

# Influence of Nonsolvents on Dissolution Characteristics of Nylon-6

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## SYNOPSIS

The dissolution of nylon-6 has been made effective by adding a nonsolvent to the primary solvents that in turn created potential combined contact sites and enhanced the process of dissolution. It is found that 50% of a primary solvent like m-cresol or phenol could be replaced by solvents that are relatively economical and safe to handle. Nylon-6 is found to get dissolved at a faster rate and with ease in a blend of 45 : 55 phenol-toluene compared to other solvent blends. The dependence of limiting viscosity on solute-binary solvent interactions is used as a measure of the solvency power of solvent blends for nylon. The lowering of temperature is found to favour the dissolution of nylon-6 in m-cresol. Its dissolution is found to be optimum in phenol at 55°C and further increase in temperature has adverse effects on it.

*Key words.* Nylon-6, limiting viscosity, radius of gyration, onset of precipitation, non-solvent and solvent blends.

## INTRODUCTION

In a dilute solution, the dimensions of random coils of a polymer depend on quality of solvent and they are also influenced by short- and long-range interactions. In good solvents, coils expand by excluded volume effects,<sup>1</sup> and in  $\Theta$  solvents the coils remain unperturbed over all concentration ranges.<sup>2</sup> The dimensions of the coil change on heating or cooling as the quality of the solvent in a particular polymer-solvent system changes with temperature. Because of this, a solvent acts as  $\Theta$  solvent for a particular polymer at  $\Theta$  temperature.

The change in temperature may produce extended uncoiled conformations or collapsed state of polymer chains in solution<sup>3</sup> and result in contracted chain configuration of the molecule even in good solvents. Several workers<sup>3-7</sup> reported the conformational transition of polymers with increase in temperature. Tanaka et al.<sup>8,9</sup> found a transition of polyacrylamide

being produced by changing the composition of water-acetone mixture or the temperature. They also observed a transition of this kind in solutions of polystyrene in cyclohexane.<sup>10,11</sup>

Nose et al.<sup>12</sup> calculated unperturbed dimensions, radius of gyration, and hydrodynamic radius by using limiting viscosity data for polystyrene in cyclohexane, 2-butanone, and toluene. They elucidated the excluded volume effects and compared the results with theoretical predictions of current thermal blob theories<sup>13,14</sup> and the Pade approximant theory.<sup>15</sup> Sun et al.<sup>16</sup> calculated the unperturbed dimensions of star-shaped polystyrene near  $\Theta$  temperature using limiting viscosity data and found its radius of gyration much smaller than that of the linear polystyrene. Janeczek and Turska<sup>17</sup> found the conformational transitions of polyamide-6 macromolecules to occur in mixtures of m-cresol and methanol. They observed a decrease in limiting viscosity that they interpreted in terms of coil-globule conformational change.

The aim of the present work is to establish solvents and solvent blends for nylon-6 and study the conformational changes of the polymer chain.

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**Table I Solvents and Nonsolvents for Nylon-6**

Solvent	Nonsolvent	Solubility Parameter $\delta$ , (cal/cc) <sup>1/2</sup> at 25°C
m-cresol		11.11
Phenol		11.38
	Toluene	8.91
	Xylene	8.80

## EXPERIMENTAL AND RESULTS

### Material

Nylon-6 (supplied by M/s Gujarat State Fertilizers Co. Ltd., Baroda, India) free from any admixtures and having viscosity average molecular weight,  $M_v$ , 35,000 (determined in m-cresol at 30°C), was used.

### Solvents and Solutions

Analytical reagent grade solvents and nonsolvents used for viscosity measurements are listed in Table I.

A number of solvent/nonsolvent blends were prepared and their solubility parameter values (reported in Table II) were calculated using the following equation<sup>18</sup>:

$$\delta_m = V_1\delta_1 + V_2\delta_2 + \dots \quad (1)$$

Here,  $\delta_1, \delta_2, \dots$  are solubility parameters of individual solvents and  $V_1, V_2, \dots$  are their volume fractions.

