

## Preparation and Some Properties of Nylon 46

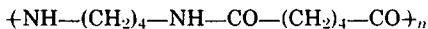
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### Synopsis

Nylon 46 was synthesized from the salt of 1,4-diaminobutane and adipic acid. High molecular weight polymers could be obtained by reaction for 1 hr at 215°C in a closed system and at least for 1 hr *in vacuo* at a temperature in the range 290–305°C. The reactions at 290°C were found to have taken place in the solid state and those at 305°C in the melt. The highest molecular weights ( $\bar{M}_w$  ca. 45,000) were obtained by reaction at 290°C with a nylon salt with a pH of 7.8–8.0. The molecular weight characteristics were studied with end-group analysis, viscometry, light scattering, and ultracentrifugation. The polymers were found to be gel-free and monodisperse ( $\bar{M}_w/\bar{M}_n \sim 1.15$ ). Films could be cast from formic acid. From x-ray diffraction patterns, measured on such films, spacings of 3.74 and 4.30 Å were calculated, whereas a long period of 66 Å was also found. The infrared spectra showed all the usual amide bands of even–even polyamides. The melting temperature was found to vary between 283 and 319°C, depending on the thermal history of the sample. Water absorption measured on a cast film showed this to be very hygroscopic (7.5% at 65% RH), while a highly crystalline sample absorbed only little water (1.6% at 65% RH).

### INTRODUCTION

Nylon 46 has a symmetrical molecular structure and a fairly high amide content:



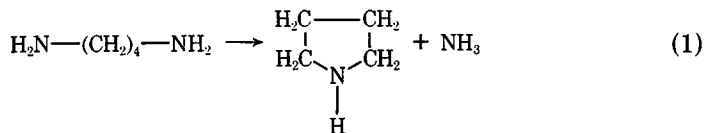
Consequently, properties like crystallinity and tensile strength should be at least comparable with those of nylon 66 or, possibly, even better with respect to practical uses. Surprisingly, rather little is known about synthesis and properties of nylon 46.

Carothers<sup>1</sup> mentioned nylon 46 as early as 1938. He reported a melting point of 278°C, which was confirmed by Coffman et al.<sup>2</sup> ten years later. Beaman and Cramer<sup>3</sup> found for the bulk polymer a melting point of 308°C and for a melt-spun fiber 283°C. Their product has been synthesized by a two-step melt-polymerization process. The inherent viscosity  $\eta_{\text{inh}}$  was 0.84 in a 0.5% solution in *m*-cresol at 30°C. They reported also some film and fiber properties of nylon 46.

Ke et al.<sup>4</sup> described the synthesis of some polyamides by interfacial polymerization. Their nylon 46 had a melting point of 293°C. More recently Aubineau et al.<sup>5</sup> prepared nylon 46 from adipoyl chloride in chloroform solution ( $\eta_{\text{inh}}$  was 0.48 in a 0.5% solution in 96% sulfuric acid).

One of the reasons for the little attention which this polymer got might be the difficulty of synthesizing a high molecular weight product. The melt polymer-

ization of nylon 46 is rather difficult, because of the high melting point. During the reaction, oxidative and thermal degradation may occur as well as cyclization of 1,4-diaminobutane to pyrrolidine [eq. (1)].



Interfacial polymerization of this polymer is not as easy as that of the longer-chain polyamides 66 and 610. Due to its hydrophilic nature, 1,4-diaminobutane is highly soluble in water but much less so in the second solvent which is required. Thus, the ratio of the concentration of diaminobutane in water to that in the second solvent is high. Consequently, the reaction is slow, so that hydrolysis of the acid chloride may occur.<sup>6</sup> Solution polymerization is interesting only when the acid hydrochloride can be efficiently extracted.

In this report, we will present the results of a study of the preparation of nylon 46 by melt polymerization and some properties of this polymer.

## EXPERIMENTAL

### Polymerization

Nylon 46 salt was prepared in ethanol as described for the nylon 66 salt, and the pH of a 1% solution in water was determined.<sup>7</sup> This pH of the salt is an easy measurable variable, depending on the excess of diamine present in the salt. 1,4-Diaminobutane (Baker & Co.) was purified by distillation (159°C/760 mm Hg). Adipic acid (Fluka, purum) was used without further purification. The polymer was prepared from the salt by the method described for nylon 66,<sup>7</sup> but instead of a Carius tube we used the "capsule in autoclave" technique.<sup>8</sup> The glass capsule has a breakseal which could be broken without opening the autoclave. The steel autoclave had a manometer, temperature control, and nitrogen feed, and it could be evacuated.

