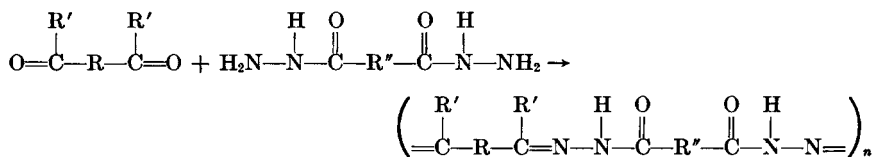


Polymers from the Condensation of Dihydrazides with Dialdehydes and Diketones

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The reaction of hydrazides with simple aldehydes and ketones has been widely used.^{1,2} However, the reaction of dihydrazides with dialdehydes, and diketones to form linear poly(acylhydrazones) has not been extensively investigated. Van Euler et al.,^{3,4} report the preparation of an insoluble, infusible polymer from 2,5-diformyl-4-methylphenol and oxalic acid dihydrazide, but did not characterize this polymer. They furthermore reported the condensation of 2,4-pentanedione and 2,5-hexanedione with sebacic and succinic acid dihydrazides. However, only low molecular weight polymers were isolated. It was therefore of interest to attempt the preparation of tractable, high molecular weight condensation polymers of this family and to examine their properties.



Discussion

A series of poly(acylhydrazones) was prepared from various combinations of the dihydrazides of isophthalic, sebacic, and adipic acids with terephthalaldehyde and glutaraldehyde. Limited attempts were also made to prepare the condensation polymers of 2,5-hexanedione and of *p*-diacetylbenzene. Equivalent quantities of dihydrazide and dicarbonyl compound reacted at room temperature in carefully purified solvents such as hexamethyl phosphoramide (HMPA), dimethyl sulfoxide (DMSO), or dimethylformamide (DMF) to give solutions containing about 10% polymer. The effect of reaction time was not studied and in some instances the reaction solutions were allowed to stand up to 8 days before the polymer was isolated. In general, reaction solutions from which the polymer precipitated did not yield high molecular weight products. It is of interest that a number of the polymers prepared in HMPA were not easily redissolved in this solvent once isolated. Some degradation was encountered when temperatures near 150°C. were used to redissolve samples for inherent

TABLE I
 Preparation and Properties of Poly(acylhydrazones)

Composition, mole ratio of dihydrazides	Polymerization medium	Reaction time, hr.	Inherent ^a viscosity, dl./g.	Fusion ^b temp., °C.	Color	Solubility				Remarks
						Hexa-methyl-phosphor-amide	Tri-fluoro-acetic acid	Di-methyl form-sulfoxide	Di-methyl form-amide	
Polymers based on terephthalaldehyde and:										
Isophthalic acid dihydrazide	HMPA	70	1.10	368	Bright yellow	Yes (limited)	No	No	No	No
Adipic acid dihydrazide	HMPA	70	0.54	>300	Light yellow	Yes	Yes	No	No	No
Sebacic acid dihydrazide	HMPA	70	0.50	300	Colorless	Yes	Yes	No	No	No
Isophthalic and adipic acid dihydrazides										
0.9/0.1	HMPA	144	1.51	>300	Light yellow	Yes	—	Yes	No	No
0.75/0.25	HMPA	144	0.76	>300	Light yellow	Yes	—	Yes	No	No
0.5/0.5	DMF	48	0.32	300	Light yellow	—	—	—	Low	Polymer precipitated during polymerization
0.5/0.5	DMSO	48	1.34	—	—	Yes	Yes	Yes	—	—

Polymers based on glutaraldehyde and: Isophthalic acid dihydrazide	HMPA	192	0.45	262	Colorless	Yes	—	Yes	—
Isophthalic and adipic acid dihydrazides 0.5/0.5	HMPA	192	0.38	175	Colorless	Yes	—	Yes	—
Polymer based on <i>p</i> -diacetyl benzene and: Isophthalic acid dihydrazide	HMPA	48	0.16	—	—	Yes (limited)	—	—	—
Polymer based on 2,5-hexadione and: Isophthalic acid dihydrazide	HMPA	48	—	—	—	No.	—	—	Polymer pre- cipitated during poly- merization

^a See experimental section.

^b Temperature at which polymer becomes fluid on a melting point block.