**Table II Solubility Parameter,  $\delta_m$ , of Various Solvent Blends at 25°C<sup>a</sup>**

Solvent : Nonsolvent (v : v)	$\delta_m$ of Solvent Blends (cal/cc) <sup>1/2</sup>		
	m-Cresol/Xylene	Phenol/Xylene	Phenol/Toluene
100 : 0	11.11	11.38	11.38
70 : 30	10.42	10.61	10.64
65 : 35	10.30	10.48	10.51
60 : 40	10.19	10.35	10.39
55 : 45	10.07	10.22	10.27
50 : 50	9.96	10.09	10.15
45 : 55	9.84	9.96	10.02
40 : 60	9.73	9.83	9.90
35 : 65	9.61	9.70	9.78
30 : 70	9.49	9.56	9.65

<sup>a</sup> Calculated by using eq. (1).

## Procedure

Solutions of nylon-6 prepared on weight basis of solute and solvent were left at  $25 \pm 1^\circ\text{C}$  for 24 h. Their viscosity was determined at  $25 \pm 0.01^\circ\text{C}$  and at other temperatures (Schott Geräte thermostatic control) using calibrated Ubbelohde capillary viscometer and AVS/N system for automatic recording of flow time to an accuracy of 0.01 of a second.

## DISCUSSION

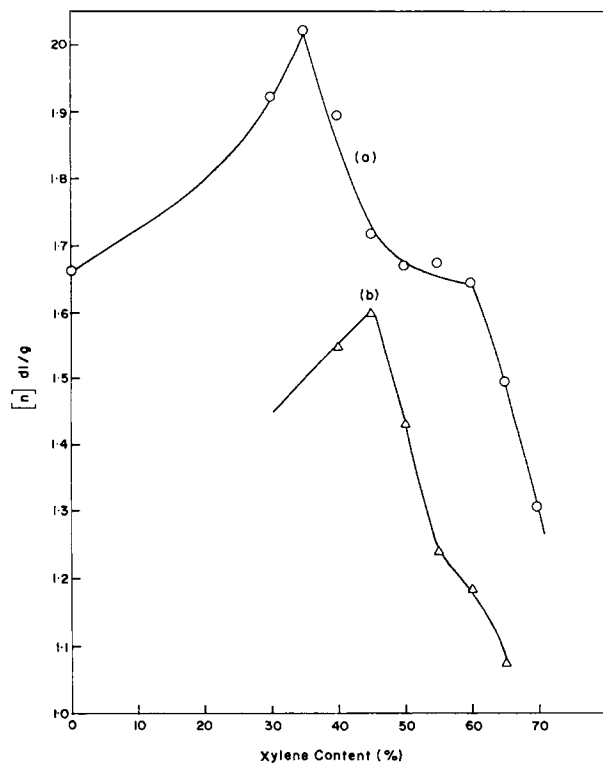
Nylon-6 is soluble in solvents that are not so safe to handle because of their peculiar odour, toxicity, and acidity. In some cases, the mixture is to be heated to a certain temperature for making the dissolution effective. These aspects have been overcome by adding a nonsolvent to primary solvents for nylon. The addition of a nonsolvent to the primary solvents creates a number of potential contact sites and the combined contacts lead to enhanced solvation of polymer chain and the dissolution.<sup>19,20</sup> The action of the nonsolvent is more effective in expanding the coil dimensions than the primary solvent alone. It has been reported earlier<sup>21</sup> that the replacement of a certain amount of primary solvent by a suitable nonsolvent produces an increase in the thermodynamic volume of the solute.

### Enhanced Solvency Power of m-Cresol and Phenol for Nylon in Presence of Nonsolvents

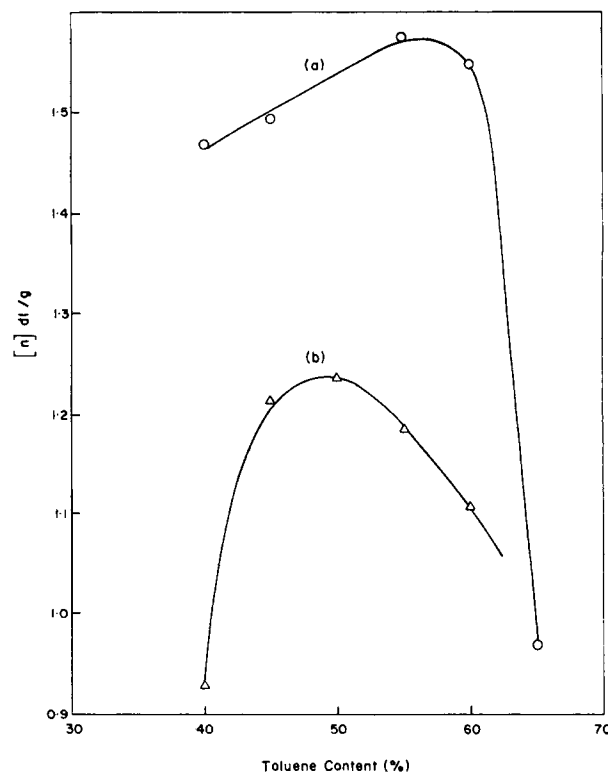
Usually, the dissolution of nylon in m-cresol takes a fairly long time at room temperature. This polymer has been dissolved at a faster rate by replacing a

