

Compared Properties of Aromatic Polyisophthalamides Containing 5-(4-Acetoxy-benzamido) Pendent Groups

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ABSTRACT: A series of aromatic polyamides containing 5-(4-acetoxy-benzamido) pendent groups have been synthesized and their properties have been characterized and compared with those of related polyamides. The polyamides have weight- and number-average molecular weights in the range of 36,680–65,700 and 12,685–35,490, respectively, and polydispersities in the range of 1.82–3.66. These polymers show good thermal stability comparable to traditional aromatic polyisophthalamides, with initial decomposition temperature between 270–320°C and glass transition temperature in the range of 230–270°C. Compared with related polyisophthalamides without any pendent groups, the present polymers show better solubility in certain solvents such as *N*-methylpyrrolidinone and dimethylacetamide and can be cast from solutions into thin transparent flexible films having dielectric constants in the range of 3.42–4.27. The polymer films display remarkable hydrophilicity, which makes them potential candidates for use as advanced materials in humidity sensors. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 650–657, 2001

Key words: aromatic polyisophthalamides; pendent acetoxy-benzamido groups; hydrophilicity; thermostability; dielectric properties

INTRODUCTION

Wholly aromatic polyamides such as poly(*p*-phenyleneterephthalamide) or poly(*p*-benzamide) are polymers with high thermal stability, good chemical resistance, and tough mechanical properties.¹ However, their high glass transition temperatures (T_g) and insolubility in organic solvents seriously limit their processability. One approach to overcome these drawbacks to some degree was the introduction of bulky thermally stable substituents in the 5-position of isophthaloyl moi-

eties.^{2–4} Thus, the solubility was enhanced, but the T_g was still too high.

To improve the solubility even more and lower the T_g while maintaining high thermal stability, we synthesized a series of polyisophthalamides which contain 5-(4-acetoxy-benzamido) pendent groups and ether bridges in the main chain. Herein, we report the study of such polymers, and we compare them with similar compounds.

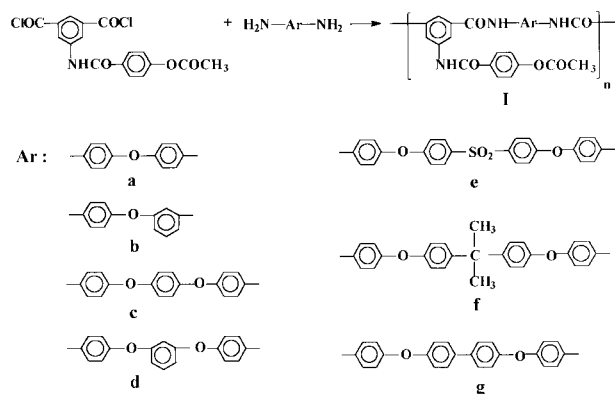
EXPERIMENTAL

Synthesis of the Polymers

The polyamides containing 5-(4-acetoxy-benzamido) groups in the side chain (**I**) were obtained

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Scheme 1 Synthesis of the polyamides containing 5-(4-acetoxy-benzamido) pendent groups (I).

by low temperature solution polycondensation reaction of equimolar amounts of aromatic diamines having ether bridges with 5-(4-acetoxy-benzamido) isophthaloyl chloride, in *N*-methylpyrrolidinone (NMP) as a solvent and in the presence of pyridine as acid acceptor, as shown in Scheme 1.

A detailed description of the synthesis of these polymers and the appropriate monomers was reported elsewhere.⁵

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 using KBr pellets.

The molecular weight distributions were measured by gel permeation chromatography with a PL-EMD 950 evaporative mass detector instrument. Polystyrene standards were used for calibration and dimethylformamide as the mobile phase.

The thermogravimetric analysis (TGA) of the precipitated polymers was performed with a Seiko Robotic TG/DTA 6200 instrument, operating at a heating rate of 10°C, in air, under a purge rate of 300 mL/min. Temperature of 5% weight loss was calculated from the resulting thermograms and it was regarded as initial decomposition temperature. Also, a temperature of 10% weight loss (T_{10}) was reported.

