SOLUTION PROPERTIES OF POLY(AMIC ACID)S AND POLYIMIDES

Doina MACOCINSCHI, Anca ȚĂRANU, Camelia HULUBEI and Silvia IOAN [*]

"Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41A, 700487-Iasi, Roumania

The influence of the structure of poly(amic acid) and polyimide structure on some solution properties is described. The aggregation phenomena in the poly(amic acid) solutions and the competition between the additional flexible linkage introduced in the chain and the effect of number of benzene rings in the poly(amic acid)s and polyimides determine the particular conformational aspects.

INTRODUCTION

The polyimides are important, both scientifically and commercially, because of their combination of outstanding key properties, including thermal, thermo-oxidative stability, high mechanical strength, high modulus, excellent electrical properties, and superior chemical resistance.[1-3]

Generally, it is known that one of the successful approaches to increase the solubility and processability without sacrificing high thermal stability is the introduction of bulky and unsymmetrical groups, flexible bonds, large pendent or polar substituents into the polymer backbone.[4-6] Therefore, it is expected that the combination of imide units, aromatic rings, flexible bonds and epiclon moieties, a cycloaliphatic anhydride with flexible and asymmetrical structure in one macromolecule, would develop new synthetic polymers offering a compromise between processability and physical and thermal characteristics. Epiclon has been used as raw material for polyimides to enhance the solubility and to render other new properties.[5,7] Thus, the enhancing of solubility becomes a major opportunity to direct study of the solution properties, such as the chain flexibility and conformation.[8] These products have their importance primarily because of their chemical properties but have the additional advantages or restrictions of their being part of a macromolecule. Advantages include cooperative effects of the functional groups, limited mobility, especially in the solid states, anchoring possibility, various polymer possibilities in compositions and distribution of the functional groups along the polymer chain. Restrictions are caused by the low mobility and possible undesirable agglomeration effects in solution. It is therefore important that in all the functional groups along the polymer chain and molecular weight distribution be taken into account. Moreover, to tailor a polyimide to satisfy specific requirements in various industries, a careful examination and control of its chain conformation are of great importance.

Previous publications in the field presented the synthesis and some properties of new soluble polyimides.[4,9] The products have been characterized from the point of view of their chemical structure and thermal behaviour. This report describes the influence of the structure on some solution properties by viscometry.

EXPERIMENTAL

Polymers presented in Scheme 1 have been obtained by polycondensation reaction between Epiclon, 5-(2,5-dioxothetrahydrofurfuryl)-3methyl-3 cyclohexene-1,2-dicarboxylic acid anhydride, and two diamines, *p*-phenylenediamine and 1,4-ethylene dianiline, respectively.[4,9]

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[*] Corresponding author: ioan_silvia@yahoo.com

poly(amic acid) I (PAAI)

polyimide I (PiI)

poly(amic acid) II (PAAII)

