Synthesis and Characterization of Block Copolymers from Aromatic Diols, Fumaric Acid, Sebacic Acid and PEG

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ABSTRACT: The syntheses of two linear unsaturated aromatic oligoesters, poly(hydroquinone fumarate-*co*-sebacate) (PHFS) and poly(resorcinol fumarate-*co*-sebacate) (PRFS), are described. PHFS, PRFS and poly(ethylene glycol) (PEG) are then used to prepare di- and tri-block copolymers. Products thus obtained are investigated in terms of molecular weight, composition, structure and thermal properties by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and NMR and FTIR spectroscopies. A number of design parameters including the molecular weights of PHFS, PRFS and PEG and the ratios of PEG to PPFS or to PEFS are varied in order to assess their effects on product yields and properties. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2358–2363, 2003

Key words: block copolymers; gel permeation chromatography, differential scanning calorimetry

INTRODUCTION

Aliphatic polyesters obtained from linear aliphatic diols and linear aliphatic diacids have been synthesized by interface polycondensation[1] and are being used in the insulation, varnish, and adhesive industries.[2]

Polyesters with aromatic groups have been prepared by the polycondensation of aromatic diols such as hydroquinone, resorcinol and bisphenol A with linear aliphatic diacids such as malonic, succinic, adipic or sebacic acid.[3–10] Another family of aromatic polyesters has been synthesized by the polycondensation of aliphatic diols such as ethylene glycol, diethylene glycol, 1,4-butanediol or 1,6-hexandiol with aromatic diacids such as isophtalic or terephtalic acid.[11,12] Aromatic polyesters are being used extensively in the plastic and rubber industries because of their high moduli, heat-resistance and liquid crystalline properties.[13–15] Aromatic-aliphatic copolyester has been prepared by the interfacial polycondensation of terephthaloyl chloride with bisphenol A and ethylene glycol.[16]

Unsaturated polyesters have been prepared by the polycondensation of unsaturated diacids such as maleic or fumaric acid with aliphatic or aromatic diols.[17–19] These low molecular weight unsaturated polyesters can be crosslinked through their double bonds via the appropriate vinyl monomers, usually styrene, in the presence of a peroxide catalyst. Both linear saturated polyesters and unsaturated polyesters have achieved commercial significance.[20]

We here report the synthesis and characterization of novel unsaturated oligoesters, poly(hydroquinone fumarate-*co*-sebasate) (PHFS) and poly(resorcinol fumarate-*co*-sebasate) (PRFS). In order to increase the hydrophilicity of PHFS or PRFS oligoesters, PHFS-*co*-PEG and PRFS-*co*-PEG di-block copolymers, as well as PEG-*co*-PHFS-*co*-PEG and PEG-*co*-PRFS-*co*-PEG tri-block copolymers have been prepared by the copolymerization of PHFS or PRFS with PEG. The resultant oligoesters and their copolymers have been characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and NMR and FTIR spectroscopies. Polyesters made by the polycondensation of hydroquinone and resorcinol with sebacic acid have been previously reported. We have used fumaric acid in order to obtain unsaturated oligoesters that can readily be crosslinked via vinyl monomers. Since PHFS and PRFS are slightly water soluble, their copolymers with PEG are potential candidates for fertilizer coatings. Study of the hydrolytic degradation of these polymers is currently in progress and will be reported in future articles.

