Viscosity studies of some polyamides dissolved in mixed solvents (cosolvents)

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The solubility of poly(octamethylene sebacamide) (POS), poly(octamethylene terephthalamide) (POT) and poly(octamethylene tetrachloroterephthalamide) (POTC1), in *m*-cresol/cyclohexane mixtures, a cosolvent system, has been studied by measuring the intrinsic viscosity [η], at 25°C. The intrinsic viscosities of POT, POS and POTC1 in various solvent/non-solvent mixtures are higher than the corresponding intrinsic viscosities in the pure solvent *m*-cresol. The POT and POTC1 polyamides exhibit a sharp increase in [η] values compared with the corresponding small increase in the POS polyamide. The POTC1 polyamide presents a true cosolvency effect in *m*-cresol/cyclohexane mixtures; *m*-cresol and cyclohexane are non-solvents for this polyamide. The cosolvent behaviour is discussed in terms of the most energetically favourable interactions. The aromatic ring in POT and POTC1 would expand the chain, would favour a better packing between neighbouring solvent molecules and would favour the selective adsorption in the cosolvent system.

INTRODUCTION

Most of the studies on polyamides in solution are limited because of the insolubility of polyamides in common solvents.

Unsubstituted polyamides prepared either from aliphatic diamines and aromatic diacids or from aliphatic diamines and aliphatic diacids are only soluble in solvents such as sulphuric acid, trifluoracetic acid, *m*-cresol, etc. This fact makes their characterization very difficult[1].

The degree of order or crystallinity shown by these polymers caused by intra- and inter-chain interactions affect their solubility and their general properties. It is known from literature that a non-solvent often increases the dissolving power of a solvent for a given polymer[2].

The main purpose in this work is to extend the range of the polyamide solubility. For this reason we consider the cosolvency effect, i.e. the synergism effect either of two non-solvents or a solvent with a non-solvent.

In this paper, the solubility of the polyamides was examined in one cosolvent system. The cosolvent behaviour is discussed in terms of the most energetically favourable interactions.

To investigate the structural effects of chemical groups on the viscometric behaviour, the linear amidic polycondensate with aromatic groups, aliphatic groups and chloroaromatic groups in the main chain were used.

EXPERIMENTAL

Poly(octamethylene sebacamide) (POS), poly(octamethylene terephthalamide) (POT) and poly(octamethylene tetrachloroterephthalamide) (POTCl) were prepared by interfacial polymerization with stirring[3]. The diamine/acid chloride molar concentration ratio was 1:1 with a little excess of acid acceptor. The highest molecular weight was obtained by using NaOH as acid acceptor and the benzene/THF–H₂O (50:50 v/v) as interface.

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The polyamides studied were soluble in *m*-cresol/cyclohexane mixtures; cyclohexane is a non-solvent for the polyamides and *m*-cresol is a non-solvent for POTCl polyamide.

Viscosity measurements were carried out using Desreux–Bischoff viscometers[4] suitably adjusted to make kinetic energy corrections unnecessary. Temperature was controlled to ±0.01°C. Intrinsic viscosities, [η], were obtained in the usual manner by extrapolation of η_{sp}/c to infinite dilution[5].

RESULTS AND DISCUSSION

Table 1 shows the solubility of polyamides POS, POT and POTCl in some solvents and mixture solvents.

Figure 1 shows [η] values in *m*-cresol and *m*-cresol/cyclohexane mixtures for poly(octamethylene terephthalamide) (POT) and poly(octamethylene sebacamide) (POS). The intrinsic viscosities of POT and POS in the different solvent/non-solvent mixtures are higher than the corresponding intrinsic viscosities in the pure solvent. These 'positive deviations' of [η] relative to the solvent *m*-cresol suggest that the *m*-cresol/cyclohexane mixture has a $G^E > 0$[6].