polyimide II (PiII)
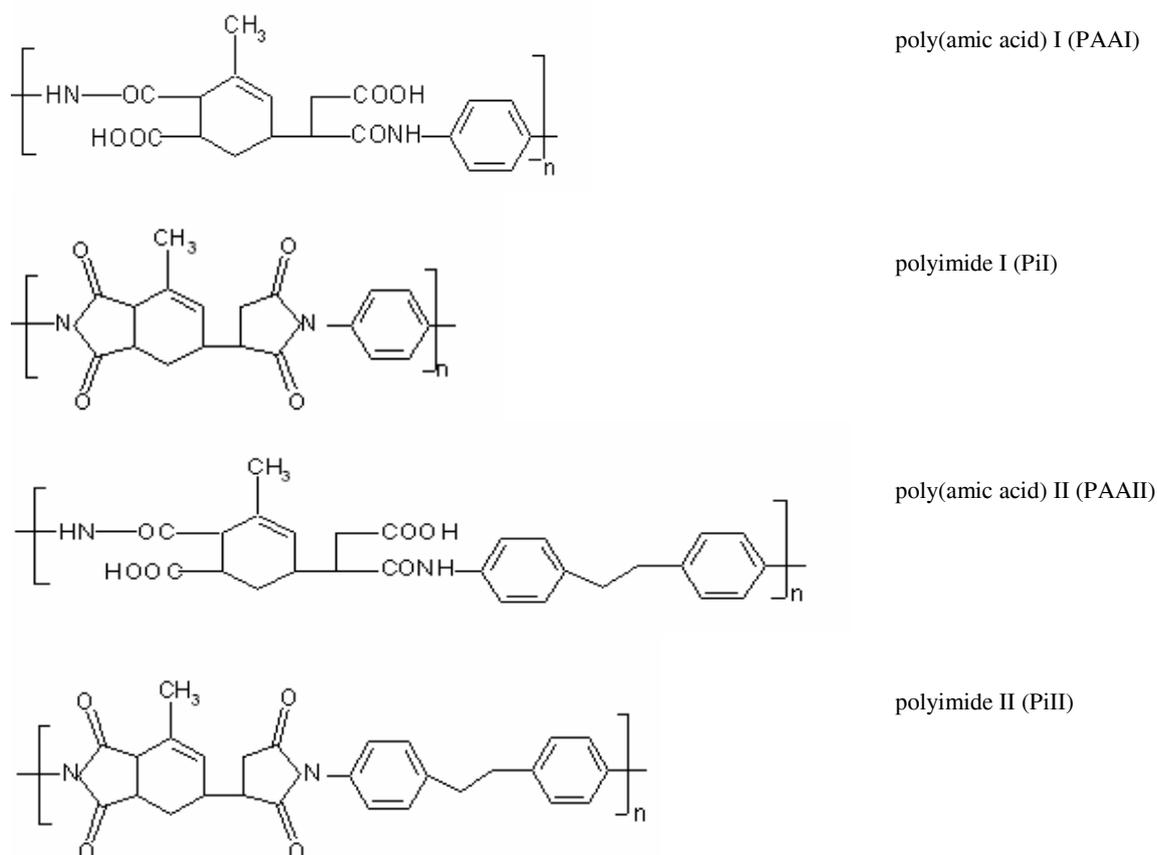
Scheme 1

Gel permeation chromatography (GPC) measurements in N,N-dimethylformamide (DMF) were conducted on a PL EMD-950 evaporative light scattering detector apparatus. The column system was thermostated at 25°C. Calibration was performed with polystyrene standards of narrow polydispersity (Polymers Laboratories Ltd.). The samples were eluted with DMF and the flow rate was 0.7 mL min^{-1}. The volume of the injected polymer solutions was always 20 μL. The analysis of the elution data was performed using computer program based on the normalization of the chromatograms. Tab. 1 shows the molecular weights of structural units, m, number average molecular weights, M_n, and polydispersity index, M_w/M_n, for the studied samples.

Table 1

Molecular weight of chain units, m, number average molecular weights, M_n, polydispersity indices, M_w/M_n, critical concentrations c* and c$^+$, intrinsic viscosities in perturbed, $[\eta]$, and unperturbed, $[\eta]_\theta$, state, gyration radii in perturbed, $R_{g,c=0}$, and unperturbed, $R_{c \geq c^+}$, state and expansion factors, α^2, of poly(amic acid)s and poly(imide)s at different temperatures

Sample	T, °C	c*, g/mL	c$^+$, g/mL	$[\eta]$, mL/g	$[\eta]_\theta$, mL/g	$R_{g,c=0} \cdot 10^8$, cm	$R_{c \geq c^+} \cdot 10^8$, cm	α^2
PAAI	20	0.0231	0.2207	32.47	9.12	87.01	56.98	2.3
m=372	25	0.0241	0.2150	31.92	8.83	86.52	56.37	2.3
M_n=63200	30	0.0255	0.2800	30.16	8.48	84.90	55.63	2.3
M_w/M_n=1.28	35	0.0243	0.2821	29.43	8.40	84.22	55.44	2.3
	40	0.0264	0.3032	29.18	7.95	83.97	54.43	2.4
	45	0.0268	0.2889	28.78	7.72	83.59	53.91	2.4
PiI	20	0.0602	0.7710	12.79	4.62	61.76	43.98	2.0
m=336	25	0.0603	0.7566	12.78	4.51	61.74	43.62	2.0
M_n=57100	30	0.0609	0.8677	12.64	4.38	61.51	43.20	2.0
M_w/M_n=1.28	35	0.0621	0.8417	12.40	4.19	61.12	42.57	2.1
	40	0.0617	0.8735	12.49	4.10	61.27	42.26	2.1
	45	0.0680	0.8598	11.32	3.89	59.30	41.53	2.0

Table 1 (continues)

Table 1 (continued)

