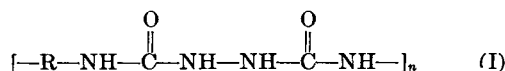


Condensation Polymers from Diisocyanates with Dihydrazides and Hydrazine

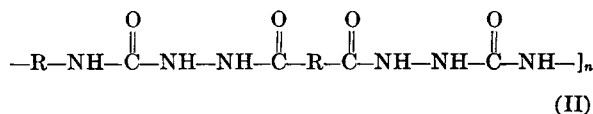
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The versatility of the reaction of the isocyanate group with various active hydrogen compounds, and some polymers made by this type of reaction, have been discussed recently.¹ Among the unusual active hydrogen compounds which have not been adequately investigated as polymer formers with diisocyanates are hydrazine² and dihydrazides, which should give linear polymers with structures (I) and (II)



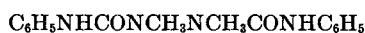
and



a polyureylene, and a poly(acylsemicarbazide), respectively.

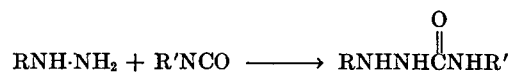
The chemistry of the reactions of monoisocyanates with hydrazines and dihydrazides has been investigated by a number of workers. Thus, Curtius and Burkhardt³ noted that hydrazine hydrate reacted with phenyl isocyanate rather violently with evolution of heat. The main products of the reaction were hydrazidicarbonyl (C₆H₅-NH·CO·NH·NH·CO·NH-C₆H₅), some carbanilide, and only a small amount of phenyl carbazide (C₆H₅NHCONHNH₂).

Busch and Frey⁴ obtained 1,4-diphenyl semicarbazide in very pure form when an equimolecular amount of phenyl isocyanate in cold ether solution was slowly added to a cold ether solution of phenylhydrazine. Phenyl isocyanate and *sym*-dimethylhydrazine⁵ reacted violently to give



Van Gelderen⁶ studied the reactions of 4-bi-

phenyl isocyanate with a series of aromatic hydrazine derivatives in benzene, toluene, or petroleum ether. In all cases, the 1,4-substituted semicarbazides resulted.



Pacilly⁷ studied the behavior of a series of aliphatic isocyanates (methyl through isopropyl) toward aromatic hydrazines. In general, the reactions were rapid and no side reactions were observed. Unfortunately, no yield of products are given, although they were presumably excellent.

Literature concerning the reaction of isocyanates with dihydrazides is very meager. An unspecified yield of 1-benzoyl-4-phenyl semicarbazide resulted⁸ when an equimolecular quantity of phenyl isocyanate was added to a cold suspension of benzhydrazide in benzene.

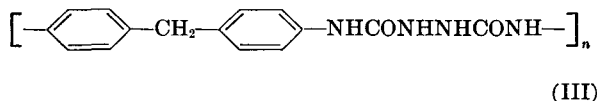
Although yields are not quoted in most of the literature cited above, it could be inferred that isocyanates react cleanly and in high yield with hydrazine and dihydrazides. These reactions should therefore be amenable to polymer formation.

DISCUSSION

The reaction of hydrazine and dihydrazides with diisocyanates has given rise to some rather unusual polymers structurally, some of which have been converted to tough films and fibers.

Hydrazine reacted readily with stoichiometric amounts of diisocyanates in appropriate solvents (dimethylformamide, dimethyl sulfoxide, etc.) to give viscous solutions, which could be cast to clear, tough films. It was not necessary to use anhydrous hydrazine in these preparations. The hydrate was employed quite satisfactorily, since reaction of the isocyanate group with the —NH₂ linkage

occurred so much more rapidly than with water that the latter reaction occurred to an insignificant degree. For example, methylene bis(4-phenyl isocyanate) reacted with the calculated amount of hydrazine hydrate in dimethylformamide solution to give a clear, viscous solution of a polymer with the structure



This polymer was cast to a clear, tough, flexible film and wet spun into 50% aqueous dimethylformamide from a 100-hole spinneret. The fiber decomposed at about 300°C., and after stretching exhibited longitudinal order in the x-ray pattern. The polymers were relatively resistant to light degradation. Thus, a film exposed 200 hr. in an Atlas Fade-Ometer was still flexible and tough.

