

## Fully Ordered Copolyhydrazides Based Upon Bisacid A2

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### Synopsis

The preparation of copolyhydrazides containing equimolar quantities of "bisacetyl A2" and terephthaloyl or isophthaloyl groups is described. The resulting copolymers were found to form clear colorless films which, when immersed in concentrated formic acid, softened but rehardened and turned white after subsequent immersion in water. The formic acid treatment did not bring about a morphological change from the amorphous to the crystalline state, but caused changes in the differential scanning calorimetry (DSC) traces which suggest that an  $\alpha/\beta$  transformation had taken place. The possible nature of this transition is discussed. The results of tensile tests on cast film are given.

### INTRODUCTION

The preparation of ordered, thermally stable polyamides, poly(amide/hydrazides), and copolyhydrazides has been reported by Preston and Black and their colleagues Culbertson, Murphy, DeWinter, Hofferbert, Holsten, and Lillyquist,<sup>1-7</sup> as well as by Frazer, Reed, and Fitzgerald.<sup>8,9,13</sup> Three earlier papers in the present bisacid A2 polymer series dealt with the *p*-phenylenediamine polyamide,<sup>10</sup> its *m*-analogue as well as with ring-substituted *p*- and *m*-phenylenediamine polyamides, with aliphatic polyamides<sup>11</sup> and with the homopolyhydrazide.<sup>12</sup> These were designated "bisparamid A2," "bismetamid A2," "nylons nA2," and "bishydrazid A2," respectively. All these polymers (except the aliphatic polyamide polymer) were made by the low-temperature solution method which had been developed by workers at du Pont, Monsanto, and elsewhere and which was acknowledged in the lists of references of Lenk and White.<sup>10,11</sup> The aliphatic polyamides of the "nylon nA2" type are more suitably made by interfacial polymerization.

The reaction scheme given in Figure 1 resulted in the production of a polymer which is of considerable interest for three reasons: (i) It affords a direct comparison with the homopolymer "bishydrazide A2" described in reference 12; (ii) it is a fully ordered copolymer and also opens up possibilities of tailoring copolyhydrazides with a variable number of ether linkages per unit length of polymer chain; (iii) the introduction of the terephthaloyl and/or isophthaloyl group would be expected to raise the softening point of the homopolyhydrazide described in reference 12.

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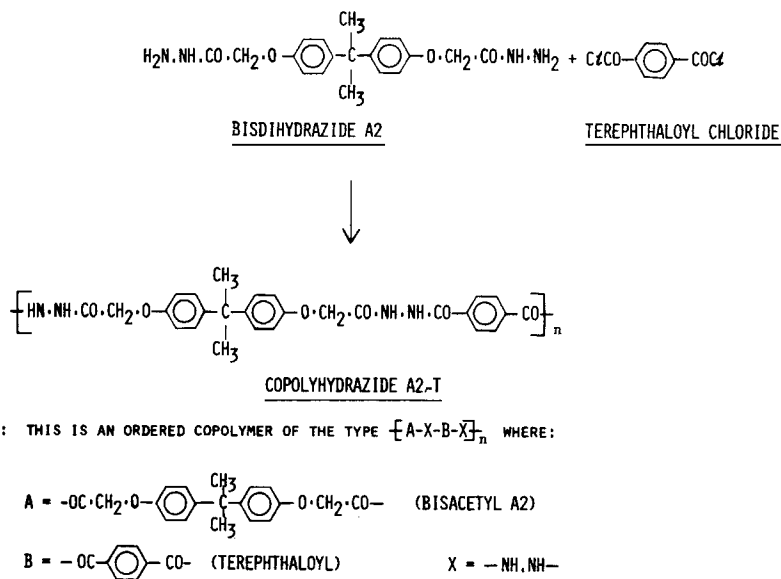


Fig. 1. Preparation of copolyhydrazide A2/T by low-temperature solution polymerization.