PAAII	20	0.0223	0.2964	34.50	9.84	94.23	62.03	2.3
M=476	25	0.0236	0.2960	32.57	9.47	92.44	61.25	2.3
M_n=75400	30	0.0.234	0.2765	32.89	9.39	92.75	61.08	2.3
M_w/M_n=1.27	35	0.0246	0.3229	31.30	8.99	92.19	60.20	2.3
	40	0.0237	0.2918	32.45	8.88	92.33	59.94	2.4
	45	0.0238	0.3130	32.30	8.44	92.19	58.94	2.4
PiII	20	0.0435	0.5508	17.70	5.04	73.56	48.40	2.3
m=440	25	0.0460	0.6258	16.73	4.83	72.19	47.71	2.3
M_n=69700	30	0.0479	0.6281	16.08	4.67	71.24	47.18	2.3
M_w/M_n=1.27	35	0.0487	0.6203	15.80	4.45	70.84	46.44	2,3
	40	0.0508	0.7146	15.15	4.20	69.84	45.56	2.4
	45	0.0497	0.6833	15.48	4.11	70.35	45.23	2.4

The viscosity measurements were carried out in DMF in the temperature range 20-45°C (±0.01°C), by using an Ubbelohde suspended-level viscometer. All measurements were performed within one day after the samples were brought into solution, in the interval of 5 h. The kinetic energy corrections were found negligible. The flow volume of the used viscometer was greater than 5 mL, making drainage errors unimportant. Flow times were obtained with an accuracy of ±0.035 % for different measurements of the same samples in DMF at a given temperature. Plots of η_{sp}/c versus c were extrapolated to zero concentration to obtain intrinsic viscosity $[\eta]$ according to the Huggins equation:

$$\eta_{sp}/c = [\eta] + k_1 \cdot [\eta]^2_{Huggins} \cdot c \tag{1}$$

in which η_{sp} is the specific viscosity and k_1 is the Huggins constant. Concentrations of the solution were between 0.6 and 1.7 g/dL for poly(amic acid)s and between 1.3 and 4 g/dL for polyimides. In this interval, the solutions are in the dilute regime where the relative viscosity is lesser than 1.9. To verify the reproducibility of the results, repeated measurements with new solutions were carried out.

Tab. 1 shows also, the intrinsic viscosity determined by Huggins equation for the studied samples in DMF at different temperatures.

RESULTS AND DISCUSSION

Coil density and dimensions

Fig. 1 shows that the intrinsic viscosity, $[\eta]$, of poly(amic acid)s and polyimides from scheme I decreases with temperature. This variation is normal for polymers in good solvents.
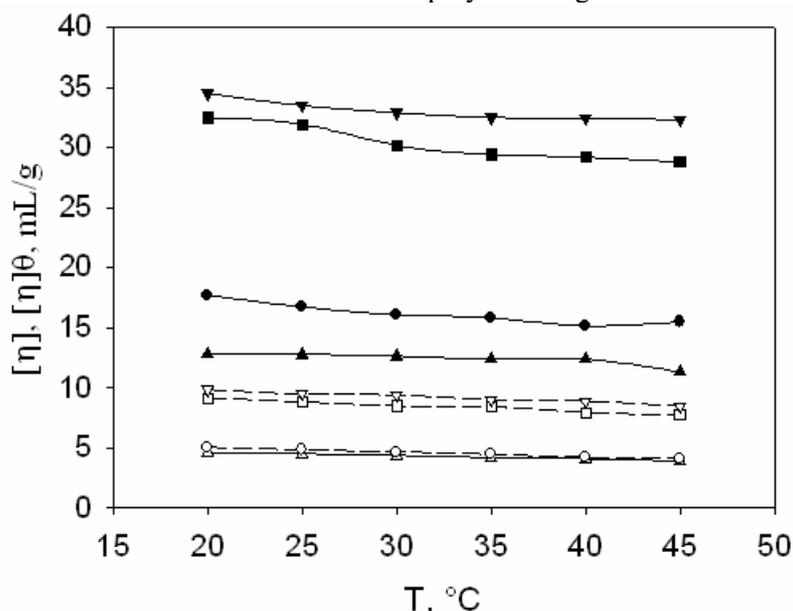

Fig. 1 – Variation of the intrinsic viscosity and intrinsic viscosity in unperturbed state for poly(amic acid)s and polyimides in DMF at different temperatures. $[\eta]$: (■)- PAAI, (▲) - PiI, (▼) - PAAII, (●) - PiII); $[\eta]_\theta$: (□)- PAAI, (△)- PiI, (▽) - PAAII, (◇) - PiII

