

# Structural memory in chromium coordinated polyamides

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It was established by X-ray diffractometry that swelling agents caused a  $\gamma \rightarrow \alpha$  transition in chromium coordinated polyamides. This structural memory effect can well be interpreted by the formation of the mixed complex,  $[\text{Cr}(\text{CO}_{\text{amide}})_n(\text{H}_2\text{O})_{6-n}]^{3+}$  proposed previously. The structure controlling the increase in the melt viscosity corresponds to  $n \geq 2$  while a treatment with a swelling agent (e.g. water) results in a complex structure of  $n \approx 1$  by ligand exchange. The latter involves a destruction of the partly crosslinked structure conferring the possibility of the structural memory.

## INTRODUCTION

Great attention has recently been given to the thermally reversible crosslinked polymers essentially because of their excellent dimensional stability. Such a thermally decomposable network structure is realized either by ionic interactions (cf. ionomers) or by coordination complexes. The latter can be synthesised by polymerizations (where the monomer itself includes coordinative bonds), polycondensations, or modification of the preformed polymer (where functional groups capable of coordination are present or can be formed by polymer-analogous or other transformations).

The thermally reversible crosslinked structure prepared by one of these methods represents a 'chemical' mode of reinforcement i.e. formation of composites, in contrast with the traditional 'physical' ways (such as incorporation of fillers, reinforcements, skeletal materials etc.).

The overwhelming majority of the reports, concerning mainly the ionomers and polyelectrolytes, emphasized principally the ionic interactions while investigations of coordination polymers have been in progress only recently.

There are, however, several analogies between the ionomers and the coordination polymers. In both cases, crosslinking involves an increase in the amorphous proportion and the structural variations are also identical, namely that an ionic cluster structure or a random distribution in the amorphous phase is realized. Based on the most recent results, the former structure appears to be accepted both for ionomers<sup>1</sup> and for coordination polymers<sup>2-4</sup>.

## EXPERIMENTAL

Nylon-6 obtained by anionic polymerization (Bonamid G-01 of the Borsod Chemical Works, Kazincbarcika, Hungary) was used for the investigations. X-ray diffractograms were recorded by a Phillips Micro III equipment using Ni-filtered  $\text{CuK}\alpha$  irradiation under the conditions of scattering of 40 kV and 20 mA. X-ray diffraction bands were resolved into their Gaussean components by means of a Du Pont 310 curve resolver. Melt viscosities were determined by a Zwick 4104 capillary plastometer (load, 2.16 kp; i.d. of nozzle, 2 mm; temperature range, 230°–270°C).

Chromium coordinated nylon-6 samples were prepared by incorporation of 0.35% of  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  using the method described previously<sup>5</sup>.

## RESULTS AND DISCUSSION

In a previous paper<sup>5</sup>, the effect of  $\text{Cr}^{3+}$  ions on the increase in melt viscosity was studied and a possible interpretation of the observed phenomena was given. In that case, the chromium coordinated polyamides were studied essentially in their morphological aspects.

X-ray diffractograms demonstrated that chromium coordinated polyamides had an increased amorphous proportion. The presence of the  $\gamma$ -pseudo-hexagonal modification was clearly observed also. The present investigations were aimed at deciding whether this  $\gamma$ -form was a non-stable modification of the chromium coordinated polyamides or not. A number of authors observed that for polyamides thermal treatments<sup>6-8</sup> or swelling<sup>9</sup> cause a  $\gamma \rightarrow \alpha$  transition. In the present study of this transition, the latter method was selected.

Samples were swollen by phenol/ethanol mixtures of different weight ratios for a certain period (1 h) then their diffractograms were recorded as shown in *Figure 1*. It can be seen that the  $\gamma$ -peak at 21° disappears and the diffractogram becomes like that of the initial (non-coordinated) polyamide. This serves as evidence that the  $\gamma$ -modification is a non-stable intermediate form.

The diffractograms were resolved into Gaussean components by a curve resolver. The hexagonal and  $\gamma$ -pseudo-hexagonal modifications were not distinguished. The location of the individual peaks were selected as follows: amorphous-1, 20°; amorphous-2, 23°; monoclinic ( $\alpha_I$ ), 19.5°; monoclinic ( $\alpha_{II}$ ), 23.5°; hexagonal, 21°.

Designations  $\alpha_I$  and  $\alpha_{II}$  are used according to Roldan<sup>10</sup>. Deviations from the above angles in the individual records were lower than  $\pm 0.2^\circ$ . Band widths of the amorphous peaks were adjusted to the upper limit of the range of the equipment, and the components of the crystalline peaks were estimated by trial-and-error fittings.

