

*Dedicated to the memory of
Professor Mircea D. Banciu (1941–2005)*

POLYISOPHTHALAMIDES WITH PENDENT ACETOXYBENZAMIDE OR IMIDE GROUPS

Ion SAVA* and Corneliu HAMCIUC

“P. Poni” Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41 A, 700487 - Iasi, Roumania

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Polycondensation reaction of diacid chlorides incorporating 3,4,5,6-tetrachlorophthalimide or 5-(4-acetoxybenzamide) pendent units with different aromatic diamines containing ether, sulfone or isopropylidene linkages gave two series of aromatic polyisophthalamides containing pendent 3,4,5,6-tetrachlorophthalimide or 5-(4-acetoxybenzamide) groups. These polymers were soluble in polar amidic solvents, gave transparent flexible films and showed good thermal stability. Conformational parameters of the polymers were calculated by the Monte Carlo method with allowance for hindered rotation. Several physical properties of these polymers such as solubility, glass transition temperature and initial decomposition temperature were experimental measured and discussed in relation with the rigidity of their chains.

INTRODUCTION

Aromatic polyamides are widely used as high temperature resistant polymers. Numerous polyamides containing different substituents on the aromatic rings have been synthesized and studied for high performance applications.¹⁻³ The polyamides containing all *para*-phenylene rings are the most interesting polymers, but they are not soluble, nor fusible which makes their processing difficult. A major parameter that contributes to insolubility is the intermolecular bonding energy developed through hydrogen bridges and through dipole-dipole interactions. Regular aromatic polyamides, obtained from symmetrical co-monomers, can develop high degree of crystallinity, a factor that works against solubility and processability.⁴

The introduction of a certain amount of *meta*-phenylene rings led to polymers with somewhat improved solubility. Thus, polyisophthalamides are soluble in highly polar solvents in the presence of inorganic salts.⁵

Another attractive synthetic approach to improve the solubility and processability is the incorporation of bulky substituents such as pendent groups along the polymer backbone. If the pendent groups are carefully chosen, it is possible to promote solubility without sacrificing the thermal and mechanical properties to a great extent. Thus, thermally stable polyamides with pendent aromatic or heteroaromatic rings have been reported.⁶⁻¹⁰

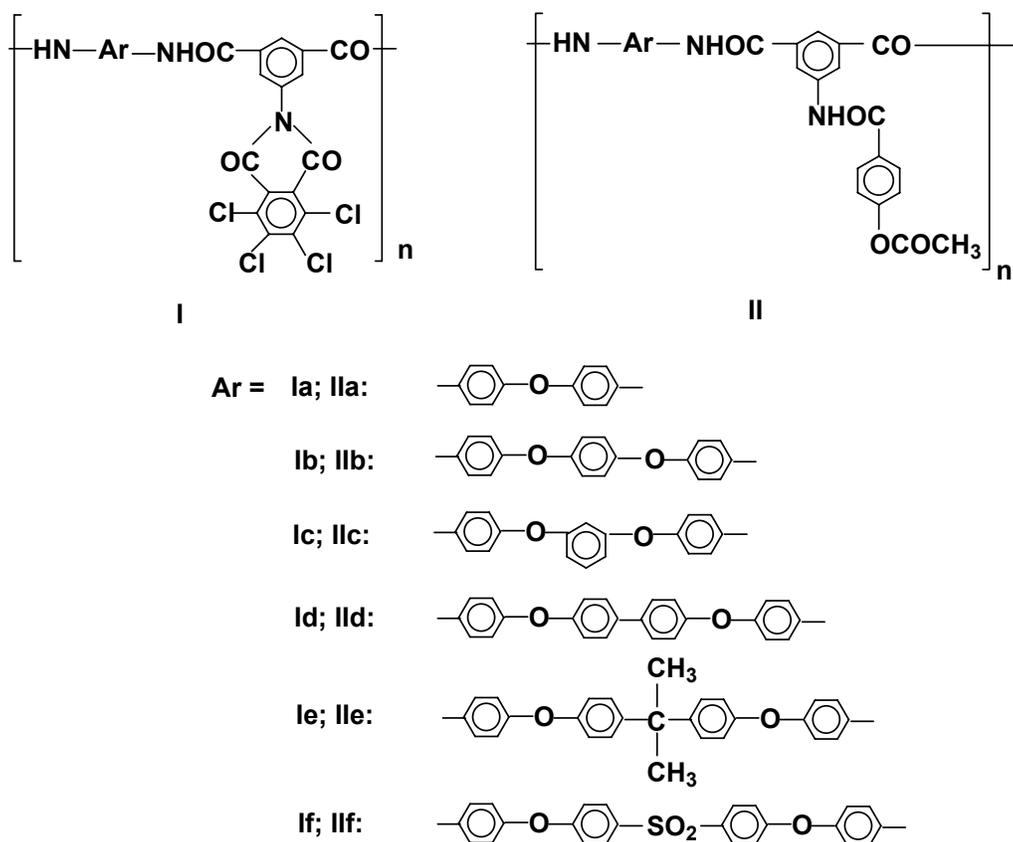
In the present work, polyisophthalamides with 3,4,5,6-tetrachlorophthalimide or 5-(4-acetoxybenzamide) pendent groups have been prepared and their properties have been evaluated and compared with respect to their chemical structure.