The T_g of the polymers was determined with a Seiko differential scanning calorimeter DSC 6200 with an EXSTAR data analysis system. A sample

size of 3 to 4 mg of each polymer was weighed in a crimped aluminium pan with a pinhole in the cover. The samples were cycled from ambient temperature to above 300°C at a heating rate of 10°C/min under a nitrogen purge of 50 mL/min. Heat flow versus temperature scans from the second heating cycle were plotted and used for reporting the T_g . The midpoint of inflection curve resulting from the typical second heating was assigned as the T_g of the respective polymers.

The dielectric constants of the polymer films having a thickness of 15–20 μm were determined by using the previously described fluid displacement method.⁶ The capacitance of the films was measured using circular gold electrodes (diameter 2.54 cm) mounted in a brass dielectric cell held at a constant temperature (25°C) and a Gen Rad Precision LC Digibridge (model 1688) operating at 10 kHz.

To determine the water absorption, polymer samples were previously conditioned at 120°C in an oven for 8 h. They were subsequently placed in a desiccator where 65% relative humidity was maintained by means of an oversaturated aqueous solution of NaNO_2 at room temperature, and were periodically weighed.

X-ray diffraction experiments were performed on a TUR-M62 diffractometer (Dresden, Germany). Nickel-filtered $\text{CuK}\alpha$ radiation was used. The wide-angle X-ray diffraction traces were recorded by a scintillation counter system with a 1.0 mm diameter pin-hole collimator. The samples were used as powders or films.

Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem program, Version 4 (Ontario).⁷ The same program was used to visualize the structures obtained after energy minimization. The calculations were performed with full geometry optimization (bond lengths, bond angles, and dihedral angles).

RESULTS AND DISCUSSION

The structure of polyamides containing 5-(4-acetoxy-benzamido) groups in the side chain (I) was identified by infrared (IR) spectra. All IR spectra showed a wide absorption band at 3440 cm^{-1} and sharp peaks at 1540 cm^{-1} characteristic for N—H and at 1670 cm^{-1} because of C=O in amide groups. The absorption band at 1760 cm^{-1} is characteristic for the COO group and it is present

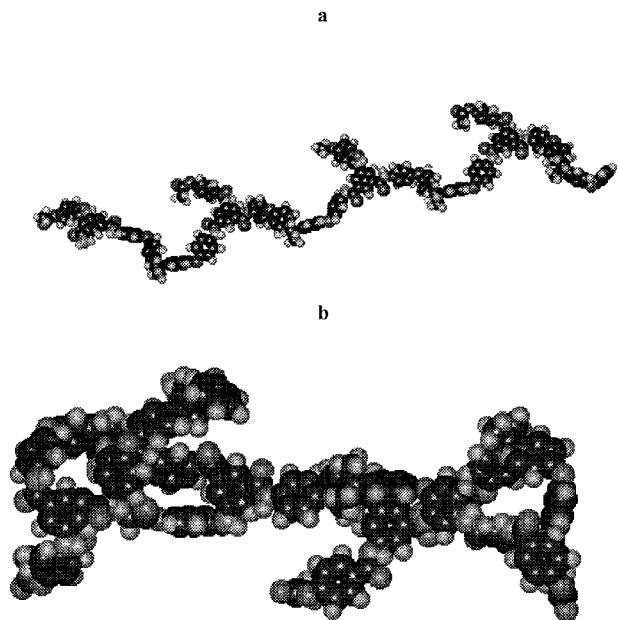


Figure 1 Representation of a single polymer chain **If** (four repeating units) in a flat (a) and a disordered conformation (b).

in all the spectra. The absorption peak at 1440 cm^{-1} was assigned to CH_3COO — group. The absorption peak at 1230 cm^{-1} was attributed to the aromatic ether Ar—O—Ar . Aromatic $\text{C}=\text{C}$ bonds were found at 1600 and 1500 cm^{-1} , whereas aromatic C—H absorptions were found at 3070 cm^{-1} .

