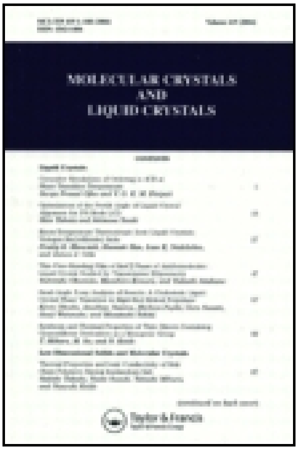

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Conformational Parameters and Some Physical Properties of Polyamides Containing Pendant Acetoxybenzamide Groups

Ion Sava [a] , Maria Bruma [a] & Inga Ronova [b]
[a] Institute of Macromolecular Chemistry “P. Poni”, Iasi, Romania
[b] Nesmeyanov Institute of Organoelement Compounds, Moscow, Russia

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CONFORMATIONAL PARAMETERS AND SOME PHYSICAL PROPERTIES OF POLYAMIDES CONTAINING PENDANT ACETOXYBENZAMIDE GROUPS

Ion Sava and Maria Bruma
Institute of Macromolecular Chemistry "P. Poni", Aleea Gr. Ghica Voda 41A, Iasi 6600, Romania

Inga Ronova
Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ulitsa Vavilova 28, Moscow 117813, Russia

Conformational parameters of some aromatic polyamides containing pendant acetoxybenzamide groups have been calculated by Monte Carlo method taking into consideration the hindered rotation produced by the side groups. Several physical properties such as solubility, glass transition temperature, initial decomposition temperature and dielectric constant have been studied with regard to the rigidity of the chain of these polyamides, and their relationships have been shown.

INTRODUCTION

Wholly aromatic polyamides are polymers with high thermal stability, chemical resistance and good mechanical properties [1]. However, their high glass transition temperature (Tg) and limited solubility in organic solvents make their processability quite difficult. To overcome these drawbacks to some degree an attractive synthetic approach to improving the solubility and processability is the incorporation of bulky substituents such as pendent groups along the polymer backbone. In this away it is possible to obtain good solubility without sacrifying the thermal and mechanical properties to a great extent [2,3]. The introduction of pendent acetoxybenzamide units in the macromolecular chain of polyamides improves the solubility while maintaining a fairly good thermal stability [4–6]. We took into

Address correspondence to Ion Sava, Institute of Macromolecular Chemistry "P. Poni", Aleea Gr. Ghica Voda 41 A, Iasi 6600, Romania. E-mail: isava@icmpp.tuiasi.ro

account that the study of physical properties of such polymers in connection with conformational parameters of the macromolecular chain is of interest for future advanced applications.

Thus, in the present work some physical properties of aromatic polyamides containing acetoxybenzamide groups in the side chain and different units such as ether, 1,3,4-oxadiazole or hexafluorisopropilidene (6F) in the main chain have been studied with regard to the conformational rigidity of the macromolecules and their relationships have been shown.

EXPERIMENTAL

Synthesis of the Polymers

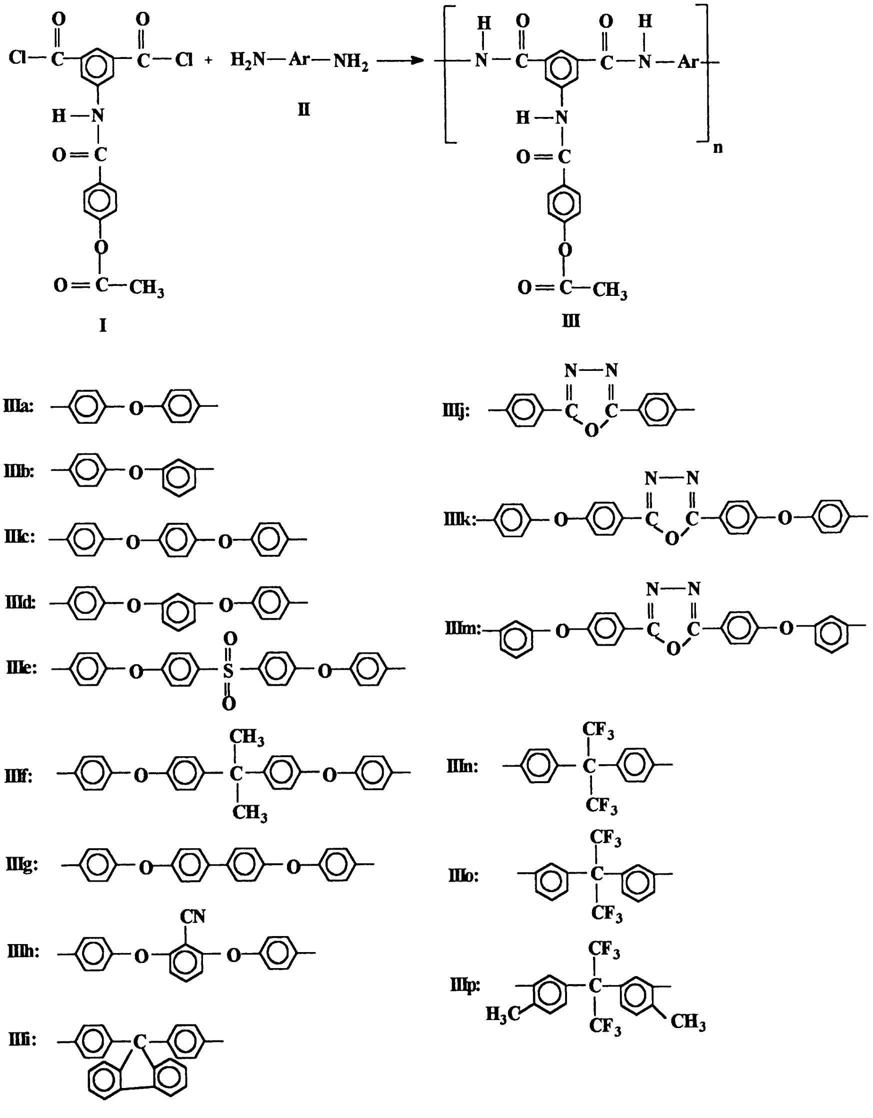
The polyamides containing acetoxybenzamide groups in the side chain were obtained by low temperature solution polycondensation reaction of equimolar amounts of 5-(4-acetoxybenzamido) isophthaloyl chloride, **I,** with various aromatic diamines containing ether linkages, preformed 1,3,4-oxadiazole ring or hexafluoroisopropylidene units **II,** in N-methylpyrrolidinone (NMP) as a solvent and in the presence of pyridine as acid acceptor, as previously reported [4–6]. These polymers have the structure **III**, as shown in Scheme 1.

