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FLUORENE-CONTAINING POLYESTERS AND POLY(ESTER-AMIDE)S

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ABSTRACT

A series of aromatic polyesters and aromatic poly(ester-amide)s have been synthesized by polycondensation of diacid chlorides containing preformed ester groups with 9,9-bis(*p*-hydroxyphenyl)fluorene or 9,9-bis(*p*-aminophenyl)fluorene, respectively. These polymers are easily soluble in polar aprotic solvents, and the polyesters are even soluble in chloroform; their solutions were cast into transparent, thin, flexible films. The polyesters are stable up to 324–335°C, while poly(ester-amide)s are stable up to 401–409°C. The dielectric constant of these polymers is in the 3.2 to 4.15 range, being lower for polyesters. All these characteristics are discussed and compared with those of related polymers without fluorene units.

INTRODUCTION

Wholly aromatic polyesters and polyamides have high thermal stabilities and find use in high strength, high modulus fibers, and engineering resins [1, 2]. Drawbacks of these systems are their insolubility and intractability, which cause difficulties in both synthesis and processing. Because high glass transition temperatures are characteristic of these polymer types, chiefly due to the rigid nature of the polymer backbones and strong interchain hydrogen bonding in the case of polyamides, several attempts have been made to reduce the transition temperatures by introducing either flexible spacer groups or kinks in the main chain, or by incorporating various substituents in the aromatic monomers [3, 4]. Another approach was the polymerization of monomers containing two or more different moieties with expectation of systems having synergetic interactions and properties. For example, the synthesis of aromatic copolyamides was reported from monomers containing preformed amide groups or various heterocycles [5]. Also, it was shown that a polymer chain having a side cardo group, such as fluorene, can cause a significant increase in solubility while providing high thermal stability [6].

In our continuing effort to develop easily processable high performance polymers which have both high thermal stability and high glass transition temperatures, we prepared a series of new polyesters and poly(ester-amide)s containing fluorene moieties by using the reaction of diacid chlorides containing preformed ester groups with a diphenol or a diamine, respectively, having fluorene groups. The solubility, film-forming ability, thermal stability, and dielectric constant of these polymers were studied.

EXPERIMENTAL

Starting Materials

9,9-Bis(*p*-hydroxyphenyl)-fluorene, **Ia**, and 9,9-bis(*p*-aminophenyl)-fluorene, **Ib**, from Hoechst-Celanese, were recrystallized from ethanol or acetone, respectively. Terephthaloyl chloride and isophtaloyl chloride were obtained from Aldrich and purified by recrystallization from *n*-hexane. *p*-Hydroxybenzoic acid, thionyl chloride, diphenylether, *N*-methyl pyrrolidinone (NMP), pyridine (Py), *n*-hexane, and chloroform were all obtained from Aldrich. Thionyl chloride was distilled before use. NMP was distilled over phosphorous pentoxide under reduced pressure.

Synthesis of the Diacid Chlorides

Terephthaloyl-bis(4-oxybenzoyl-chloride), **IIa**, and isophthaloyl-bis(4-oxybenzoyl-chloride), **IIb**, were prepared by treating with excess thionyl chloride the corresponding dicarboxylic acids, **II'a** and **II'b**, which had been obtained from the reaction of 4-hydroxybenzoic acid with terephthaloyl or isophthaloyl chloride, respectively [7, 8]. 4-Hydroxybenzoic acid, 16.6 g (0.12 mol), and 250 mL 0.5 N NaOH aqueous solution were introduced into a three-necked flask equipped with mechanical stirrer. The mixture was stirred a few minutes until complete dissolution, then it was cooled to 0°C. A solution of 10.15 g (0.05 mol) terephthaloyl or isophthaloyl chloride in 100 mL chloroform was added gradually in the flask under vigorous stirring, followed by 100 mL 1 N NaOH aqueous solution. A white product began to separate. The mixture was stirred for 3 hours at room temperature; then it was filtered and washed with water. The white precipitate was stirred with 150 mL 0.5 N HCl for 1 hour; then it was filtered, washed with water, and dried. Mp **II'a**: 382-385°C; mp **II'b**: 294-296°C.

Ten grams **II'a** or **II'b**, 100 mL thionyl chloride, and 0.2 mL dimethylformamide were heated at reflux for 5 hours. The resulting yellow solution was allowed to cool, and the white crystalline product was filtered and then recrystallized, **IIa** from benzene and **IIb** from chloroform. Mp **IIa**: 226-228°C; mp **IIb**: 208-210°C.