In a typical preparation, a thin-walled glass capsule (vol. 50 ml) was filled with 5 g of freshly prepared nylon 46 salt, purged of air, and sealed under vacuum. The sealed capsule was placed in an autoclave (250 ml). After closing and purging, the autoclave was filled with nitrogen to a pressure of 20 atm. It was heated for 2 hr at 215°C, while the pressure in the autoclave had increased to 40 atm. After the first step, it was allowed to cool to 40°C and the breakseal was broken by rocking the capsule against the lid (a pressure drop was observed on the manometer). The whole system was then evacuated (0.5 mm Hg), and heated *in vacuo* for 1 hr at a temperature in the range 290–305°C.

### Characterization

Amine end groups were determined by conductometric titrations in phenol/water at 22°C,<sup>9</sup> and carbonyl end groups by potentiometric titrations in benzyl alcohol at 200°C.<sup>10</sup> The inherent viscosities  $\eta_{\text{inh}}$  were determined in 0.5% solution in 98% formic acid.

For light-scattering measurements a Fica 50 instrument was used. Solutions 2.3M in KCl in 90% formic acid were prepared, this solvent mixture being known as a theta solvent for most nylons.<sup>11,12</sup>

The ultracentrifuge measurements were measured with a Spinco model E analytical ultracentrifuge on 0.4% solutions in 90% formic acid containing 2.3M KCl. By means of the sedimentation-diffusion equilibrium method of Scholte,<sup>11</sup> we determined  $\bar{M}_n$ ,  $\bar{M}_w$ , and  $\bar{M}_z$ . The buoyancy factor ( $1 - \bar{v}d = -0.086$ ) necessary for the calculation of these molecular weights from ultracentrifugation data was measured by means of a PEER DMA/50 digital density meter.

The melting behavior was studied with a Perkin-Elmer DSC-1B instrument at a heating rate of 16°C/min. The peak temperatures were taken as melting points.

Films were cast from formic acid solutions. The infrared spectra were obtained from thin films.

The water absorption was measured on samples which were first dried to constant weight in a vacuum oven at 80°C, and then allowed to pick up water (1 day conditioning) at 23°C, in successive atmospheres of 34, 50, 60, 84 and 100% RH, maintained in a climate chamber equipped with a balance.

## RESULTS AND DISCUSSION

### Polymerization

The polymerization was carried out in two steps. After the first step (1 hr at 215°C in a closed capsule), the polymer had an inherent viscosity of 0.18 (sample I) (Table I). High molecular weight polymer was obtained by reacting in the second step for 1 hr at 290–305°C *in vacuo*. Under these conditions, reactions at 290°C were found to have taken place in the solid state and the reactions at 305°C in the melt. 1,4-Diaminobutane should be present in excess, as it is more

TABLE I  
Reaction Conditions and Properties of Samples

Sample	Amt, g	pH salt	Extra additives <sup>a</sup>	Step 1 (closed system)		Step 2 (vacuum)		Physical state during reaction <sup>b</sup>	$\eta_{inh}$ , dl/g	Color
				Temp, °C	Time, hr	Temp, °C	Time, hr			
I	5	7.6	—	220	1	—	—		0.18	colorless
II	5	7.2	—	220	1	290	1	s	1.34	light yellow
III	5	7.4	—	220	1	290	1	s	1.32	light yellow
IV	5	7.6	—	220	1	290	1	s	1.69	light yellow
V	5	7.8	—	220	1	290	1	s	2.01	light yellow
VI	5	8.0	—	220	1	290	1	s	1.99	light yellow
VII	5	8.3	—	220	1	290	1	s	2.09	light yellow
VIII	5	7.2	—	220	1	305	1	m	1.29	yellow
IX	5	7.4	—	220	1	305	1	m	1.45	yellow
X	5	7.6	—	220	1	305	1	m	1.65	yellow
XI	5	7.7	—	220	1	305	1	m	1.56	yellow
XII	5	7.8	—	220	1	305	1	m	1.54	yellow
XIII	5	7.8	—	220	1	305	1	m	1.55	yellow
XIV	60	7.6	—	220	2	280 290	2 2	s	1.72	light yellow
XV	60	7.6	AA, 1.25% TDMA, 0.62%	220	2	280 290	2 2	s	1.03	colorless

<sup>a</sup> AA = adipic acid; TDMA = tetramethyl diammonium acetate.