Oxalyl dihydrazide reacted readily with methylene bis(4-phenyl isocyanate) in dimethyl sulfoxide solution. The highest viscosity polymer was obtained reproducibly when polymerization was carried out at room temperature at about 9% concentration. When polymerization was carried out at 100°, the viscosity of the polymer reached a maximum and then decreased with increasing reaction time, indicating that the polymer is thermally unstable at elevated temperatures when in solution. Heating isolated polymer to 100° for several hours did not affect the inherent viscosity.

This polymer, which should have the structure (IV), has a very unusual combination of alternating segments along the chain, that is, a diphenylmethane unit followed by a segment ten atoms long, consisting of six NH units and four C=O groups! Solutions of this polymer could be cast to tough, clear film. Once the film was dried at 100° in a forced draft oven for 1/2-1 hr., it was very difficult to dissolve in cold dimethyl sulfoxide. Film strips could be stretched at 220° about 200%.

Polymers were also prepared from oxalyl dihydrazide with tolylene-2,4-diisocyanate and 3,3'-dimethyl-4,4'-biphenylene diisocyanate. Both were

film-forming, but were not obtained in high enough molecular weight to be tough.

Isophthaloyl dihydrazide condensed readily with methylene bis(4-phenyl isocyanate) in dimethyl sulfoxide to a soluble high polymer with the structure (V).

Inherent viscosities of over 1.70 were obtained reproducibly. The polymerization at room temperature was fast and polymer was obtained in greater than 90% yield. Tough, dimethyl sulfoxide-soluble films could be cast either from the polymerization mixture directly or from a dimethyl sulfoxide or dimethylformamide solution of the polymer. Highest viscosity polymer was obtained when the reaction was run in dimethyl sulfoxide at room temperature and at about 9% concentration.

TABLE I

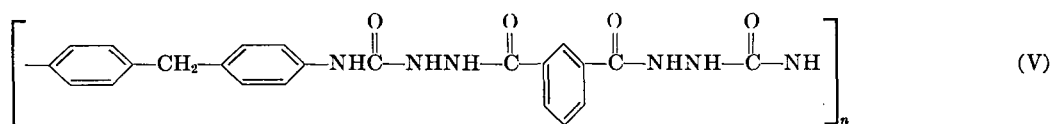
Fiber Properties of Yarn^a from Methylene Bis(4-phenyl Isocyanate) and Isophthaloyl Dihydrazide (see ref. 11)

Fiber stick temperature	240°C.
Inherent viscosity	0.98 (in dimethyl sulfoxide)
Tenacity	3.7 g. per denier
Elongation at break	31%
Initial modulus	42 g. per denier

^a Yarn sample spun from dimethylformamide and stretched 3X at about 100°C.

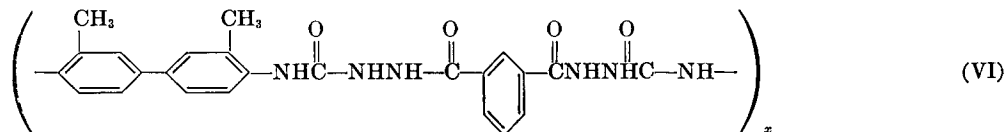
It was found that the inherent viscosity of this polymer decreased markedly when the solid polymer was kept at 100° for several hours. Efforts to stabilize the polymer by reacting it with a monoisocyanate or an acid chloride were unsuccessful. Monoisocyanates ruptured the chain (sharp decrease in viscosity), while no reaction took place with *o*-chlorobenzoyl chloride (as determined by chlorine analysis).

Polymer of $\eta_1 = 0.98$ was successfully dry-spun from dimethylformamide. Spinning proceeded continuously and the resulting fibers could be steam-drawn 3X. The undrawn fiber was amorphous and unoriented. The drawn fiber showed no lateral perfection but low longitudinal perfection, with an orientation angle of about 70° by x-ray. Fiber properties are shown in Table I.



High-viscosity polymer was also obtained from isophthaloyl dihydrazide and 3,3'-dimethyl-4,4'-biphenylene diisocyanate:

(compare IV) was obtained when the reactants were mixed in dimethyl sulfoxide. Polymers isolated by precipitation in water were insoluble in



The polymer was again prepared in dimethyl sulfoxide at room temperature, with $\eta_i = 1.00$ for air-dried samples. The viscosity dropped to 0.28 when samples were oven-dried at 100° overnight, and to 0.38 when kept at that temperature for 2½ hr. The melting point of the polymer was 260°; it was not soluble in dimethylformamide, but soluble in dimethyl sulfoxide.

