phillips generator, PW-1730) and a Nickel filtered cuKα radiations

RESULTS AND DISCUSSION

The diacids 4-OEDA and 3-OEDA were converted into diacyl chlorides by refluxing with thionyl chloride. Both the diacyl chlorides were characterized by IR and ^{1}H-NMR spectra. The IR spectra of diacyl chlorides showed the strong absorption band at 1785-1790 cm^{-1} characteristic of the C=O of acid chloride.



Scheme-1

Table 1. Synthesis of Copolyesters

Code	BPA (mol)	TPC (mol)	IPC (mol)	4-OEDAC (mol)	3-OEDAC (mol)	Yield (%)	η_{inh} dL/g
PE-1	1	0.50	0.50	-	-	98	1.05
PE-2	1	-	-	1	-	92	0.38
PE-3	1	-	-	-	1	99	0.86
PE-4	1	0.50	0.45	0.05	-	99	1.02
PE-5	1	0.50	0.40	0.10	-	99	0.97
PE-6	1	0.50	0.35	0.15	-	99	0.91
PE-7	1	0.50	0.25	0.25	-	99	0.76
PE-8	1	0.50	-	0.50	-	94	0.50
PE-9	1	0.50	0.45	-	0.05	99	0.90
PE-10	1	0.50	0.40	-	0.10	99	0.84
PE-11	1	0.50	0.35	-	0.15	99	0.64
PE-12	1	0.50	0.25	-	0.25	99	0.53
PE-13	1	0.50	-	-	0.50	98	0.35

Copolyesters containing 4-OEDAC as the comonomer exhibited slightly higher inherent viscosities than the copolyesters containing 3-OEDAC units.

Table 2. Solubility of Polyesters

Polymer	Methylene Chloride	Chloroform	Tetrachloroethane	Nitrobenzene	Dimethyl acetamide	Dimethyl sulfoxide
PE-1	+	+	+	+	*	*
PE-2	+	+	+	+	*	*
PE-3	+	+	+	+	*	*
PE-4	+	+	+	+	*	*
PE-5	+	+	+	+	*	*
PE-7	+	+	+	+	*	*
PE-7	+	+	+	+	*	*
PE-8	+	+	+	+	*	*
PE-9	+	+	+	+	*	*
PE-10	+	+	+	+	*	*
PE-11	+	+	+	+	*	*
PE-12	+	+	+	+	*	*
PE-13	+	+	+	+	*	*

+ = Soluble at room temperature, * = Soluble after heating.

Copolyesters were synthesized by copolymerization of bisphenol-A and diacyl chloride containing oxyethylene linkages, TPC and IPC by interfacial polymerization method *Scheme 1*.

Table 1 summarises the monomers used, and inherent viscosities of the copolyesters. Polyester PE-1 is a wholly aromatic copolyester prepared from BPA, terephthaloyl chloride and isophthaloyl chloride. Polyester PE-2 and PE-3 are homopolyesters prepared from BPA and 4-OEDAC and 3-OEDAC, respectively. The inherent viscosities of copolyesters containing oxyethylene linkages varied from 0.35 to 1.02 dl/g

The formation of copolyesters was confirmed from IR and ^{1}H-NMR spectra. The IR spectra of copolyesters synthesized showed a characteristic ester absorption at 1740 cm^{-1}. Absorption at 1240 cm^{-1} is attributed to C-O-C linkages of oxyethylene containing polyesters. ^{1}H-NMR spectra were in good agreement with the structure of the copolyesters.

The powder X-ray diffraction studies indicated that the homopolyester prepared from BPA and 4-OEDAC (PE-2) and copolyester prepared from BPA, terephthaloyl chloride and 4-OEDAC (PE-8) showed semicrystalline pattern. This could be attributed to the relatively symmetrical rigid structure of the polymer chain. All other copolyesters prepared from BPA, TPC, IPC and 4-OEDAC exhibited amorphous pattern. The homopolyester prepared from BPA and 3-OEDAC (PE-3) exhibited amorphous pattern. Copolyester synthesized from BPA, TPC, IPC and 3-OEDAC exhibited amorphous pattern except copolyester PE-13. Copolyester PE-13 exhibited semicrystalline pattern which can be attributed to the relatively rigid structure of the polymer chains.

Table 2 presents the solubility characteristics of the homopolyesters and copolyesters. The copolyesters were soluble in common organic solvents such as chloroform, methylene chloride,

Table 3. Thermal Characteristics of Copolyesters

Polymer Code	T_{10} (°C)	T_{max} (°C)	T_g (°C)
PE-1	475	495	188
PE-2	390	460	88
PE-3	440	460	81
PE-4	435	490	172
PE-5	455	495	156
PE-6	450	500	160
PE-7	420	470	157
PE-8	410	465	150
PE-9	455	495	169
PE-10	470	510	160
PE-11	410	495	121
PE-12	435	495	110
PE-13	435	465	-

tetrachloroethane, nitrobenzene, tetrahydrofuran etc. A 1% solution was taken as a criterion for solubility.

Thermal properties of these polymers were evaluated by TGA and DSC. A single step degradation was observed in all the polyesters with no weight loss below 380°C. Table 3 summarises the thermal behavior data of polyesters. The temperature of 10 % weight loss (T_{10}) ranges from 390 to 475°C in nitrogen. The polymer maximum decomposition temperature (T_{max}) was in the range of 460 to 510°C.

The glasstransition temperature (T_g) recorded by DSC showed decrease in T_g in copolyesters where diacyl chloride containing oxyethylene linkages has been used along with terephthaloyl chloride and isophthaloyl chloride. The wholly aromatic copolyesters (PE-1) has T_g of 188°C.

CONCLUSIONS

Aromatic copolyesters containing oxyethylene linkages in the backbone were synthesized with fairly high thermal stability and excellent solubility in organic solvents. These copolyesters may find applications in processable high stable polymers.

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