<sup>b</sup> s = solid state; m = melt.

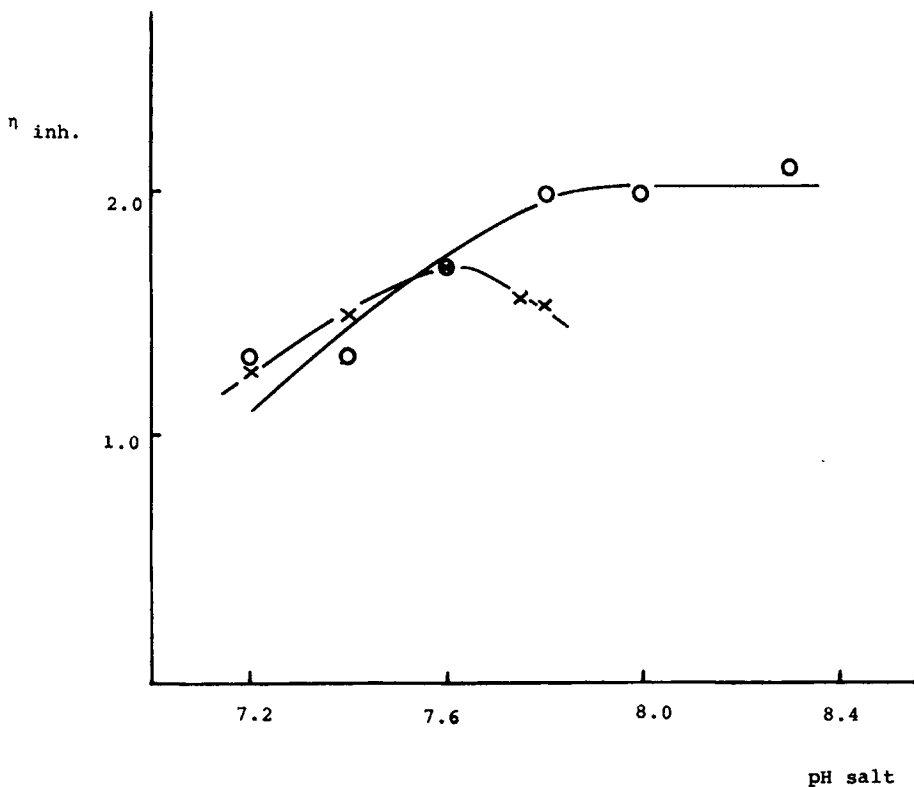


Fig. 1. Influence of the salt pH on  $\eta_{inh}$  of the polymers prepared: (x) sample polymerized at 308°C in the melt; (O) sample polymerized at 290°C in the solid state.

volatile than adipic acid and can cyclize to pyrrolidine. In order to study the effect of excess diaminobutane, starting salts with variable pH (1% solution in water) were prepared. The polymers prepared at 290°C (in the solid state) had a maximum in  $\eta_{inh}$  when the pH of the salt was 7.8–8.3 (Table I, Fig. 1). The polymers prepared at 305°C (in the melt) had a lower maximum in  $\eta_{inh}$  at a lower salt pH (7.6). In the pH range 7.2–7.6 there is no detectable difference in  $\eta_{inh}$  between the polymers prepared at 290°C and 305°C. Under the reaction conditions used (290–305°C, *in vacuo*), nylon 66 would normally form branched structures and gels.<sup>13,14</sup> Therefore, we studied the molecular weight characteristics of samples II–VII in detail (Table II).