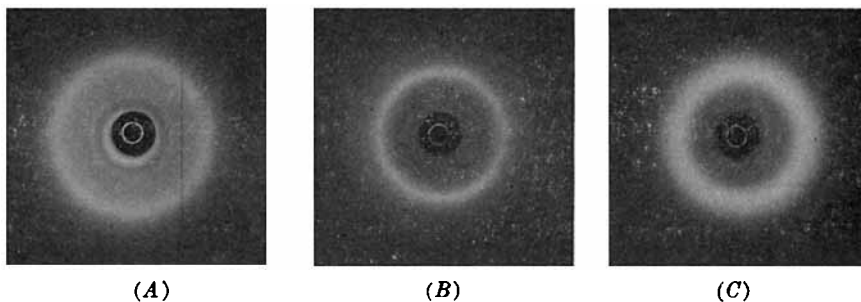


Fig. 1. X-ray diffraction patterns of poly(acylhydrazones) (using copper target and a nickel filter): (A) polymer from terephthalaldehyde and isophthalic acid dihydrazide; (B) polymer from terephthalaldehyde and adipic acid dihydrazide; (C) polymer from terephthalaldehyde and a 1:1 mixture of isophthalic and adipic acid dihydrazides.

viscosity measurements. Hence, solution viscosities measured in this solvent are to be considered only as minimum values.

Table I summarizes the various polymerizations which were carried out and some of the characteristics of the polymers formed. It can be seen that high molecular weight polymers were obtained with terephthalaldehyde and that at least medium molecular weights were obtained with glutaraldehyde. The product from 2,5-hexanedione and isophthalic acid dihydrazide was intractable, while that from *p*-diacetylbenzene was of low molecular weight.

The color of the polymers varied from bright yellow for all-aromatic poly(acylhydrazones) to light yellow or colorless for polymers containing substantial aliphatic portions.

Of the polymers derived from terephthalaldehyde, only those prepared with a mixture of dihydrazides were significantly soluble in anything but HMPA and trifluoroacetic acid. The x-ray diffraction pattern (see Fig. 1) of such a copolymer showed it to be essentially amorphous, in contrast

TABLE II
Physical Properties of Poly(acylhydrazone) Films

Polymer composition, mole ratio of dihydrazides	Inherent viscosity, dl./g.	Casting ^a solvent	Tensile ^b modulus, psi	Tensile strength, psi	Elongation, %
Terephthalaldehyde, isophthalic, and adipic acid dihydrazides	0.9-0.1	Hexamethyl phosphoramidate	299,000	7,200	6
	0.75-0.25	Hexamethyl phosphoramidate	210,000	4,300	11
	0.5-0.5	Dimethyl sulfoxide	497,000	13,000	22

^a Dried at 100°C. under vacuum for 2 to 3 days.

^b Measured by Instron apparatus.

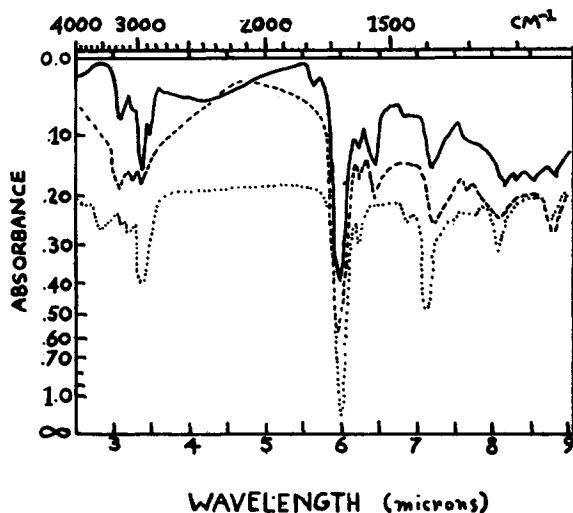


Fig. 2. Infrared spectra: (···) Model compound, terephthalaldehyde bis(butyrylhydrazone) in KBr pellet; polymer films cast from trifluoroacetic acid; (—) polymer from terephthalaldehyde and sebamic acid dihydrazide; (---) polymer from terephthalaldehyde and adipic acid dihydrazide.

to the more crystalline polymers from terephthalaldehyde and either pure adipic or pure isophthalic acid dihydrazide. Furthermore, the fusion point of the copolymer was lower than that of polymer from either straight aliphatic or aromatic dihydrazide. The glutaraldehyde-based polymers were found to be generally more soluble than the terephthalaldehyde-based polymers. The polymers from terephthalaldehyde and aliphatic dihydrazides were soluble in trifluoroacetic acid. Fairly tough films could be cast from these solutions so that, if degradation due to the solvent did occur, it was not extensive.