EXPERIMENTAL

Materials

All compounds and solvents used were reagent grade obtained from Merck (Darmstadt, Germany). These
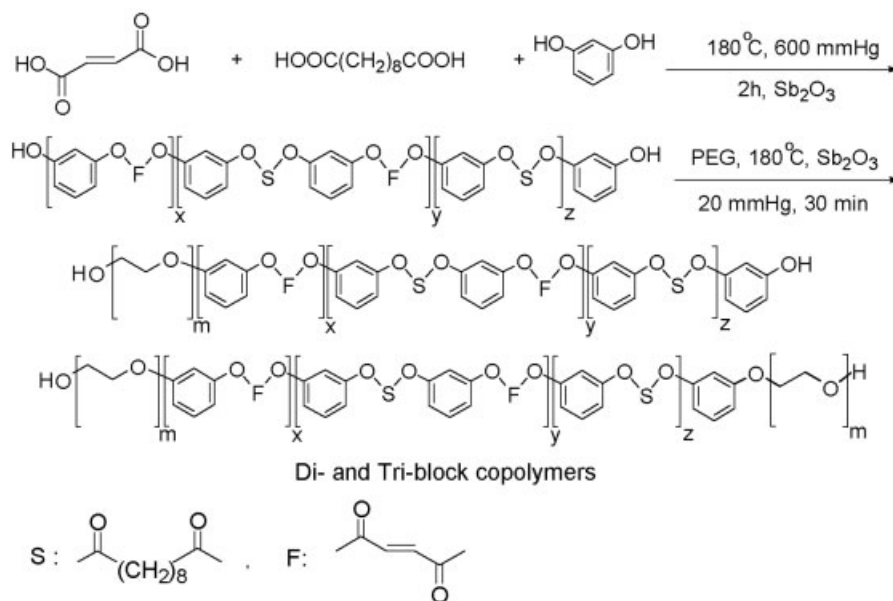
Scheme 1

include sebacic acid (SA), fumaric acid (FA), hydroquinone (HQ), resorcinol (RC), polyethylene glycol (PEG), chloroform, petroleum ether, diethyl ether, antimony trioxide, deuterated chloroform and dimethylsulfoxide.

Instrumentation

Infrared spectra were recorded on a Shimadzu-4300 FTIR spectrophotometer (Kyoto, Japan). Polymeric samples were either in the form of solid films or liquid spreads on NaCl plates. Polymeric powder samples were pressed into KBr pellets. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Brucker AC80 spectrophotometer (Germany) using deuterated solvents and tetramethylsilane (TMS) as an internal reference. Molecular weight and molecular weight distribution of the polymers were determined by GPC of the polymer solutions in tetrahydrofuran, using a Waters 150C model equipped with Styragel columns, a flow rate of 1 mL/min at 30°C, and polystyrenes of low polydispersity as standards. DSC thermograms were obtained on a DSC 4 (Perkin Elmer, U.S.A.) at a constant heat-

ing rate of 10°C/min. TGA were obtained on V5.1A DuPont 2000 (Delaware, U.S.A.) at a constant heating rate of 10°C/min.

Oligoester Syntheses

Oligoesters of FA or SA with HQ or RC were synthesized by melt polycondensation of an equimolar mixture of FA and SA with 2.2 equimoles of HQ (at 180°C) or RC (at 160°C), with stirring in the presence of an antimony trioxide catalyst for 2 h under mild vacuum (about 600 mmHg). The H$_2$O evolved was trapped in an ice water bath. The resulting oligoesters were purified by pouring their chloroform solutions into petroleum ether (non-solvent). Precipitates were washed with dry ether and dried under vacuum at 40°C for 4 h.

Copolymers Synthesis

The PHFS-*co*-PEG and PRFS-*co*-PEG di-block copolymers and PEG-*co*-PHFS-*co*-PEG and PEG-*co*-PRFS-*co*-PEG tri-block copolymers were prepared by adding

TABLE I
Monomer Composition and Average Molecular Weights of Oligoesters

Oligoesters	Monomer Composition (mol)	Molecular Weight[a]		Yield
		$\bar{M}_n$	$\bar{M}_w$	
PHFS	2.2 HQ, 1 FA, 1SA	3629	3983	84
PRFS	2.2 RC, 1 FA, 1SA	2206	4661	78

[a] Obtained by GPC experiment using a Waters 150C model equipped with three Stragel columns (10^4, 10^5, 10^6) in series and THF as the solvent, with a flow rate 1 mL/min at 30°C.
FA: Fumaric acid SA: Sebacic acid HQ: Hydroquinone RC: Rosercinol