Table 1 Solubility of polyamides*

Polyamides	POS	POT	POTCl
m-Cresol	+	+	−
Formic acid	−	−	−
Sulphuric Acid	+	+	+
Trifluoroacetic acid	+	−	−
Dimethyl sulphoxide	−	−	−
Dimethylformamide	−	−	−
Tetrachloroethane	−	−	−
Cyclohexane	−	−	−
m-Cresol/cyclohexane	+	+	+

* Solubility was determined at 1% concentration; +, soluble at room temperature; −, insoluble at room temperature

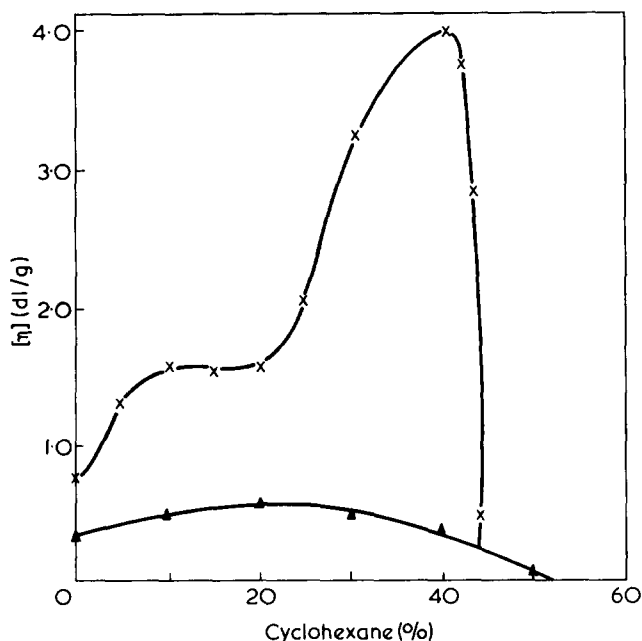*Figure 1* Intrinsic viscosities of ▲, poly(octamethylene sebacamide) (POS) and X, poly(octamethylene terephthalamide) (POT) in *m*-cresol/cyclohexane mixtures at 25°C
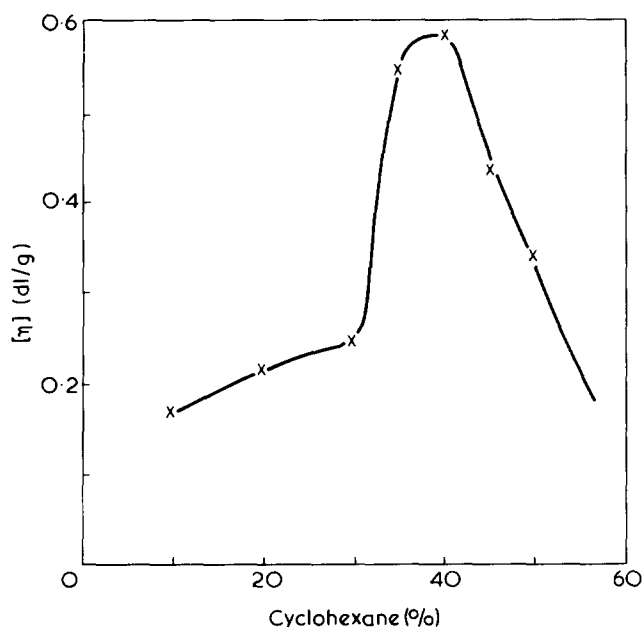

Figure 2 Intrinsic viscosities of poly(octamethylene tetrachloro-terephthalamide) with composition of the solvent mixture (*m*-cresol/cyclohexane) at 25°C

From *Figure 1* it follows that the increase of $[\eta]$ is much more pronounced in the case of POT than in POS. In both cases, once a particular composition mixture is reached, $[\eta]$ decreases to a composition mixture which may be the theta (θ) condition, where phase separation takes place[7].

Figure 2, shows $[\eta]$ values in *m*-cresol/cyclohexane mixtures for POTCl. When $[\eta]$ is plotted against solvent composition for POT polyamide, (*Figure 1*) this plot shows a maximum at 40 vol% cyclohexane. This feature of attaining a maximum has also been observed in the cosolvent system: POTCl in *m*-cresol/cyclohexane at the same solvent composition. (*Figure 2*).

