

Soluble Aromatic Polyimides Based on 2,2-Bis(3-amino-4-hydroxyphenyl)Hexafluoropropane: Synthesis and Properties

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SYNOPSIS

Aromatic polyimides were synthesized from 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6F-OH diamine) and different aromatic dianhydrides by a one-step high-temperature polycondensation, or by a two-step procedure using either thermal or chemical imidization of poly(amic acids), PAA. The obtained polyimides were compared in terms of their chemical structure, molecular weight, mechanical and thermal properties. The reaction of 6F-OH diamine with different aromatic dianhydrides in amide solvents at room temperature resulted in the formation of PAA with moderate molecular weight ($\eta_{inh} \leq 0.7$ g/dL). The thermal imidization of these PAAs led to brittle hydroxy polyimides (PI-6F-OH). In contrast, chemical imidization of similar PAAs in acetic anhydride and pyridine brought about flexible self-supporting polyimide films. The FTIR analysis indicated that the latter process was accompanied by an esterification of the OH groups in the diamine moieties, resulting in the formation of the polymers with side acetate groups (PI-6F-Ac). The high molecular weight hydroxy polyimides, suitable for preparation of films with good tensile properties, were synthesized by a one-step high-temperature polycondensation in phenolic solvents. All obtained polyimides were well soluble in common organic solvents. The highest solubility was observed for PI-6F-Ac. It was found by means of FTIR and TGA that the polyimides with the R group (R = OH or acetate) in ortho position to the nitrogen atom in the diamine moiety underwent a rearrangement to benzoxazoles above 300°C. The starting temperature and conversion of this rearrangement reaction were controlled by the type of R group. The imide-to-benzoxazole rearrangement shifted to lower temperatures, and higher conversion was encountered for the polyimides with side acetate group, PI-6F-Ac, obtained by chemical imidization. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic polyimides have been widely accepted as thermally stable high-performance engineering plastics and have been used in many branches of modern industry as reliable materials. Recently, considerable efforts have been taken in the field of these polymers to modify their chemical and super molecular structure with regard to a specific application or particular property.

Some hydroxy polyimides with one or two free OH groups per repeating unit were synthesized recently from trimethylsilylated 2,4-diaminophenol¹ or 4,6-diamino-resorcinol dichloride,² respectively. These polymers look very promising for further functionalization. They were reported to be interesting for membranes, photoresists^{1,2} or for nonlinear optic applications.³

Another monomer—2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6F-OH diamine, see the scheme on page 727) has been also used for similar purposes.⁴⁻⁸ In contrast to the above-mentioned monomers,^{1,2} 6F-OH diamine is stable under normal conditions and the conventional synthetic procedures can be applied to obtain a desired hydroxy

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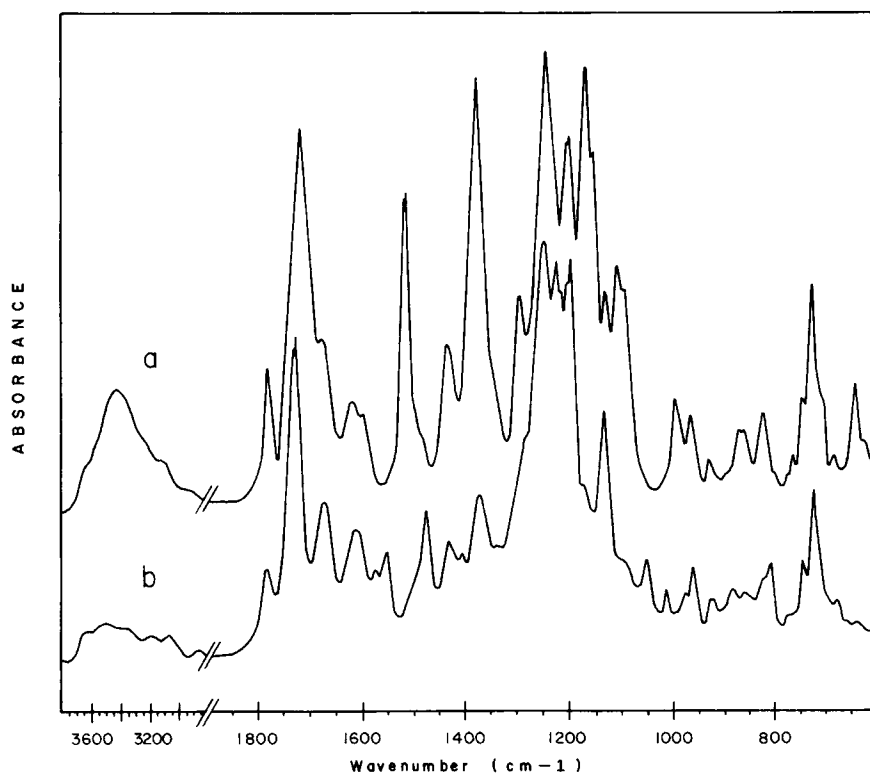


Figure 1 IR-spectra of BT-6F-OH obtained by thermal imidization: (A) BT-6F-OH after thermal imidization at 275°C for 1 h; (B) T-6F-OH after thermal treatment at 425°C for 1 h under vacuum.

polyimide. In addition, the hexafluoroisopropylidene (6F) group of this monomer provides significantly higher solubility of the resulting polymers in common organic solvents, e.g., acetone, tetrahydrofuran, amide, and phenolic solvents.⁸

In most cited works⁵⁻⁸ 6F-OH diamine-based polyimides have been prepared via a routine two-step polycondensation technique with thermal imidization of the prepolymer poly(amic acid): PAA. The resulting polymers were of moderate molecular weight with an inherent viscosity, $\eta_{inh} \leq 0.5$ dL/g. These low molecular weight hydroxy polyimides have been used as thin films on a substrate to produce both negative and positive photoresists. A one-step high-temperature polycondensation was also used for synthesis of several 6F-OH-based polyimides,⁴ but the reported molecular weight was practically the same as for the two-step method.

