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Aromatic Polyamides Containing Pendent Acetoxybenzamide Groups

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Summary: Polycondensation reaction of 5-(4-acetoxy-benzamide) isophthaloylchloride with different aromatic diamines gave a series of polyisophthalamides with good solubility in organic solvents. These polymers showed good thermal stability with initial decomposition temperature above 300 °C and glass transition temperature in the range of 220–335 °C. Thin, flexible, transparent films were cast from solutions, having good electroinsulating properties.

Keywords: acetoxybenzamide groups; aromatic polyamides; thermal properties; thin films

Introduction

Aromatic thermostable polymers are used in applications that demand service at high temperatures, while maintaining their structural integrity, and an excellent combination of chemical, physical and mechanical properties. The most important polymers in this respect are aromatic polyamides, polyimides and poly(1,3,4-oxadiazole)s.[1–4] However, all of these polymers have the common problem of being difficult to process owing to their infusibility and poor solubility in organic solvents. The introduction of pendent bulky groups along the polymer backbone results in a less ordered polymer matrix, thus increasing the solubility characteristics without affecting thermal and mechanical properties to any great extent.[5–8] On the other hand, it is shown that poly(phenylquinoxaline)s are a family of aromatic polymers known for excellent thermal and chemical stability, which can be stored at ambient temperature.[9,10] The phenyl substituents in quinoxaline rings improve the solubility and processing characteristics of these polymers as well as the thermo-oxidative stability over the unsubstituted polymers.[11,12] Here, we present the synthesis and study of aromatic polyamides containing pendent acetoxybenzamide groups based on aromatic diamines containing flexible bridges such as ether, sulfone or isopropylidene, or on heterocyclic diamines containing phenyl-substituted quinoxaline rings. The incorporation of acetoxybenzamide as side groups and of flexible bridges and/or voluminous phenylquinoxaline rings in the main chain was expected to give products with a superior balance of properties and processing capabilities, which would be useful for various high-performance applications.

Experimental

Materials

N-Methyl-2-pyrrolidinone (NMP) from Merck was dried over phosphorous pentoxide and distilled under reduced pressure. Thionyl chloride, from Merck, was freshly distilled. Pyridine (Py), *p*-hydroxybenzoic acid, N,N-dimethylformamide, acetic anhydride and 5-aminoisophthalic acid were provided by different commercial sources and used as received.

Monomers

5-(4-Acetoxybenzamide)-isophthaloyl chloride was prepared by a sequence of reactions in which *p*-hydroxybenzoic acid reacted with acetic anhydride to give

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p-acetoxy-benzoic acid that by further treatment with thionyl chloride gave the corresponding acid chloride; the latter reacted with 5-aminoisophthalic acid to produce *p*-acetoxy-benzamide-isophthalic acid which, by further treatment with thionyl chloride, gave *p*-acetoxy-benzamide-isophthaloyl chloride.[6,8] Scheme 1 presents the synthesis of 5-(4-acetoxybenzamide)-isophthaloyl chloride.

Aromatic diamines containing ether bridges were provided by different commercial sources and used as received. Diaminophenylquinoxalines were synthesized as previously reported in the literature.[11]