## EXPERIMENTAL

Figure 1 shows the scheme of reaction for the preparation of a fully ordered copolyhydrazide of the type  $\left[ \text{A-X-B-X} \right]_n$ . The polymer which results from the specific reaction given in Figure 1 is the terephthalic copolyhydrazide ("copolyhydrazide A2/T"). The isophthalic copolyhydrazide ("copolyhydrazide A2/I") is made in exactly analogous fashion. The preparative details are given below.

### "Copolyhydrazide A2/T"

An 8.3366-g (0.02239 mole) portion of bisdihydrazide A2 was dissolved in 50 ml N-methylpyrrolidone (NMP) and cooled to  $-40^\circ\text{C}$ , whereupon 4.544 g (0.02239 mole) solid terephthaloyl chloride (recrystallized twice from *n*-hexane) was added all at once while dry nitrogen was passed through the reaction flask which was also fitted with a drying tube. After 10 min, another 5 ml NMP was used to rinse into the reaction zone any solid material from the neck through which the terephthaloyl chloride had been added. The cooling bath was removed after 20 min and the mixture was allowed to regain room temperature. The mixture was then an almost colorless viscous liquid which did not appear to wet glass readily. It was precipitated without neutralization or dilution by dropping it from a funnel into a large volume of water with agitation, giving snow white pearls, left to wash for 24 hr, similarly washed by suspension in methanol for 24 hr, and finally dried *in vacuo* at  $50^\circ\text{C}$ . It was also seen that the reaction mixture could be readily wet spun into fiber. The concentration during reaction was 18.4%, and the final concentration was 17.0%. The yield was 11.0 g (theory: 11.2 g) and the inherent viscosity (0.5% solution in dimethylacetamide containing 5% LiCl) was 0.58.

TABLE I  
Inherent Viscosities of Copolyhydrazides A2/T and A2/I in 5%  
LiCl/DMA and pure DMA

	$\eta_{inh}$	
	In 5% LiCl/DMA	In pure DMA
Terephthalic copolyhydrazide (A2/T)	0.63	0.45
Isophthalic copolyhydrazide (A2/I)	0.38	0.29

TABLE II  
Tensile Tests on Copolyhydrazide A2/T<sup>a</sup>

	A2/T	A2/T(X)	A2/T	A2/T(X)	A2/T	A2/T(X)
Strain rate, cm/min	2.54	2.54	1.27	1.27	0.508	0.508
Maximum stress, (dynes/cm <sup>2</sup> ) × 10 <sup>-8</sup>						
Mean	6.93	1.46	9.13	1.55	8.21	1.31
S.D.	---	---	---	---	1.07	0.25
% Strain of break						
Mean	1.50	6.17	2.10	8.70	2.90	6.53
S.D.	---	---	---	---	0.37	1.26
Initial modulus, (dynes/cm <sup>2</sup> ) × 10 <sup>-10</sup>						
Mean	5.15	0.66	10.68	0.63	4.15	0.66
S.D.	---	---	---	---	0.33	0.07
No. of specimens	3	3	3	2	8	7

<sup>a</sup> All samples failed after reaching a yield point (tough failure); X denotes formic acid-treated film

### "Copolyhydrazide A2/I"

A 10.4693-g (0.02814 mole) portion of bisdihydrazide A2 was dissolved in 50 ml NMP and chilled to -40°C, whereupon 5.7131 g (0.02814 mole) solid isophthaloyl chloride (freshly opened jar of reagent grade but not recrystallized) was added, followed by 5 ml additional NMP in order to flush any solid material down the neck into the reaction zone. The viscosity increased quickly, and the slightly straw-yellow solution was left to stir for 2 hr during which time the bath temperature rose to ambient. The resulting solution (20.6% polymer) was precipitated into water and washed and dried as in the previous preparation. The pure-white pearls obtained represented a yield of 13.4 g (theory: 14.1 g), and the inherent viscosity (solvent and concentration as before) was 0.38.