Synthesis of the Polymers

Polycondensations were performed with equimolar amounts of the two monomers. Reaction of 9,9-bis(4-hydroxyphenyl)fluorene, **Ia**, with diacid chlorides, **II**, was performed in diphenylether as a solvent at reflux temperature to give the polyesters **III**. A mixture of 2.1 g (0.006 mol) **Ia**, 2.658 g (0.006 mol) **IIa** or **IIb**, and 30 mL diphenyl-ether was heated with stirring under argon in a 100-mL three-necked flask. Complete dissolution took place at 150°C. Heating was continued at reflux for 3-4 hours. The clear solution was cooled and the polymers **III** were precipitated with ethanol, filtered, washed twice with ethanol, and dried in vacuum at 150°C for 5 hours. Inherent viscosities are in the 0.5 to 0.6 dL/g range. One gram of each polymer was redissolved in 12 mL chloroform, and the solution was filtered and cast onto glass plates 100 × 100 mm and dried in an oven at 100°C. Transparent, colorless, flexible films were obtained which were used for various measurements.

Reaction of 9,9-bis(*p*-aminophenyl)fluorene, **Ib**, with diacid chlorides, **II**, was performed in *N*-methylpyrrolidinone using pyridine as acid acceptor at 0°C to room temperature. **Ib**, 2.088 g (0.006 mol), was dissolved in 50 mL NMP and 1 mL Py, and the solution was cooled to 0°C. **IIa** or **IIb**, 2.658 g (0.006 mol), was added at once and the mixture was stirred under argon for 30 minutes at 0°C and 3 hours at room temperature. A portion of the resulting viscous solution was cast onto glass plates (100 × 100 mm) and dried at 100, 125, 150, and 175°C each for 1 hour. Heating was continued in a vacuum oven at 150°C for 5 hours. Transparent, yellow, flexible films were stripped off the glass plates and used for further studies.

The remaining polymer solution was diluted with 20 mL NMP and poured into water under rapid stirring. The precipitated fibrous white product was filtered, washed twice with water and once with ethanol under stirring, and dried in a vacuum oven at 150°C for 5 hours. Inherent viscosities are in the 0.9 to 1.1 dL/g range.

Measurements

The inherent viscosity of the polymers was determined at 20°C for solutions having a concentration of 0.5 g polymer/100 mL NMP, using an Ubbelohde viscometer. Infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier Transform Infrared (FT-IR) Spectrometer at 4 cm^{-1} resolution and 16 scans, using polymer films of 3-6 μm thickness. Glass transition temperatures of the precipitated polymers were determined by differential scanning calorimetry (DSC) at a heating rate of 5°C/min in nitrogen using a Seiko DSC 220C equipment. All transition temperatures reported here result from the second heating run, and they were taken as the midpoint of the change in slope of the base line.

Thermal stability was investigated by thermogravimetric analysis (TGA) at a heating rate of 5°C/min in nitrogen using a Seiko TG/DTA 220 thermobalance.

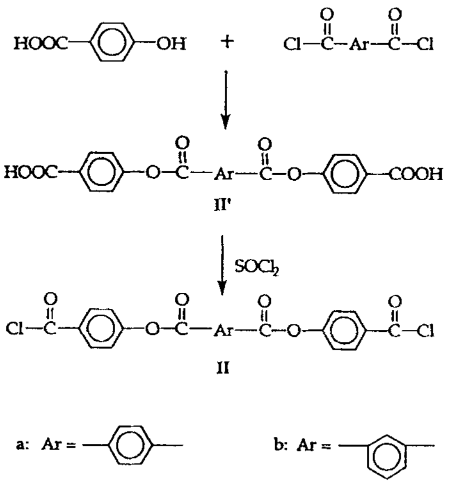
Dielectric constants were determined on polymer films of 20-30 μm thickness, using the previously described fluid displacement method [9]. The capacitance of the films was measured using circular gold electrodes (diameter 2.54 cm) mounted in a brass dielectric cell held at constant temperature (25°C) and a Gen Rad Precision LC Digibridge (model 1688) at 10 kHz. Relative humidity (RH) was measured by a General Eastern Dew Point Hygrometer (system 1100 DP).