The intrinsic viscosity in unperturbed state was computed according to the Qian *et al* method, [10-13] and is based on the following relationship:

$$[\eta]_\theta = \frac{[\eta]\left[1 - \exp\left(-\dfrac{c}{c^*}\right)\right]}{\dfrac{0.77^3 \rho}{c^*} - \exp\left(-\dfrac{c}{c^*}\right)} \tag{2}$$

Here, c^* is the critical concentration at which the polymer coils begin to overlap each other, as defined by equation (3), N_A is the Avogadro number, and ρ is coil density, approximated by equation (4) or (5):

$$c^* = \frac{3M}{4\pi N_A R_g^3} = \frac{3\phi'}{4\pi N_A [\eta]} \tag{3}$$

$$\rho = \frac{c}{\eta_{sp}}\left(1.25 + 0.5\sqrt{56.4\eta_{sp} + 6.25}\right) \tag{4}$$

$$\rho = \frac{c^*}{0.77^3\left\{1 + \dfrac{[\eta] - [\eta]_\theta}{[\eta]_\theta}\left[1 - \exp\left(-\dfrac{c}{c^*}\right)\right]\right\}} \tag{5}$$

where R_g is the radius of gyration of the polymer molecule in solution, M is the number average molecular weight, and $\phi' = 3.1 \times 10^{24}$.

In order to know the coil density of the poly(amic acid)s and polyimides chains in solution, ρ, Equation (4) was applied. Figs. 2 and 3 show the concentration dependence on coil density for poly(amic acid) II and polyimide II respectively, in DMF at different temperatures, in the dilute range and for a large concentration domain. The small plot corresponds to experimental data in dilute solution.
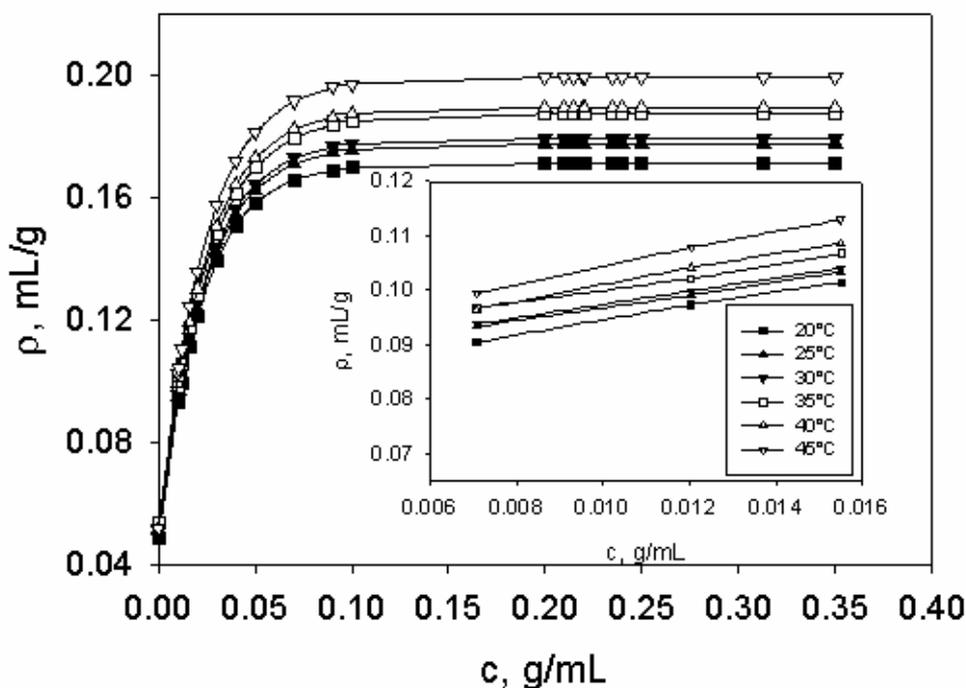