Block Copolymers[a]	Block Composition	Molecular Weight[b]	Yield
PHFS-co-PEG	1g PHFS 1g PEG 4000	8799	65
PEG-co-PHFS-co-PEG	1g PHFS 2g PEG 4000	11983	71
PRFS-co-PEG	1g PRFS 1g PEG 4000	7433	61
PEG-co-PRFS-co-PEG	1g PRFS 2g PEG 4000	11403	79

[a] Insoluble in THF
[b] Determination of molecular weight by ^{1}H-NMR

PEG to the PHFS (at 180°C) or PRFS (at 160°C) oligoesters, under a 20 mmHg vacuum using the antimony trioxide catalyst for 30 min. The formatiom reaction of the unsaturated di-and tri-block copolymers from FA, SA, HQ and PEG is shown in Scheme 1. The resulting copolymers were purified by pouring their chloroform solutions into petroleum ether (nonsolvent). Then, to remove the residues of PEG, precipitates were washed with hot water. Precipitates were washed with dry ether and dried under vacuum at 40°C for 4 h. Dryness was further verified FTIR and NMR spectroscopies.

RESULTS AND DISCUSSION

Characterization

Table I shows the monomer composition and the average molecular weights of the unsaturated aromatic oligoesters, PHFS and PRFS. PHFS is a gray solid, while PRFS is an orange viscous paste. Oligoesters are insoluble in water but soluble in tetrahydrofuran, dimethylsolfoxide and chloroform.

The PHFS-co-PEG and PRFS-co-PEG di-block copolymers and PEG-co-PHFS-co-PEG and PEG-co-PRFS-co-PEG tri-block copolymers were synthesized by adding poly(ethylene glycol) 4000 to either of the oligoesters, PHFS or PRFS. Table II shows the block composition and the average molecular weights of di- and tri-block copolymers as determined by ^{1}H-NMR. As expected, the solubility of the copolymers in water rises with the increase in weight percent of PEG. In di-block copolymers, a PHFS or PRFS block is connected to a PEG block, but in tri-block copolymers, thay are located in the middle of two PEG blocks.

Figure 1 shows the ^{1}H-NMR spectra of the PRFS obtained in deuterated dimethylsolfoxide. The phenolic OH-groups belonging to the chain ends of aromatic oligoesters are seen as a wide peak at 10 ppm.
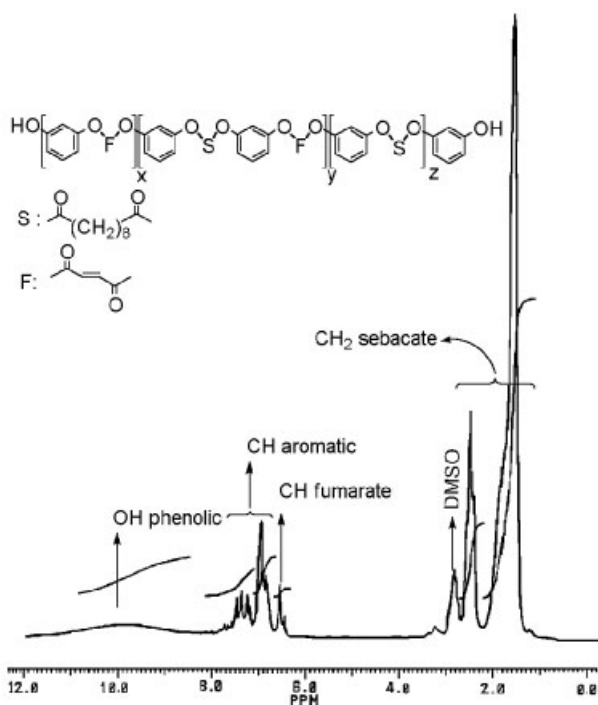