RESULTS AND DISCUSSION

Aromatic diamine, **Ia**, and diphenol, **Ib**, containing fluorene units were commercially available and were purified by recrystallization.

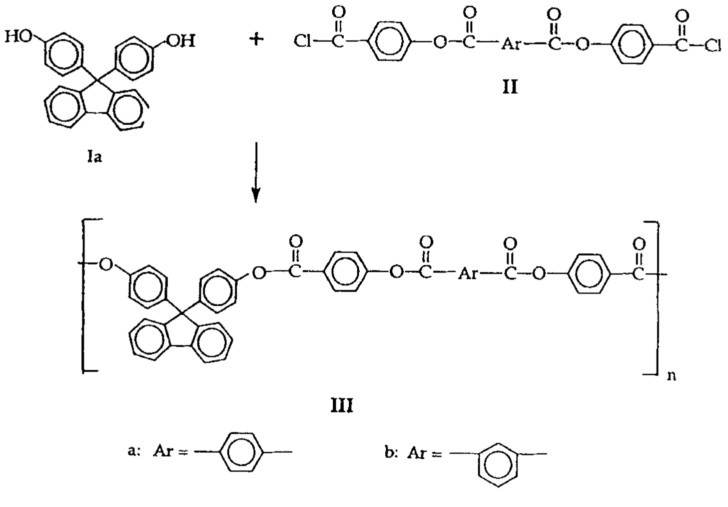
Diacid chlorides containing ester groups, **II**, were readily prepared by treating with thionyl chloride the corresponding dicarboxylic acids, **II**′, resulting from the reaction of *p*-hydroxybenzoic acid with terephthaloyl chloride or isophthaloyl chloride. *p*-Hydroxybenzoic acid was first transformed into its sodium salt, in aqueous solution, and then the one-pot interfacial reaction with terephthaloyl chloride or isophthaloyl chloride, dissolved in chloroform, followed by neutralization with hydrochloric acid, afforded the dicarboxylic acids containing ester groups, **II**′. Subsequent reaction with thionyl chloride gave the diacid chlorides, **II**, as shown in Scheme 1.

Polycondensation of equimolar amounts of 9,9-bis(*p*-hydroxyphenyl)-fluorene, **Ia**, and diacid chlorides, **II**, in diphenylether at reflux temperature at 10–15% concentration of total solids yielded polyesters containing fluorene, **III** (Scheme 2). No acid acceptor was used; the hydrogen chloride evolved by polycondensation was swept away by passing a slow stream of argon through the reaction mixture. The resulting polymer solution was poured in ethanol, and the precipitated polymer was thoroughly washed with ethanol to remove the residual diphenylether and dried. Diphenylether proved to be the most efficient solvent for preparing the present polyesters. These polycondensations were also attempted in NMP, at low temperature or at high temperature, using pyridine or quinoline as acid acceptor, but the inherent viscosity was very low ($\approx$0.1 dL/g) and no films could be obtained. The use of high-boiling-point solvents for the synthesis of other aromatic polyesters has been reported [10]. Flexible, transparent films were cast from solutions of these polymers in chloroform.

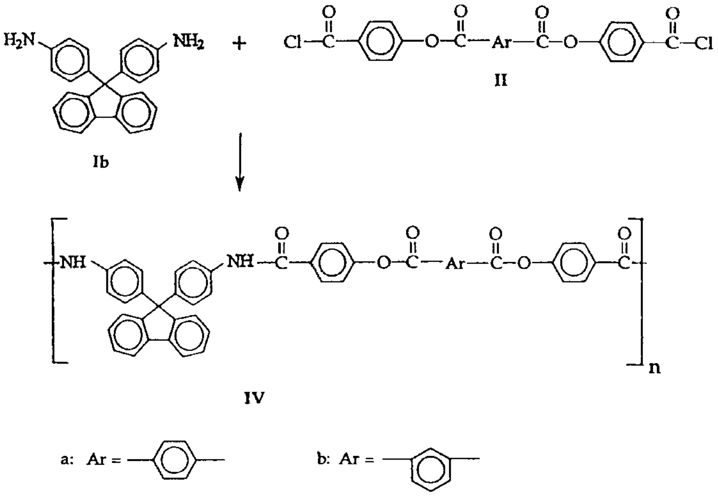


SCHEME 1.