Fig. 2 – Variation of coil density with concentration for poly(amic acid) II in DMF at different temperatures. The small plot corresponds to experimental data in dilute solution
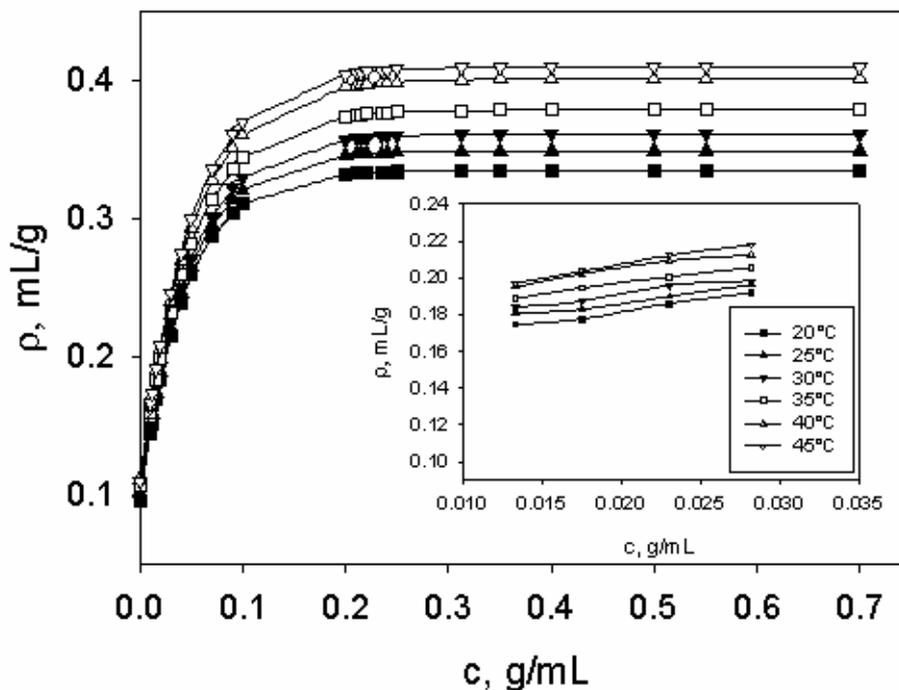
Fig. 3 – Variation of coil density with concentration for polyimide II in DMF at different temperatures. The small plot corresponds to experimental data in dilute solution

It is observed that the polymer coil density increases with increasing polymer concentration while, at a critical concentration c^+ from the semidilute domain, approximated by $c^+ \cong 8c*$, [14,15] coil density remains constant. Thus, the density at $c \geq c^+$ corresponds to the density in unperturbed state. The critical concentrations $c*$ and c^+ are presented in Tab. 1.

Coil density in solution is higher for Pi than for PAA and increases with the increasing of the temperature.

Modification of the coil density is reflected in the variation of the gyration radius with concentration. The concentration dependence of the radius gyration is calculated with Equation (6):

$$R_g^3 = \frac{3M[\eta]}{3\phi\left\{1 + \dfrac{[\eta] - [\eta]_\theta}{[\eta]_\theta}\left[1 - \exp\left(-\dfrac{c}{c*}\right)\right]\right\}} \tag{6}$$

