

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

INFLUENCE OF CONFORMATIONAL PARAMETERS ON PHYSICAL PROPERTIES OF SOME POLY(AMIDE-ESTER)S

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Conformational parameters of a series of aromatic polyamides containing esters groups were calculated by the Monte Carlo method. Some physical properties of these polymers, such as solubility, glass transition temperature and initial decomposition temperature were experimentally measured and discussed in relation with the rigidity of their chains. The conformational rigidity parameters values of the polymers correlates well with their solubility and glass transition temperatures.

INTRODUCTION

Wholly aromatic polyamides (aramids) and polyimides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties. However, rigidity of the backbone and strong intermolecular interactions through hydrogen bonding (in polyamides) and charge-transfer complex formation (in polyimides) result in high melting or glass transition temperature and limited solubility in most organic solvents.¹⁻⁴ These properties make them generally intractable or difficult to process, thus restricting their applications. Therefore, intense efforts have been made to try to improve the processing characteristics of the relatively intractable polymers.⁵⁻¹²

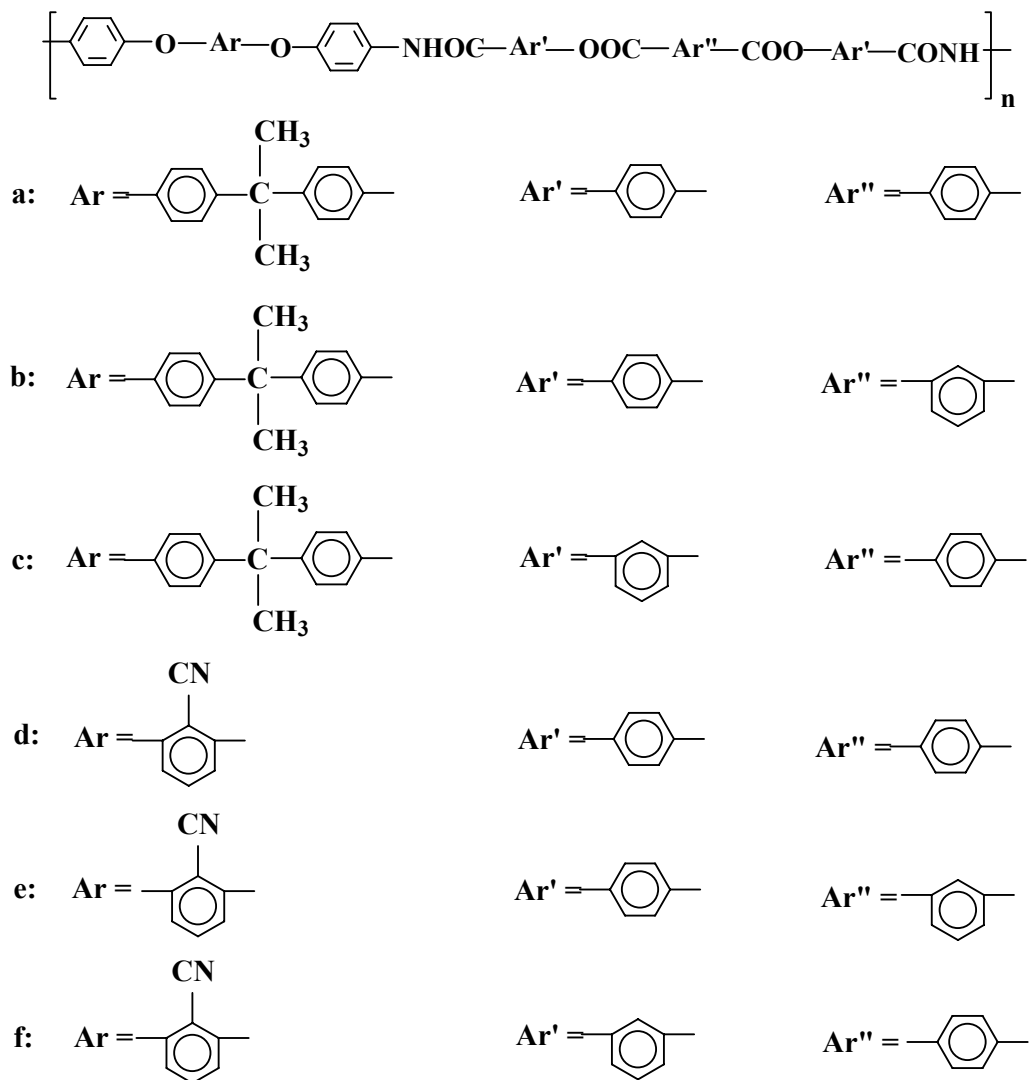
These studies include introducing flexible segments into the polymer chain replacing symmetrical aromatic rings by unsymmetrical ones, which lead to a reduction in crystallinity; introducing bulky pendant groups to minimize crystallization, and forming a non-coplanar structure, thereby making crystallization impossible.