Measurements

The Kuhn segments were calculated by using the Monte Carlo method as described earlier [7]. The glass transition temperature (Tg) of the polymers was determined with a Seiko differential scanning calorimeter DSC 220 C, operating at a heating rate of 10°C min^{-1} in nitrogen. The decomposition temperature was investigated by using Seiko TGA/DTA 220 thermobalance operating at a heating rate of 20°C min^{-1} in air. The dielectric constant of polymer films was measured by using the previously described fluid displacement method [8].

RESULTS AND DISCUSSION

The Kuhn segment ($\mathbf{A_{fr}}$), the characteristic ratio ($\mathbf{C}_\infty$), 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 [7,9].



SCHEME 1 Synthesis of polyamides **III**.

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

$$A = \lim_{n \to \infty} \left(\frac{\langle R^2 \rangle}{n l_0} \right)$$

where $\langle R^2 \rangle / n l_0$ 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 midpoints of the virtual bonds is taken as the contour length. The Kuhn segment lengths were calculated by Monte Carlo method. Knowing the value of Kuhn segment allows one to calculate the characteristic ratio $\mathbf{C}_\infty$

$$C_\infty = \frac{A}{l_0}$$

and 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 ($\mathbf{A_{fr}}$) and under the assumption of hindered rotation ($\mathbf{A_{hin}}$) are nearly equal; in case of the polymers **IIIf, IIIi, IIIn, IIIo** and **IIIp** there is a slight difference between $\mathbf{A_{fr}}$ and $\mathbf{A_{hin}}$. It means that the acetoxybenzamide 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 bulk acetoxybenzamide groups influence only on packing of macromolecules in solid state.

We have studied some of the physical properties of the polymers **III** such as solubility, glass transition temperature, initial decomposition temperature (IDT), and dielectric constant (ε), and we have made correlations with their conformational rigidity (Table 1).

The solubility of the polymers 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 having low values of Kuhn segment (13.85–44.77). The voluminous pendent groups together with ether, oxadiazole or hexafluoroisopropylidene (6F) units do not allow the macromolecular chains to pack tightly through hydrogen bonds between amide groups and thus increase the solubility of the polymers. The polymers containing 6F groups in the main chain, have the best solubility and that can be explained by the combined action of 6F groups and pendant acetoxybenzamide units which introduced a factor of asymmetry and steric hindrance that prevent a dense packing of the chains.

TABLE 1 Conformational Rigidity Parameters and Some Properties of the Polymers III

Polymer	l_0 (Å)	A_{fr} (Å)	A_{hin} (Å)	C_∞	p	IDT (°C)	Tg (°C)	Dielectric constant
IIIa	17.57	30.73	30.75	1.75	7.00	295	273	–
IIIb	17.56	20.91	20.89	1.19	4.77	270	251	–
IIIc	24.48	28.52	28.56	1.16	5.82	290	251	4.27
IIId	22.73	21.63	21.61	0.95	4.76	275	230	4.36
IIIe	27.54	23.55	23.52	0.86	5.13	305	263	3.42
IIIf	27.25	24.58	25.32	0.93	5.57	310	243	3.53
IIIg	26.41	33.58	33.56	1.27	7.62	290	252	4.13
IIIh	22.75	21.63	21.61	0.95	4.75	291	260	4.5
IIIi	17.47	24.08	25.28	1.45	8.68	303	320	–
IIIj	20.25	44.77	44.78	2.21	8.84	263	280	4.9
IIIk	30.05	34.23	34.21	1.14	6.83	292	270	3.93
IIIm	30.03	20.48	20.49	0.68	4.09	299	270	4.65
IIIn	17.47	24.08	25.28	1.45	5.78	307	280	–
IIIo	17.38	13.85	14.54	0.84	3.35	305	245	–
IIIp	17.38	13.85	14.54	0.84	3.35	311	225	–

IDT = initial decomposition temperature = temperature of 5% weight loss.
Tg = glass transition temperature.