Figure 1 ^{1}H-NMR spectra of poly(resorcinol fumarate-co-sebacate), PRFS in deuterated dimethylsolfoxide.
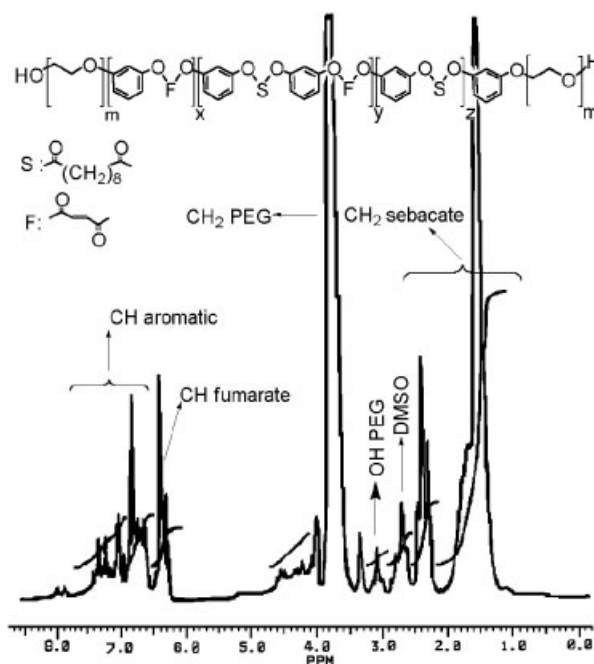

Figure 2 ^{1}H-NMR spectra of the PEG-co-PRFS-co-PEG tri-block copolymer in deuterated dimethylsolfoxide.
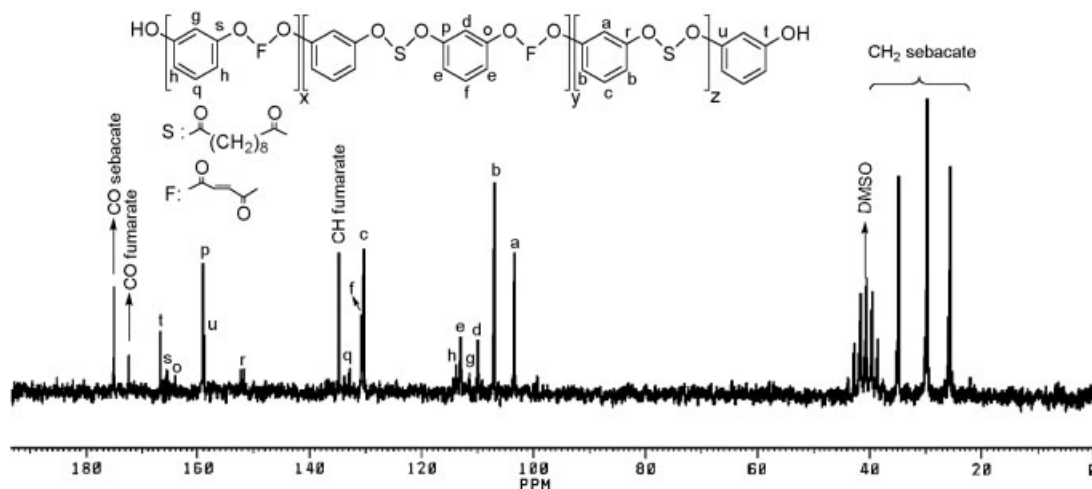
Figure 3 ^{13}C-NMR spectra of poly (resorcinol fumarate-*co*-sebacate), PRFS in deuterated dimethylsolfoxide.

The peak due to the CH$_2$ protons of sebacate appears at 1.3-2.3 ppm, and that of the CH protons in fumarate appears at 6.1-6.4 pmm. The ^{1}H-NMR spectra of the PHFS oligoester is almost identical to that of PRFS.

Figure 2 shows the ^{1}H-NMR spectra of the PEG-*co*-PRFS-*co*-PEG tri-block copolymer in deuterated dimethylsolfoxide, where it is seen that the wide peak belonging to phenolic OH has disappeared. The OH protons of the PEG blocks in the tri-block copolymers are seen as a small triplet at δ = 3.1 ppm.