We took into account that the study of physical properties of such polymers in connection with the influence of the esters linkages on the chain conformation is of great interest for future advanced applications. Thus, in the present work some physical properties of aromatic polyamides containing esters groups have been studied with regard to the conformational rigidity of the polymer chains and the relation between conformational parameters and thermal properties have been shown.

RESULTS AND DISCUSSION

The poly(amid-ester)s have been prepared by polycondensation of equimolar amounts of three diacid chlorides incorporating ester linkages with 1,4-bis(*p*-aminophenoxy-phenyl)-2,2-isopropane or with 2,6-bis(*p*-aminophenoxy)-benzotrile in *N*-methylpyrrolidinone (NMP) as a solvent and in the presence of pyridine as acid acceptor, as previously reported.¹³ The structures of these polymers are shown in scheme 1.

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Scheme 1 – Structure of polymers.

The Kuhn segment (A_{fr}), the characteristic ratio (C_∞) 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.^{14,15}

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

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

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 and 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 as shown in the literature,¹⁶ under the assumption of free rotation around virtual bonds (Table 1). We used the Volkenstein rotational isomeric

state approximation by consideration of only discrete values of rotation angles, and the Flory approximation by the assumption that rotations around virtual bonds are independent.¹⁷ The term «virtual bonds» is used to indicate a rigid section of a chain approximated by a straight line about which rotation is possible. In a particular case, it can be an ordinary valence bond; more generally, it can contain rings as well. The conformational energy maps for several aromatic polyesters and polycarbonates were calculated and the minimum energy structures were found, in which the rotation angles about virtual bonds passing through aromatic rings were 0° and 180°, both values being equally probable.¹⁸

Table 1

Conformational parameters and physical properties of polymers

Polymer	l_0	A_{fr}	C_∞	p	T_g (°C)	T_g calc. (°C)	ITD (°C)	T_d (°C)
a	40.28	49.66	1.233	8.63	210	211.32*	370	400
b	40.05	35.17	0.878	6.15	203	199.024*	370	410
c	39.78	27.57	0.693	4.85	190	192.576*	380	405
d	35.80	46.82	1.308	7.85	215	214.81**	375	410
e	35.57	33.17	0.933	5.60	218	218.517**	365	390
f	35.30	25.41	0.714	4.29	221	220.67**	380	410

l_0 = contour length of a repeat unit; A_{fr} = Kuhn segment; C_∞ = characteristic ratio; p = parameter of conformational rigidity; T_g = glass transition temperature; T_g calc. = glass transition temperature calculated with equations: * $T_g = 168.52 + 4.96 p$; ** $T_g = 227.74 - 1.65 p$; ITD = Onset temperature of initial decomposition; T_d = temperature of 10% weight loss.

Knowing the value of Kuhn segment allows the calculation of 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. A comparison between the experimental values of the Kuhn segment (A_{exp}) for polyheteroarylenes and those calculated under the assumption of a free rotation (A_{fr}) showed they are nearly equal.^{19,20} In the case of the present polymers we suppose that the ester 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.

The solubility of the polymers correlates well with their conformational rigidity. All these polymers are soluble in polar amidic solvents such as NMP and DMF. The solubility is due to the relatively high flexibility of the macromolecular chains of these polymers having low values of Kuhn segment (25.41 – 49.66) (Tab. 1). The arrangement of macromolecular chain was evidenced by molecular modeling as shown in Fig. 1.