We took into account that the study of physical properties of such polymers in connection with the influence of the pendent units on the chain conformation is of great interest for future advanced applications. Some physical properties of these polymers such as solubility, glass transition temperature and initial decomposition temperature have been discussed in relation with the conformational rigidity of their chains and some relationships have been shown.

* Corresponding author: Email: isava@icmpp.ro

RESULTS AND DISCUSSION

Aromatic polyisophthalamides containing pendent groups **I** and **II** have been synthesized with the aim to have highly thermostable, easy soluble and processable products. These polymers were prepared by the polycondensation reaction of 5-(3,4,5,6-tetrachlorophthalimide) isophthaloyl chloride or with 5-(4-acetoxycarbonylbenzamide) isophthaloyl chloride with different aromatic diamines containing ether, sulfone or isopropylidene linkages. The reaction was run with equimolar amounts of the two monomers, in N-methylpyrrolidinone (NMP) as a solvent and in the presence of pyridine as acid acceptor. The structures of these polymers are shown in Scheme 1.



Scheme 1 – The structures of the polymers **I** and **II**.

The structure of polyisophthalamides containing pendent groups in the side chain (**I** and **II**) was identified by IR spectra. All IR spectra of polymers **I** and **II** 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} due to C = O in amide groups. In the infrared spectra of polymers **I**, the absorptions at 1780 cm^{-1} and 1720 cm^{-1} are commonly attributed to the symmetrical and asymmetrical stretching vibrations of carbonyl groups of imide rings; the absorptions at 1375 cm^{-1} and 720 cm^{-1} are possibly due to imide ring deformations. In the case of IR spectra of polymers **II** 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 $\text{CH}_3\text{COO-}$ group. The absorption peak at 1230 cm^{-1} was attributed to the aromatic ether Ar - O - Ar. Aromatic C = C bonds were found at 1600 cm^{-1} and 1500 cm^{-1} , while aromatic C - H absorptions were found at 3070 cm^{-1} .

All these polymers are soluble in polar aprotic solvents such as NMP and dimethylacetamide (DMA). This behavior is in agreement with the fact that the presence of voluminous imide or acetoxybenzamide side units introduces a factor of asymmetry and sterical hindrance that prevents a dense packing and enhances the solubility. The good solubility compared with that of aromatic polyamides that do not contain side

5-(4-acetoxybenzamide) groups nor ether bridges is due to the presence of voluminous side groups which prevent the packing of the macromolecules through hydrogen bonds between amide groups in the main chain. Thus, the present polymers containing pendent tetrachlorophthalimide or acetoxybenzamide groups have better solubility in organic solvents compared to polyisophthalamides which are only soluble in polar amidic solvents.⁵ The good solubility of the present polymers is due to the relatively high free volume of macromolecular chains which was obtained by the introduction of pendent groups and ether linkages. Thus, the shape of a macromolecule is far from a linear rigid rod, which is characteristic to wholly aromatic insoluble structures. Model molecules of the polymers **Ic** and **IIf** are shown in Figure 1. Due to such a shape, the dense packing of the chains is disturbed, the diffusion of small molecules of solvents between the polymer chains is facilitated and that leads to better solubility.