Clear, tough films were cast from the polymerization mixture; these films, however, were insoluble in dimethylsulfoxide after drying for 1 hr at 100°. A 26% solids solution was prepared at 60°C., which was very viscous. When it was heated to 90°, the viscosity of the solution decreased almost instantly and did not increase on addition of 10 g. more solid polymer. Apparently, the polymer is very unstable in solution at elevated temperature.

Polymers were also prepared from isophthaloyl dihydrazide and tolylene-2,4-diisocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, and hexamethylene diisocyanate.

Terephthaloyl dihydrazide reacted readily with diisocyanates, but the products were less soluble and lower in molecular weight.

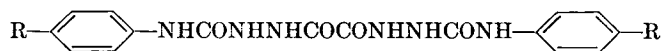
dimethyl sulfoxide. To get at least an approximate indication of the viscosity of the polymer, polymerizations with methylene bis(4-phenyl isocyanate), and 3,3'-dimethylbenzidine diisocyanate at 5% concentration were run, and aliquots of the reaction mixture were diluted to the required concentration for determination of the inherent viscosity. With methylene bis(4-phenyl isocyanate) and carbonyldiurea, polymer of $\eta_i = 0.33$ which decomposed at its PMT* of 260° was obtained in this manner. With 3,3'-dimethyl-4,4'-biphenylene diisocyanate, the polymerization solution became very viscous, almost gel-like, and a polymer with very high molecular weight was obtained.

It was observed repeatedly that the inherent viscosity of the polymers obtained from dihydrazides and diisocyanates decreased remarkably when kept at elevated temperature, and that the nitrogen analyses were low. Model compounds were prepared from oxalyl dihydrazide and two monoisocyanates, *p*-tolylisocyanate (VIII) and *p*-chlorophenyl isocyanate (IX), and also from isophthaloyl dihydrazide and *p*-tolylisocyanate (X) under conditions similar to polymerization.



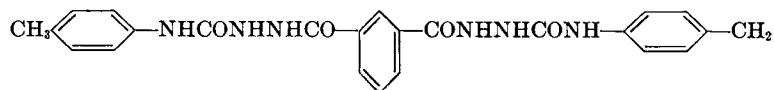
Carbonyldiurea, $\text{NH}_2\text{NHCONHNH}_2$, reacted readily with diisocyanates to give polymers. For example, with methylene bis(4-phenyl isocyanate), a polymer with the presumed structure of (VII)

These compounds were white, crystalline materials, and their analyses for carbon, hydrogen, nitrogen, and chlorine agreed well with theoretical values. Their heat stability was determined by comparing



1,1'-Oxalyl bis [2-(*p*-tolylcarbonyl)hydrazine] (VIII) (R = CH₃)

1,1'-Oxalyl bis[2(*p*-chlorophenylcarbonyl)hydrazine] (IX) (R = Cl)



1,1'-Isophthaloyl bis[2-(*p*-tolylcarbonyl)hydrazine] (X)

* PMT = polymer melt temperature.¹¹

the infrared spectra of samples which were kept at 100°C. for 3 hr. with the spectra of the unexposed compound. No change in characteristic bands was observed. The compounds did not show any marked tendency to solvate strongly.

EXPERIMENTAL

(All melting points taken on Kofler hot stage with polarizing microscope.)

Isophthaloyl Dihydrazide

To a rapidly stirred mixture of 100 g. hydrazine hydrate and 250 ml. toluene was added in small portions 80.3 g. dimethyl isophthalate dissolved in 250 ml. toluene. The reaction mixture was heated at reflux for 20 hr. After this period, about 300 ml. of solvents was distilled. The reaction mixture was cooled to room temperature and the white, crystalline product was collected on a filter, thoroughly washed with 300 ml. of boiling water to remove the excess hydrazine, and dried in a vacuum oven at 100°. The product was then extracted with benzene in a Soxhlet extractor for 16 hr., dried in vacuum at room temperature and in a vacuum oven at 100°. The yield was 60 g., m.p. 224–225.6°.⁹

Anal. calc'd. for C₈H₁₀N₄O₂: N, 28.8. Found: N, 28.31, 28.37.