In this article we report the synthesis of soluble polyimides based on 6F-OH diamine by using the three most general methods (see scheme on page 727): one-step high-temperature polycondensation in phenolic solvents (I) and the standard two step procedure with both thermal (II) or chemical (III) imidization of PAA. The obtained polyimides were

compared in terms of their chemical structure, molecular weight, solubility, thermal, and mechanical properties. The main objective of this study was to establish an appropriate route and synthesis conditions for producing high molecular weight polyimides based on 6F-OH diamine, suitable for preparation of self-supporting films, with a reasonable level of mechanical properties. Taking into consideration previous reports,⁴⁻⁸ these polymers appear to be promising candidates for a wide and diversified range of applications in electronic and optoelectronic devices.

EXPERIMENTAL

Materials

A 6F-OH diamine (Chriskev Co.) was recrystallized from *n*-propanol and sublimated at 240°C under 10^{-6} mmHg, to produce polymer grade monomer with mp 245°C. The 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride, PMDA, Aldrich) was sublimated twice at 245°C under vacuum (mp 287°C). The 4,4'-oxydiphthalic anhydride

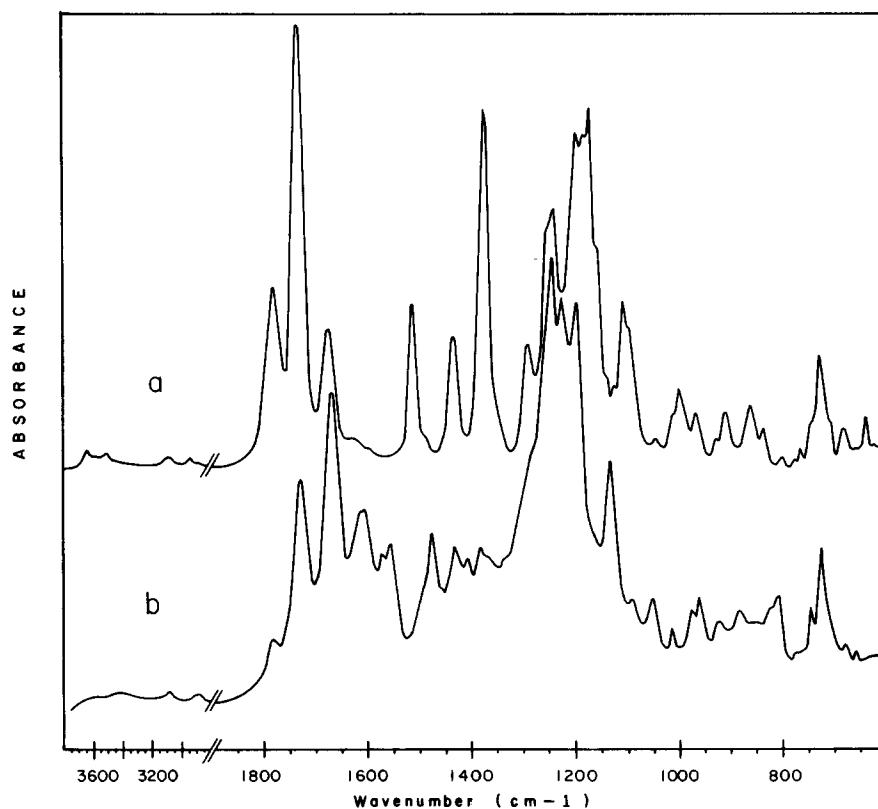
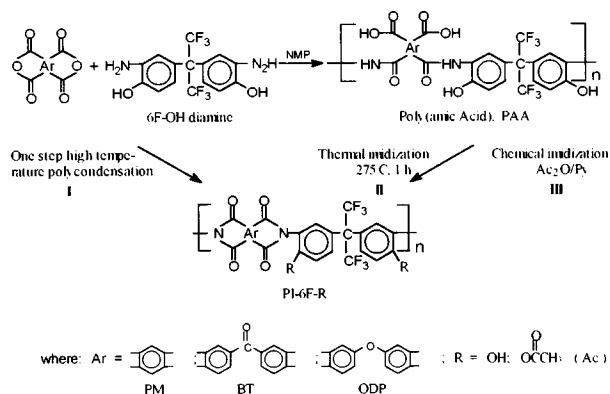


Figure 2 IR-spectra of BT-6F-Ac obtained by chemical imidization: (A) BT-6F-OH after chemical imidization and drying at 275°C for 1 h; (B) BT-6F-OH after thermal treatment at 425°C for 1 h under vacuum.

(ODPA) was recrystallized from acetic anhydride and sublimated at 200°C under vacuum (mp 221°C). The 3,3', 4,4'-benzophenonetetracarboxylic dianhydride (BTDA, Aldrich, sublimated, purity 98%) was used without purification. All solvents were obtained from Aldrich Chem. Corp., and amide solvents *N*-methyl-2-pyrrolidone, (NMP), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMAc) were fractionally distilled under vacuum over barium oxide and stored over 4 Å molecular sieves. The phenolic solvents—*p*-chlorophenol, *m*-cresol, and nitrobenzene—were distilled under vacuum prior to use. Tetrahydrofuran (THF) was dried over KOH, distilled over a potassium wire, and stored over a potassium mirror. The other solvents were used as received.