certain amount of *m*-cresol by xylene (nonsolvent). The solvency power of the mixture was found to increase with xylene content up to a certain percentage. The optimum value of limiting viscosity of nylon-6 in a blend of 35% *m*-cresol and 65% xylene indicates that the resin has maximum degree of solvation and interaction in this blend of solvent and nonsolvent. The further increase of xylene in the blend produces adverse effects, and at 60% xylene content the abrupt decrease in limiting viscosity is indicative of polymer coil collapse phenomenon, i.e., coil globule transition (Fig. 1). These observations indicate the onset of precipitation of nylon-6 in a 40 : 60 *m*-cresol : xylene mixture at 25°C.

Phenol melts at 40–41°C and the dissolution of nylon in it can be made effective only above this temperature. However, in blends of nonsolvent and phenol, nylon-6 could be dissolved even at room temperature. It is observed that nylon dissolves at a much faster rate in blends of phenol-xylene than in pure phenol or in *m*-cresol. This made it possible to study solution properties of nylon in phenol-xylene blends at 25°C. The limiting viscosity of nylon-6 attains an optimum value when 45% phenol is replaced by xylene in the blend. The further increase of xylene content in blends results in continuous



**Figure 1** Limiting viscosity  $[\eta]$  of nylon-6 in (a) *m*-cresol/xylene and (b) phenol/xylene at 25°C.



**Figure 2** Limiting viscosity  $[\eta]$  of nylon-6 in phenol/toluene (a) at 25°C and (b) at 50°C.

decrease of limiting viscosity of the solution, which in turn reaches to the stage of coil-globule transition (Fig. 2). Hence, for better dissolution of nylon-6 at room temperature a blend of phenol : xylene (55 : 45) may be used.

At 25°C, limiting viscosity of nylon is found to attain a maximum value when 55% of phenol is replaced by toluene; further increase of toluene content in the blend produces adverse effects. An onset of precipitation is observed in 35 : 65 phenol-toluene mixture (Fig. 2). At 50°C, the dissolution of nylon is found to be optimum in 50 : 50 phenol : toluene blend, and on further increase of toluene content the limiting viscosity decreases gradually but not so suddenly as was observed at 25°C (Fig. 2). No onset of precipitation was observed at 50°C, even when 70% phenol was replaced by toluene.

#### Radius of Gyration of Nylon-6

Radius of gyration,  $\langle S^2 \rangle$ , defined as the average distance between the centre of gravity of the molecular coil and the chain ends, was calculated by using the Flory-Fox equation<sup>1,3</sup>:

$$[\eta] = 6^{3/2} \cdot \phi \cdot (\langle S^2 \rangle^{3/2}) / M_v \quad (2)$$

**Table III Limiting Viscosity,  $[\eta]$  (dL/g), and Radius of Gyration,  $\langle S^2 \rangle$  (nm), of Nylon-6 Solution in Different Solvent/Nonsolvent Blends**