TABLE II  
Characterization Data

pH	$\eta_{inh}$ , dl/g	End-group analysis, ends/10 <sup>6</sup> g			Light scattering $\bar{M}_w$	Ultracentrifugation			
		-NH <sub>2</sub>	-COOH	$\bar{M}_n$		$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	
II	7.2	1.34	5.3	60.3	31,000	23,000	27,000	30,000	35,000
III	7.4	1.32	8.6	53.9	32,000	22,000	—	—	—
IV	7.6	1.69	10.1	32.7	47,000	31,000	30,000	34,000	39,000
V	7.8	2.01	16.1	21.5	53,000	43,000	—	—	—
VI	8.0	1.99	14.2	23.6	53,000	40,000	37,000	42,000	49,000
VII	8.3	2.09	40.3	9.7	40,000	47,000	—	—	—

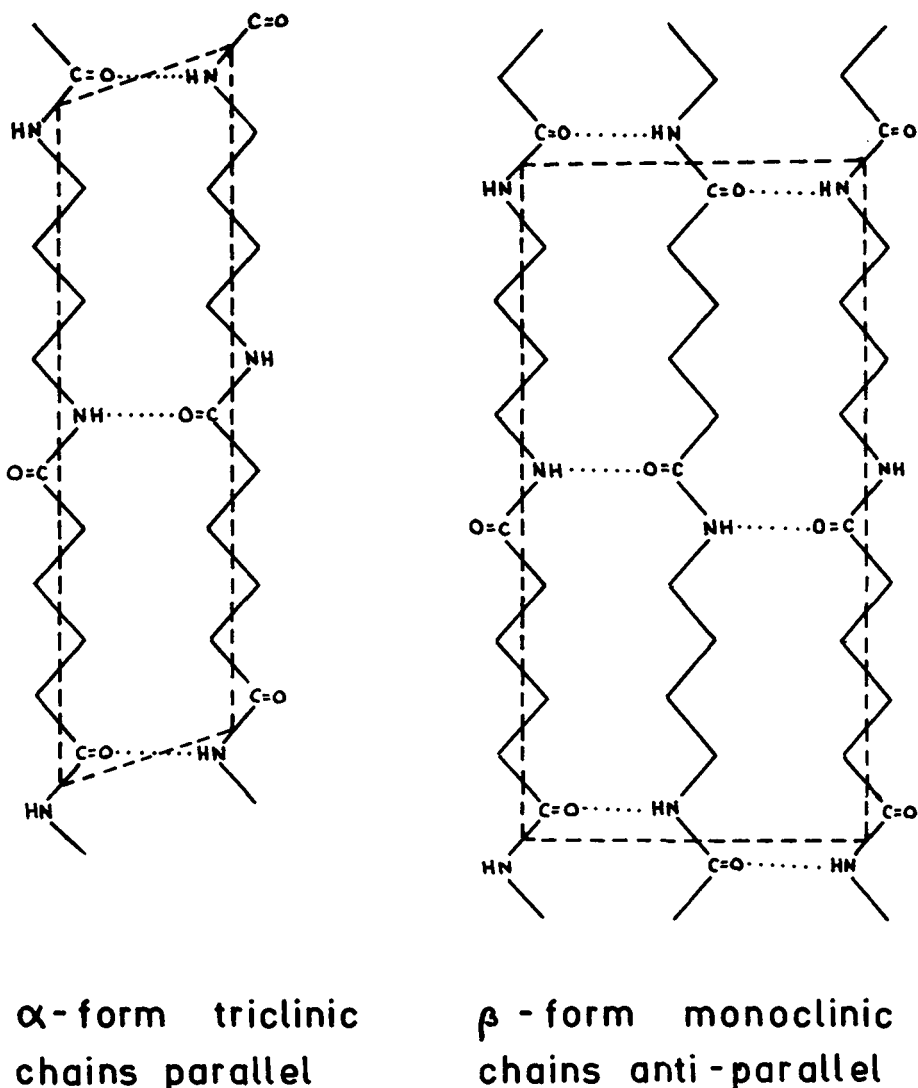


Fig. 2. Schematic view of two possible crystal arrays in nylon 46.

The  $\bar{M}_n$  obtained from end-group analysis is found to be higher than the  $\bar{M}_w$  from light scattering. Thus, it seems that with our end-group analysis not all end groups were determined. This is confirmed by the ultracentrifugation measurements of  $\bar{M}_n$  for II, IV, and VI. The  $\bar{M}_w$  determined by light scattering gave similar increases with the pH of the salt as  $\eta_{inh}$ . No bottom layer was observed during ultracentrifugation runs, and from this we can conclude that no gel was present in the samples studied. Moreover, the polydispersity was found to be surprisingly low ( $\bar{M}_w/\bar{M}_n \sim 1.15$ ). This suggests that no branched structures or gels were formed during the high-temperature polymerization *in vacuo*.