The inherent viscosities are in the range of 0.45-0.88 dL/g (Table 1).

The thermal stability of the polymers was studied by thermogravimetric analysis (TGA). All these polymers are thermally stable in air over 400°C for polymers **I** and up to above 300°C in the case of polymers **II**, as indicated by the temperature of 5% weight loss in TGA thermograms (Table 1). As can be seen the initial decomposition temperature of polymers **I** is higher than the initial decomposition temperature of polymers **II** due to the presence of high thermostable imide groups. Also, the presence of acetoxy group in the side chain of the polymers **II** is the most vulnerable part of the macromolecule and consequently reduce the thermostability.

Comparison of these polymers with previously synthesized polyisophthalamides with pendent phthalimide groups but not containing any chlorine substituents shows that their thermooxidative stabilities are very similar.

Table 1
Properties of the polymers **I** and **II**

Polymer	η_{inh}^a (dL/g)	T_d^b (°C)	T_{10}^c (°C)	T_g^d (°C)	Dielectric constant	l_0 (Å)	A_{fr} (Å)	p
Ia	0.53	415	465	Nd	4.03	17.56	31.40	7.15
Ib	0.78	400	448	Nd	3.96	22.30	28.70	6.43
Ic	0.84	405	452	Nd	3.72	22.75	20.60	4.52
Id	0.88	420	467	Nd	3.91	26.40	30.50	6.93
Ie	0.69	400	430	Nd	3.63	27.25	22.70	4.99
If	0.72	442	472	Nd	4.06	27.54	24.10	5.25
IIa	0.71	295	340	273	-	17.57	30.73	7.00
IIb	0.46	290	360	251	4.27	24.48	28.52	5.82
IIc	0.70	275	345	230	4.36	22.73	21.63	4.76
IId	0.54	290	360	252	4.13	26.41	33.58	7.62
IIe	0.63	310	380	243	3.53	27.25	24.58	5.57
IIIf	0.45	305	370	263	3.42	27.54	23.55	5.13

^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; ^cTemperature 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;

l_0 = contour length of the repeat unit; A_{fr} = Kuhn segment; p = parameter of rigidity.

Polyisophthalamides with pendent 3,4,5,6-tetrachlorophthalimide groups, **I**, did not melt, nor soften (visually) under 350°C. Likewise, they did not show any fusion peak, nor clear T_g inflections in DSC curves, up to 350°C.

The glass transition temperatures of polymers **II** as shown by DSC analysis are in the range of 230-270°C, being lower than that of related polyisophthalamides without pendent groups.¹¹ 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 *para* position has the highest T_g and the one with triphenylether groups in *meta*-position has the lowest T_g (Table 1).

Electroinsulating properties of these polymers have been evaluated on the basis of dielectric constant values. All these polymers have low dielectric constants, in the range of 3.6-4.27 (Table 1). However, these values are slightly higher than that (3.5) of the polyimide film (Kapton) obtained from pyromellitic dianhydride and 4,4'-diaminodiphenylether which is one of the most used dielectrics in high performance applications. These polymers containing 3,4,5,6-tetrachlorophthalimide or acetoxybenzamide groups have slightly increased dielectric constants when compared with related polymers containing non-chlorinated or without side acetoxybenzamide units.¹⁰ Since the dielectric constant is a function of the total polarizability of the molecule,¹² the polymers which display higher dielectric constants should also have higher polarizabilities. The higher dielectric constants of the present polymers are determined by high polarizability of the polar groups, which are present into macromolecular chains.

