Investigation of conformational transitions in polyamide-6 macromolecules in mixtures of *m*-cresol and methanol

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The intrinsic viscosity of polyamide-6 (PA-6) solutions in mixtures of *m*-cresol and methanol decreases with increasing methanol concentration. A conformational transition occurs in the 50–60% methanol concentration range. This phenomenon has been studied by viscometric measurements for various methanol concentrations, a two-fold decrease of intrinsic viscosity having been observed. The results are interpreted by assuming that the observed decrease in intrinsic viscosity is due to a coil–globule conformational change in the polyamide-6 molecules. A decrease of intrinsic viscosity also occurs on increasing the temperature at which the viscometric measurements are carried out. This is explained by the possibility of occurrence of a *cis-trans* isomerisation, and of a partial helix–coil conformational change.

Keywords Polyamide-6; coil–globule; intrinsic viscosity; chain conformation

INTRODUCTION

Precipitation of polymers from solution is a complex process, and many of its aspects have not been established until recently.

It is known from the literature that the processes of aggregation and precipitation of many polymeric substances are accompanied by conformational changes of polymer chains in solution[1]. The same phenomenon has been observed by Koenhen *et al.*[2] for the process of crystallization from solution. These authors suggested that crystallization of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) from dilute toluene solutions proceeds in two stages. In the first stage, there occurs a conformational transition of the PPO chain, while in the other the processes of nucleation and crystallite growth occur.

The aim of this work was to study conformational changes of a polymer chain accompanying the precipitation of polyamide-6 from solution, and to ascertain whether the precipitation is indeed accompanied by a coil–globule conformational change.

At higher temperatures and in thermodynamically favourable solvents a polymer has an extended coil conformation, while at low temperatures and in a poor solvent it is in a collapsed globule state[3]. This transition is connected with the 'goodness' of the solvent, and can be initiated, therefore, by decreasing the 'goodness' of the solvent in the following three ways: (1) by lowering the temperature below the θ temperature for solutions of infinitely long chains exhibiting the upper consolute temperature; (2) by means of suitable pressure changes; and (3) by adding to the solution a non-solvent for the given polymer. In the present work the last of these three approaches was examined.

The coil–globule transition theory has been developed independently by Ptitsyn[4], de Gennes[5] and Lifschitz[6] and transitions of this type have been observed for several polymers. Tanaka *et al.*[8–10] found such a transition to occur in solutions of polyacrylamide in water–acetone mixtures, the initiation of the transition being produced by changing the composition of the mixture or the temperature.

A complete transition of this kind has been observed in solutions of polystyrene in cyclohexane[11,12], and also in DNA solutions[13]. In the latter case, the transition was initiated by adding a non-solvent (polyethylene oxide of low molecular weight).

Authors of numerous other works have observed either the probable onset of the coil–globule transition, or postulate the possibility of such a process occurring[14]. In the present work the intrinsic viscosity of solutions of polyamide-6 in *m*-cresol–methanol mixtures was studied as a function of temperature and methanol content.

Viscometric measurements were used owing to the fact that, besides light scattering, differential refractometry and neutron scattering, it is known to provide very useful information about the thermodynamic and conformational properties of macromolecules in solution[2,14].

EXPERIMENTAL

Materials

Commercial grade polyamide-6, made by the ZWS 'STILON' Works, Gorzów Wielkopolski, was supplied in the form of fibres and free from any admixtures. It had viscosity average molecular weight $\bar{M}_v = 22000$ (determined in *m*-cresol at 30°C). Before use, the PA-6 was extracted with water and dried carefully in a vacuum dryer at an elevated temperature.

Solvents and solutions

Methanol (analytical grade; supplier REANAL, Hungary) was used without further purification. The *m*-cresol (pure grade; supplier REACHIM, USSR) was purified by fractional distillation at reduced pressure under argon,

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Table 1 The intrinsic viscosity of polyamide-6 in *m*-cresol/methanol mixtures and the viscosity average radii of gyration $\bar{R}_{gv}$ calculated from the Flory–Fox equation and expressed as a function of methanol concentration. Temperature, 25°C; $\bar{M}_v$, 22 000

Methanol concentration (vol%)	$[\eta]$ (ml g^{-1})	$\bar{R}_{gv}$[a] (nm)
0	120.0	9.43
20.00	94.5	8.75
30.76	89.0	8.53
40.00	88.0	8.50
40.80	87.0	8.47
46.10	84.0	8.37
50.00	81.0	8.27
55.75	78.5	8.18
57.69	73.0	7.99
59.61	64.7	7.67
61.53	64.2	7.65
64.46	64.0	7.64

[a] Calculated from equation (2) with $\Phi = 2.1 \times 10^{23} mol^{-1}$

resulting in a colourless fraction with a refractive index of $n_D^{20}=1.5398$.

Polymer solutions were obtained by dissolving carefully weighed amounts of the PA-6 in a known weight of the solvent (a mixture of *m*-cresol and methanol at a suitable concentration of the components), at a suitable temperature, and then sorted at room temperature. Measurements were carried out at different temperatures after the prior heating or cooling of the solution to the required temperature.