Terephthaloyl Dihydrazide

The above procedure was used in the preparation of this compound starting with 32.1 g. of dimethyl terephthalate, with the exception that toluene was used as the extracting solvent. The yield was 29 g. The compound started to decompose at 325°. ¹⁰

Anal. calc'd. for C₈H₁₀N₄O₂: C, 49.5; H, 5.15; N, 28.8. Found: C, 49.67, 49.63; H, 5.24, 5.13; N, 27.95, 27.96.

The infrared spectrum was consistent with the assigned structure.

Preparation of a Polymer from Anhydrous Hydrazine and a Diisocyanate

One milliliter of anhydrous hydrazine was dissolved in 30 ml. of pure dimethylformamide and added to a solution of 5.3 g. of tolylene-2,4-diisocyanate in 20 ml. of dimethylformamide. The polymer solution became viscous and could be cast to a clear, flexible film. The polymer was isolated by precipitation in water and had an inherent viscosity of 0.15 in dimethylformamide ($\eta_{inh} = 2 \ln \eta_{rel}$).

A solution of 1.2 g. of hydrazine (anhydrous) in

20 ml. of dimethyl sulfoxide was added to 9.32 g. of methylene bis(4-phenyl isocyanate) in 100 ml. of dimethyl sulfoxide. Immediate exothermic reaction occurred and the mixture became quite viscous. After 30 min. it was poured into water to give a lump of polymer which could not be redissolved in dimethyl sulfoxide or dimethylformamide.

Substitution of 3,3'-dimethoxy-4,4'-biphenylene diisocyanate gave a more soluble product. Thus, 5.92 g. of 3,3'-dimethoxy-4,4'-biphenylene diisocyanate in about 75 cc. of dimethyl sulfoxide was mixed with 0.64 g. of hydrazine in 20 ml. of dimethyl sulfoxide at about 60°C. The solution became quite viscous and was cast on a glass plate after 1 hr. and dried in a forced-draft oven at 130°C. The film was quite tough and could be flexed and creased repeatedly. The polymer had a PMT of 275° and was soluble in dimethylformamide. The inherent viscosity was 0.60 in this solvent.

In a similar experiment, 2.57 g. of 4,4'-biphenylene diisocyanate in 20 ml. of dimethyl sulfoxide was reacted with 0.35 g. of hydrazine in 8 ml. of dimethyl sulfoxide at about 40°. There was an immediate exothermic reaction and a viscous solution formed which eventually became slightly grainy. The reaction mixture was scraped out of the flask and cut up in a home mixer with water. The polymer did not melt at 400°, although it did darken and show evidence of decomposition. The inherent viscosity was 1.60 in dimethyl sulfoxide.

Preparation of III from Methylene Bis(4-phenyl Isocyanate) with Hydrazine Hydrate

A mixture of 23.0 g. of methylene bis(4-phenyl isocyanate) and 100 ml. of dimethylformamide was treated with a solution of an equivalent amount of hydrazine hydrate in 50 cc. of dimethylformamide. An immediate exothermic reaction occurred, and the solution became very viscous. This solution could be cast to clear, tough film.

A wet spinning experiment was carried out using conventional wet spinning equipment and a 100-hole spinneret. The precipitant was 50% dimethylformamide/water. Spinning was satisfactory.

Reaction of Dimethoxy Biphenylene Diisocyanate with Hydrazine Hydrate

A solution of 59.6 g. of the diisocyanate in 300 ml. of dimethylformamide was treated with 10 g. of hydrazine hydrate in 50 ml. of dimethylformamide. An immediate exothermic reaction occurred and the solution became very viscous. The polymer did

not precipitate and a stable solution was obtained. A cast film was prepared and studied after exposure to ultraviolet radiation in an Atlas Fade-Ometer. The film was very strongly yellowed after 24 hr. and after 200 hr. was dark. However, the film was still coherent and strong. Before exposure, the film strips showed a PMT of 280°.