Polycondensation of 9,9-bis(*p*-aminophenyl)fluorene, **Ib**, and diacid chlorides, **II**, taken into 1:1 molar ratio, in *N*-methylpyrrolidinone at low to room temperature, at a concentration of 8-10% of total solids, afforded the poly(ester-amide)s containing fluorene, **IV** (Scheme 3). Pyridine was used as acid acceptor. Solutions of these polymers as they resulted from polycondensation were coated onto glass substrates and dried to yield transparent, flexible films. These films were yellow, while those of polyesters **III** were colorless. Parallel workup in water of NMP solutions yielded white fibrous products, showing that the yellow color of the films is probably due to some decomposition of NMP when drying the films. For



SCHEME 2.

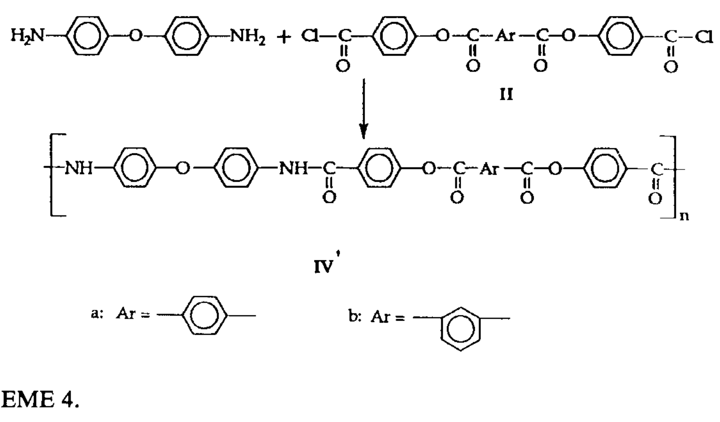


SCHEME 3.

comparison, related poly(ester-amide)s, **IV**′, without fluorene units, were synthesized from 4,4′-diaminodiphenylether and the same diacid chlorides, **II** (Scheme 4). Polymers **IV**′ were prepared in NMP + 5% LiCl, since they precipitated when polycondensations were attempted in plain NMP. Solutions of the polymers **IV**′ in trifluoroactic acid/chloroform (1/3 volume) were coated onto glass substrates and dried to yield transparent, flexible, colorless films.

The expected structures of polyesters, **III**, and poly(ester-amide)s, **IV** and **IV**′, were confirmed by FT-IR data as follows. The IR spectra of all the polymers showed strong absorptions at 1742 and 1258 cm^{-1} due to ester carbonyl and C—O—C stretching. The spectra of poly(ester-amide)s **IV** and **IV**′ exhibited broad absorptions at 3342-3324 cm^{-1} characteristic for N—H stretching, and sharp bands at 1672-1670 cm^{-1} due to amide carbonyl stretching.

Polymers **III** and **IV**, containing fluorene, are easily soluble at room temperature in polar aprotic solvents such as *N*-methylpyrrolidinone, dimethylformamide,



SCHEME 4.

and dimethylacetamide. Polyesters, **III**, are even soluble at room temperature in chloroform, while polymers **IV**′, without fluorene, are completely insoluble in common organic solvents, and only slightly soluble, less than 1%, in NMP + LiCl. The improved solubility of fluorene-containing polymers as compared to that of related aromatic polyesters and polyamides can be explained by the presence of the bulky fluorene moieties. Due to the kink introduced with these groups, the rodlike structure of the macromolecules is probably disturbed, the tight packing of the chains cannot be achieved, and consequently the solvent molecules can penetrate easily to solubilize the chains.

Inherent viscosities are 0.5–1.1 dL/g. The poly(ester-amide)s, **IV**, have higher viscosities (0.9–1.1 dL/g) than those of polyesters, **III** (0.5–0.6 dL/g), which could be explained by the higher reactivity of the 9,9-bis(*p*-aminophenyl)fluorene as compared to the 9,9-bis(*p*-hydroxyphenyl)fluorene. Due to its higher reactivity, 9,9-bis(*p*-aminophenyl)fluorene reacted easily with the diacid chlorides, **II**, at low to room temperature, while the corresponding dihydroxy compound reacted with the same diacid chlorides, **II**, only at very high temperature. Also it was noticed that the polymers **IIIa** and **IVa** have slightly higher viscosities (0.6 and 1.1 dL/g, respectively) than those of the related polymers **IIIb** and **IVb** (0.5 and 0.9 dL/g, respectively), which is probably due to the higher reactivity of the diacid chloride **IIa** containing all *para*-substituted phenylene rings.