Figures 4-7 plot these dependences for studied samples. The radii of gyration, R_g, decrease with increasing concentration while at critical concentration c^+ (identical values with those from Figs. 2 and 3) they are considered to shrink to their unperturbed dimensions. Thus, for c=0 and for $c \geq c^+$, the perturbed gyration radii, $R_{g,c=0} \equiv \left(R^2\right)^{1/2}$, and the unperturbed gyration radii, $R_{g,c \geq c^+} \equiv R_\theta$, respectively, were obtained.
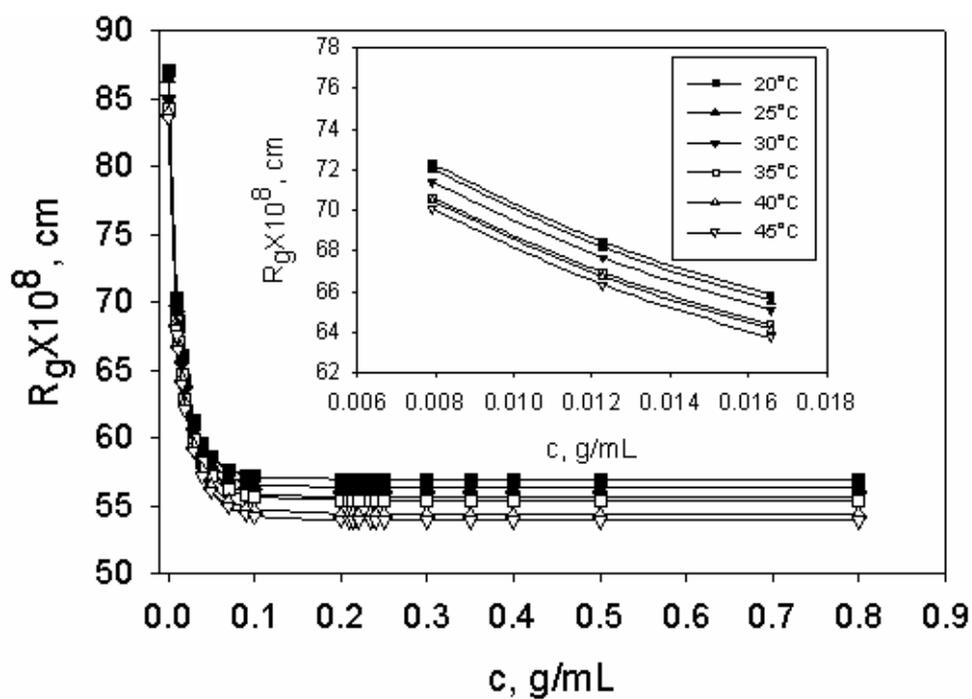
Fig. 4 – Variation of gyration radius with concentration for PAAI in DMF at different temperatures. The small plot corresponds to experimental data
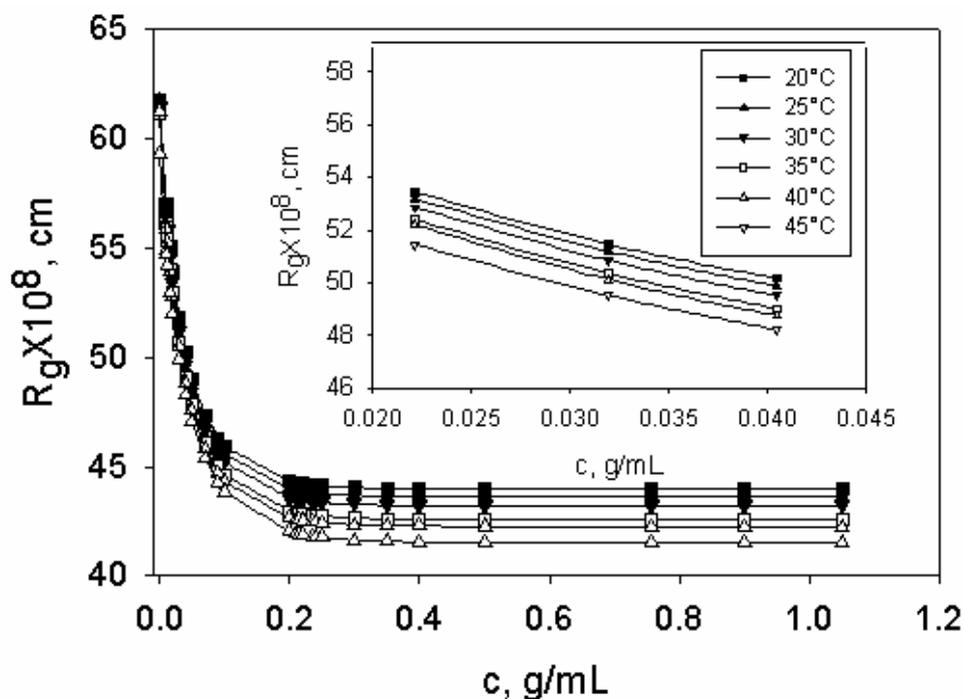