Polymer (IV) from Methylene Bis(4-phenyl Isocyanate) and Oxalyl Dihydrazide

Oxalyl dihydrazide (1.18 g.) was dissolved in dimethyl sulfoxide (25 ml.) by heating to about 100°. This solution was added to a solution of methylene bis(4-phenyl isocyanate) (2.50 g.) in dimethyl sulfoxide (15 ml.). The mixture became quite viscous and was cast on a glass plate and dried in a forced-draft oven at 100°C. The film was clear and very tough. It exhibited a PMT of about 270° and could be stretched 2.5 times over a hot surface. The drawn samples showed a slight degree of orientation, but no crystallinity. Strong birefringence was observed under the polarizing microscope which disappeared at about 260°C. The viscosity was 0.43 in dimethylformamide.

A film sample rapidly turned bright yellow on exposure to light in an Atlas Fade-Ometer. After 30 hr., the film was completely decomposed.

Oxalyl Dihydrazide and Toluene-2,4-diisocyanate

Polymerization was carried out as reported in the above experiment using 1.18 g. (0.01 mole) oxalyl dihydrazide, 40 ml. dimethyl sulfoxide, and 1.74 g. (0.01 mole) toluene-2,4-diisocyanate. The solution was stirred at room temperature for 2 hr. without becoming viscous. A clear but weak film could be cast from the solution. The remaining portion was precipitated in 200 ml. water, the solid polymer was washed with water and methanol, then was dried. The yield was 2.6 g. with a PMT of 290° and $\eta_i = 0.28$ in dimethyl sulfoxide.

Oxalyl Dihydrazide and 3,3'-Dimethyl Biphenylene Biphenylene Diisocyanate

Polymerization was carried out as reported in the above experiments using 1.18 g. (0.01 mole) of oxalyl dihydrazide, 50 ml. of dimethyl sulfoxide, and 2.64 g. (0.01 mole) sublimed 3,3'-dimethyl biphenylene diisocyanate. The reaction mixture was stirred at room temperature for 1 hr. After this period, an opaque and weak film was cast from the solution, the remaining portion was precipitated in 300 ml. water, and was worked up as in previous experiments. The yield was 3.1 g. (81%) with a

PMT of 300° (dec.). Both the air-dried and oven-dried (100°, 18 hr.) samples were insoluble in cold or hot dimethyl sulfoxide.

Reaction of Oxalyl Dihydrazide with Hexamethylene Diisocyanate

A solution of 2.36 g. of oxalyl dihydrazide in 50 ml. of dimethyl sulfoxide at about 100°C. was added to 3.36 g. of the diisocyanate in an Erlenmeyer flask. The solution became moderately viscous after 3 to 4 hr. at 60°C. After standing for 60 hr. at room temperature, the relatively dilute solution could be cast to film which was clear and tough but very water sensitive. The polymer was soluble in formic acid and dimethyl sulfoxide. The inherent viscosity was 0.37 in dimethyl sulfoxide. The yield was 4.3 g. and the PMT was 216°C.

Preparation of (V) from Isophthaloyl Dihydrazide and Methylene Bis(4-phenyl Isocyanate)

To a solution of 1.94 g. (0.01 mole) isophthaloyl dihydrazide in 50 ml. dimethyl sulfoxide was added at room temperature 2.50 g. (0.01 mole) methylene bis(4-phenyl isocyanate). The reaction mixture warmed up slightly and became viscous immediately. Stirring at room temperature under nitrogen was continued for 2 hr. The polymer was isolated by pouring the solution into 300 ml. of water, and was washed twice with water. One portion of the solid was dried in air (η_i in dimethyl sulfoxide 1.84), one in a vacuum oven at 100° for 15 hr. (η_i in dimethyl sulfoxide 1.18). Yield: 3.5 g. (78%); PMT: 250°C. The polymer was soluble in cold *N*-methyl pyrrolidone, sulfuric acid, dimethyl sulfoxide, and dimethylformamide and in hot hexamethylphosphoramide.

A 20% solution in dimethyl sulfoxide was prepared from the oven-dried sample and a tough, clear film was cast. After drying the film for 1/2 hr. at 100° in a forced-draft oven, it dissolved easily in dimethyl sulfoxide.

Anal. calc'd. for $(C_{23}H_{26}N_6O_4)_x$: N, 18.9. Found: N, 17.9, 17.6.

A viscous solution was prepared by dissolving 39 g. of polymer in 150 ml. dimethylformamide. This solution was dry-spun easily. Properties of the yarn are shown in Table I.