It was noted that neither of the two copolyhydrazides dissolved readily in dimethylacetamide (DMA) containing 5% LiCl at room temperature even at the low concentration of 0.5%, but that gentle warming quickly produced a clear solution. In contrast, solutions of high concentration (10–20%) would be readily obtained at room temperature with DMA in the *absence* of LiCl. Inherent viscosity measurements in pure DMA gave lower results for both copolyhydrazides than did DMA containing 5% LiCl, as shown in Table I.

Both copolyhydrazides were made into film by casting from solution in DMA. The terephthalic copolyhydrazide film was tested in tension at three different

TABLE III  
Tensile Tests on Copolyhydrazide A2/I

	A2/I(X)
Strain rate, cm/min	0.508
Maximum stress, (dynes/cm <sup>2</sup> ) × 10 <sup>-8</sup>	
Mean	0.65
S.D.	0.10
% Strain	
Tough failure (4 specimens)	3.4
Brittle failure (3 specimens)	1.5
Initial modulus, (dynes/cm <sup>2</sup> ) × 10 <sup>-10</sup>	
Mean	0.43
S.D.	0.12
No. of specimens	7

strain rates both before and after treatment with concentrated formic acid, washing, and drawing. The isophthalic copolyhydrazide film was weak and brittle as cast, but formic acid treatment gave a film which was suitable for tensile testing. This was done at one strain rate only. The results of the tests which were done at 23°C/65% R.H. are given in Tables II and III.

It was observed that the appearance of the cast film following exposure to concentrated formic acid was different in the copolyhydrazides from that shown by the bispolyaramides and bishydrazide A2: The last-mentioned films opacified instantaneously,<sup>10-12</sup> while the copolyhydrazides softened but remained clear until they were taken out of the formic acid and immersed in water, when they developed opacity and turned pure white instantaneously.

X-ray scattering (WAXS) patterns showed no sharp concentric rings. The copolyhydrazides are thus amorphous both as-cast and after formic acid treatment (Fig. 4).

### Differential Scanning Calorimetry (DSC)

The DSC traces for both copolyhydrazides (as virgin polymer and as formic acid-treated film) are given in Figures 2 and 3.

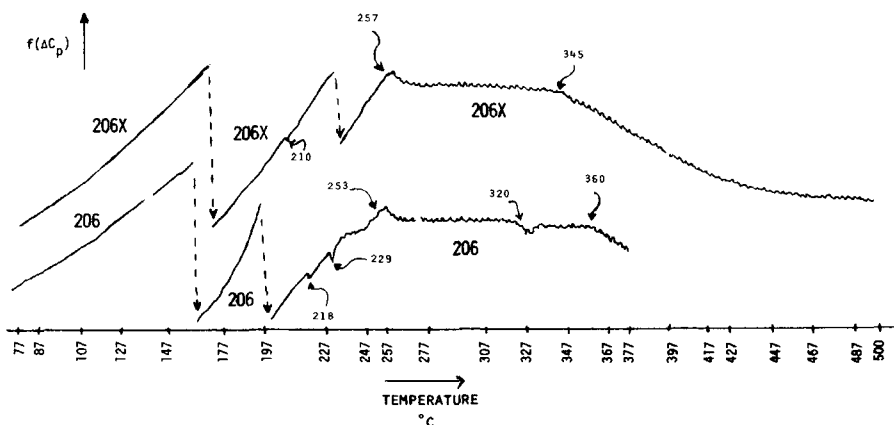


Fig. 2. Differential scanning calorimetry (DSC) traces of copolyhydrazide

## DISCUSSION

It is clear that the reaction scheme as given in Figure 1 affords an excellent method for preparing fully ordered copolyhydrazides. The lower inherent viscosity of the isophthalic copolyhydrazide compared to its terephthalic analogue may have been due to the fact that the isophthaloyl chloride was used as received (although from a fresh bottle of good reagent grade), while the terephthaloyl chloride was recrystallized twice from *n*-hexane. It was significant to note that tough film was obtained from the terephthalic copolyhydrazide film (both as-cast and formic acid treated) at all three strain rates, while three out of seven specimens of even the formic acid-treated isophthalic copolyhydrazide film failed in brittle manner at the lowest strain rate. (It should be remembered that formic acid treatment always tends to toughen as-cast film.) The implication is that an inherent viscosity of around 0.60 is suitable for making good copolyhydrazide film (both clear and opaque, i.e., formic acid treated), but that a value of about 0.40 is too low to ensure toughness even after formic acid treatment which reduces the probability of brittle failure. Moreover, those specimens of the low inherent viscosity formic acid-treated isophthalic copolyhydrazide film which failed after first yielding (and which were, therefore, tough) had only a rather lower elongation at failure than is common after formic acid treatment of bisacid A2 polyamides and polyhydrazides.