Synthesis

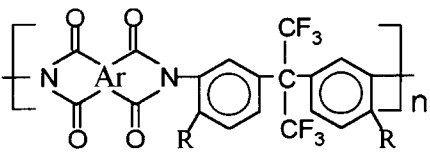
The synthetic pathways applied in this study for preparation of the polyimides based on 6F-OH diamine are presented in the following scheme:



The corresponding polyimides prepared by one-step polycondensation or by thermal imidization of PAA are named below as PM-6F-OH, BT-6F-OH, and ODP-6F-OH, respectively, and those produced by chemical imidization as PM-6F-Ac, BT-6F-Ac, and ODP-6F-Ac.

Synthesis of Poly(amic acid)s

Poly(amic acid)s were prepared by low-temperature solution polycondensation of 6F-OH diamine and

Table I Inherent Viscosity and Mechanical Properties of PI-6F-R Polyimides Produced by Different Methods


The chemical structure shows a polyimide repeating unit with a central aromatic group (Ar) and a 6-fluoro-2,2,2-trifluorophenyl group (6F-R). The structure is enclosed in brackets with a subscript 'n'.

Ar	Synthetic Route	R	η_{inh}^a , dL/g	Young's Modulus, GPa	Tensile Strength, MPa	Elongation at Break, %
PM	Thermal imidization of PAA	OH	0.5	—	—	brittle
	Chemical imidization of PAA	Ac	0.9	1.7	137	8
	One-step polycondensation ^b	OH	—	—	—	—
BT	Thermal imidization of PAA	OH	0.4	—	—	brittle
	Chemical imidization of PAA	Ac	0.7	1.2	116	12
	One-step polycondensation	OH	1.8	1.5	129	25
ODP	Thermal imidization of PAA	OH	0.4	—	—	brittle
	Chemical imidization of PAA	Ac	0.8	1.1	109	7
	One-step polycondensation	OH	1.5	1.3	119	18

^a η_{inh} was determined in 0.5 g/dL DMF solutions at 25°C; for the thermally imidized samples it was determined using the soluble fraction.

^b The polymer precipitates from solution during polymerization reaction.

the correspondent dianhydride. The diamine was dissolved in dry NMP (DMF, DMAc, or THF) and the solution was cooled to 0°C. After a stoichiometric amount of the solid dianhydride was added, the continuously stirred mixture was gradually heated to room temperature. After the monomers were dissolved completely, the reaction solution, having a concentration of 25 wt %, was stirred for 4–5 h. The PAA solutions were stored at 0°C.

Thermal Imidization of PAA

The reaction solutions of PAA were cast onto glass plates and dried at 60°C under vacuum for 5 h to produce solid transparent PAA films. The dry films were stripped off the glass plates, placed into metal frames, and heated at 275°C for 1 h under nitrogen flow to produce the desired polyimides.

Chemical Imidization of PAA

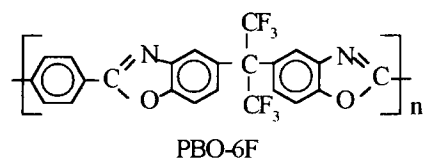
The imidization mixture Ac₂O/Pyridine (1/1 by volume) was added to the reaction solutions of PAA: 5 mol of Ac₂O per repeating unit of the prepolymer. The resulting solutions were stirred for 24 h at room temperature, then cast onto glass plates and dried at 150°C under 10⁻⁶ mmHg for 5 h. The obtained polyimide films were stripped off the plates, placed into metal frames, and heated at 275°C under 10⁻⁶ mmHg for 1 h.

One-Step High-Temperature Polycondensation

Stoichiometric amounts of 6F-OH diamine and the dianhydride were loaded into a three-neck round-bottom flask, equipped with a reflux condenser and a mechanical stirrer. After a phenolic solvent was added, the mixture with a concentration of solids 15–25 wt % was heated under intensive stirring and nitrogen flow to the boiling temperature of the solvent and it was kept under these conditions for 3 h. Films were cast from hot reaction solutions onto glass plates, preheated to 140–150°C, and dried at 150°C under 10⁻⁶ mmHg for 48 h. The residual phenolic solvent was extracted by hot benzene for a period of 5 h. The resulting polyimide films were placed in metal frames and heated under 10⁻⁶ mmHg and 250°C for 48 h, and then at 275°C for 1 h.

Synthesis of Polybenzoxazole

A polybenzoxazole of the following chemical structure



was prepared in two steps.⁹ A prepolymer poly(*o*-hydroxybenzamide) was synthesized from 6F-OH

Table II Solubility of PI-6F-R Polyimides^{a,b}

Solvent/Polymer	PM		BT		ODP	
	OH	Ac	OH	Ac	OH	Ac
DMF (DMAA, NMP)	±	++	+	++	+	++
<i>p</i> -Chlorophenol ^c (<i>m</i> -cresol, nitrobenzene)	—	++	++	++	++	++
Acetone or MEK	±	+	+	++	+	++
MeOH or EtOH	—	±	±	+	±	+
THF or <i>n</i> -Dioxane	—	+	±	++	±	++
Ethylacetate	—	+	±	+	±	+
Acrylonitrile	—	±	±	++	±	++
Chloroform	—	+	—	++	—	++

^a —, insoluble; ±, partially soluble, or swells; +, soluble up to concentration of 10 wt % at room temperature for 24 h; ++, soluble up to concentrations higher than 25 wt % for less than 1 h at room temperature.

^b OH containing polyimides used for solubility tests were produced by one-step polycondensation; for BT-6F-OH and ODP-6F-OH η_{inh} was about 1.5 dL/g; PM-6F-OH was used as a precipitate; PI-6F-Ac were produced via chemical imidization of PAA (η_{inh} , 0.5–0.7 dL/g).