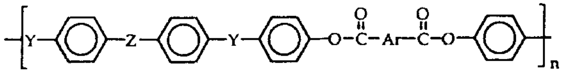
All of the new polymers possess outstanding film-forming properties. Transparent flexible films have been obtained by casting the solutions of polymers **III** in chloroform or solutions of polymers **IV** in NMP onto glass plates, followed by heating to remove the solvent. Even the polymers **III** which had lower viscosities gave quite flexible films. This can be explained by the flexibilizing effect of fluorene units present in the main chain. Films prepared from polymers **III** are colorless, while those made from polymers **IV** are yellow, probably due to the decomposition of NMP traces while heating the films.

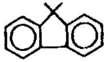
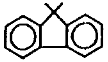
Thermogravimetric analysis shows that these polymers are highly thermostable. The polyesters, **III**, begin to decompose at 324–335°C, while poly(ester-amide)s, **IV**, begin to decompose at 401–409°C, which is similar to the related poly(ester-amide)s, **IV**′, whose initial decomposition temperature is 406–408°C (Table 1). It means that the incorporation of fluorene units into poly(ester-amides) didn't influence significantly the thermal stability of these polymers.

Glass transition temperatures (T_g) of the fluorene-containing polyesters, **III**, are in the 233 to 235°C range, while those of fluorene-containing poly(ester-amide)s, **IV**, are in the 317 to 321°C range. This shows that all these polymers have a reasonable window, of 80–100°C, between their decomposition and glass transition temperatures, which could be advantageous in their processing. At the same time, poly(ester-amide)s, **IV**′, without fluorene units didn't show any T_g up to 400°C.

The electrical insulating property of these polymers was evaluated on the basis of dielectric constant values at different relative humidity (RH) levels. The dielectric constants of polymer films are in the 3.20 to 4.15 range (Table 1). Polyesters, **III**, have dielectric constants of 3.2–3.26 which is similar to the values (3.0) reported for related heat-resistant polyesters [11] and to that (3.5) of the polyimide "film" prepared from 4,4′-diaminodiphenyl ether and pyromellitic dianhydride, which is one of the most common heat-resistant dielectrics used in microelectronic applica-

TABLE 1. Properties of the Polymers



Polymer	Y	Z	Ar	η_{inh}, dL/g	T_g, °C	IDT,[a] °C	Dielectric constant at		
							0% RH	30% RH	60% RH
IIIa	—COO—			0.62	235	335	3.26	3.54	3.87
IIIb	—COO—			0.50	233	324	3.20	3.51	3.89
IVa	—CO—NH—			1.12	321	409	3.98	4.65	5.42
IVb	—CO—NH—			0.91	317	401	4.15	4.80	5.58
IV′a	—CO—NH—	—O—		1.08[b]	—	408	3.91	4.50	5.02
IV′b	—CO—NH—	—O—		1.04[b]	—	406	4.00	4.57	5.14

[a] Initial decomposition temperature, from TG measurements.

[b] Determined in NMP + 7% LiCl.

tions [12]. Poly(ester-amide)s, **IV** and **IV′**, have slightly higher dielectric constant values (3.91–4.15) which can be explained by the increased polarizability of the polymer chains containing polar amide groups. With increasing relative humidity, an increase in dielectric constant takes place: 3.87–5.58 at 60% RH. That can be explained by moisture absorption to the polar carbonyl groups. It can be noticed that the increase of dielectric constant with relative humidity in the case of polyesters, **III**, is slower (3.87–3.89) than that of poly(ester-amide)s, **IV** and **IV′** (5.02–5.58), which suggests that among these fluorene-containing polymers, the polyesters, **III**, are more suitable for some uses as dielectric materials.

CONCLUSIONS

New aromatic polyesters and poly(ester-amide)s containing fluorene units in the main chain have been prepared and compared with related polymers which do not have such groups. Incorporation of fluorene units into the polymer backbone produced easily soluble compounds while maintaining their high thermal stability and a reasonable window between decomposition and glass transition temperature. These polymers also show outstanding capability to be processed into thin, flexible films or coatings having a low dielectric constant. All these properties make these polymers, particularly the polyesters, potential candidates for high performance applications, such as in microelectronics, optics, or related industries.

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