Isophthaloyl Dihydrazide and Toluene-2,4-diisocyanate

Polymerization was carried out as reported in the above experiment using 1.94 g. (0.01 mole) iso-

phthaloyl dihydrazide, 1.74 g. (0.01 mole) tolylene-2,4-diisocyanate, and 40 ml. dimethyl sulfoxide. On addition of the diisocyanate the solution became viscous. It was stirred at room temperature under nitrogen for 2 hr. and the polymer was isolated and dried as reported above. Yield: 3.6 g. (100%); PMT: 230°; η_i in dimethyl sulfoxide of air-dried sample: 0.41; of oven-dried sample: 0.30.

Preparation of VI from Isophthaloyl Dihydrazide and 3,3'-Dimethoxy-4,4'-benzidine Diisocyanate

To a solution of 1.94 g. isophthaloyl dihydrazide in 50 ml. dimethyl sulfoxide was added 2.96 g. of 3,3'-dimethoxy-4,4'-biphenylene diisocyanate. The resulting suspension was warmed on the steam bath for a few minutes to dissolve all of the diisocyanate. A clear, viscous solution resulted which did not change in consistency overnight. The polymer was isolated by pouring the solution into water. The solid was washed with water and dried in air. A 20% solution in dimethyl sulfoxide was prepared from the solid polymer and cast to a clear but brittle film.

Yield of polymer 5 g.; PMT: 230°; $\eta_i = 0.51$ (dimethyl sulfoxide).

Anal. calc'd. for $(C_{24}H_{22}N_6O_6)_x$: N, 17.1. Found: N, 16.19, 16.28.

Isophthaloyl Dihydrazide and 3,3'-Dimethyl-4,4'-biphenylene Diisocyanate

To a solution of 1.94 g. isophthaloyl dihydrazide in 50 ml. dimethyl sulfoxide was added at room temperature with stirring under nitrogen 2.64 g. of the diisocyanate. The solution warmed up and became viscous almost immediately. It was stirred for 1 hr., then a film was cast from the solution. The film was dried at 100° in a forced-draft oven for 1 hr. and soaked in water overnight to remove residual solvent. It was clear and tough but insoluble in dimethyl sulfoxide.

The remaining portion of the solution was precipitated in water. The polymer was worked up as in previous experiments. Yield: 3.8 g.; PMT: 260°; η_i air-dried sample: 1.32 (dimethyl sulfoxide).

Anal. calc'd. for $(C_{24}H_{22}N_6O_4)_x$: N, 18.3. Found: N, 16.97, 17.10.

This polymer dissolved at room temperature in dimethyl sulfoxide to about 28% by weight to give a very viscous solution. This solution became almost water-thin on warming to 85–90°C.

Isophthaloyl Dihydrazide and Hexamethylene Diisocyanate

Polymerization was carried out as in the above experiment using 1.94 g. isophthaloyl dihydrazide, 1.64 g. of the diisocyanate, and 50 ml. dimethyl sulfoxide. The reaction mixture was stirred for 18 hr., but the viscosity of the solution did not increase appreciably. Polymer was isolated as usual. Yield: 3.2 g.; PMT: 220°; η_i (dimethyl sulfoxide) 0.19 (sample was dried in air).

Anal. calc'd. for $(C_{18}H_{24}N_6O_4)_x$: N, 23.4. Found: N, 22.2, 22.7, 22.9.

Terephthaloyl Dihydrazide and Methylene Bis(4-phenyl Isocyanate)

To a suspension of 1.94 g. terephthaloyl dihydrazide in 50 ml. dimethyl sulfoxide was added at room temperature 2.50 g. of the diisocyanate. The reaction mixture warmed up and cleared up almost completely. It was heated with stirring under nitrogen to 60° for 1 hr. to bring about complete solution and then cooled to room temperature. A clear, stable, viscous solution resulted. The polymer was isolated in the usual manner. Yield: 3.3 g.; PMT: 240°; η_i (dimethyl sulfoxide) 0.41 (for both, air-dried and oven-dried samples).

Anal. calc'd. for $(C_{23}H_{18}N_6O_4)_x$: N, 17.8. Found: N, 17.3, 16.8.

Terephthaloyl Dihydrazide and Tolylene-2,4-diisocyanate

Polymerization was first run under the usual conditions but the isolated polymer proved insoluble in dimethyl sulfoxide.