^c Solubility in phenolic solvents was determined at 150°C.

diamine and terephthaloylchloride in NMP. The solution of the prepolymer with a concentration of 25 wt % was poured onto a glass plate and dried at 60°C under vacuum for 5 h. The resulting film was converted to PBO-6F by thermal cyclodehydration at 350°C for 1 h under nitrogen.

Measurements

The chemical structure of the obtained polymers was studied by FTIR-spectroscopy. This spectra are shown in Figures 1–3. The degree of imidization, i , was monitored using an IR-spectral technique.¹⁰ For all polyimides, i was very close to 100% and did not change under further treatment. Infrared spectra were recorded by using a FTIR spectrometer NICOLET 510P.

Solubility tests were performed by the following procedures. The 1.0 g polyimide specimens were gradually immersed into 3.0 g of solvent in a stoppered glass tube (concentration 25 wt %). This was stirred at room temperature for 3 h. If the specimen did not dissolve after this time, another 6 g of solvent were added to the mixture (up to a concentration of 10 wt %), and it was stirred for 24 h at room temperature. Solubility tests in phenolic solvents (*p*-chlorophenol, *m*-cresol, and nitrobenzene) were carried out by a similar procedure, at 150°C.

The inherent viscosity (η_{inh}) of the soluble polymers was determined in 0.5 g/dL *N,N*-dimethylformamide (DMF) solutions, by using a Ubbelohde viscometer at 25°C. A Du Pont, high-resolution

Thermogravimetric Analyzer, TGA 2950, was used for the thermal analysis at a heating rate of 5°C/min. Mechanical tests of the polymer films (about 25 μ m thickness) were performed by using an Instron Tester, Model 111, at a drawing rate 50 mm/min, on samples of 5 × 20 mm. All specimens for mechanical tests were checked by TGA for the presence of residual low molecular compounds in order to exclude their possible plasticizing effect.

RESULTS AND DISCUSSION

Synthesis of Polyimides from 6F-OH Diamine

The preparation of aromatic polyimides by the conventional two-step polycondensation is known to be very sensitive to the stoichiometry of the reactants.^{11,12} It requires monomers and solvents of very high purity. A small excess of the dianhydride has often been used to increase the molecular weight of the prepolymer, poly(amic acid), on the first stage of this synthesis.

In this work, 6F-OH diamine and aromatic dianhydrides were rigorously purified by repeated high-vacuum sublimation. The diamine/dianhydride ratio in the polycondensation reaction was varied from exact stoichiometry to 0.5–3 wt % excess of the dianhydride. The reaction was carried out at the most appropriate time-temperature regime, favorable for the formation of high molecular PAA,¹³ in four different solvents: NMP, DMF, DMAc, and THF.

Table III Weight Loss Temperature of PI-6F-R

Polymer		Weight Loss by TGA (°C)					
		Nitrogen				Air ^b	
Ar	R	T _s ^a	T _p ^a	5% ^b	10% ^b	5%	10%
PM	OH	397	448	496	517	466	493
	Ac	325	378	504	521	465	490
BT	OH	385	427	502	522	495	514
	Ac	322	376	502	519	473	496
ODP	OH	379	422	506	515	486	498
	Ac	314	373	507	525	478	490

^a The starting temperature of weight loss and temperature at peak, on the first stage of the weight loss (see Fig. 4).

^b Weight loss was measured using polymer samples preheated at 425°C for 1 h under vacuum.

This optimization of synthesis conditions did not succeed in giving a notable increase of PAA molecular weight. In this study, the prepolymers with highest inherent viscosity, η_{inh} , of about 0.7 dL/g, were obtained in NMP or DMF at exact stoichiometry of reagents. The average value of η_{inh} ranged between 0.3–0.6 dL/g, a figure that is very similar to that reported in previous articles.^{4–8} Thus, the very moderate molecular weight of poly(amic acids), prepared from 6F-OH diamine by conventional procedures, appears to be determined by objective factors, such as the possible screening effect of the polar

OH group in the ortho position to the reactive amino group, and the impact of the 6F bridging unit, which is known usually to decrease the reactivity of the monomers in the condensation reaction between aromatic diamines and dianhydrides.¹¹

The molecular weight of the obtained PAAs was enough to produce flexible colorless films. The thermal imidization of these films at 275°C induced a dramatic embrittlement of resulting PI-6F-OH. Thermal imidization in solution^{4–8} also brought about the formation of very brittle polymers, not suitable for producing self-supporting films or for tensile tests. Such result can be explained by taking into consideration the reduction of molecular weight typical for this technique,¹² and possible crosslinking of the polymer under the severe conditions of the thermal process.^{14,15}

An alternative method to cyclodehydrate PAA to desired polyimide is chemical imidization. It can be carried out at room temperature and is known to be free of the above-mentioned drawbacks.^{16,17} This method was at first applied to PI-6F-R in this study. The results of the mechanical tests listed in Table I show that, in contrast to thermal imidization, the chemically induced process allowed us to prepare transparent self-supporting films with a reasonable level of tensile properties and elongation at break. As it was reported for polyimides of various structures,^{13,16–18} better mechanical properties of the chemically imidized polymers could be attributed

Table IV Infrared Spectral Changes upon Thermal Treatment of BT-6F-Ac Films under Vacuum at 425°C for 1 h^a

Initial Polymer, cm ⁻¹	After 1 h at 425°C, cm ⁻¹	Probable Assignment of the Band
[3400 (s, br)]	3500 (w, br)	ν (O—H)] ^b
1782 (m)	1784 (sh)	ν (C=O) in-phase
1736 (vs)	1733 (m)	ν (C=O) out-of-phase
[1619 (w)] ^b	1617 (m)	C=N stretching of benzoxazoles (oxazole I) ^{20–23}
no	1577 (sh)	} Typical band of benzoxazoles (oxazole II) ^{9,20–21}
no	1556 (m)	
1512 (m)	no	ν (19a) of substituted phenyl ring
[1480 (sh)] ^b	1479 (m)	Typical band of benzoxazoles ^{20–21}
1375 (vs)	1386 (w)	ν (CNC) axial imide II
1108 (m)	no	ν (CNC) transverse imide III
no	1054 (m)	Ar-O-C stretching of benzoxazoles ^{9,20–23}
no	810 (m)	Benzoxazole ring deformation ^{20–23}

^a vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

^b These bands appear only in the spectrum of BT-6F-OH.