It may be supposed that an effective approach towards the understanding of the solubility of polyamides in co-

solvent media should take into account both thermodynamic as well as structural aspects. To explain the observed cosolvent effect, one can postulate that the polyamides containing amidic groups can be solvated by solvents like *m*-cresol through hydrogen bonding, provided that the interactions between *m*-cresol molecules themselves are not too strong or weakened by introducing other suitable substances. Cyclohexane is a non-polar liquid and may cause a shift in the dissociation of *m*-cresol. The free *m*-cresol molecules may then attach themselves to the

$$\begin{array}{cc} -C-N- \\ \| \quad | \\ O \quad H \end{array}$$

groups of the polyamide chains thus breaking the interchain hydrogen bonding[8]. The chains can then expand and cyclohexane molecules solvate the hydrocarbon chain skeleton. There would be selective adsorption of one of the liquid components by the polyamide. A similar case is reported by Deb and Palit[9] for the PMMA molecules in mixtures of methanol/carbon tetrachloride (cosolvent mixture). In order to analyse the greater increase of $[\eta]$ values in POT and POTCl than in POS it is necessary to take into account the effect of the terephthalic group in the polyamides POT and POTCl. The presence of this group would produce a weakening of the intermolecular interactions between the amidic groups (hydrogen bonding), and this effect would favour the selective adsorption of cyclohexane on the skeletal chain. Thus, higher rigidity of the chains and steric effects seem to play a very important part together with the strength of interactions between amidic groups in the organization of these polyamides.

Poly(octamethylene sebacamide) (POS), presents a peculiar viscometric behaviour. A problem arises when evaluating the $[\eta]$ by extrapolation of η_{sp}/c to infinite dilution because the η_{sp}/c values increase with the dilution. In order to evaluate $[\eta]$, it was necessary to prepare new solutions each time. *Figure 3* illustrates the phenomenon
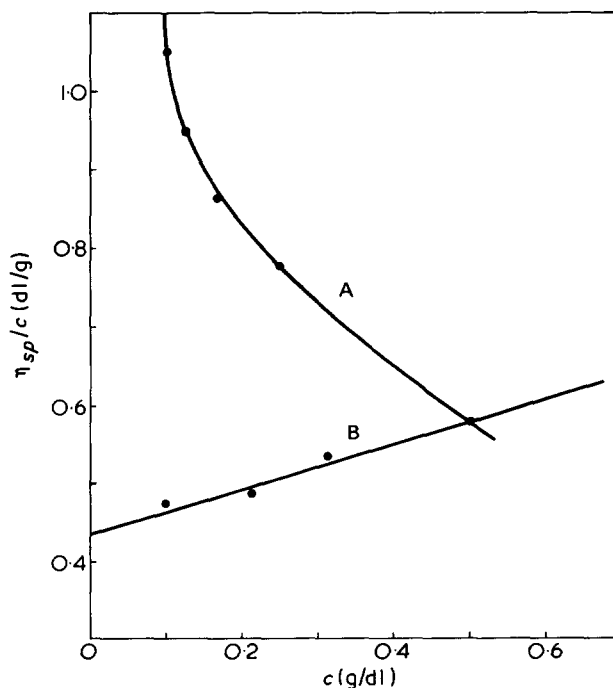

Figure 3 Solution viscosity—concentration relationships for poly(octamethylene sebacamide) (POS) in cyclohexane mixtures 40% at 25°C, $[\eta]$ = 0.435 A, Solutions prepared by diluting an original sample; B, solutions directly prepared

just described for the solvent mixture 40% v/v in cyclo-
hexane, which can be extended to all the solvent mixtures
studied for this polyamide. It is difficult to give an inter-
pretation of this result but it can be attributed to a kinetic
effect.

In conclusion, it is interesting to note that the mixture
solvent m-cresol/cyclohexane is a good solvent for the
polyamides studied; the organization of these polyamides
would play an important role in the viscometric behaviour
in cosolvent mixtures.

Further studies on these and related polyamides are
currently in progress.

ACKNOWLEDGEMENT

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