We can explain this difference between nylon 46 and nylon 66 synthesis as follows. For nylon 66, one of the important steps in the formation of a gelled structure is the formation of the trifunctional dimer of 1,6-diaminohexane [eq. (2)].<sup>13,15</sup>

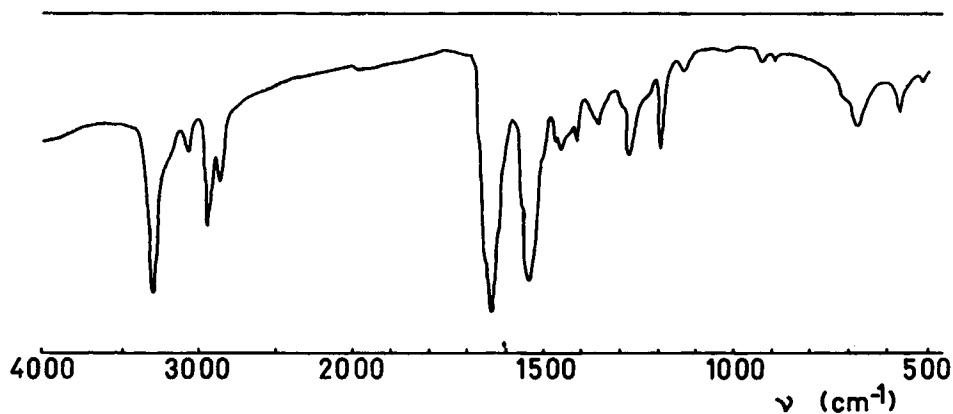


Fig. 3. Infrared spectrum of a solution-cast film.



The formation of a similar dimer from 1,4-diaminobutane is less likely, as it has a strong tendency to react with its own amine group and cyclize to pyrrolidine.

Larger quantities of polymer could easily be prepared with the same method (XIV, XV). Sample XV was synthesized in the presence of the additives adipic acid and tetramethylene diammonium acetate.<sup>2</sup>

The "capsule in autoclave" method has the advantage of being a safe and simple technique of conducting the first step in a closed system at high temperatures and high pressures and conducting the second step *in vacuo* under good oxygen-free conditions.

### Structure Analysis

Nylon 46 has a symmetrical structure and should be able to form, in analogy with nylon 7,<sup>16</sup> a triclinic parallel structure and a monoclinic antiparallel structure (Fig. 2). Both structures might occur simultaneously. It is expected that the crystallinity will be high.

TABLE III  
Main Bands in the Infrared Spectrum of Cast Film

Band, $\text{cm}^{-1}$	Intensity <sup>a</sup>	Assignment
3300	vs	N-H band
3070	m	N-H band
2945	s	$\text{C}_{\text{H}_2}$ -
2870	m	$\text{C}_{\text{H}_2}$ -
1638	vvs	amide I
1540	vvs	amide II
1280	m	amide III
940	w	amide IV
730	sh	amide V ( $\gamma$ -structure)
690	s (broad)	amide V ( $\alpha$ -en $\beta$ -structure)
575	m	amide VI
520	w	amide VI

<sup>a</sup> Intensity: vs = very strong; m = medium; s = strong; vvs = very very strong; w = weak; sh = shoulder.