The dependence of the Tg (determined from DSC curves) on the parameter of conformational rigidity **p** is shown in Table 1. As can be seen, the polymer **IIIi,** with higher value of rigidity parameter (8.68) has the highest Tg (320°C). The introduction of ether linkages in the macromolecular chain of the polyamides led to a decrease of Tg values, by comparison with the polymer **IIIi** which does not have any ether linkages. The polymer **IIId**, containing both ether groups and a *meta*-catenated phenylene ring, has the lowest value of rigidity parameter (4.76) and exhibits the lowest value of Tg (230°C). All the other polymers have intermediate values of Tg and of rigidity parameter.

In the case of polymers which contain 1,3,4-oxadiazole rings in the macromolecular chains, it can be observed that the polymers **IIIk** and **IIIm** containing ether linkages have a slightly lower Tg values (270°C, each) by comparing with polymer **IIIj** whose Tg is 280°C and which does not have any ether and which has a higher rigidity parameter (8.84) than the polymers **IIIk** and **IIIm** whose rigidity parameter is 6.83 and 4.09, respectively. The introduction of 6F units in the macromolecular chain of the polyamides **IIIn, IIIo** and **IIIp** increases the flexibility of the backbone and the Tg of these polymers is lower especially when the polymers contain *meta*-catenated phenylene rings (**IIIo** and **IIIp**) and this fact is in concordance with the values of rigidity parameter. The polymer **IIIn** having a higher value of rigidity parameter (5.78) shows a higher value of Tg (280°C), while the polymer **IIIp** which has a low value of rigidity parameter (3.35) exhibits a lower value of Tg (225°C).

The initial decomposition temperature (IDT) of these polymers (determined from TG curves) does not show a very significant dependence of their chain rigidity. Even more, the polymers **IIIn, IIIo** and **IIIp** have the IDT very close to each other, being 305–311°C, while their rigidity parameters are quite different 3.35–5.78. This fact is probably due to the presence of acetoxybenzamide groups which are more sensitive to thermal degradation than all the other aromatic units and begin to decompose at about 300°C. The polymers **III** have IDT in the range of 270–310°C, the lowest IDT being shown by the polymers **IIIb** and **IIId** due to the presence of *meta*-catenated phenylene units in the macromolecular chain (270°C and 275°C, respectively); the values of rigidity parameter of these two polymers are low (4.77 and 4.76, respectively). The polymers **IIIe** and **IIIf** have the highest IDT (305°C and 310°C, respectively) although the values of conformational rigidity parameter **p** (5.13 and 5.57, respectively) are not significantly higher than in the case of their analogs **IIIa, IIIc, IIId** and **IIIh** which have the conformational rigidity parameter **p** of 7.0, 5.82, 4.76 and 4.75, respectively, and whose IDT is in the range of 290°–295°C. This means that the presence of flexible SO_2, isopropylidene or voluminous rigid fluorene groups in the polymers **IIIe**, **IIIf** and **IIIi** or hexafluoroisopropylidene bridges in the polymers **IIIn, IIIo** and **IIIp** leads to a slightly higher thermal stability, probably due to a higher thermal resistance of these groups.

The dielectric constant of the present polymers is in the range of 3.42–4.9. 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. In the case of these polymers the presence of side acetoxybenzamide units affects the dielectric properties of the polymers because it introduces a high dipole moment in the aromatic ring it is bonded to in the polymer backbone. This dipole moment will distort the electron cloud of the aromatic ring and increase the electronic polarizability in the polymer chain. Compared with conventional aromatic polyamides whose dielectric constant is usually below 3.6, most of the present polymers having pendant acetoxybenzamide groups exhibit slightly higher dielectric constant [10].

CONCLUSIONS

The solubility of the present polyamides containing pendant acetoxybenzamide groups correlates well with Kuhn segment values. On the other hand the solubility is dependent on the presence of hexafluoroisopropylidene groups and of the architecture of the molecules. The glass transition temperature of these polyamides is in the range of 230°–320°C and it increases with increasing the chain rigidity which is described by the conformational rigidity parameter **p** being in the domain of 3.35–8.84. All these polymers have a good thermal stability with the initial decomposition temperature being in the range of 270°C–311°C; we did not find a significant dependence of the initial decomposition temperature on the chain rigidity probably due to the fact that acetoxybenzamide groups begin to decompose at lower temperature and the decomposition is mainly determined by these groups. The dielectric constant of these polymers is not associated with the conformational rigidity parameters. The value of the dielectric constant is in the range of 3.42–4.9 and it is slightly higher compared with conventional aromatic polyamides due to the presence of highly polar amide groups in the pendant unit which make the total polarizability of the macromolecular chains to be higher.

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