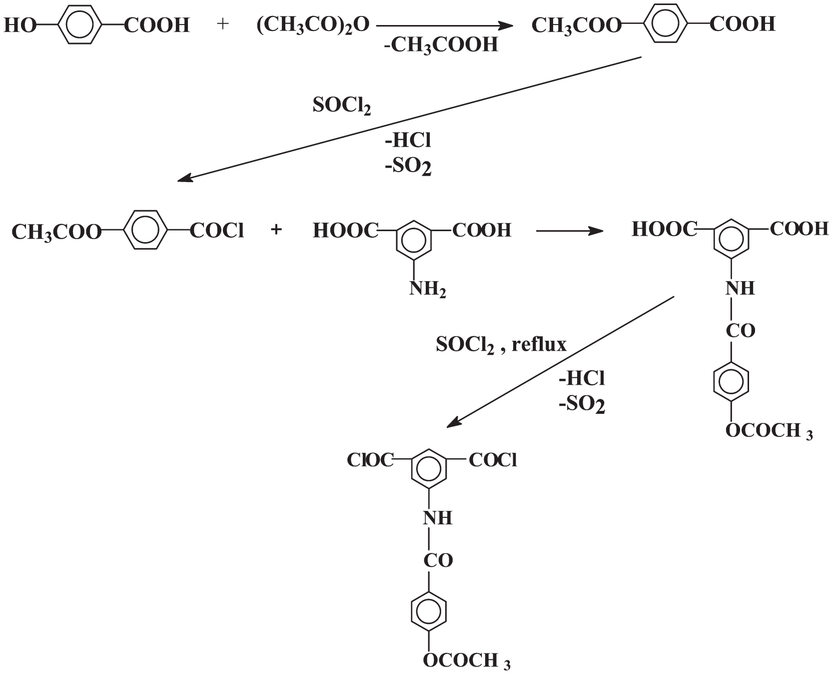
Synthesis of the Polymers

Low temperature solution polycondensation reaction of equimolar amounts of 5-(4-acetoxy-benzamide)-isophthaloyl chloride with different aromatic diamines was carried out in NMP using pyridine as acid acceptor, and gave new polyamides with pendent acetoxybenzamide groups as shown in Scheme 2.

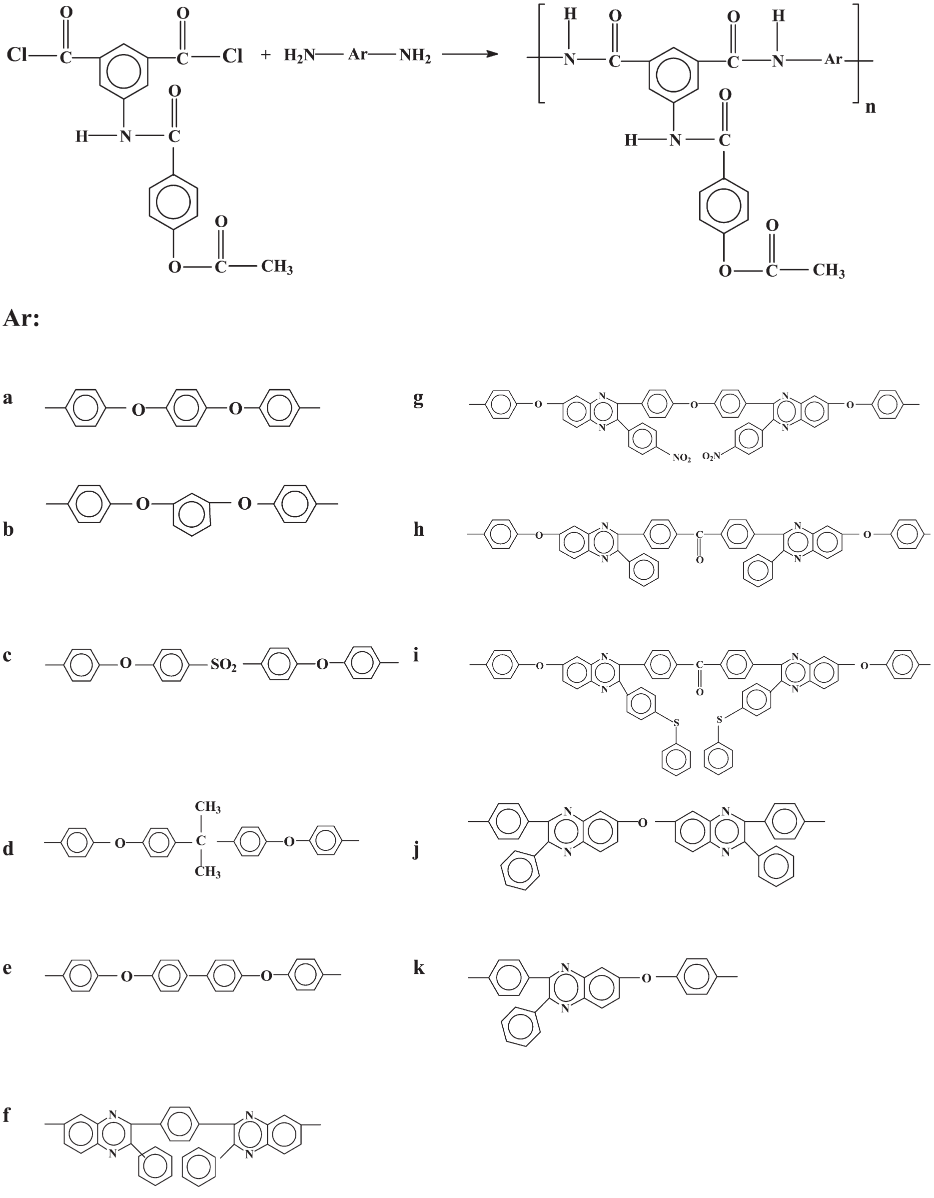
Measurements

The inherent viscosity (η_{inh}) was determined at 20 °C for polymer solutions of 0.5 g/L in NMP by using an Ubbelohde viscometer.