All these polymers are soluble in polar aprotic solvents such as NMP and dimethylacetamide. The good solubility compared with that of aromatic polyamides that do not contain side 5-(4-acetoxy-benzamido) groups nor ether bridges is attributed to the presence of voluminous side groups which prevent the packing of the macromolecules through hydrogen bonds between amide groups in the main chain.

Potential energy calculations were performed on the polymer **If** by molecular mechanics (MM+) to obtain information on the most probable conformations and to gain insight into the behavior observed when the polymers are thermally treated. For these calculations, a model chain involving four repeating units was adopted. The calculations show that the lowest energy conformation of an isolated chain does not correspond to a regular flat structure [Fig. 1(a)]. Other less-ordered conformations have lower energy than the flat structure; an example of one of these conformations is shown in Figure 1(b). 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. The close superposition of two chains in the conformation shown in Figure 1(b) causes a decrease of enthalpy of 21 kcal/mol . In the case of the flat structure shown in Figure 1(a), two possibilities of close packing can be considered: one by intercalation of the side chains, as seen in Figure 2, with a drop in energy of about 35 kcal/mol , and another one by superimposing the main and the side chains in parallel layers. In the second case, a higher drop in energy, of 46 kcal/mol of chain, is observed.

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, estimated at 50.3 kcal/mol of chain.

All these data indicate the high tendency of these polymers with 5-acetoxy-benzamido 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 possi-

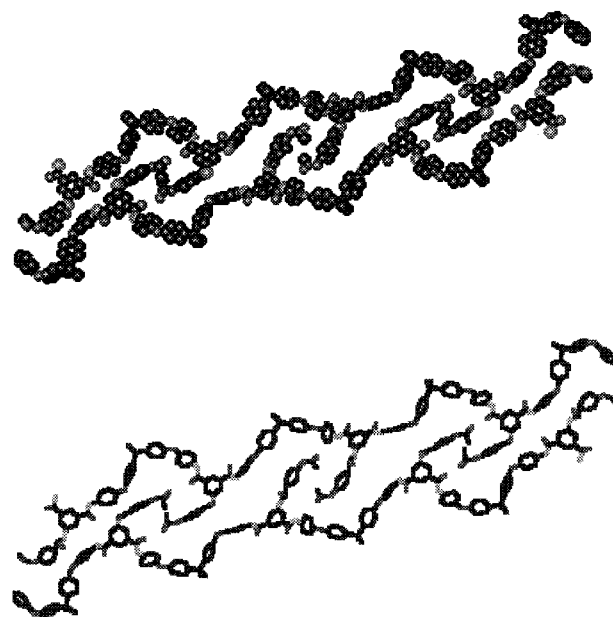


Figure 2 Representation of two intercalated flat chains of polymer **If** (the hydrogen atoms were omitted for clarity). Top: model with spheres; Bottom: model with sticks.

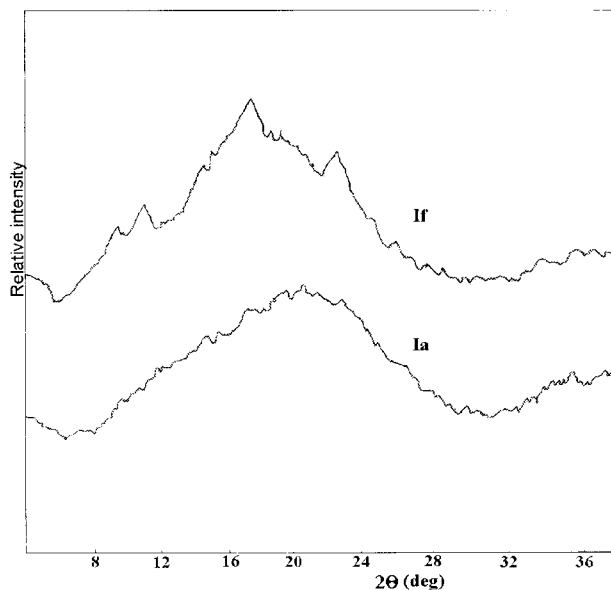


Figure 3 X-ray traces of polymers **Ia** and **If**.