The presence of *two* blips in the DSC trace of the virgin polymers and the appearance of one (*and only one*) of these after formic acid treatment is interesting. The bisacid A2 polyaramides and the homopolyhydrazide have only one blip, which disappears on formic acid treatment. It is taken to signify that such treatment has caused an  $\alpha/\beta$  transition.<sup>10-12</sup> Evidently, the same transformation occurs in the copolyhydrazide, and the second blip is presumably associated with the second acyl group. The one which disappears on formic acid treatment is evidently the one associated with the bisacetyl group.

The precise nature of the  $\alpha/\beta$  transformation has not yet been established, but there is good circumstantial evidence which points to a reasonable interpretation.

Sweeny,<sup>14</sup> in a du Pont patent dealing with the preparation, properties, and structure of polyaramides, specifically poly(*m*-phenyleneisophthalamide), suggested that the essentially helical and *intramolecularly* hydrogen-bonded

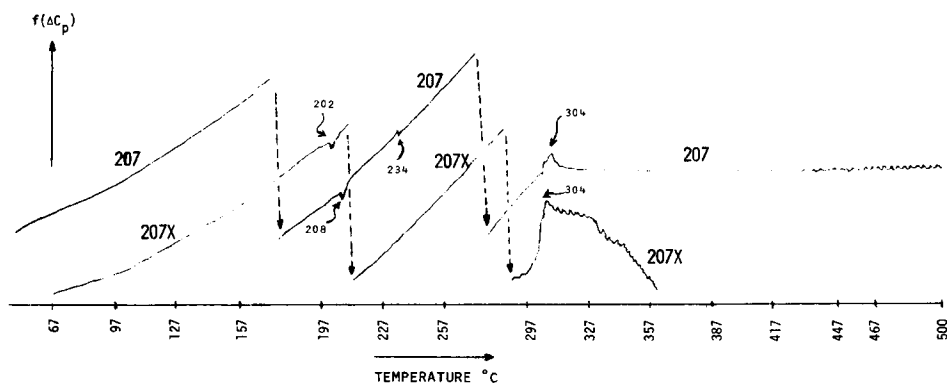


Fig. 3. Differential scanning calorimetry (DSC) traces of copolyhydrazide A2/I film: 206, as cast; 206X, formic acid treated.

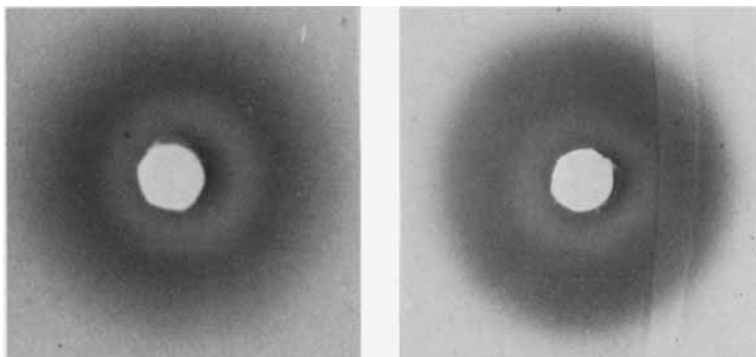


Fig. 4. Wide-angle x-ray scattering (WAXS) of formic acid-treated films of bisacid A2 ordered copolyhydrazides.

polymer presumably transforms to a pseudocrosslinked *intermolecularly* hydrogen-bonded structure and that the conditions under which this would tend to be favored include: the action of acids, notably strong formic acid; heat; and high-shearing stresses.