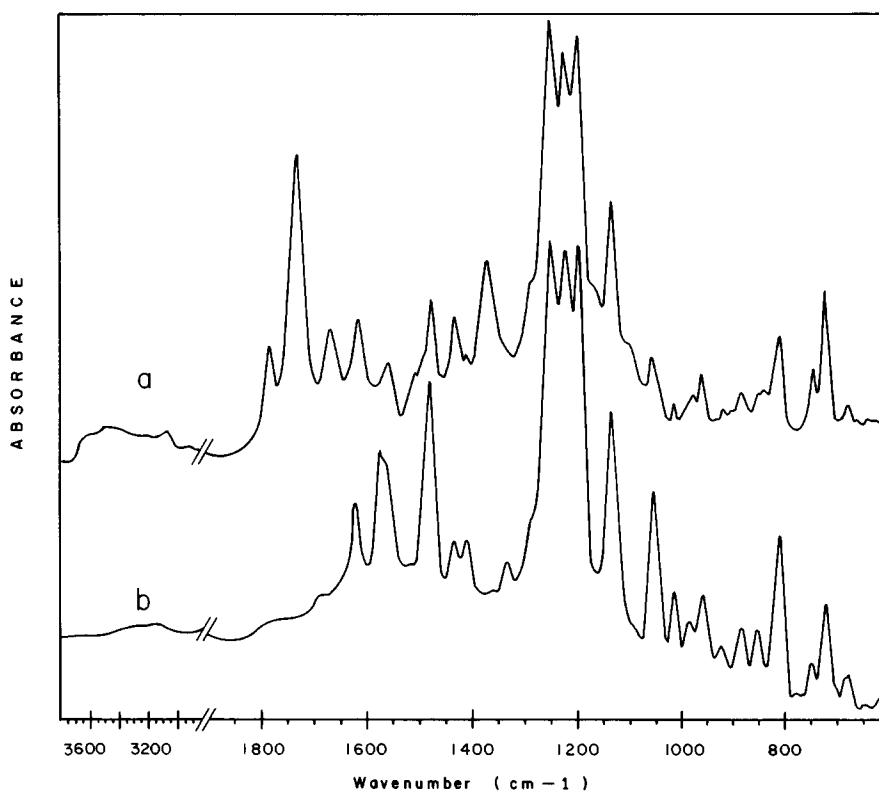


Figure 3 IR-spectra of PM-6F-Ac after thermal treatment at 425°C for 1 h under vacuum (A), and polybenzoxazole PBO-6F (B).

to both their higher molecular weight, and their less ordered super molecular structure.¹⁹ However, it is very complicated to consider a more detailed contribution of these factors in the particular case of PI-6F-R, obtained by thermal and chemical imidization, because of the different structure of the side group R. Analysis of IR-spectra of these polymers indicated that the most notable difference between them is the presence or absence of an OH band [Figs. 1(a) and 2(a)]. There is a strong and broad peak at 3200–3600 cm^{-1} , typical for ν (O—H) of a hydrogen bonded hydroxyl group in the spectrum of polyimides produced via the thermal imidization of PAA [Fig. 1(a)]. The absence of this band in the spectra of polyimides, obtained by chemical imidization of PAA in the mixture $\text{Ac}_2\text{O}/\text{Py}$ [Fig. 2(a)], means that the OH groups have been esterified during the cyclodehydration process, resulting in the formation of an acetate ester group. It is very difficult to detect other spectral differences caused by this esterification, because the ester carbonyl vibration, at 1730–1750 cm^{-1} , is covered by a very strong imide I band around 1730 cm^{-1} (imide ν C=O out-of-phase), and ν (Ar—O—Ac), at 1100–1250 cm^{-1} , is also hidden by the fluorine bands dominating the spectra in this region.

Infrared spectra of PI-6F-OH obtained by one-step high-temperature polycondensation in phenolic solvents (route I, scheme on page 727) are practically identical to the spectrum of thermally imidized polymers [see example on Fig. 1(a)]. This synthetic route is known to be effective toward sterically and/or electronically hindered monomers.¹¹

As it can be seen from Table I, after the optimization of the reaction conditions it is possible to form hydroxyl containing polyimides BT-6F-OH and ODP-6F-OH with the highest values of η_{inh} , in comparison to the other synthetic routes. The higher molecular weight of PI-6F-OH, produced by the one-step method, is obviously one of the most important reasons for their better mechanical properties, because the type of R group and chemical structure in this case are similar to those of the thermally imidized polymers; therefore, a direct comparison is possible. It should be noted that elongations at break as high as 70–80% were registered for several samples produced by this method. The lower average values of ϵ_b listed in Table I can be explained by insufficient quality of the surface of the films, cast from hot solutions under laboratory conditions.