Solvent : Nonsolvent (v : v)	m-Cresol/Xylene		Phenol/Xylene		Phenol/Toluene		Phenol/Toluene	
	at 25°C							
	$[\eta]$	$\langle S^2 \rangle$	$[\eta]$	$\langle S^2 \rangle$	$[\eta]$	$\langle S^2 \rangle$	$[\eta]$	$\langle S^2 \rangle$
100 : 0	1.662	12.35	—	—	—	—	—	—
70 : 30	1.922	12.97	—	—	—	—	—	—
65 : 35	2.021	13.18	—	—	—	—	—	—
60 : 40	1.894	12.90	1.545	12.06	1.468	11.85	0.928	10.17
55 : 45	1.720	12.49	1.598	12.19	1.492	11.92	1.209	11.11
50 : 50	1.670	12.37	1.429	11.75	1.541	12.05	1.237	11.20
45 : 55	1.677	12.39	1.239	11.20	1.575	12.67	1.185	10.03
40 : 60	1.644	12.30	1.183	11.03	1.548	12.06	1.106	10.79
35 : 65	1.492	11.92	1.073	10.67	1.035	10.55	—	—
30 : 70	1.305	11.39	—	—	—	—	—	—

Here, Flory's universal constant,  $\phi = 2.1 \times 10^{23}$  (for limiting viscosity expressed in mL/g).

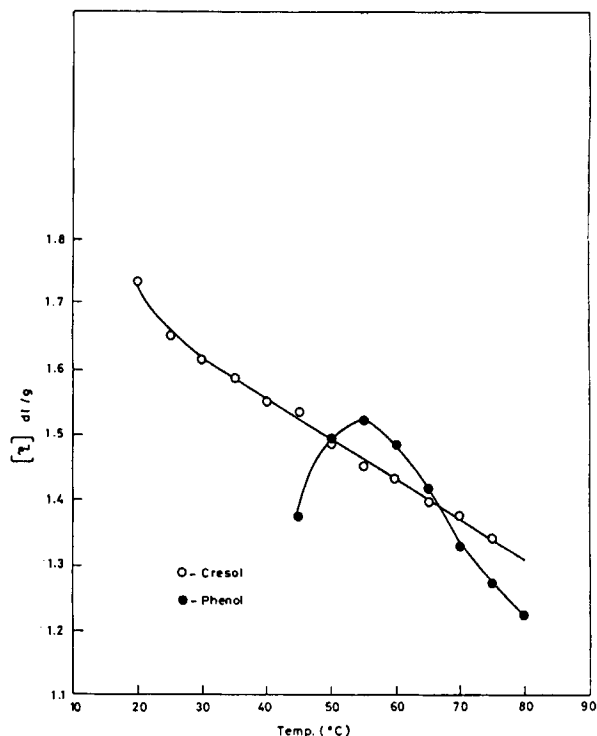
Like  $[\eta]$ , radius of gyration  $\langle S^2 \rangle$  is found to increase with increase of nonsolvent content in blends and then decrease. It attains maximum value in blends of 65 : 35 m-cresol : xylene and 55 : 45 phenol : xylene, which indicates the maximum extent of stretching of nylon-6 chain in them. In phenol-toluene blends at 25°C, the radius of gyration increases and attains the maximum value when 55% phenol is replaced by toluene. However, at 50°C the fully stretched condition of the coil is attained in 50 : 50 phenol : toluene blend (Table III).

#### Influence of Temperature on Conformational Transition of Nylon-6 in m-Cresol and Phenol

The continuous decrease in limiting viscosity of nylon-6 in m-cresol at temperatures ranging from 20–75°C, indicates contraction of the dimensions of polymer coil (Fig. 3, Table IV). This is in accordance with the findings of other workers.<sup>3,5</sup> Flory and Williams<sup>19</sup> explained that the amide bond is capable of cis-trans isomerization, and at higher temperatures the equilibrium between the two isomeric forms is probably shifted towards the cis-isomer,<sup>20</sup> which results in the contraction of the polyamide chain.<sup>22</sup> Janeczek and Turska<sup>17</sup> explained that a partial helix-coil type polymer chain transition may occur in polyamide-6 in solution. This is supported by the fact that m-cresol is a helicogenic solvent and polyamides occur in helix form in this particular solvent.<sup>23</sup> The results show that lowering of temperature favours the dissolution properties of nylon

in m-cresol. It is likely that a nylon-m-cresol system may attain a state of optimum interaction at lower temperatures as certain nylon chain sequences may be present partly in helix form.