In our earlier work on bisacid A2 polyaramides,<sup>10,11</sup> we have observed: (i) That treatment of the clear as-cast polymer film caused instantaneous opacification which we consider to be not merely a surface etching phenomenon, but a more fundamental chemical or morphological change; (ii) that the blip in the DSC trace found in both virgin polymer granules and in specimens of clear (i.e., untreated) as-cast film is not found when the transition region is retraversed in the reverse direction or when the same specimen is rerun on the DSC; the transition is not, therefore, spontaneously reversible; (iii) that during the primary reaction of bischloride A2 and aromatic diamines (carried out at low temperature in an anhydrous acid-acceptor solvent with vigorous stirring), the polyaramides form a gel-like mass as they are formed. This is quite likely due to the influence of the HCl which is simultaneously produced and which, even in the presence of the acid acceptor, causes formation of the  $\beta$  species even as the latter is formed from the  $\alpha$  species under the action of formic acid upon as-cast film. This may well be further favored by the fast stirring during the initial reaction which produces a high-shear field, all the more so because the oxymethylene units present in the structure of bisacid A2 polyaramides make these chains quite flexible and so facilitate interchain hydrogen bonding. The gel-like mass is not readily broken up by dilution, but neutralization (or even partial neutralization) of the HCl with lithium hydroxide does break up the gel after a few hours, especially when a little more solvent is added; a still viscous (but definitely free flowing) liquid characteristic of a solution of a high polymer results. It is not thought that *short-term* exposure of the solution to lithium hydroxide causes extensive hydrolysis, although prolonged exposure (a week or more) *does* cause loss of viscosity and reduction in molecular weight as indicated by a determination of inherent viscosity.

It is thus reasonable to assume that the observed  $\alpha/\beta$  transition of polyhydrazides and copolyhydrazides of bisacid A2 is analogous to that observed with phthalic polyaramides<sup>14</sup> and with bisacid A2 polyaramides<sup>10,11</sup> which Sweeny<sup>14</sup> attributes to the existence of *intramolecularly* and *intermolecularly* hydrogen bonded  $\alpha$  and  $\beta$  forms, respectively.

Since the  $\beta$  form (heat-treated or formic acid-treated material) does not spontaneously revert to the  $\alpha$  form, we can account for the fact that the  $\alpha$  form (virgin granules or as-cast clear film material) shows a transition blip on the DSC trace, while the  $\beta$  form, having already undergone the transition, does not.

It is worth noting additionally that the solubility characteristics of poly(*m*-phenyleneisophthalamide) may also be profoundly affected by heat treatment. Thus, Sweeny<sup>14</sup> reports that heat-treated film of this material—as distinct from untreated film—was no longer soluble in amide solvents and that heat treatment of a polymer solution in amide solvents even caused the polymer to precipitate. In the case of bisacid A2 polyaramides and polyhydrazides, we did *not* find any significant solubility differences between the  $\alpha$  and  $\beta$  forms, but this is scarcely surprising in view of the much greater flexibility of these polymers compared with the phthalic polyaramides.

Comparing the terephthalic copolymer with the homopolymer “bishydrazid A2,”<sup>12</sup> it is seen that decomposition with evolution of volatile matter starts in the range of 320° to 360°C for both, but that the process is more gradual in the copolymer. The fusion peak is around 290°C in the homopolymer and some 30°C lower in the copolymer. On the other hand, the  $\alpha/\beta$  transition in the homopolymer was at about 170°C (rather lower than in the bisacid A2 polyaramides), around 220°C in the copolymer (terephthalic: first blip at 218°C, second blip at 229°C; isophthalic: first blip at 208°C, second blip at 234°C). The DSC traces of the terephthalic and the isophthalic polymers have many similarities. But the fact that the blips indicate a much higher  $\alpha/\beta$  transformation temperature than that of the bisacid A2 polyaramides and of bishydrazid A2 presumably reflects the very much smaller number of oxymethylene groups per unit chain length in the copolymers compared to the number present in the others.

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