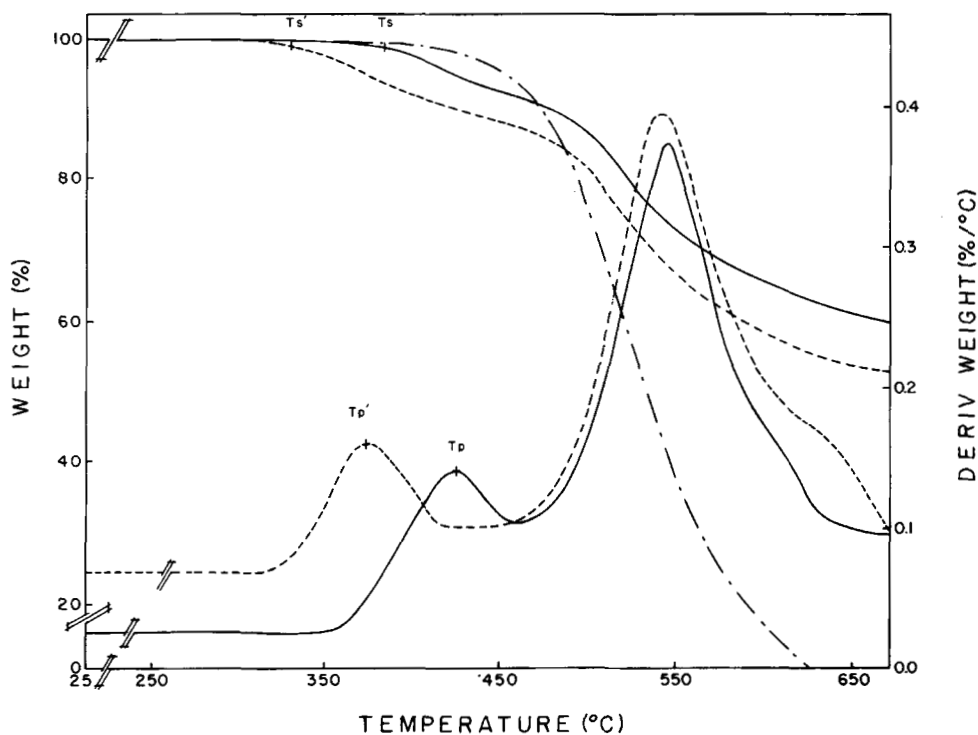


Figure 4 TGA and DTA curves of BT-6F-OH and BT-6F-Ac obtained at a heating rate of 5°C/min; solid line (—): BT-6F-OH in nitrogen; dotted line (- -): BT-6F-Ac in nitrogen; dot-dash line (- · - · -): TGA curve of BT-6F-OH in air.

Solubility

As it has been discussed above, depending on the chosen synthetic method, PI-6F-R polyimides differ in the type of R side group and molecular weight, and it was found that this also controlled their solubility. The poorest solubility was registered for PI-6F-OH films obtained by the thermal imidization in the condensed state. They dissolved slowly and incompletely even in amide solvents. The usual amount of the insoluble fraction was about 5 wt % for BT-6F-OH and ODP-6F-OH, and it was 8–15 wt % for PM-6F-OH. The solubility of thermally imidized samples decreased notably when they were heated to a temperature higher than 275°C.

The poor solubility of PI-6F-OH films produced by thermal imidization in the condensed state might originate from crosslinking during this process. In addition to the possible crosslinking mechanisms reported for conventional polyimides,^{14,15} free hydroxyl group of the PI-6F-OH may also participate in interchain reactions. However, the small changes in the intensity of the ν (O—H) band up to 300°C indicated that in this range of temperatures such reactions took place only to a moderate extent.

Hydroxy polyimides with a bridging group in the dianhydride moiety, BT-6F-OH and ODP-6F-OH,

obtained by one-step polycondensation were completely soluble in amide solvents, or in ketones (acetone or MEK); nevertheless, their molecular weight was markedly higher in comparison to the thermally imidized polymers. They were partially soluble in various organic solvents at room temperature, and could be easily dissolved in hot phenolic solvents (see Table II). The insolubility of the more rigid PM-6F-OH in phenolic solvents made it unsuitable for the one-step synthesis. The solubility of all PI-6F-OH polyimides prepared by this method decreased for samples heated at temperatures higher than 275°C.

As it can be seen in Table II, PI-6F-Ac polyimides resulting from chemical imidization show remarkably higher solubility in a wide range of organic solvents. Concentrated solutions ($C \leq 25$ wt %) of BT-6F-Ac or ODP-6F-Ac in common organic solvents such as chloroform, dioxane, or acetone could be rapidly prepared at room temperature. Solubility of the more rigid PM-6F-Ac is lower, but it should be mentioned that, in contrast to PM-6F-OH, it was soluble in phenolic solvents. It is obvious that the higher solubility of PI-6F-Ac resulted from the replacement of the OH hydrogen by the bigger acetate group that cannot produce an intermolecular hy-

drogen bonded network. The moderate molecular weight of the chemically imidized polyimides could also contribute to this phenomenon.

Thermal Properties

Thermal properties of hydroxy polyimides based on 6F-OH diamine were recently studied by Lee et al.⁸ They related the thermal and thermooxidative stability of six PI-6F-OH polymers with various structures of the dianhydride moiety to the 10% weight loss temperature in nitrogen and air, measured by TGA. It was found that, for most of the polyimides, degradation in air started at higher temperatures than in inert atmosphere. For example, the 10% weight loss temperature in air reported for ODP-6F-OH was 38°C higher than the corresponding degradation temperature determined in nitrogen.