ble. However, even if less regular chains were present, the tendency of side chains to intercalate would still be favored by polar interactions and hydrogen bridges.³

From all the polymers only **If** shows a slight order, which is seen in a calculated degree of crystallinity $\chi = 25\%$. This polymer exhibited three peaks: 11.2° corresponding to an interplanar distance of 7.9 \AA ; 17.2° corresponding to 5.15 \AA , and 22.2° corresponding to 4.0 \AA (Fig. 3). The other polymers were amorphous, showing very broad peaks at about 21° .

The degree of crystallinity (χ_c) has been calculated with the ratio of the integrated crystalline scattering to the total scattering, both crystalline and amorphous, and is given by the following equation^{8,9}:

$$\chi_c = \frac{\int_0^\infty s^2 I_c(s) ds}{\int_0^\infty s^2 I(s) ds}$$

where s is the magnitude of the reciprocal lattice vector and is given by $s = (2\sin\theta)/\lambda$; θ is one-half the angle of deviation of the diffracted rays from the incident X-rays; λ is the X-ray wavelength; $I(s)$ is the intensity of coherent X-ray scatter from a specimen (both crystalline and amorphous); and $I_c(s)$ is the intensity of coherent X-ray scatter from the crystalline region.

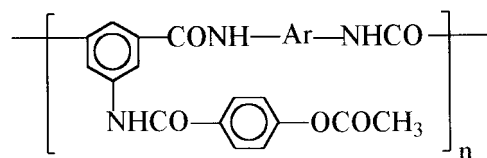
The molecular weight values M_n are in the range of 12,685–35,490, M_w in the range of 36,680–65,700, and M_w/M_n in the range 1.82–3.66 (Table I). It should be noted that gel permeation chromatography measurements by using polystyrene as standard provide only a crude estimate of molecular weights and not an accurate evaluation. As can be seen in Table I, the polymers have quite a broad molecular weight distribution and a low quantity of oligomers. The inherent viscosities are in the range of 0.45–0.7 dL/g (Table II).

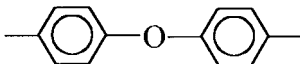
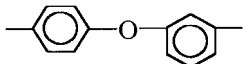
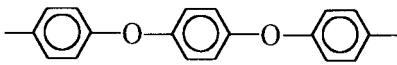

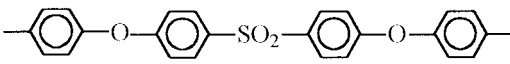
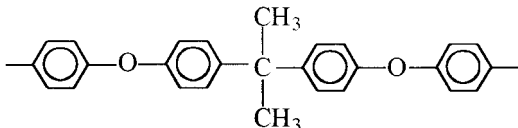
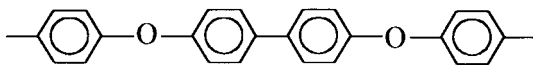
The equilibrium water absorption for these polyamides was studied as a function of the time exposed. Polyamides with 5-(4-acetoxy-benzamido) pendent groups showed a water uptake of 2.23–2.92% after 72 h exposure time (Table II). These values correspond to those of other similar polyamides that contain esters or amido groups in the pendent chain.^{10,11} It is seen that these polymers display a remarkable hydrophilicity probably because the pendent groups cause less dense chain packing, which increases the water accessibility.

The thermal stability of the polymers was studied by thermogravimetric analysis. All these polymers are thermally stable in air up to above 300°C as indicated by the weight loss in TGA thermograms (Table II). A typical TGA curve is shown in Figure 4.