As can be seen the shape of macromolecular chains is far from a linear rigid form which is characteristic to aromatic polyamide. Due to such a shape, the packing of chains through hydrogen bonds between amide groups is disturbed and thus the small molecules of solvent can diffuse easily among the chains, leading to better solubility. The polymers which contain all *para*-catenated benzene rings, **a** and **d**, having higher Kuhn segment values were not soluble in N,N'-dimethylformamide (DMF) after precipitation. The other polymers having lower Kuhn segment values are more flexible and are soluble in neat polar aprotic solvents. The polymers containing *meta*-disubstituted phenylene rings have lower Kuhn segment values than the corresponding ones containing *para*-disubstituted phenylene rings and better solubility. Moreover, the polymers **b**, **c**, **e** and **f** are also soluble in other polar amidic solvents, such as N,N'-dimethylacetamide (DMA) or DMF. It is believed that the presence of one *meta*-catenated benzene ring in each repeating unit of these polymers introduces more flexibility in the chain and makes the polymers soluble in a large variety of solvents. This is proved by the values of rigidity parameter as can be seen in the Tab. 1.

The glass transition temperature (T_g) and the initial decomposition temperature values (IDT) 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 as the value of the conformational rigidity parameter increases.

Previously,²¹ it was shown that there was a relationship between glass transition temperature and initial decomposition temperature for several polymers: $IDT = aT_g$.

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 IDT 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 dependence of glass transition temperature (determined from DSC curves) for polymers **a**, **b**, **c** and **d**, **e** and **f** on conformational parameters (A_{fr} and p) are shown in Fig. 2 a and 2 b.

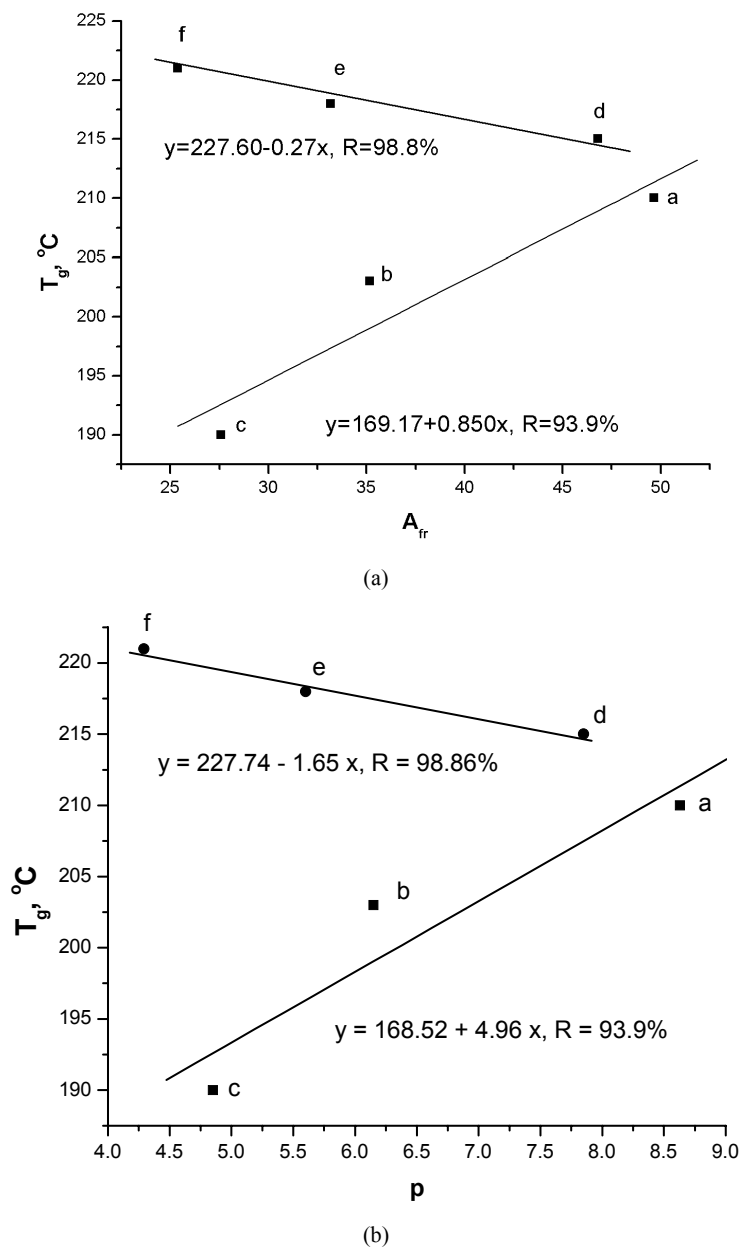


Fig. 2 – (a) Dependence of glass transition temperature on Kuhn segment A_{fr} ;
(b) Dependence of glass transition temperature on rigidity parameter p .