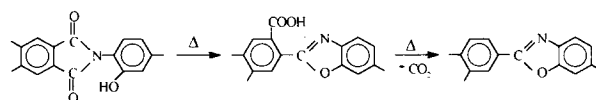
This observation might result from remarkable differences in the shape of TGA curves registered in air and nitrogen.⁸ Similar curves of BT-6F-R obtained in our study are shown in Figure 4. In contrast to common thermooxidative behavior of this and other hydroxy polyimides, the weight loss process in nitrogen occurred in two well-distinct stages. The first stage started between 314–397°C, depending on the structure of dianhydride moiety, Ar, and on the type of R side group (see Table III); and it was completed at 450–460°C for all PI-6F-R. The total weight loss at this stage was found to be about 7–8% for PI-6F-OH and 13–15% for PI-6F-Ac.

The TGA curves of all studied polymers became practically flat above 460°C, and the second stage of weight loss started around 500°C. The starting temperature and temperature at peak of this stage depended on the structure of Ar and are practically insensitive to the type of R side group.

The structure of a product resulting from the first stage of weight loss was studied by FTIR spectroscopy. Spectrum of BT-6F-R films heated at 425°C for 1 h under vacuum are shown in Figures 1 and 2 (curves b), and Table IV summarizes the most obvious spectral changes caused by this treatment.

A dramatic decrease in the intensity of ν (O—H) at 3200–3600 cm^{-1} was observed for all studied hydroxy polyimides PI-6F-OH. This decrease was greater for higher temperatures and longer times of treatment; however, complete conversion could not be reached even at temperatures of active thermal decomposition. The rest of the spectrum changed in a very similar way for both PI-6F-OH and PI-6F-Ac. This included the decrease of most of the imide and some aromatic bands, and the appearance of some new bands (see Table IV).

The frequency and the shape of these new bands look very similar to the FTIR signature of aromatic benzoxazoles.^{9,20–23} We propose that the first stage of weight loss of PI-6F-R in nitrogen originates, not from thermal decomposition, but from a chemical reaction of the R group with the imide cycle resulting in its rearrangement to a benzoxazole. The possibility of such rearrangement was reported by Kardash and Pravednikov for poly(3,3'-dihydroxy 4,4'-diphenylene)pyromellitimide in 1967.²⁴ The proposed mechanism of this reaction is shown in the following scheme:



It includes the rearrangement of the hydroxy imide to the benzoxazole with a free carboxylic group, followed by a decarboxylation reaction. This scheme was supported by comparing the IR-spectra of the final product and a standard polybenzoxazole, and by mass-spectrometry of volatile compounds resulting from aging the sample at 450°C.²⁴

The analysis of the IR-spectra of PI-6F-OH and PI-6F-Ac films after high-temperature thermal treatment shows that the acetate group can also be active in this rearrangement. In Figure 3, the spectrum of PM-6F-Ac heated at 425°C for 1 h is compared to the spectrum of a standard polybenzoxazole PBO-6F (see structure in the Experimental section). It can be seen that the treatment led to the formation of a copolymer consisting of benzoxazole and residual imide cycles.

The conversion of the imide to benzoxazole rearrangement in PI-6F-R is believed to be restricted by insufficient mobility of the macrochains (required for restructuring of cycles) and by side reactions that are possible at high temperatures. However, a remarkable increase in conversion was observed when the OH group was replaced by Ac. The FTIR-spectra of BT-6F-OH and BT-6F-Ac after 1 h at 425°C under vacuum [Figs. 1(b) and 2(b)] are qualitatively similar, but the spectral changes resulting from the rearrangement are more notable for the latter.

The effect of the R side group became more evident when the TGA and DTA data was considered. Figure 4 shows the TGA and DTA curves of both BT-6F-OH and BT-6F-Ac. The starting temperature and peak temperature at the first stage of weight loss for BT-6F-Ac were shifted to lower temperatures, related to the values obtained for BT-6F-OH, by 63 and 51°C, respectively. For the

other polyimides studied, this shift of the rearrangement temperatures ranged from 49 to 72°C (see Table III).

The rearrangement of PI-6F-R polyimide to poly(imide-benzoxazoles) also appeared to take place when the polymers were heated in air. However, the temperature of the active thermooxidative degradation was too close to the reaction temperature, and these two processes were difficult to be resolved well enough. Better resolution could be reached for the PI-6F-Ac, which underwent the rearrangement at lower temperatures. But the picture was still significantly less obvious than if the polyimides had been tested in nitrogen.

A small amount of the benzoxazole cycles might probably be formed even during thermal imidization of PAA based on 6-F-OH diamine, at 275–300°C. The IR-spectra of the hydroxy polyimides prepared by this method showed a low intensity band around 1620 cm⁻¹, which is usually associated with benzoxazole absorption. This band was not observed in spectra of similar polyimides obtained by the more selective chemical imidization at ambient temperature.

In order to collect more reliable characteristics of the thermal and thermooxidative stability for a material based on PI-6F-R polyimides, it is better to exclude from the estimation of the weight loss temperature the volatile products resulting from the rearrangement of heterocycles. This was done by preheating the samples in an inert atmosphere above 400°C. The temperatures of 5 and 10% weight loss both in nitrogen and air are listed in Table III for PI-6F-R films, preheated for 1 h at 425°C under vacuum. As it can be seen in the corresponding TGA curves shown in Figure 4, this treatment allowed obtaining the highest rearrangement conversion without reaching the onset of the thermal decomposition process. After such treatment, PI-6F-R samples demonstrated conventional TGA behavior, and the parameters of their thermal stability in nitrogen were superior to corresponding characteristics obtained in air, as expected.

CONCLUSIONS

Three synthetic methods for producing PI-6F-R polyimides suitable for preparation of self-supporting films were compared. The polymers obtained by one-step high-temperature polycondensation, or by the two-step method using either thermal or chemical imidization of PAA were studied in terms of

their chemical structure, molecular weight, solubility, thermal and mechanical properties.