Viscometry

Suspended-meniscus Ubbelohde capillary viscometers were used. The efflux time for *m*-cresol was 164 s, and 222 s for a 50:50 % vol. mixture of *m*-cresol and methanol (measurements at 25 ± 0.01°C). The viscometric measurements were carried out at 25, 30, 40, 50 and 60°C, the viscometers being immersed in a thermostated water bath.

The Hagenback–Couett kinetic energy loss correction factor was taken into account for each measurement. The values of the correction factors were obtained from correction tables supplied by the manufacturers of the viscometers. The solvents and solutions were filtered through a glass frit (1 G-2) before the measurements.

The intrinsic viscosity $[\eta]$ was determined from Huggin's plots obtained for 4–5 concentrations in the range of from 10^{-4}–10^{-2} g ml^{-1}. For each series of measurements, the relation $(\eta_r{}^{-1})/c$ was determined as a function of concentration; $\eta_r{}^{-1}$ is the relative viscosity found from the ratio of efflux times recorded for the polymer solution and solvent, respectively.

For higher methanol concentrations (50% vol) solutions with concentrations of polymer $< 3 \times 10^{-3}$ g ml^{-1} were used to avoid the occurence of aggregation and precipitation phenomena. Rectilinear plots were obtained, the values of intrinsic viscosity being given by the point of intersection of the respective Huggin's plots with the ordinate.

Results and discussion

Results of viscometric measurements carried out for polyamide-6 solutions in *m*-cresol were used to calculate its viscosity average molecular weight using the Mark–Houwink relation[3]:

$$[\eta]=KM^a \qquad (1)$$

For the temperature of 30°C the literature values[15] of the Mark–Houwink coefficients are: $K=0.00107$ and $a=0.7$. The calculated value of $\bar{M}_v$ was 22000.

The intrinsic viscosity values $[\eta]$ and those of the radii of gyration found for polyamide-6 in *m*-cresol/methanol mixtures are listed in *Table 1*.

The radii of gyration $\bar{R}_{gv}$ were calculated based on the experimental intrinsic viscosity data obtained, using the Flory–Fox equation[3,17]:

$$[\eta]=6^{3/2}\Phi\frac{(\bar{R}_{gv})^3}{\bar{M}_v} \qquad (2)$$

in which Flory's universal constant Φ_0 was assumed to be $\Phi = 2.1 \times 10^{23}$ mol^{-1} (for $[\eta]$ expressed in ml g^{-1})[3]. As Φ is related to the macromolecular coil expansion (α) and may change up to the value of 2.8×10^{23} mol^{-1} (for $\alpha=1$)[16,17], the values of the radii of gyration found for larger methanol concentrations may be decreased by 10–15% with respect to the real size of the macromolecular coil[16]. $\bar{M}_v$ is the viscosity average molecular mass.

Dependence of the intrinsic viscosity $[\eta]$ of polyamide-6 solutions in *m*-cresol/methanol mixtures on methanol concentration at several temperature is shown in *Figure 1a*.

Figures 1a and *1b* show that the results of intrinsic viscosity measurements indicate that a conformational transition of the polymer chain does indeed occur.

For low methanol concentrations, the intrinsic viscosity $[\eta]$ and the radii of gyration $\bar{R}_{gv}$ (e.g. at 25°C) are large, and in the limiting case of zero methanol concentration they are equal to 120 ml g^{-1} and 9.43 nm. With increasing methanol concentration, the values of intrinsic viscosities and radii of gyration decrease. In the region of methanol concentration equal to 50–60 vol% the curve showing the

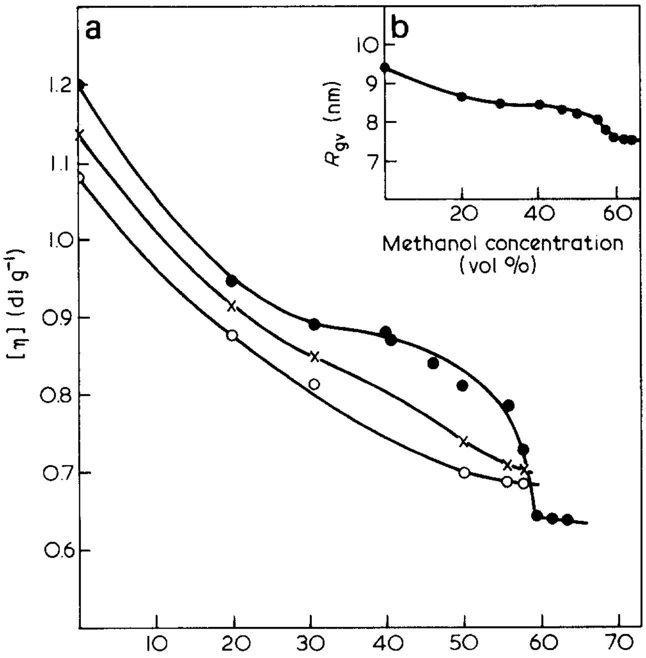

Figure 1 (a) Dependence of the intrinsic viscosity $[\eta]$ of polyamide-6 solutions in *m*-cresol/methanol mixtures on methanol concentration (results for several measurement temperatures). (b) Dependence of the viscosity average radius of gyration $\bar{R}_{gv}$ of the polyamide-6 in these same solutions on methanol concentration at 25°C. Measurement temperatures: ●, –25, x, –40; ○, –60°C