Unlike m-cresol, phenol melts at 40–41°C, so the determination could be conducted at 45°C and

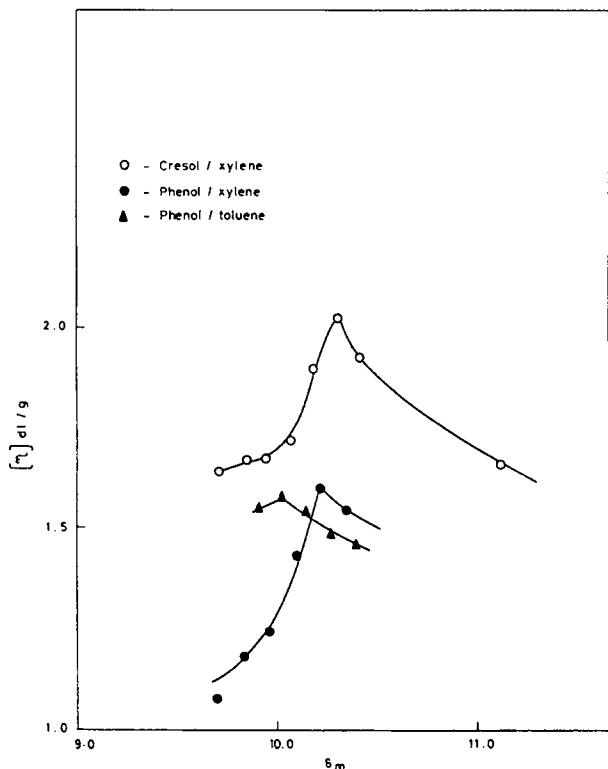


**Figure 3** Limiting viscosity  $[\eta]$  of nylon-6 in m-cresol and in phenol as function of temperature.

**Table IV Limiting Viscosity,  $[\eta]$ , and Radii of Gyration of Nylon-6 in m-Cresol and Phenol at Different Temperatures**

Temperature (°C)	$[\eta]$ (dL/g)		$\langle S^2 \rangle$ (nm)	
	m-Cresol	Phenol	m-Cresol	Phenol
20	1.729	—	12.52	—
25	1.651	—	12.32	—
30	1.612	—	12.24	—
35	1.587	—	12.16	—
40	1.551	—	12.07	—
45	1.536	1.374	12.03	11.59
50	1.483	1.494	11.89	11.92
55	1.451	1.521	11.81	11.99
60	1.433	1.481	11.76	11.89
65	1.393	1.414	11.65	11.70
70	1.376	1.332	11.60	11.47
75	1.341	1.270	11.50	11.29
80	—	1.224	—	11.15

above. It is observed that in nylon-phenol solution the interaction among the solute-solvent molecules increases with the increase in temperature and attains a state of optimum dissolution at 55°C. How-

**Figure 4** Limiting viscosity  $[\eta]$  of nylon-6 as function of the solubility parameter  $\delta_m$  of solvent blends.**Table V Solubility Parameter of Nylon-6 Derived from Fig. 4**

Solvent Blend	Solubility Parameter, $\delta$ , of Nylon-6 at 25°C
m-Cresol : xylene (65 : 35)	10.30
Phenol : xylene (55 : 45)	10.22
Phenol : toluene (45 : 55)	10.02

ever, the further increase in temperature does not favour the dissolution of nylon, and the solvency power of phenol is found to be fairly low at 80°C (Fig. 3).

### Solubility Parameter of Nylon-6

The dependence of limiting viscosity on solute-binary solvent interactions is taken as a measure of the solvency power of solvent blend for resins.<sup>21,24</sup> Limiting viscosity data are plotted in Figure 4 as a function of solubility parameter of the solvent blends. The plots pass through a maximum, and the solubility parameter of the solvent blends corresponding to the maxima of the plot is taken as equivalent to the solubility parameter of nylon-6. The values of solubility parameter for nylon-6 in different solvent blends obtained from the plots are listed in Table V.

### CONCLUSIONS

The findings reported here indicate that in the dissolution of nylon almost 50% of the primary solvents could be replaced by solvents that are relatively economical and safe to handle. Moreover, nylon gets dissolved in such blends at a faster rate and with ease. The blend of 45 : 55 phenol : toluene is found to have optimum solvency for nylon-6 compared to other solvent blends. Many such solvent blends could be designed for polymers that are usually difficult to be dissolved or take a longer time to go into solution. Flow properties of polymer solution can be used as one of techniques for this purpose.

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