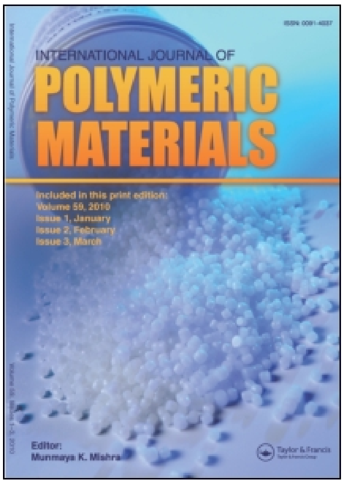

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On The Aggregation of Aromatic Polyamides in DMAc/LiCl

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The tendency of linear para-aromatic polyamides to aggregate in DMAc/LiCl solutions is well documented in the literature. In this note it is shown that this tendency is retained even when the polyamides are rendered much more soluble in DMAc/LiCl through the introduction of a nitro group on every third aromatic ring along the stiff chain. When the polyamides are highly branched, they conform with the fractal model. These fractal polyamides agglomerate in several distinct size aggregates; the size of the aggregates and the fraction of the polymer in them are affected by both the solution temperature and the molecular weight of the polymer. With respect to aggregate sizes, the temperature effects are reversible.

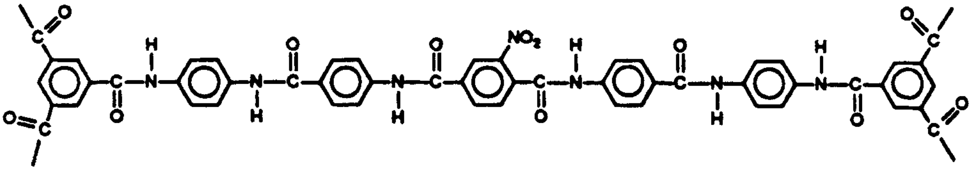
KEY WORDS Linear polyamides, fractal polyamides, branched polyamides, aromatic polyamides, solution properties, aggregation, light scattering, temperature effects.

INTRODUCTION

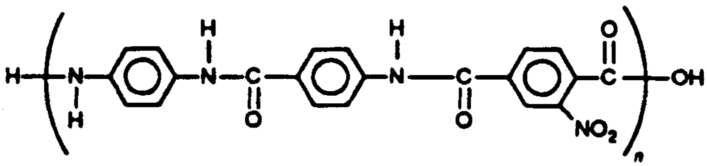
Linear para-aromatic polyamides have created much commercial interest because of their remarkable tensile properties and thermal stability. Their backbone stiffness and interchain hydrogen bonding demand the use of highly corrosive viscous solvents such as concentrated sulfuric acid or chlorosulfonic acid for their processing and the preparation of solutions for the purpose of measuring many of their properties. Several less corrosive solvent systems for these polymers are commonly used on the laboratory scale; the most popular among them is a solution of LiCl in *N,N*-dimethylacetamide (DMAc).[1-6] However, molecular weight measurement in DMAc/LiCl yield results reflecting strong aggregation effects. For example, studies of poly(*p*-benzamide) in DMAc/3% LiCl gave Mark-Houwink exponents far larger than the most common values (1.85 *vs.* 1.1–1.2),[1] while other light scattering studies with multiple solvent systems have shown molecular weights up to an order of magnitude greater in the mixed solvent than the strong acids.[2] This effect has been shown[3] to vary both with the concentration of LiCl and with temperature. In our work we have been concerned with highly branched fractal polyamide systems characterized by stiff segments connected by rigid trifunctional branchpoint.[7-11] When allowed to further react in solution, these systems form rigid gels. By stopping the reaction before the gel point, we obtained pre-gel fractal polymers. These polymers have weight average molecular weights (M_W) from less than 10 000 to almost a million, depending on when the reaction was arrested. In this study, we measured the apparent hydrodynamic radius, R_H, of fractal and linear aromatic polyamides in the mixed solvent DMAc/5% LiCl using photon correlation spectroscopy (PCS).[12–14] From past experience[7–11, 15] we know that the addition of nitro groups on some of the aromatic rings along linear para-aromatic polyamide chains or the segments of the branched analogues greatly increases the solubility in both conc. sulfuric acid and DMAc/LiCl. The enhanced solubility is expected to minimize the aggregation effects. In this communication we will show that these nitro-substituted polymers still aggregate considerably and that the aggregation changes with both temperature and the molecular weight of the sample.

EXPERIMENT

The polymers were prepared in solution in one step by the Yamazaki procedure[16] modified for the preparation of networks as described previously.[7–10] Samples F59E, F72A and F45XB were fractal polyamides with molecular weights M_W = 9 600, 320 000, and 410 000, respectively. A typical stiff segment with two rigid trifunctional branches is shown:



The linear sample NL51D is characterized by the following nitro-containing repeat unit:



Its M_W is 12 700 and its intrinsic viscosity is $[\eta]$ = 0.83 dL/g.

The PCS measurements on 1% solutions were made over a temperature range of 25°C to 85°C at a scattering angle of 90° using a 50 mW HeNe laser as the light source. All solutions were filtered through a 0.2 micron pore size poly(tetrafluoroethylene) filter prior to measurement. For the size calculations we assumed our mixed solvent would have the same percentage change in viscosity with temperature as that given in the literature[17] for pure DMAc, and used these values to correct the value of the mixed solvent measured at 25°C to the other temperatures.

RESULTS

From CONTIN[18, 19] analyses of the PCS spectra, we obtained multimodal distributions consisting of a peak at the expected molecular size and other peaks, due to aggregation, at larger sizes (see Figure 1). Higher molecular weights also had increased fractions of these larger species. This is clearly visible in Figure 2. At present we do not understand why the fractal polyamides prefer to agglomerate in several distinct size aggregates instead of a single, broad and smoothly decaying distribution.