The infrared spectra of the polymers were recorded on a Specord M-80 spectrophotometer in transmission mode by using KBr pellets. The molecular weight values were determined by gel permeation chromatography (GPC) using a Waters GPC apparatus provided with refraction and UV detectors and PL Mixed C Column. Measurements were carried out with polymer solutions of 2% concentration in DMF containing 0.1M $NaNO_3$ and by using DMF with 0.1M $NaNO_3$ as eluent. Polystyrene standards of known molecular weight were used for calibration. The dielectric constant of polymer films was measured at 10 kHz and 20 °C, by using the previously described



Scheme 1.
Synthesis of the 5-(4-acetoxybenzamide)-isophthaloyl chloride.



Scheme 2.
Synthesis of the polymers.

fluid displacement method.[12] Thermogravimetric analyses (TGA) were performed on a MOM derivatograph made in Budapest, Hungary, at a heating rate of 12 °C/min in air. The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieves 5% weight loss. The temperature of 10% weight loss (T_{10}) was also recorded. The glass transition temperatures (T_g) of the precipitated polymers were determined with a Mettler differential scanning calorimeter DSC 12E. The samples were heated from ambient temperature to above 300 °C at a heating rate of 10 °C/min under nitrogen. Heat flow versus temperature scans from the second heating run were plotted and used for reporting the glass transition temperature. The mid-point of the inflection curve resulting from the typical second heating was assigned as the glass transition temperature of the respective polymers. The surfaces of the very thin films as-deposited on silicon wafers were studied by atomic force microscopy (AFM) with a SA1/BD2 apparatus (Park Scientific Instruments) in the contact mode. Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem program, Version 6. [13] The same program was used to visualize the structures obtained after energy minimization. The calculations were carried out with full geometry optimization (bond lengths, bond angles and dihedral angles).

Results and Discussion

Aromatic polyamides with pendent substituted benzamide groups have been synthesized with the aim of attaining better solubility and processability. The structures of these polymers were identified by IR spectra. All polymers showed a wide absorption band at 3440 cm^{-1} and a sharp peak at 1540 cm^{-1} characteristic for N-H, and another peak at 1670 cm^{-1} due to C=O in amide groups. The absorption band at 1760 cm^{-1} is characteristic for COO group and it is present in all the spectra. The absorption peak at 1440 cm^{-1} was assigned to CH_3COO- group.

All these polymers are soluble in polar aprotic solvents such as N-methylpyrrolidinone (NMP), dimethylformamide (DMF) and dimethylacetamide (DMA). The good solubility compared with that of related aromatic polyamides, which do not contain any pendent groups, is due to the presence of voluminous side groups, which prevent the packing of the macromolecules through hydrogen bonds between amide groups in the chain.

Potential energy calculations were performed on the polymer **d** by molecular mechanics (MM+) to obtain information on the most probable conformations and to gain insight into the behaviour observed when the polymers are thermally treated. For these calculations, a model chain involving four repeating units was adopted and these calculations showed that the lowest energy conformation of an isolated chain does not correspond to a regular flat structure. When more than one chain is considered and minimized, the packing of the chains causes a decrease in energy related to that of the isolated chains, a lowering that is proportional to the regularity of the packing. In the case of the flat structure two possibilities of close packing can be considered: one by intercalation of the side chains, as seen in Figure 1, and another one by superimposing the main and the side chains in parallel layers.[14] Of course, both types of packing are possible simultaneously and, in this case, the system formed by four chains, in two layers of intercalated chains each gives a much greater decrease in energy. All these data indicate the high tendency of these polymers with acetoxybenzamide pendent groups to pack tightly, in an ordered structure. If only this ideal structure was present, the polymer would be expected to be crystalline, but this was not confirmed by X-ray diffraction. This indicates that other conformations are also possible. However, even if less regular chains were present, the tendency of side chains to intercalate would still be favoured by polar interactions and hydrogen bridges.[5]

Inherent viscosity values of these polymers are in the range of 0.17–0.7 dL/g showing a moderate molecular weight. The number average molecular weight values, Mn, are in the range of 13000–54500 g/mol, the weight average molecular weight values, Mw, are in the range of 29000–91000 g/mol and polydispersity Mw/Mn is in the range of 1.4–2.89. These values indicate that the polymers have quite a narrow molecular weight distribution and a low quantity of oligomers (Table 1).