Films of the more soluble copolymers were solvent-cast, and tensile properties were determined. These properties, which are listed in Table II, show the poly(acylhydrazones) to be moderately tough.

The hydrolytic and thermal stabilities of the poly(acylhydrazone) from terephthalaldehyde and a 1:1 mixture of isophthalic and adipic acid dihydrazides were examined. While these properties are not outstanding, they are surprisingly good for a completely amorphous condensation polymer with $-C=N-$ linkages. Three days in water at 97°C . reduced the inherent viscosity from 1.31 to 0.86 (in DMSO). Six days in air at 180°C . reduced the viscosity to 0.90.

An interesting reaction occurred when a film of the DMSO-soluble poly(acylhydrazone), derived from terephthalaldehyde and a 1:1 mixture of the adipic acid and isophthalic acid dihydrazides, was immersed in a DMSO solution of cupric acetate. The film retained its shape, turned brown, and did not dissolve in pure DMSO when subsequently transferred to this solvent. After approximately 16 hrs. of immersion, followed by

drying, such film was analyzed and showed 18.7% by weight copper. This corresponds very closely to one cupric ion for each pair of acylhydrazone groups (18.3% calculated). The mechanism of insolubilization requires further investigation since it is not clear whether a simple cupric salt or a more complex chelate is formed.

The structure of the condensation products of dihydrazides and dicarbonyls was confirmed for at least one polymer by spectral and elemental analysis. Figure 2 compares the infrared spectra of the model compound terephthalaldehyde bis(butyrylhydrazone) and of the polymers derived from terephthalaldehyde and two aliphatic dihydrazides. There are many points of similarity. Two noteworthy features of the model compound's spectrum are the weakness of the N—H band at 3.1 and the absence of the 6.5 μ band present in the polymers. A Dumas nitrogen analysis of the polymer based on adipic acid dihydrazide agrees well with the calculated value for this material:

ANAL. Calculated $(C_{14}H_{16}O_2N_2)_x$: N, 19.17; found: N, 19.01.

Experimental

Inherent Viscosity Measurement

The inherent viscosity of the polymers was determined as follows: The polymer was dissolved in hexamethylphosphoramide (0.25%) using vigorous stirring and heat. In some instances temperatures of up to 150°C. for 30 min. were required. The solution was then cooled to 30°C. The time of efflux of this solution and of the solvent through a viscometer was measured. The viscosity was calculated as follows:

$$\eta_{(\text{inherent viscosity})} = \frac{\ln \eta_{\text{rel}}}{C}$$

where C = concentration in g./100 ml. and η_{rel} = ratio of flow times of solution and of solvent

Materials

Polymerization Solvents. Dimethylformamide (Eastman) was used directly. Hexamethylphosphoramide (Dow Chemical) and dimethyl sulfoxide (Crown Zellerbach) were distilled from Molecular Sieve, Type 4A (Linde) at reduced pressure.

*Polymer Intermediates.** *p*-Diacetylbenzene was purchased from Eastman and 2,5-hexanedione from Olin Mathieson. The terephthalaldehyde was a commercial product, m.p. 111–112°C.; lit. 115–116°C.⁵ Glutaraldehyde was isolated from a 25% aqueous solution by ether extraction and distillation, b.p. 57°C. (3 mm.), 71–72°C. (10 mm.).⁶ Dimethyl adipate, dimethyl sebacate, and dimethyl isophthalate used in the preparation of the hydrazides were purchased from Eastman.

* All melting points were taken by Fisher-Johns apparatus.