Fig. 5 – Variation of gyration radius with concentration for PiI in DMF at different temperatures. The small plot corresponds to experimental data
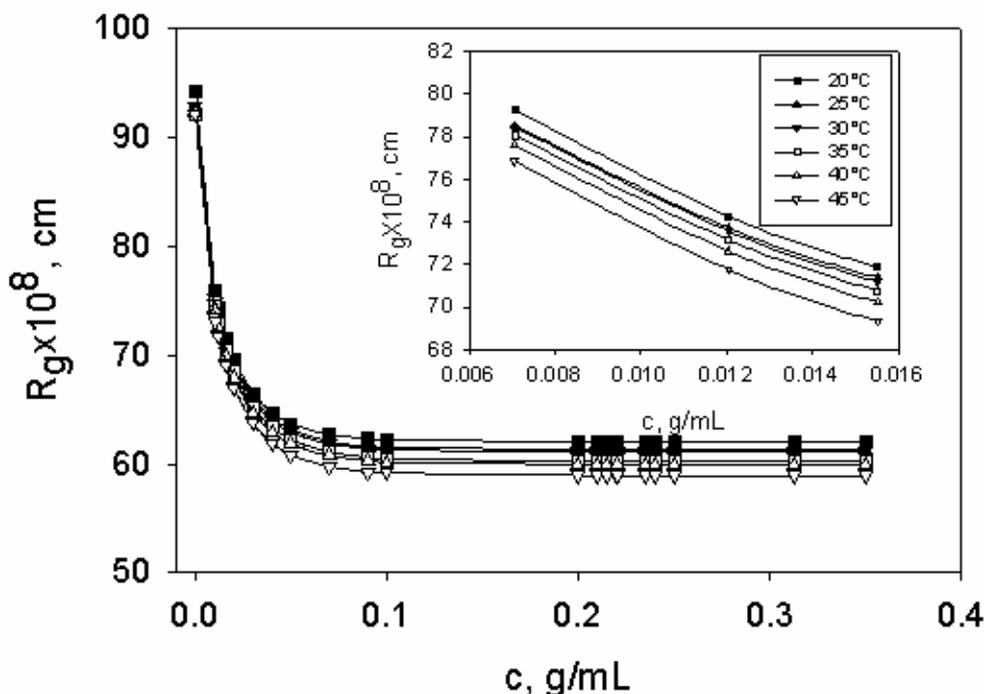
Fig. 6 – Variation of gyration radius with concentration for PAAII in DMF at different temperatures. The small plot corresponds to experimental data
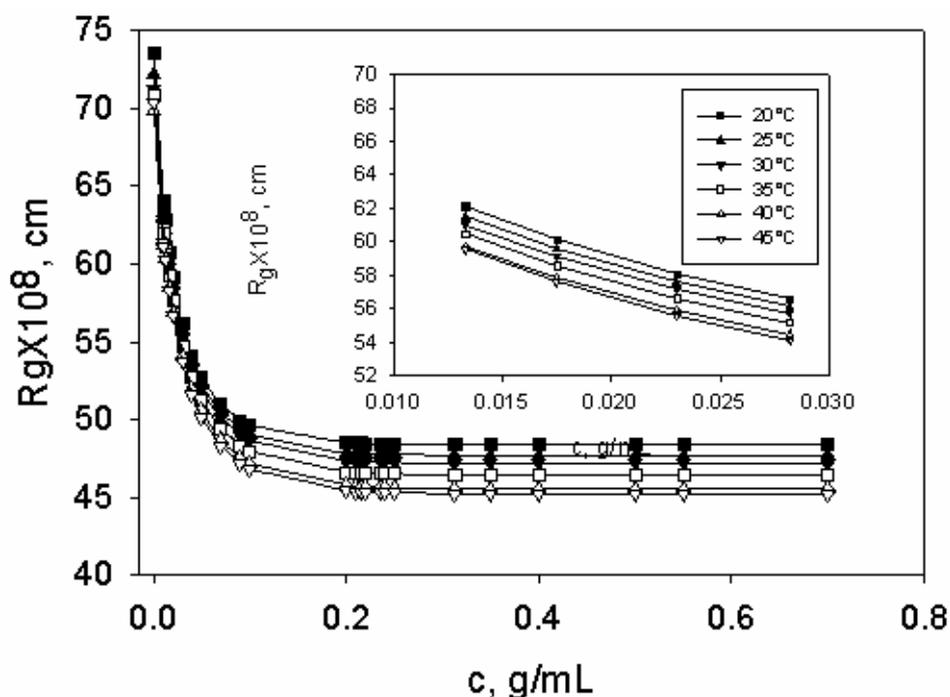

Fig. 7 – Variation of gyration radius with concentration for PiII in DMF at different temperatures. The small plot corresponds to experimental data

$R_{g,c=0}$ and $R_{g,c\geq0}$ values presented in Tab. 1 are smaller for polyimides than for poly(amic acid)s, decreasing with the increasing of temperature. Furthermore, it was observed the differences between the radii of gyration of PAAI and PAAII or PiI and PiII samples.

The results reflect the aggregation phenomena in solution which conduct to high dimensions of poly(amic acid)s. Thus, from the point of view of chemical structures, the poly(amic acid)s have higher molecular weight of the structural units and higher flexibility than corresponding values of polyimides.