Results of the curve resolution are shown in *Figure 2* for the chromium coordinated polyamide in an intermediate stage of swelling (cf. the diffractogram of a sample swollen

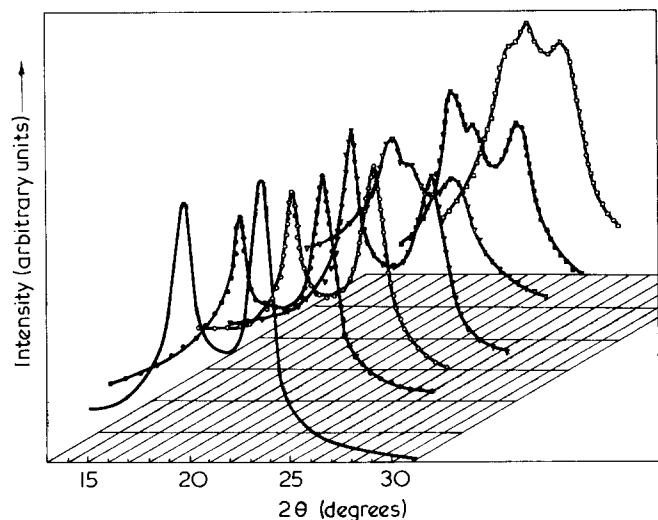


Figure 1 X-ray diffractograms for demonstration of  $\gamma \rightarrow \alpha$  transition in the chromium coordinated polyamide-6 induced by swelling in phenol/ethanol mixtures:  $\square$ , without swelling;  $\blacksquare$ , swollen in phenol/ethanol mixture of 15:85;  $\nabla$ , swollen in phenol/ethanol mixture of 30:70;  $\blacktriangledown$ , swollen in phenol/ethanol mixture of 50:50;  $\circ$ , swollen in phenol/ethanol mixture of 60:40;  $\bullet$ , swollen in phenol/ethanol mixture of 70:30; —, non-coordinated initial polyamide-6 without swelling

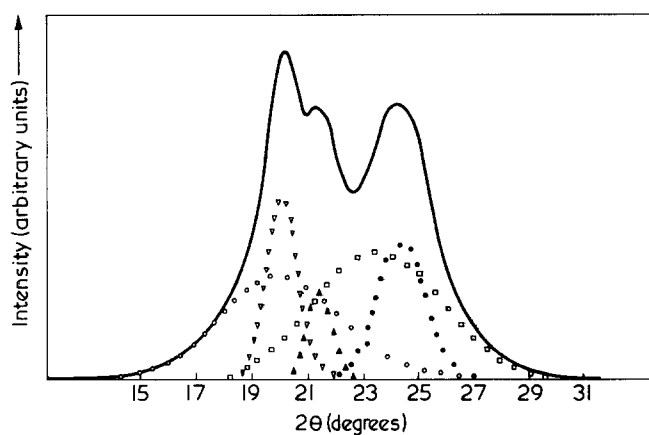


Figure 2 Gaussian components of the X-ray diffractogram for the chromium coordinated polyamide-6 swollen in phenol/ethanol mixture of 15:85:  $\circ$ , amorphous-1;  $\square$ , amorphous-2;  $\nabla$ ,  $\alpha_I$ ;  $\bullet$ ,  $\alpha_{II}$ ;  $\blacktriangle$ ,  $\gamma$

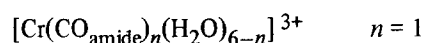
in phenol/ethanol of 15:85 w/w in Figure 1). Figure 3 represents the diffractogram and its Gaussian components for the initial non-modified nylon-6 corresponding to the full line in Figure 1.

Detailed results of the curve resolution are presented in Table 1. However, the results are approximate since, on the one hand, the Gaussian function is actually not an exact mathematical interpretation of the corresponding structures, and on the other hand, the accuracy of fittings during the curve resolution is rather doubtful. It can be established from the data of the Table that, due to the coordination, the ratio of  $\Sigma am./\Sigma cryst.$  increased considerably on account of the monoclinic modifications. It is also apparent that the  $\gamma$ -hexagonal modification is only transient and is present at a low percentage.

It can be seen in Figure 1 and concluded from the results collected in Table 1 that the structural memory exists in the chromium coordinated polyamides, as the sample tends to reach or approximate the structure of the initial material.

Due to the incorporation of the chromium compound, however, a permanent structural change takes place in the amorphous-to-crystalline ratio as compared with the initial polyamide.

An analogous structural change (i.e.  $\gamma \rightarrow \alpha$  transition) was observed, even though as a much slower process, by water treatment. Since water is competitive with the carbonyl group of  $n$ -donor nature in the polyamide<sup>5</sup> with respect to coordination, formation of a cationic mixed complex is possible in the range of the amorphous phase (except for the sites where stable chelate bonds have been formed due to the folding of the polymer chain of multidentate ligands) as follows:



Under the conditions of processing preceded by drying, it transforms into a complex structure of  $n \geq 2$ , i.e. into a partly crosslinked polyamide product that controls the increase in melt viscosity.