The initial decomposition temperature of these polymers is in the range of 270 – 310°C , being comparable with those of aromatic polyisophthalamides reported in the literature.¹² The temperature of 10% weight loss (T_{10}) is in the range of 320 – 380°C and is about 100°C lower than those of related aramides containing unsubstituted benzamide groups³ and 50°C lower than those of polyterephthalamides containing ester pendent groups.¹⁰

The polymers' T_g s as shown by differential scanning calorimetric (DSC) analysis are in the range of 230 – 270°C , being lower than that of related polyisophthalamides without pendent groups.³ Such behavior of the present polymers could be attributed to the higher free volume determined by the presence of pendent groups. The polymer with diphenylether group in the para position has the highest T_g and the one with triphenylether groups in meta position has the lowest T_g (Table II). A typical DSC diagram is shown in Figure 5. We expected that the presence of acetoxy-benzamido side groups would generate

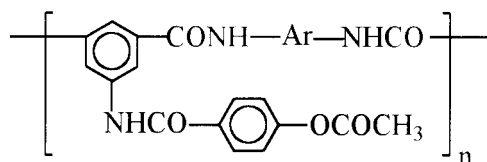
Table I GPC Measurements of Aromatic Polyamides Containing 5-(4-Acetoxy-benzamido) Pendent Groups, I; The General Formula:

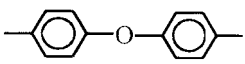
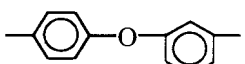

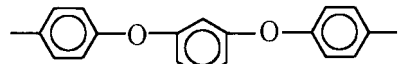
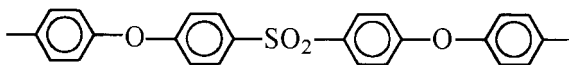
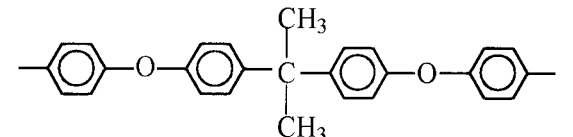
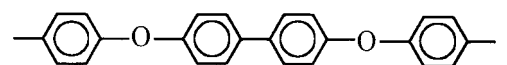
| Polymer | Ar | M_w | M_n | M_w/M_n |
|---------|---|--------|--------|-----------|
| Ia |  | 64,640 | 35,490 | 1.82 |
| Ib |  | 52,750 | 14,380 | 3.66 |
| Ic |  | 61,000 | 29,200 | 2.08 |
| Id |  | 46,780 | 17,915 | 2.61 |
| Ie |  | 36,680 | 12,685 | 2.89 |
| If |  | 65,700 | 25,280 | 2.59 |
| Ig |  | 48,740 | 21,600 | 2.25 |

some liquid crystalline behavior of these polymers, but no clear evidence of such behavior was found in DSC curves, or in microscopic investigations under polarized light.

When polymer films were heated at $T > 200^\circ\text{C}$ for 2 h or more, they did not redissolve readily in concentrated sulphuric acid. This behavior is in contrast with that of traditional polyisophthalamide films which redissolve very easily after heating at high temperature even for longer periods of time. It is believed that during thermal treatment of the present polymers, some crosslinking takes place through

hydrogen bonds between amide groups of the side chain and/or through the ester groups ---OCOCH_3 , which become mobile so that they can be rearranged in a favorable position as to interact with each other. However, the IR spectra of the thermally treated polymer films do not show significant change, which means that the amount of crosslinks is not high enough to be visible in IR, but it is sufficient to produce the insolubility. This phenomenon is in concordance with observations of other authors for polyisophthalamides with similar structure having other pendent units containing amide

Table II Properties of the Aromatic Polyamides Containing 5-(4-Acetoxy-benzamido) Pendent Groups, I; The General Formula:

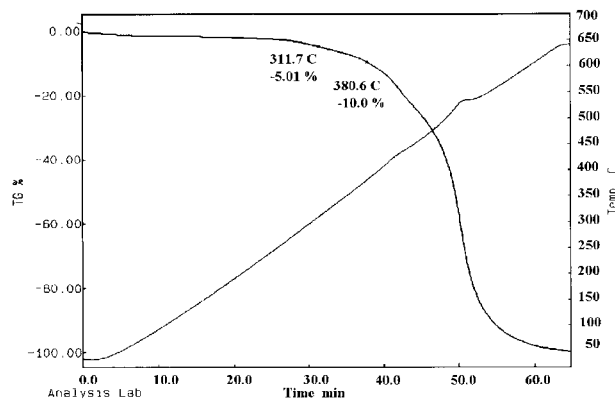
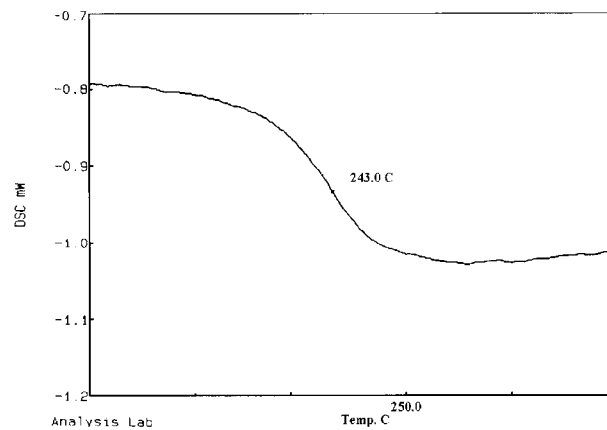
| Polymer | Ar | η_{inh}^a (dL/g) | IDT ^b (°C) | T_{10}^c (°C) | T_g^d (°C) | Dielectric Constant | Water Absorption (%) |
|---------|---|--------------------------|--------------------------|--------------------|-----------------|------------------------|----------------------------|
| Ia |  | 0.708 | 295 | 340 | 273 | — | 2.78 |
| Ib |  | 0.466 | 270 | 320 | 251 | — | 2.92 |
| Ic |  | 0.462 | 290 | 360 | 251 | 4.27 | 2.5 |
| Id |  | 0.697 | 275 | 345 | 230 | 4.36 | 2.37 |
| Ie |  | 0.446 | 305 | 370 | 263 | 3.42 | 2.23 |
| If |  | 0.630 | 310 | 380 | 243 | 3.53 | 2.90 |
| Ig |  | 0.544 | 290 | 360 | 252 | 4.13 | 2.45 |

^a Determined for polymer solutions of 0.5% conc. in NMP at 20°C.

^b Temperature of 5% weight loss, determined by TGA in air at a heating rate of 10°C/min.

^c Temperature of 10% weight loss, determined by TGA in air at a heating rate of 10°C/min.

^d Determined by DSC with a heating rate of 10°C/min in air.

**Figure 4** TGA curve of the polymer If.**Figure 5** DSC curve of the polymer If.

linkages³ and it is different from that of polyisophthalamides containing cinnamoyl groups.¹³

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 (Table II). There are a number of factors affecting the dielectric properties of materials.¹⁴ The dielectric constant of polymer is a function of the total polarizability, αT .¹⁵ There are three components to the polarizability of a polymer: 1. the electronic polarizability, αE , which results from electrons being displaced from their equilibrium positions about the nucleus; 2. atomic polarizability, αA which results from nonsymmetrical displacement of one atom to another; and 3. orientational polarizability, αO , which results from a change in alignment of the permanent dipole moments in the polymer to that of an applied electric field by physical movement of the group associated with the dipole. The electronic and atomic components of the dielectric constant are generally much smaller than the orientational components of polarization of a polar molecule. An exception to this is with conjugated systems where electron displacement can take place over a larger area and substantially increase electronic polarizability.¹⁶

The amide side groups affect the dielectric properties of the resulting polymers in two ways. First, the amide side groups 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. Because the polymer repeating unit molecular weights in **Ic**, **Id**, and **Ig** are lower than in **Ie** and **If**, the total polarizability of **Ic**, **Id**, and **Ig** would be higher. As a result, we would expect these polymers to have higher dielectric constants than the polymers **Ie** and **If**. 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, αT , of the polymer and will result in polymers having higher dielectric constants.