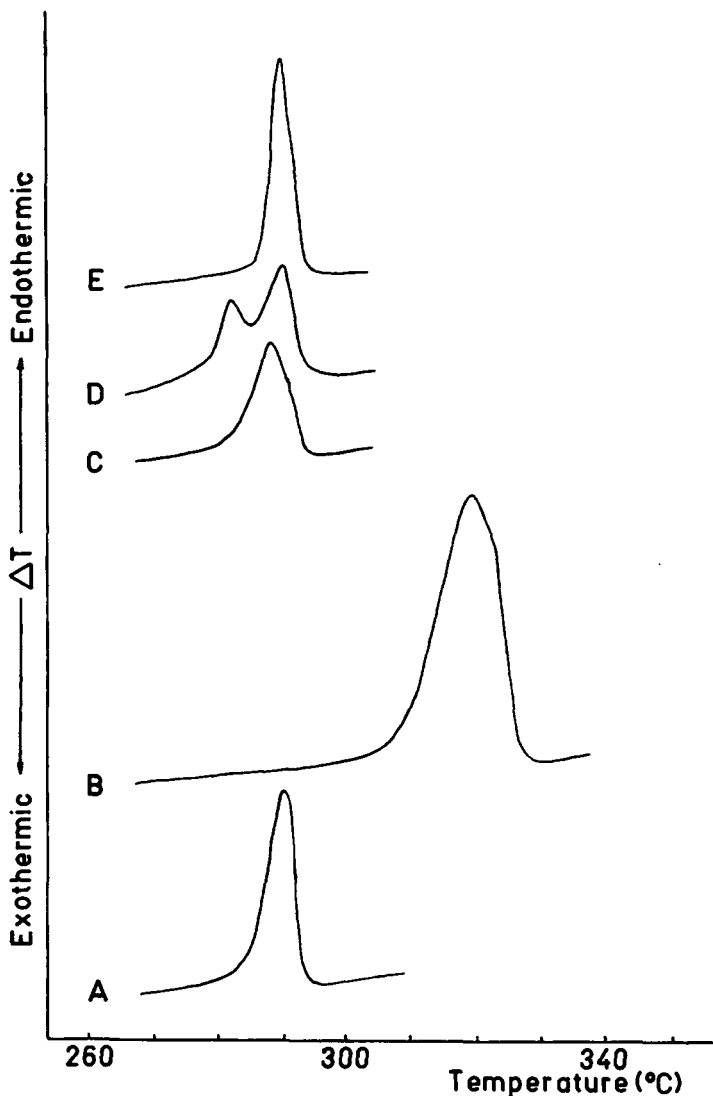


Fig. 4. DSC curves at 16°C/min heating rate: (A) melt-polymerized sample; (B) sample polymerized in the solid state; (C) cast film; (D) quenched sample; (E) sample, quenched and annealed for 5 min at 279°C.

From x-ray studies on cast films of XIV, we found the following interplanar spacings:  $d_{010} = 3.74 \text{ \AA}$ , and  $d_{100} = 4.30 \text{ \AA}$ ; a long period of 66 Å was also found. These results are similar to those reported for other even-even polyamides with an  $\alpha$ -structure.<sup>17</sup>

The infrared spectra of the polymer XIV (Fig. 3, Table III) show amide bands at the frequencies of polyamides with an  $\alpha$ -structure.<sup>18,19</sup>

### Properties

The most frequently quoted property of nylon 46 is its melting point, which ranges from 278 to 308°C.<sup>1-5</sup> Particularly interesting is the finding of Beaman,<sup>3</sup> who obtained a melting point of 308°C on the bulk polymer and a melting point of 283°C after melt spinning and drawing. Our melt-polymerized polymer X