All these polymers are capable to give thin flexible films by casting their NMP solutions onto glass plates, followed by

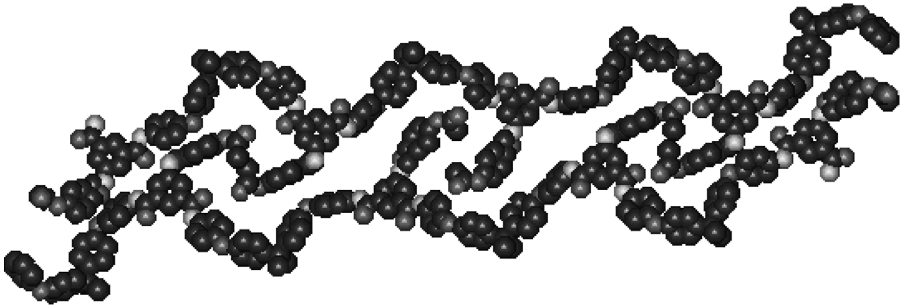


Figure 1.
Representation of two intercalated flat chains of polymer **d**.

drying to remove the solvent. Very thin films having a thickness in the range of tens of nanometres have been prepared from diluted NMP-solutions (conc. 2%) by spin-coating onto silicon wafers. The quality of such films as-deposited on substrates was studied by atomic force microscopy. The films exhibited smooth surfaces over a large scanning ranges (1–100 μm); the values of root mean square (rms) roughness calculated from the AFM data are in the range of 0.5–3 nm. They do not show any pinholes or cracks and are practically defectless. A typical AFM image is shown in Figure 2.

All the polymers show good thermal stability. Their decomposition, in air, begins at about 300 °C as indicated by the temperature of 5% weight loss in TGA thermograms (Table 1).

The initial decomposition temperature (IDT) of these polymers is comparable with that of related aromatic polyisophthalamides having pendent substituted benzamide groups.[5] The temperature of 10% weight loss (T_{10}) is in the range of 345–445 °C and is about 80 °C lower than those of related aramides containing pendent unsubstituted benzamide groups and 40 °C lower than those of polyterephthalamides containing ester groups in the side chain.[15] It means that the acetoxy group in the side chain of the present polymers is the most vulnerable part of the macromolecule. On the other hand when compare the polymers **a–e** with the polymers **f–k** it can be seen that the initial decomposition temperature is slightly higher in the case of polymers which contain phenylquinoxaline units, **f–k**. That means that the phenyl-

Table 1.
Properties of the polymers

Polymer	η_{inh}	Mw	Mn	Mw/Mn	IDT	T_{10}	Tg	Diel.
	dL/g	g/mol	g/mol		(°C)	(°C)	(°C)	(Const.
a	0.462	61000	29000	2.08	290	360	251	4.27
b	0.697	47000	18000	2.61	275	345	230	4.36
c	0.446	37000	13000	2.89	305	370	263	3.42
d	0.630	66000	25000	2.59	310	380	243	3.53
e	0.544	49000	22000	2.25	290	360	252	4.13
f	0.560	78000	54500	1.43	380	445	335	-
g	0.310	34500	23000	1.50	365	415	265	-
h	0.230	54000	22000	2.50	330	420	255	-
i	0.190	91000	42000	2.15	375	420	220	-
j	0.190	46000	29000	1.60	350	375	283	-
k	0.170	29000	14000	2.08	350	395	222	-

IDT = Temperature of 5% weight loss; T_{10} = Temperature of 10% weight loss; Tg = Glass transition temperature.

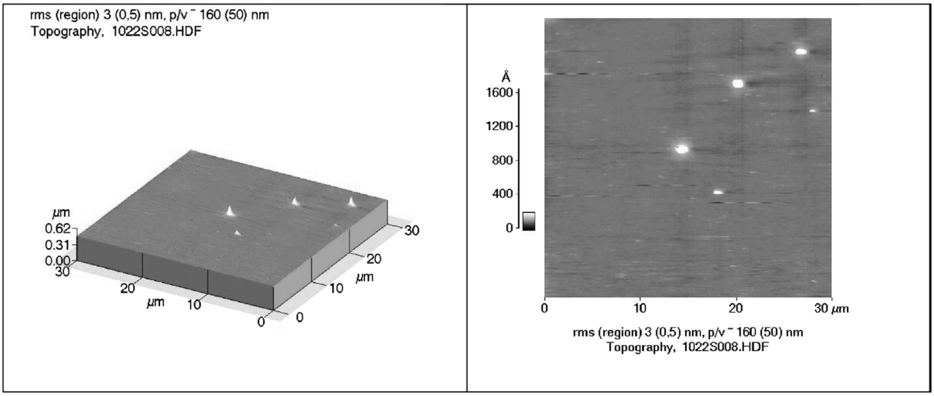


Figure 2.
Atomic force microscopy images of polymer film **f** (left: side view; right: top-view).