Figures 3 and 4 show the ^{13}C-NMR spectra of the PRFS oligoester and the PEG-*co*-PRFS-*co*-PEG tri-block copolymer, respectively. In the former, the peak belonging to the carbon next to the OH terminal group is seen at δ = 166 ppm. In the latter spectrum, the PEG carbons are seen at about δ = 70 ppm. The peak at δ = 166 ppm has disappeared in the ^{13}C-NMR spectra of the tri-block copolymer and instead a small peak at δ = 145 ppm, due to ipso aromatic carbons attached to PEG appears, indicating that the PEG blocks are connected to the PRFS block oligoester. A broad stretch-

ing band belonging to the C—O group in the PEG block appears at about 1090 cm^{-1} in the FTIR spectra of the di- and tri-block copolymers.

Thermal Analysis

The DSC thermograms of the PHFS and PRFS, Figures 5 and 6, show small wide endothermic peaks at 61°C and 97°C, respectively, which correspond to their respective melting points. The DSC thermogram of the PHFS shows an exothermic process that starts at about 200°C and slowly increases until 250°C, indicating the detachment and sublimation of HQ units, leading to an increase in molecular weight (due to joining of neighboring oligoesters). The wide endothermic peak at about 280°C corresponds to the melting point of the newly formed PHFS polyester. On the other hand, the DSC thermogram of PRFS shows an exothermic process that starts at about 100°C and slowly increases until 300°C.
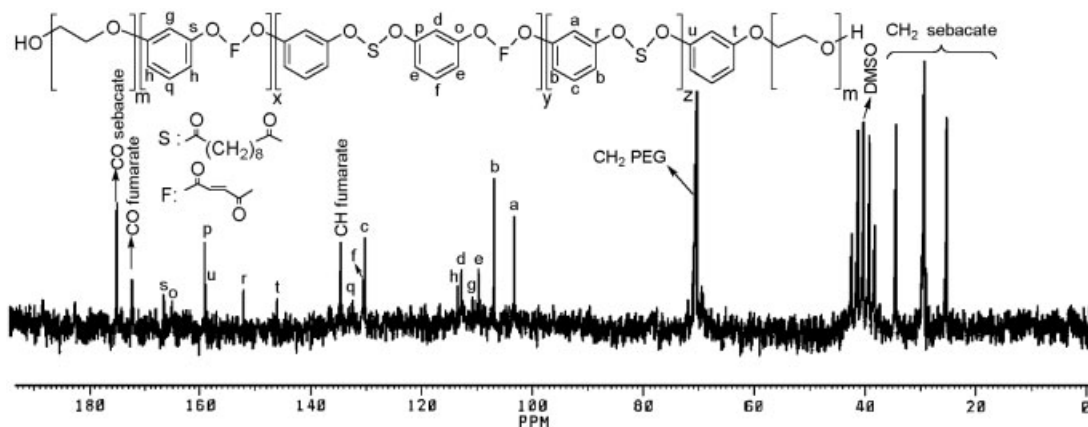

Figure 4 ^{13}C-NMR spectra of the PEG-*co*-PRFS-*co*-PEG tri-block copolymer in deuterated dimethylsolfoxide.
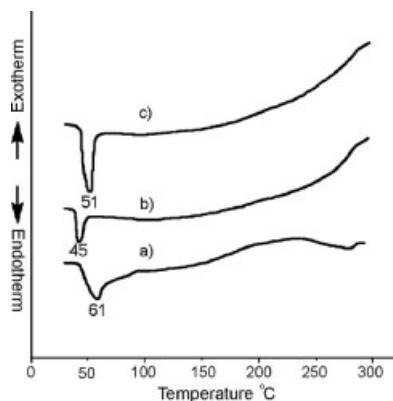
Figure 5 DSC thermograms of a) PHFS, b) PEG-*co*-PHFS c) PEG-*co*-PHFS-*co*-PEG at a constant heating rate of 10°C/min in the range 30–300°C.