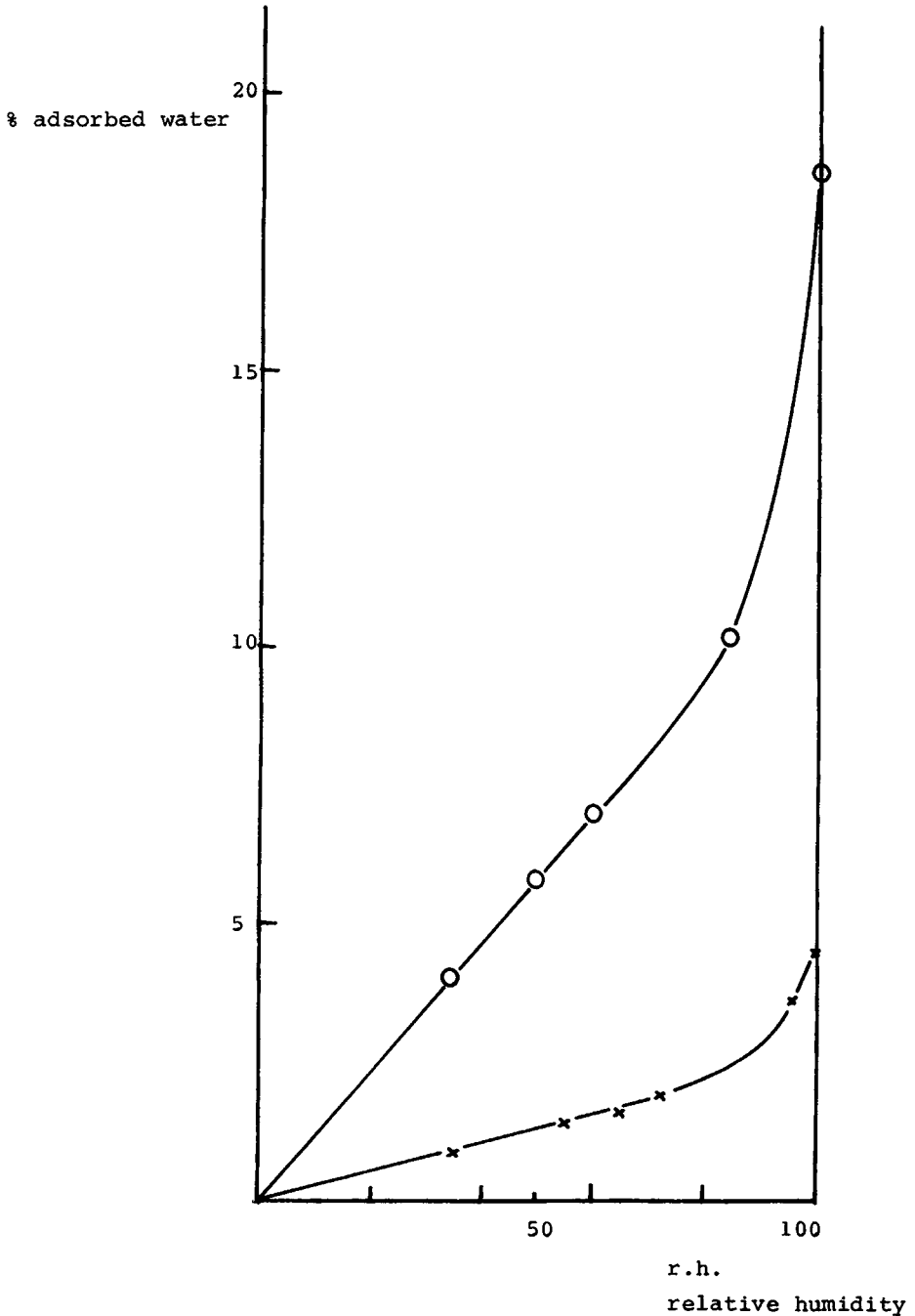


Fig. 5. Water absorption isotherms at 23°C: (O) cast film; (x) solid-state polymerized particle.

had an endotherm with a peak temperature of 284°C (Fig. 4A). The product polymerized in the solid phase (XIV) had a very strong endotherm with a peak temperature at 319°C (Fig. 4B). A solution-cast film had a melting temperature of 278°C (Fig. 4C). A quenched sample had a double melting peak (283–291°C)



(Fig. 4D), but if a quenched sample was annealed for 5 min at 279°C, a sharp single melting peak was obtained at 291°C (Fig. 4E).

These results show that the melting point is strongly dependent on the thermal history of the sample and can be changed reversibly. The shift to a higher melting temperature suggests an increase in the crystallite perfection or size. The sometimes observed double melting peak suggests the presence of another structure. The heats of fusion corresponding with the samples A–E were 15.7, 31.3, 13.7, 14.6, and 15.1 kJ/mole, respectively. Samples which had previously been melted (A and D) gave results which seem to be dependent on the rate of cooling of the molten samples.

The density of a solid-state polymerized polymer was 1.24 g/cm<sup>3</sup> and that of a solution-cast film 1.20 g/cm<sup>3</sup>. The polymer is rather difficult to dissolve.<sup>3</sup> A good solvent is formic acid and, to a lesser extent, trifluoroacetic acid. Concentrations up to 45% polymer could be obtained in 98% formic acid. Even in 60% formic acid nylon 46 is soluble. Polyamides absorb water, the amount of which is strongly dependent on the amide group concentration<sup>20</sup> and crystallinity.<sup>21</sup>

The highly crystalline sample XIV absorbed little water, while the cast film was very hygroscopic (Fig. 5).

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