The reaction of 6F-OH diamine with different aromatic dianhydrides in amide solvents at room temperature brought about PAA with a moderate molecular weight ($\eta_{inh} \leq 0.7$ g/dL). The thermal imidization of these PAA led to very brittle PI-6F-OH, while the chemically induced process gave flexible self-supporting films. The FTIR analysis of these films indicated that the imidization of the PAA based on 6F-OH diamine in the mixture of acetic anhydride and pyridine was accompanied by an esterification of the hydroxy groups resulting in the formation of the polyimides with side acetate groups (PI-6F-Ac).

The high molecular weight hydroxy polyimides PI-6F-OH could be obtained via the one-step high-temperature polycondensation in phenolic solvents. These polymers were suitable for producing flexible films with good elasticity and tensile properties.

All obtained PI-6F-R polyimides were well soluble in common organic solvents. The highest solubility was observed for the PI-6F-Ac polyimides prepared by the chemical imidization. Their increased solubility appeared to result from the replacement of the side OH groups (responsible for the formation of a intermolecular network by hydrogen bonds) by the intermolecular inactive acetate groups. The moderate molecular weight of the PI-6F-Ac could also contribute to this phenomena.

It was found by means of FTIR and TGA/DTA that the polyimides with the R group (R = OH or acetate) in *ortho* position to the nitrogen atom in the diamine moiety underwent a rearrangement to benzoxazoles above 300°C. The starting temperature and conversion of the imide-to-benzoxazole rearrangement were controlled by the type of R group. The rearrangement shifted to lower temperatures, and higher conversion was encountered for the polyimides with the acetate group (PI-6F-Ac) obtained by chemical imidization.

The authors gratefully acknowledge the contributions of Dr. Larissa Alexandrova and Carmen Vázquez Ramos for their contribution to this work. We also wish to thank Lucia Vera and Dr. S. Muhl Saunders for valuable discussions of this article.

REFERENCES

1. Y. Oishi, M. Shirasaki, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 293 (1993).
2. T. M. Moy and J. E. McGrath, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 1903 (1994).

3. D. Yu, A. Gharavi, and L. Yu, *Macromolecules*, **28**, 784 (1995).
4. D. N. Khanna and W. H. Mueller, *Polym. Eng. Sci.*, **29**, 954 (1989).
5. T. Omote, Guo-Jin, K. Koseki, and T. Yamaoka, *J. Appl. Polym. Sci.*, **41**, 929 (1990).
6. T. Omote, K. Koseki, and T. Yamaoka, *Macromolecules*, **23**, 4788 (1990).
7. T. Omote, H. Mochizuki, K. Koseki, and T. Yamaoka, *Macromolecules*, **23**, 4796 (1990).
8. B.-C. Ho, Y.-S. Lin, and Y.-D. Lee, *J. Appl. Polym. Sci.*, **53**, 1513 (1994).
9. I. Ye. Kardash, A. Ya. Ardashnikov, V. S. Yakubovich, G. I. Braz, A. Ya. Yakubovich, and A. N. Pravednikov, *Vyskomol. Soedin.*, **A9**, 1914 (1967).
10. I. Ye. Kardash, D. Yu. Likhatchev, N. V. Nikitin, A. Ya. Ardashnikov, N. V. Koslova, and A. N. Pravednikov, *Polym. Sci. USSR*, **27**, 1961 (1985).
11. C. E. Sroog, *Prog. Polym. Sci.*, **16**, 561 (1991).
12. R. A. Dine-Hart and W. W. Wright, *J. Appl. Polym. Sci.*, **11**, 609 (1967).
13. D. Yu. Likhatchev, M. S. Arzhakov, S. N. Chvalun, Ye. A. Sinevich, Yu. A. Zubov, and I. Ye. Kardash, *Vysokomol. Soyed.*, **B27**, 723 (1985).
14. A. K. Saini, C. M. Carlin, and H. H. Patterson, *J. Polym. Sci., Polym. Chem.*, **31**, 2751 (1993).
15. R. W. Snyder, B. Thomson, B. Bartges, D. Czerniawski, and P. C. Painter, *Macromolecules*, **22**, 4166 (1989).
16. M. L. Wallach, *J. Polym. Sci.*, **A-2**, 1995 (1969).
17. M. I. Bessonov, M. M. Koton, V. V. Kudryavtsev, and L. A. Laius, *Polyimides—Thermally Stable Polymers*, Plenum, New York, 1987.
18. D. Likhatchev, L. Alexandrova, M. Tlenkopatchev, R. Vilar, and R. Vera-Graziano, *J. Appl. Polym. Sci.*, **57**, 37 (1995).
19. D. Yu. Likhatchev, S. N. Chvalun, Yu. A. Zubov, and I. Ye. Kardash, *Polym. Sci. USSR*, **33**, 2010 (1991).
20. A. P. Simonov, V. P. Bazov, G. I. Braz, N. N. Voznesenskaya, A. Ya. Yakubovich, *Khim. Geterotsikl. Soedin.*, **2**, 292 (1970).
21. P. Bassignana, C. Cogrossi, and M. Gandino, *Spectrochim. Acta*, **19**, 1855 (1963).
22. G. F. L. Ehlers, K. R. Fishch, and W. R. Powell, *J. Polym. Sci. Symp.*, **43**, 55 (1973).
23. M. Bruma, F. Mercer, B. Schulz, R. Dietel, and W. Neumann, *Polym. Adv. Technol.*, **5**, 535 (1994).
24. I. Ye. Kardash, and A. N. Pravednikov, *Vysokomol. Soyed.*, **B9**, 873 (1967).

Received June 7, 1995

Accepted August 28, 1995