Chemical stability of polymer films was evaluated by examining their aspect upon immersion in acidic or basic media for periods up to one month. Free standing films were kept in glacial acetic acid, in 10% HCl or in 10% NaOH solution. After one month the films, which were kept in acidic media, were flexible and apparently unchanged. Indeed, IR spectra of the acid treated films were identical to those of the initial, untreated films. Also, UV spectra of the acidic solution in which the polymer film was immersed didn't exhibit any absorption, which might be attributed to some fragments of hydrolysis. When immersed in 10% NaOH solution for one month, the films became brittle, but they were still films. At the same time a sample film prepared from the polyimide "H" (synthesized by polycondensation of pyromellitic dianhydride with 4,4'-diaminodiphenylether) became a gel after immersion for only three days in 10% NaOH solution. Therefore it can be observed that the present polymer films have a good stability towards acidic media, but they lose their integrity in basic media.¹³

The Kuhn segment (A_{fr}) and the number of aromatic rings in the Kuhn segment (p) were chosen as the conformational parameters and were discussed in correlation with some physical properties of the present polymers. The parameter p was included because in previous work the correlation of physical properties with the number of aromatic rings in Kuhn segment was shown.¹⁴⁻¹⁶

As is known, the Kuhn statistical segment can be written as:

$$A = \lim_{n \rightarrow \infty} \left(\frac{\langle R^2 \rangle}{nl_0} \right)$$

where $\langle R^2 \rangle / nl_0$ is the ratio of the average square end-to-end distance of a chain to its contour length; n is the number of repeat units; l_0 is the contour length of a repeat unit. In the case of polyheteroarylenes in which the macromolecular unit contains virtual bonds with different length and different angles between them, the length of the zig-zag line connecting the mid-points of the virtual bonds is taken as the contour length. The Kuhn segment lengths were calculated by Monte Carlo method.¹⁷

Knowing the value of Kuhn segment allows one to calculate the parameter of conformational rigidity p

$$p = \frac{A}{l_0} k$$

where k is the number of aromatic rings in a polymer structural unit. The conformational parameter p takes into account both factors: aromatic character of polyheteroarylenes and their rigidity. In the case of the present polymers we have found that the Kuhn segment values calculated under the assumption of free rotation (A_{fr}) and under the assumption of hindered rotation (A_{hin}) are equal. It means that the acetoxybenzamide or imide pendant groups do not cause a significant hindrance, since they allow rotation around virtual bond going through phenyl ring in *meta*-position despite the narrow distance between phenyl hydrogen and hydrogen of amide group. These bulky acetoxybenzamide or imide groups influence only on packing of macromolecules in solid state. Conformational parameters A_{fr} and p are shown in Table 1.

The solubility of the polymers **I** and **II** correlates well with their conformational rigidity. All these polymers are soluble in polar amidic solvents such as NMP and dimethylformamide (DMF). The solubility is due to the relatively high flexibility of the macromolecular chains of these polymers, which is in agreement with relatively low values of Kuhn segment (20.6 – 33.58). The voluminous pendent groups together with ether units do not allow the macromolecular chains to pack tightly through hydrogen bonds between amide

groups and thus increase the solubility of the polymers.^{15,16} The polymer **Ie** was soluble even in tetrahydrofuran probably due to the presence of isopropylidene units that introduce a supplementary kink in the chain.

The glass transition temperature and the initial decomposition temperature values (T_d) are known to be significantly dependent on the presence of aromatic rings in the polymeric chain. In the case of the present polymers, T_g values increased while increasing the value of the conformational rigidity parameter. Previously,¹⁸ it was shown that there was a relationship between glass transition temperature and initial decomposition temperature for several polymers: $T_d = aT_g$

The value of a for polyamides and polyimides lies in the range of 1.15 – 1.25 depending on the structure of the polymer repeating unit. Since the dependence between the glass transition temperature and the conformational rigidity exists, it would be reasonable to assume the existence of a relation between the initial decomposition temperature and the conformational rigidity. It is known that T_g and T_d values are to an essential degree dependent on the presence of aromatic rings in the polymeric chain. Therefore, one can try to find a correlation between these parameters and the number p of aromatic rings in the fragment of polymeric chain equivalent to Kuhn segment. The initial decomposition temperature (T_d) of the polymers does not show a very significant dependence of their chain rigidity. This fact is probably due to the presence of amide groups, which are more sensitive to thermal degradation.^{15,16} The presence of acetoxy groups in the side chain of polymers **II**, which are more sensitive to degradation dictates the T_d . Also, the presence of amide units in the macromolecular chains, which are more vulnerable to thermal degradation, influences the decomposition temperature of the polymers. A similar behavior was reported for related heterocyclic polymers containing amide groups.¹⁹

We can not say that the dielectric constant is associated with the hindrance of rotation of the polymers or with conformational rigidity parameter. The dielectric constant of a polymer is a function of total polarizability.