The T_g of the polymers which contains isopropylidene groups (**a**, **b** and **c**) is slightly lower by comparing with the corresponding polymers which contain benzonitrile units (**d**, **e**, and **f**), probably due to the presence of isopropylidene groups, which have a strong influence on the flexibility of the chains.

Using the least-squares method, the dependence of T_g on conformational parameter **p** can be described by a linear equation. The factor of convergence **R** is relatively high: $R = 93.9\%$ for polymers with isopropylidene units and 98.85% for polymers with benzonitrile groups. As mentioned in the literature,^{15,22} if the dependence is linear with a good factor of convergence, this equation can be used for the theoretical estimation of glass transition temperatures for polymers having similar structures in case their experimental determination is difficult. Thus, the glass transition temperatures of polymers **a**, **b** and **c** can be calculated by equation $T_g = 168.52 + 4.96 \mathbf{p}$ and those of polymers **d**, **e** and **f** can be calculated by equation $T_g = 227.74 - 1.65 \mathbf{p}$. Tab. 1 presents the calculated values of T_g in comparison with those found experimentally. It can be seen that it is a very good correlation between the obtained values. It can be concluded that the glass transition temperature of polymers are correlated in a good manner with the conformational rigidity parameters of these polymers, suggesting a linear dependence.

The initial decomposition temperature of these polymers (determined from thermogravimetric curves) does not show a significant dependence on their chain rigidity. This fact is due to the presence of ester groups which are more sensitive to thermal degradation and begin to decompose at lower temperatures. In polymers **c** and **f** the presence of the three phenyl rings, one of which is *meta*-connected between amide and ester groups, leads to thermal stabilization of these polymers. Therefore, these polymers exhibit higher decomposition temperature, although they are the most flexible among all the investigated polymers.

EXPERIMENTAL

Synthesis of the polymers

Low temperature solution polycondensation reaction of equimolar amounts of diacid chlorides which contain preformed ester groups with aromatic diamines, namely 2,6-bis(*p*-aminophenoxy-phenyl)-2,2'-isopropane or 2,6-bis(*p*-aminophenoxy)-benzonitrile units, was carried out in NMP using pyridine as acid acceptor and the new polyamide-esters **a-f** were obtained as previously described.¹³ Diacid chlorides containing preformed esters linkages were prepared by treating the corresponding dicarboxylic acids with thionyl chloride. They had been obtained from the reaction of 4-hydroxybenzoic acid or 3-hydroxybenzoic acid with terephthaloyl- or isophthaloyl chloride, respectively, as previously reported.²³

Measurements

The Kuhn segments were calculated by using Monte Carlo method as described earlier.¹⁸

Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem program, Version 7.5.²⁴ The same program was used to visualise the structures obtained after the energy minimisation. The calculations were carried out with full geometry optimisation (bond lengths, bond angles and dihedral angles).

Thermogravimetric analysis (TGA) was performed on a MOM-type Derivatograph made in Budapest, Hungary, operating in air at a heating rate of $12^\circ\text{C}/\text{min}$.

The glass transition temperature (T_g) was measured on a Mettler DSC 12E apparatus in nitrogen with a heating rate of $10^\circ\text{C}/\text{min}$. Approximately 7 to 10 mg of polymers were crimped in Al pans and run in nitrogen purge of 50 ml/min with a heat-cool-heat profile from 30°C to 320°C at $10^\circ\text{C}/\text{min}$, with 3 min isothermal stabilization times at the temperature extremes. The mid-point of the inflection curve resulting from the typical second heating cycle was assigned as the T_g of polymers.

CONCLUSIONS

A series of aromatic poly(amide-ester)s containing flexible isopropylidene or benzonitril substituents on the benzene rings have been characterized by physical properties such as solubility, glass transition temperature and initial decomposition temperature and correlated with the conformational rigidity of their chains. The improved solubility of these polymers having ester and ether linkages compared with fully aromatic polyamides correlates well with the low values of their Kuhn segment. The glass transition temperatures have a linear dependence on conformational rigidity parameters with a high convergence factor.

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