Preparation of Hydrazides

The hydrazides were all prepared by essentially the same technique. Into a three-necked 3-l. flask equipped with a stirrer, a dropping funnel, and a condenser were placed 174.2 g. dimethyl adipate, 3 lbs. benzene, and 500 g. hydrazine hydrate. The mixture was refluxed and stirred overnight. It was allowed to cool and the product was collected on a filter, recrystallized once from water, and dried at 50°C. under vacuum. The yield was 145.5 g. The melting points of the hydrazides were as follows:

Adipic acid dihydrazide	180–181°C., lit. 178°C. ⁷
Sebacic acid dihydrazide	186°C., lit. 187–188°C. ⁷
Isophthalic acid dihydrazide	227°C., lit. 224–225.6°C. ⁸

Preparation of Poly(acylhydrazones)

The following is a typical procedure for the preparation of a poly(acylhydrazone). A 250-ml. three-necked flask equipped with a stirrer and two glass stoppers was charged with 100 ml. dimethyl sulfoxide, 3.48 g. adipic acid dihydrazide, and 3.88 g. isophthalic acid dihydrazide. After all the hydrazide had dissolved, 5.36 g. terephthalaldehyde was added and the solution allowed to stir at room temperature for 48 hrs. The polymer solution was stirred into methanol. The precipitated polymer was repeatedly washed with methanol in a blender and then dried under vacuum.

Preparation of Model Compound

Butyric Acid Hydrazide. To 50 ml. refluxing benzene in a three-necked stirred flask were added 6.5 g. propyl butyrate and 25 ml. hydrazine hydrate. After 5 hrs. of refluxing the reaction mixture was allowed to cool. The aqueous layer was separated and allowed to evaporate to dryness, first in the air, and then over P₂O₅ in a desiccator. A waxy solid melting near room temperature was isolated (reported m.p. 44°C.).⁹

Terephthalaldehyde Bis(butyrylhydrazone). To 20 ml. dimethyl sulfoxide was added 2.06 g. crude butyric acid hydrazide and 1.3 g. terephthalaldehyde. The mixture was stirred until all was in solution. After standing 3 days at room temperature, 0.6 g. of yellow powder was collected on a filter and 1.25 g. more was isolated when the solution was poured into water. Several recrystallizations from dimethylformamide gave a yellow product, m.p. 307°C.

ANAL. Calculated for C₁₆H₂₂O₂N₄: C, 63.55; H, 7.34; N, 18.53; found: C, 63.70; H, 7.32; N, 18.71.

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Synopsis

A series of poly(acylhydrazones) has been prepared by the condensation of dihydrazides with dialdehydes and diketones. The dihydrazides included those derived from isophthalic, sebacic, and adipic acids. Terephthalaldehyde, glutaraldehyde, *p*-diacetylbenzene, and 2,5-hexanedione were the dicarbonyl compounds used. Polymers derived from terephthalaldehyde were of high molecular weight. The polymers varied in crystallinity, fusion point, and solubility in the expected manner. Thermal and hydrolytic stabilities were moderately good. Tough films were cast from a number of the soluble polymers. These films could be insolubilized by reaction with cupric acetate.

Résumé

On a préparé une série de poly-acryl-hydrazones par condensation de dihydrazides avec des dialdéhydes et des dicétones. Les dihydrazides utilisées proviennent des acides isophthalique; sébacique et adipique. Les composés dicarbonyliques sont l'aldéhyde téréphtalique, l'aldéhyde glutarique, le *p*-diacétyl-benzène et la 2,5-hexanedione. Les polymères obtenus à partir d'aldéhyde téréphtalique sont de haut poids moléculaire. Les polymères varient du point de vue cristallinité, point de fusion et solubilité comme on l'avait prévu. Les stabilités thermiques et hydrolytiques sont raisonnablement bonnes. On a obtenu des films durs à partir d'un certain nombre de polymères solubles, ces films pouvant être insolubilisés par réaction avec l'acétate de cuivre.

Zusammenfassung

Eine Reihe von Polyacylhydrazonen wurde durch Kondensation von Dihydraziden mit Dialdehyden und Diketonen dargestellt. Die Dihydrazide der Isophthal-, Sebacin- und Adipinsäure wurden verwendet. Als Dikarbonylverbindung kamen Terephthalaldehyd, Glutardialdehyd, *p*-Diacetylbenzol und 2,5-Hexandion zur Anwendung. Die vom Terephthalaldehyd abgeleiteten Polymeren waren hochmolekular. Die Abhängigkeit der Kristallinität, des Schmelzpunktes und der Löslichkeit von der Natur des Polymeren zeigte den erwarteten Verlauf. Thermische und hydrolytische Stabilität waren mässig gut. Aus einer Anzahl der löslichen Polymeren wurden zähe Filme gegossen. Die Filme konnten durch Reaktion mit Kupferacetat unlöslich gemacht werden.

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