EXPERIMENTAL

Synthesis of the monomers

Synthesis of diacid chlorides

5-(3,4,5,6-Tetrachlorophthalimide) isophthaloyl chloride, has been synthesized in two steps. In the first step a dicarboxylic acid, namely 5-(3,4,5,6-tetrachlorophthalimide) isophthalic acid have been prepared by the reaction of 5-aminoisophthalic acid with 3,4,5,6-tetrachlorophthalic anhydride, in glacial acetic acid at reflux temperature. In the second step, this dicarboxylic acid containing preformed imide ring reacted with thionyl chloride to give the corresponding diacid chloride. Melting point: 268°C - 270°C.¹¹

5-(4-Acetoxybenzamido)-isophthaloyl chloride was synthesized by a sequence of reactions in which *p*-hydroxybenzoic acid reacted with acetic anhydride to give *p*-acetoxybenzoic acid that by further treatment with thionyl chloride gave the corresponding acid chloride; the latter reacted with 5-aminoisophthalic acid to produce *p*-acetoxybenzamide isophthalic acid which, by further treatment with thionyl chloride, gave *p*-acetoxybenzamide isophthaloyl chloride. It was purified by recrystallization from ligroin. Melting point: 132°C – 134°C.¹²

Aromatic diamines containing ether, sulfone or isopropylidene units were provided from different commercial sources and were used as received.

Synthesis of the polymers

The polymers containing pendent 3,4,5,6-tetrachlorophthalimide or acetoxybenzamide unit, **I** and **II**, respectively, were obtained by low temperature solution polycondensation reaction of equimolar amounts of 5-(3,4,5,6-tetrachlorophthalimide) isophthaloyl chloride or 5-(4-acetoxy-benzamide) isophthaloyl chloride with aromatic diamines having ether, sulfone or isopropylidene bridges in NMP as a solvent and in the presence of pyridine as acid acceptor.^{15,16} (Scheme 1).

Measurements

Infrared spectra were recorded on a Specord M-80 spectrometer with resolution of 4 cm⁻¹, using KBr pellets. Inherent viscosity (η_{inh}) was determined at 20°C for polymer solutions of 0.5 g/dL in NMP with an Ubbelohde viscometer. 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 0.1 M NaNO₃ and by using DMF with 0.1 M NaNO₃ as eluent. Polystyrene standards of known molecular weight were used for calibration. The thermogravimetric analysis (TGA) of the polymers was performed with a Seiko Robotic TG/DTA 6200 instrument, operating at a heating rate of 10°C/min, in air. The initial decomposition temperature (T_d) is characterized as the temperature at which the sample achieves 5% weight loss. Glass transition temperatures (T_g) of the polymers were determined with a Seiko differential scanning calorimeter DSC 6200. The dielectric constant of polymer films was measured at 10 kHz and 20°C, by using the previously described fluid displacement method.²⁰ Model molecules for a polymer fragment were obtained by molecular

mechanics (MM+) by means of the Hyperchem program, Version 6.²¹ 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).

CONCLUSIONS

By introducing tetrachlorophthalimide or acetoxybenzamide groups pendent to polyisophthalamide chain a significant increase of the polymer solubility was achieved, thus allowing easy processing into films or coatings by casting from polymer solution. 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. These polymers show good thermal stability with initial decomposition temperature being between 400-442°C for polymers, which contain pendent imides units, and in the range of 275-310°C for polymers with acetoxybenzamide groups in the side chain. The glass transition temperature is situated in the range of 230-270°C for the polymers, which contain pendent acetoxybenzamide units, and the polymers with pendent imides group didn't show any T_g. These polymers are highly thermostable and have good electroinsulating properties, being potential candidates for application in microelectronics and related industries.

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