The DSC thermograms of the PHFS-*co*-PEG di-block and PEG-*co*-PRFS-*co*-PEG tri-block copolymers, Figure 5, show endothermic peaks at about 45°C for di-block and 51°C for tri-block copolymers, which correspond to the melting points of the PEG blocks. The endothermic peak corresponding to the melting point of the PEG blocks in the block copolymer becomes sharper and more intense as the percentage of the PEG in the copolymer increases. In di- and tri-block copolymers of PHFS, an exothermic process starts at about 175°C, which slowly increases until 300°C. Such is not the case with di- and tri-block copolymers of PRFS.

The TGA diagram of PHFS, Figure 7, shows that about 50% of the weight loss occurs in the range 150–250°C, due to detachment of the HQ units; about 18% in the range 250–350°C, due to detachment of the fumarate units and about 26% in the range 350–550°C, due to departure of sebacate units. The TGA diagram of PRFS, Figure 8, shows that its thermal degradation
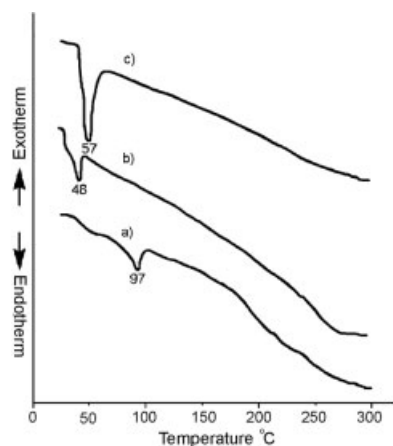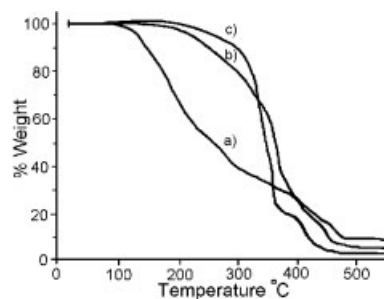

Figure 7 TGA diagrams of a) PHFS, b) PEG-*co*-PHFS c) PEG-*co*-PHFS-*co*-PEG at a constant heating rate of 10°C/min in the range 25–550°C.

starts at 200°C and it is thermally more stable than PHFS. Most of the weight loss from PRFS occurs in the range of 200–300°C (about 75%).

Figures 7 and 8 show the thermal stabilities of di- and tri-block copolymers larger than PHFS and PRFS increase as the percent of PEG increases. This may be attributed to the presence of hetro-atoms in the PEG blocks.

CONCLUSIONS

Two linear unsaturated aromatic oligoesters, PHFS and PRFS, have been synthesized. PHFS, PRFS and PEG have been used to prepare the di-block copolymers PHFS-*co*-PEG and PRFS-*co*-PEG and the tri-block copolymers PEG-*co*-PHFS-*co*-PEG, PEG-*co*-PRFS-*co*-PEG. Their molecular structures were confirmed by GPC, DSC, TGA, NMR and FTIR spectroscopies. The results of thermal analysis show that thermal stability of the block copolymers is higher than that of either PHFS or PRFS and tends to increase with increasing PEG content.

Figure 6 DSC thermograms of a) PRFS, b) PEG-*co*-PRFS c) PEG-*co*-PRFS-*co*-PEG at a constant heating rate of 10°C/min in the range 30–300°C.
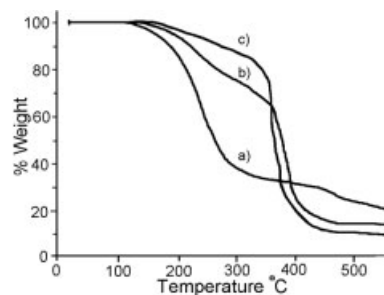

Figure 8 TGA diagrams of a) PRFS, b) PEG-*co*-PRFS c) PEG-*co*-PRFS-*co*-PEG at a constant heating rate of 10°C/min in the range 25–550°C.

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