Based on the Arrhenius plot of melt viscosity against the temperature (Figure 4), it can be stated that, at the same moisture content (0.02% determined by the vacuum

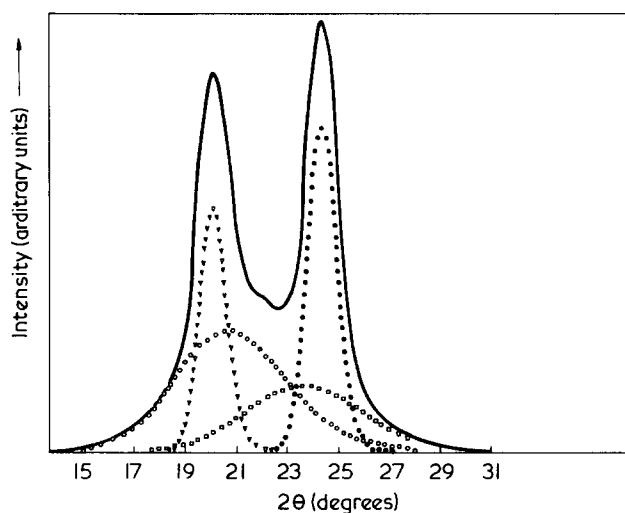


Figure 3 Gaussian components of the X-ray diffractogram for the initial polyamide-6 sample. (For symbols see Figure 2)

Table 1 Changes ( $\gamma \rightarrow \alpha$  transition) in the structure of chromium coordinated polyamide-6 caused by swelling as studied by the Gaussian components of X-ray diffractograms

Sample	Structural forms (%)						
	$\alpha_I$	$\alpha_{II}$	$\gamma$	amor- phous 1	amor- phous 2	$\Sigma$ cryst. (%)	$\Sigma$ am. (%)
Chromium coordinated							
Polyamide-6							
Non-swollen	5.5	8.5	2.5	46.5	37	16.5	83.5
Swollen in phenol/ethanol:							
15:85	11.5	8.5	1	48.5	30.5	21	79
30:70	13.5	15.5	5	29	37	34	66
50:50	13	21	0	43	23	34	66
60:40	10.5	24.5	0	36	29	35	65
70:30	7	28	0	40	25	35	65
Non-coordinated							
Non-swollen	18	26	0	36	20	44	56

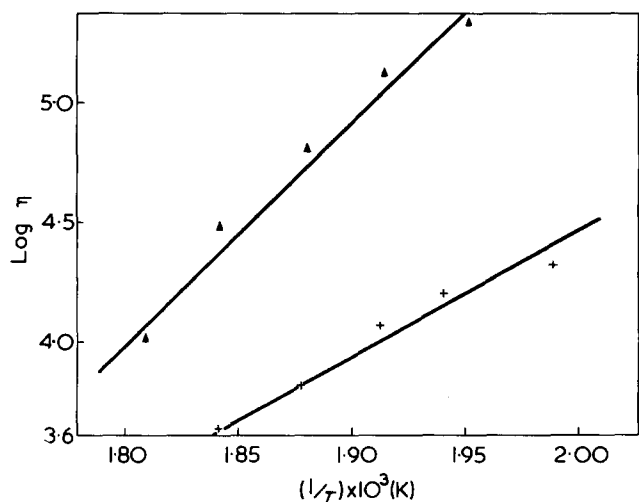


Figure 4 Arrhenius plot of the melt viscosity against temperature: ▲, chromium coordinated polyamide-6; +, initial polyamide-6

technique method), the activation energy of the chromium coordinated polyamide (46.2 kcal/mol) is higher than that of the initial polyamide (25.7 kcal/mol). Such an increase in the activation energy of the viscous flow indicates a stiffening of the chain i.e. it contributes evidence for the existence of a thermally reversible intermolecular crosslinked structure.

To summarize, it can be concluded that the phenomenon of structural memory exists in the chromium coordinated polyamides under the given experimental conditions. Morphologically, the  $\gamma$ -form is non-stable as shown by the data of curve resolutions. This observation is in accordance with the suggested mixed complex structure (where water is a competitive ligand) which takes part in the structural memory since the carbonyl groups can be replaced by water becoming incorporated into the coordination sphere through ligand exchange. The suggested mixed cationic complex structure at  $n \geq 2$  gives a correct interpretation for the increase in melt viscosity. The existence of such a partly crosslinked structure is supported by the changes in activation energies of viscous flow (cf. Figure 4).

Water, being a competitive ligand as illustrated by the suggested mixed complex structure, may lead to a structure that can reach the condition of  $n = 1$  as a limiting value.

This latter structure is analogous to that of the so-called I coordination type of Dunn and Sanson<sup>11</sup> suggested for metal-salt/polymer systems. In fact,  $n$  tends to 1 under favourable steric conditions when chelate structure can also be formed. Such a coordination, corresponding to the above conditions, is also supported by the observation that the incorporated chromium compound can not be removed from the matrix by boiling with hot water. In studies on the interactions in polar polymer/inorganic salt systems<sup>12</sup>, participation of water in the coordination was observed. It leads to the conclusion for the present instance that the crosslink density in chromium coordinated polyamides can be controlled by the moisture content of the system.

The morphological conclusion can be summarized by the fact that the amount of inorganic salt that can be incorporated depends on the proportion of the amorphous phase in the initial crystalline polymer, i.e. the more amorphous the initial substance is, the higher the amount of chromium compound that can be incorporated into the polymer. This is the reason why the *in situ* incorporation of the chromium compound is sometimes used during the polymerization process.

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