However, the intrinsic viscosity and dimensions of poly(amic acid)s are higher than those of polyimides not only because of the differences of molecular weights, but also, because of the solution parameters. The functional groups along the poly(amic acid)s chain determine the aggregations by intermolecular interactions in solution due to hydrogen bonding. These aggregations lead to higher intrinsic viscosity. This conclusion is asserted by literature data which show that the solution properties of poly(amic acid) rise serious problems, including effects of polyelectrolytes and the differences in chain rigidity between a poly(amic acid) and its corresponding polyimide chain. Moreover, information obtained from the study of those soluble poly(amic acid)s can be strongly influenced by both the nature of imidization and the reversible reaction. [8,16] Also, there is a competition between the additional flexible linkage introduced in the chain, which decreases the persistence length of the poly(amic acid) and polyimide, and the effect of number of benzene rings, which can be more important than the nature of diamine.

Unperturbed dimension parameters

In the present study, $[\eta]_\theta$ was calculated according to equations (2-5), using the data of η_{sp}/c at different concentrations. The results for PAA and Pi at different temperatures are shown in Tab. 1. It was observed that the $[\eta]_\theta$ values are approximatively constant for different concentrations, but slightly decrease with the increasing of temperature.

The relative unperturbed dimensions K_θ parameters (Fig. 8) and the viscosity expansion factors, α^2, (Tab. 1) were calculated with equations (7) and (8), respectively. The K_θ values are comparable with those from the literature data. [17] Also, the same expansion of poly(amic acid) and polyimide chains in solution was obtained (Table 1).

$$[\eta]_\theta = K_\theta M^{1/2} \tag{7}$$

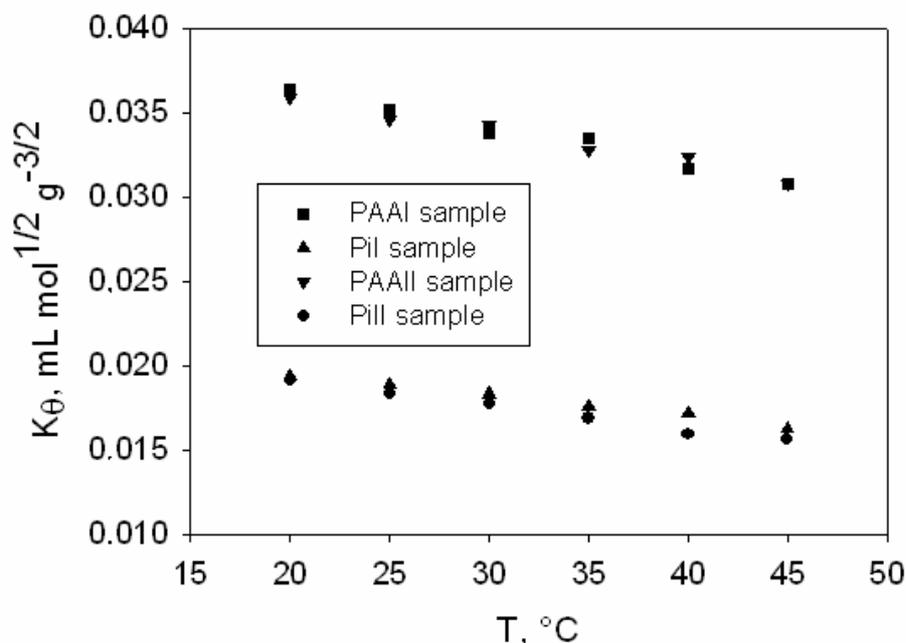$$\alpha^2 = \frac{R^2_{g,c=0}}{R^2_{g,c\geq c^+}} \tag{8}$$

Fig. 8 – Variation of unperturbed dimension parameters K_θ with temperature for poly(amic acid)s and polyimides in DMF

These results seem to indicate that the unperturbed dimension parameters easily decrease with increasing temperature for all studied samples. Also, the -CH₂-CH₂- group from structural units of PAAII or PiII samples transmits a more flexibility in unperturbed state on macromolecular chain comparatively with PAAI or PiI samples.

CONCLUSIONS

In the present study, information on coil density, the radius of gyration at different concentration and the unperturbed dimension of poly(amic acid)s and polyimides as a function of temperature are presented, along with their interpretation *versus* their chemical structures. Thus, the solution properties of poly(amic acid)s and polyimides rise some problems. The aggregation phenomenon depends on the competition between the additional flexible linkage introduced in the chain and the number of benzene rings. This competition modifies the persistence length of the poly(amic acid) and polyimide more than the nature of diamine.

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