The multimodal distributions were found to reach sizes larger than the filter pore size and to change with temperature for both the fractal and the linear polyamides. Thus, some, if not all, of the larger non-gel species must be due to aggregation.

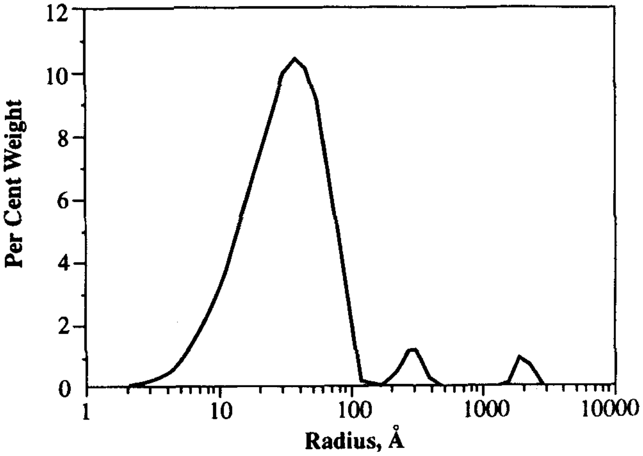


FIGURE 1 Size distribution of the fractal polyamide F72A at 45°C

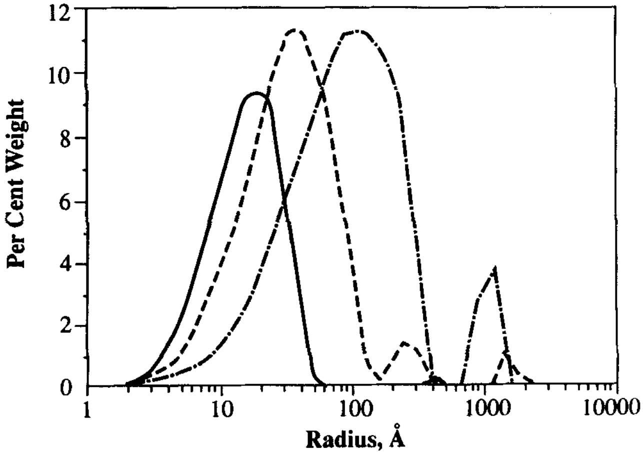


FIGURE 2 Size distribution of three fractal polyamides as a function of their molecular weight (all at 25°C). The solid line is for F59E (M_w = 9 600), the dashed line is for F72A (M_w = 320 000) and the dash-dot-dash line is for F45XB (M_w = 410 000).

Both the size and weight fraction of the aggregates reversibly vary with temperature, but the data were not of sufficient quality to obtain consistent distributions from the complex CONTIN analyses. To simplify the analyses we used a 9-cumulant fit to obtain a single average hydrodynamic radius. Since cumulant fits give *z*-average diffusions coefficients, the R_H obtained should be dominated by the largest species and would thus give an indication of the extent of aggregation. As a simple treatment, we then postulated the aggregation would have an Arrhenius-type behavior and, consequently, made semi-log plots of radii against reciprocal temperature. The slope of these plots can be related to an activation energy for the breakdown of aggregates.

The fractal polyamide (F72A) has a fast initial drop in the level of aggregation which then almost levels off. This is seen as two lines in Figure 3, intersecting at about 45°C, indicating a change in the state of aggregation. From the slopes of the two lines we estimate an activation energy of 5 kcal/mole from 25°C to 45°C and only 1 kcal/mole for the higher temperatures. Thus, the structure breakdown appears to occur in two steps. As the temperature increases, the largest aggregates break up first, with an activation energy in the range of the activation energy for hydrogen-bond breaking. Next, the smaller aggregates are broken up causing a further small decrease in size. Changes in chain rigidity may appear at the transition temperatures[20] but these may require higher activation energy[21] than was obtained from the Arrhenius plot in Figure 3. The plot for the linear polyamide NL51D also showed two lines indicating the presence of a transition temperature at about 50°C separating two rates of aggregates size decrease with increasing temperature. The details of this plot are, however, not straightforward and do not lend themselves to the same explanation as previously.

Most importantly, based on the previous and the cited literature, we would like to point out that drawing conclusions on para-aromatic polyamides on the *sole*

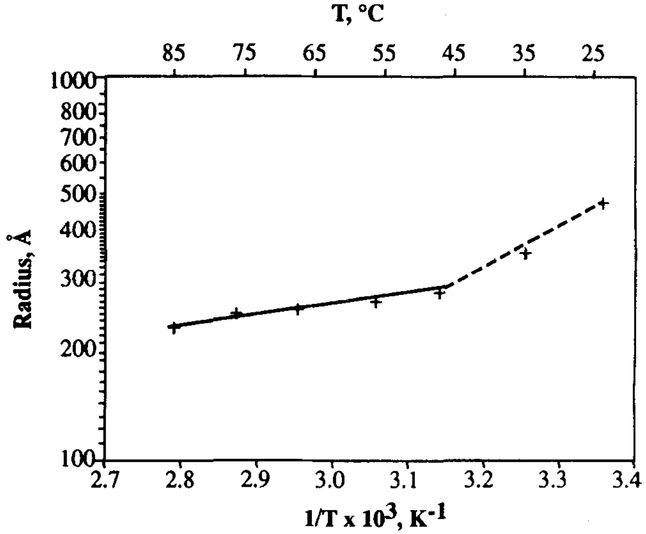


FIGURE 3 Arrhenius plot of the radii of the fractal polyamide F72A as a function of temperature, *T*.

basis of their solution behavior in DMAc/LiCl is fraught with danger and might lead to erroneous results.

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