quinoxaline units preseve the high thermal stability, even if we introduce the acetoxybenzamide group which is more vulnerable to thermal degradation. The polymers' glass transition temperatures as shown by DSC analysis are in the range of 220–335 °C, being lower than those of related polyisophthalamides without pendent groups. Such behavior of the present polymers could be attributed to the higher free volume determined by the presence of pendent groups and phenyl substituents on quinoxaline rings. It can also be seen that there is a large interval between Tg and decomposition temperature, which could be advantageous in the processing of these polymers. Electroinsulating properties of these polymers have been evaluated on the basis of dielectric constant values. The dielectric constant of the polymer films is in the range of 3.42–4.27. The dielectric constant of the polymer films is a function of the total polarizability of the macromolecular chain, αT. The amide side groups affect the dielectric properties of the resulting polymers in two ways. First, an amide side group should cause a high dipole moment in the aromatic ring it is bonded to in the polymer backbone. This dipole will distort the electron cloud of the aromatic ring and increase the electronic polarizability in the polymer chain. Second, the acetoxy units in the side groups will also cause a high dipole moment in the aromatic ring of the side group. This resulting high dipole moment of the side group will add to the total polarizability of the polymer and will result in polymers having higher dielectric constant. Also, the present polymers showed a slightly higher dielectric constant values in comparison with that (3.5) of "H film", a polyimide which is prepared from pyromellitic dianhydride and 4,4′-diaminodiphenylether and which is one of the most prefered dielectric for use in microelectronic applications.[16]

Conclusion

The incorporation of acetoxybenzamide units as pendent groups on a polyamide backbone containing some flexible bridges or voluminous rings gave products having a remarkable solubility in polar amidic solvents and excellent processability into thin defects-free films. These polymers maintained a high thermal stability, although slightly diminished compared with that of related aromatic polyamide which do not contain any pendent groups.

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[1] B. Sillion, in: "*Comprehensive Polymer Science*", Allen G, editor., Pergamon Press: Oxford, vol 5, **1989**, p 499.
[2] T. Yokozawa, M. Ogawa, A. Sekino, R. Sugi, A. Yokoyama, *Macromol Symp.* **2002**, *199*, 187.

[3] C. D. Diakoumakos, J. A. Mikroyannidis, *Polymer* **1994**, *35*, 1986.

[4] B. Schulz, M. Bruma, L. Brehmer, *Adv Mater.* **1997**, *9*, 601.

[5] A. E. Lozano, J. G. de la Campa, J. de Abajo, J. Preston, *J. Polym Sci, Part A, Polym Chem.* **1995**, *33*, 1987.

[6] I. Sava, E. Hamciuc, C. Hamciuc, M. Bruma, F. W. Mercer, V. N. Reddy, *High Perform. Polym.* **1999**, *11*, 307.

[7] D. J. Liaw, P. N. Hsu, J. J. Chen, B. Y. Liaw, C. Y. Hwang, *J Polym Sci, Part A, Polym. Chem.* **2001**, *39*, 1557.

[8] I. Sava, M. D. Iosip, M. Bruma, C. Hamciuc, J. Robison, L. Okrasa, T. Pakula, *Eur. Polym. J.*, **2003**, *39*, 725.

[9] E. S. Krongauz, *Visokomol. Soedin.., Ser. A*, **1984**, *26*, 227.

[10] M. Bruma, *Handbook of Thermoplastics* ed. O. Olabisi, New York: M. Dekker, **1997**, p 771.

[11] V. V. Korshak, E. S. Krongauz, N. M. Belomoina, H. Raubach, D. Hein, *Acta Polym.*, **1983**, *34*, 213.

[12] F. W. Mercer, T. D. Goodman, *High Perform. Polym.*, **1991**, *3*, 297.

[13] Hypercube Inc. (Ontario) *Hyperchem Version 6*, **2000**.

[14] I. Sava, M. Bruma, C. Hamciuc, E. Hamciuc, D. Timpu, F. Mercer, *J. Appl. Polym. Sci.*, **2001**, *80*, 650.

[15] I. K. Spiliopoulos, J. A. Mikroyannidis, *J. Polym. Sci. Part A, Polym. Chem.*, **1996**, *34*, 1703.

[16] T. Liang, Y. Makita, S. Kimura, *Polymer*, **2001**, *42*, 4867.