dependence of intrinsic viscosity $[\eta]$ on polyamide-6 concentration exhibits a sudden, marked decrease in the $[\eta]$ value, which indicates a large decrease of the size of the polymer coil. On increasing methanol concentration further, the intrinsic viscosity remains constant $[\eta]=64$ ml g^{-1}, which is equivalent to a radius of gyration equal to 76 nm. The decrease in the intrinsic viscosity in the whole range of methanol concentrations may be interpreted as indicative of a polymer coil collapse phenomenon, i.e. a coil–globule transition.

The onset of precipitation at the temperature of 25°C corresponds to a 55.75 vol% methanol concentration (polymer concentration of $\approx 4\times 10^{-3}$ g ml^{-1}).

By reducing the polymer concentration to $<3\times 10^{-3}$ g ml^{-1} it was possible to avoid polymer aggregation and precipitation, thus allowing observation of the changes occurring on further increasing the concentration of methanol.

The necessity of using high dilutions is due to the fact that the 'collapse' of individual polymer chains can be observed in very dilute solutions in which the globule state may be attained before polymer aggregation occurs[3,11,18]. The coil–globule transition observed here is not a discrete phenomenon, due to the shortness of the polymer chain. According to theory, an infinitely long chain should exhibit a discrete transition[19]. However, here this transition occured at all measured temperatures.

The dependence of intrinsic viscosity on methanol concentration, obtained at several temperatures, is shown in *Figure 1*. For clarity, only the curves obtained for the temperatures of 25, 40 and 60°C are shown. At higher temperatures, a less pronounced decrease in intrinsic viscosity was observed, indicating a less sudden occurrence of the coil–globule conformational transition.

The intrinsic viscosity decreases with increasing temperature for all polyamide-6 solutions investigated, which suggests that the size of the polymer coil decreases instead of being expanded[3].

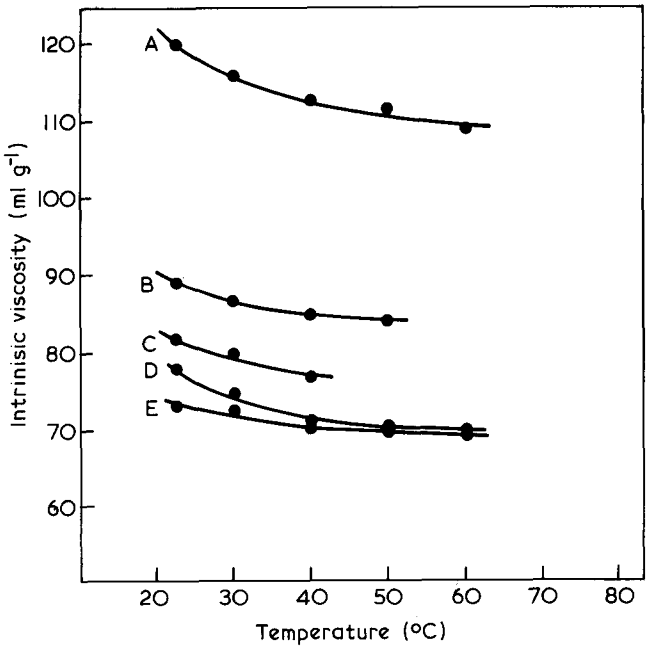

Figure 2 Intrinsic viscosity $[\eta]$ of PA-6 as a function of temperature, determined in *m*-cresol/methanol mixtures with different methanol content. Methanol content: A, 0; B, 30.76; C, 50; D, 55.75; E, 57.65 vol%

The decrease of intrinsic viscosity on increasing the temperature has been observed previously for polyamide-6 and several other polymers[2,3,20], but so far no satisfactory explanation has been given. One possible explanation of this phenomenon, according to Flory and Williams[21], is to assume that the amide bond is capable of *cis–trans* isomerization[22]. On increasing the temperature, the equilibrium between the two isomeric froms is probably shifted towards the *cis*-isomer, which would result in a shortening of the polyamide chain[20].

Here, it is proposed that another possible explanation of this phenomenon is to assume that a partial helix–coil-type polymer chain transition may occur in solution.

At lower temperatures, certain polyamide-6 chain sequences may be present partly in helix form. In this case, a lowering of temperature would lead to an increase of the number of helical sequences and, therefore, to coil expansion.

This assumption is supported by the fact that *m*-cresol is a helicogenic solvent, and that polyamides occur in helix-form in this particular solvent[23]. Flory's calculations of the conformation of poly(oxymetylene) chains as a function of the helical component content and temperature[24] indicate the possibility of interpreting that phenomenon in this way.

Consequently, the conformational helix–coil transition occurring with increasing temperature and leading to a more compact polymer coil structure, manifests itself on a macroscopic scale by a decrease of the intrinsic viscosity function. The integer *n* has a value between 1 and 4

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