In summary, the dielectric properties of these polyamides are due in large part to the amide side group. Both the electronic polarizability of the side group itself and the fact that these highly polar amide side groups also induce high dipole moments in the aromatic electron clouds of the aromatic rings they are attached to, both contrib-

ute to the relatively high dielectric constants observed.

These results are important because they indicate a good way to prepare polymers having high dielectric constants. That is, to get a high dielectric constant, prepare polymers with highly polarizable side groups. The polymers having relatively high dielectric constant are important for use in passive components (resistors, capacitors, inductors) in electronic packaging technologies.

CONCLUSIONS

By introducing 5-(4-acetoxy-benzamido) pendent groups together with ether bridges into the repeating unit of aromatic polyamides, polymers with good solubility and reasonably low T_g , while preserving the high thermal stability, were obtained. They were cast from solutions into flexible films having dielectric constants in the range of 3.42–4.27 and with a strong adhesion to glass. The polymers have weight- and number-average molecular weights in the range of 36,680–65,700 and 12,685–35,490, respectively, and polydispersities in the range of 1.82–3.66. These polymers show good thermal stability, comparable to traditional aromatic polyisophthalamides, with initial decomposition temperature between 270–320°C and T_g in the range of 230–270°C. The polymer films display remarkable hydrophilicity, which makes them potential candidates for use as advanced materials in humidity sensors. Other applications based on their dielectric constant value are also foreseen.

REFERENCES

1. Preston, J. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley-Interscience: New York, 1988; Vol. 11; p. 381.
2. Lozano, A. E.; de la Campa, J. G.; Preston, J. *J Polym Sci Part A Polym Chem* 1992, 30, 1327.
3. Lozano, A. E.; de Abajo, J.; de la Campa, J. G.; Preston, J. *J Polym Sci Part A Polym Chem* 1995, 33, 1987.
4. Hamciuc, C.; Hamciuc, E.; Mercer, F. W.; Bruma, M. *J Macromol Sci Pure Appl Chem* 1997, 34, 143.
5. Sava, I.; Hamciuc, E.; Hamciuc, C.; Bruma, M.; Mercer, F. W.; Reddy, V. N. *High Perform Polym* 1999, 11, 307.

6. Mercer, F. W.; Goodman, T. D. *High Perform Polym* 1991, 3, 297.
7. Hypercube Inc. (Ontario) *Hyperchem* Version 4, 1994.
8. Alexander, L. E. *X-Ray Diffraction Methods in Polymer Science*; Wiley: New York, 1969; p.137.
9. Rabek, J. F. *Experimental Methods in Polymer Chemistry*; Wiley: New York, 1980; p. 507.
10. Spiliopoulos, I. K.; Mikroyannidis, J. A. *J Polym Sci Part A Polym Chem* 1996, 34, 1703.
11. Spiliopoulos, I. K.; Mikroyannidis, J. A. *J Polym Sci Part A Polym Chem* 1996, 34, 1685.
12. Diakoumakos, C. D.; Mikroyannidis, J. A. *Polymer* 1994, 35, 1986.
13. Ommer, H. J.; Ritter, H. *Makromol Chem* 1993, 194, 767.
14. Feynman, R. P.; Leighton, R. B.; Sands, M. *The Feynman Lectures of Physics*; Addison-Wesley Publishing: Reading, PA, 1977; Vol. 2.
15. Hougham, G.; Tesoro, G.; Shaw, J. *Polym Mater Sci Eng* 1989, 61, 369.
16. Ku, C. C.; Liepins, R. *Electrical Properties of Polymers: Chemical Principles*; Hanser: New York, 1987.