To get at least an approximate value of the inherent viscosity of the polymer, a polymerization was run at exactly 5% concentration (assuming 100% conversion) using 0.90 g. carbonyl dihydrazide, 2.50 g. methylene bis(4-phenylene isocyanate), and 68 ml. dimethyl sulfoxide. After the reaction was stirred for 1½ hr. under nitrogen at room temperature, an aliquot of 5 ml. was diluted to 50 ml. with dimethyl sulfoxide and the inherent viscosity of this solution was determined (0.33). The remaining portion of the solution was precipitated in water and worked up in the usual manner. PMT: 260° (dec.). The polymer was only slightly soluble in dimethyl sulfoxide after precipitation.

Carbonyl dihydrazide and 3,3'-Dimethyl-4,4'-biphenyl Diisocyanate

Polymerization was carried out as in the previous experiment using 0.90 g. carbonyl dihydrazide, 2.64 g. of

the diisocyanate, and 70.8 ml. dimethyl sulfoxide (to give a 5% concentration). On addition of the diisocyanate, the solution became very viscous and at the end of 1½ hr. reaction time it was almost gel-like. The η_i of an aliquot was 1.46. The polymer was isolated as usual, PMT: 280°. It was slightly soluble in dimethyl sulfoxide.

Preparation of (X) by the Reaction of Isophthaloyl Dihydrazide and *p*-Tolyl Isocyanate

To a solution of 3.88 g. isophthaloyl dihydrazide in 80 ml. dimethyl sulfoxide was added at room temperature 5.32 g. *p*-tolyl isocyanate. An immediate exothermic reaction took place. The resulting solution was kept at room temperature for 90 min., was then heated to ca. 80° and enough water was added at this temperature to make the solution cloudy. A white, crystalline precipitate separated as the mixture cooled. It was collected and washed with ether. The crude product was recrystallized from dimethylformamide/water, washed with ether and dried in vacuo at 80°. The yield was 1.5 g., M.P. 296°.

Anal. calc'd. for $C_{24}H_{24}N_6O_4$: C, 62.6; H, 5.22; N, 18.2. Found: C, 62.53, 62.59; H, 5.27, 5.26; N, 18.39, 18.50.

The infrared spectrum was consistent with the assigned structure and showed no changes in characteristic bands after the compound was kept at 100° for 3 hr. in air.

Preparation of (VIII) by the Reaction of Oxalyl Dihydrazide and *p*-Tolyl Isocyanate

A solution of 2.36 g. oxalyl dihydrazide in 80 ml. dimethyl sulfoxide was prepared at 80°. The solution was cooled to room temperature; the dihydrazide separated as a very fine precipitate. When 5.32 g. of *p*-tolyl isocyanate was added, an exothermic reaction took place, and a clear solution resulted. It was set aside at room temperature for 1 hr. After this period it was heated to 95°; water was added at this temperature to the cloud point. A white, crystalline precipitate formed; it was collected on a filter, washed with ether and dried in vacuo. The compound was recrystallized from dimethylformamide/water, washed with ether and dried in vacuo at 80°. The compound decomposed at 310° (hot bar) without melting.

Anal. calc'd. for $C_{18}H_{20}N_6O_4$: N, 21.8. Found: N, 21.6, 21.7.

The infrared spectrum was consistent with the proposed structure and showed no changes in charac-

teristic bands after the compound was kept at 100° for 3 hr. in air.

Reaction of Oxalyl Dihydrazide and *p*-Chlorophenyl Isocyanate

This reaction was carried out exactly as reported above using 2.36 g. oxalyl dihydrazide, 80 ml. dimethyl sulfoxide, and 6.12 g. *p*-tolyl isocyanate. M.P.: 330° (dec.).

Anal. calc'd. for $C_{16}H_{14}N_6O_4Cl_2$: C, 45.1; H, 3.3; N, 19.7; Cl, 16.7. Found: C, 44.8, 44.9; H, 3.95, 4.00; N, 19.7, 19.8; Cl, 16.7, 16.5.

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Synopsis

Diisocyanates condense readily with hydrazine or hydrazine hydrate to give polyureylenes with the structure:



Similarly, dihydrazides ($NH_2NH-COR'/CONHNH_2$) condense with diisocyanates to give polymers with the structure:



Tough films and fibers can be prepared from these polymers by conventional techniques. Solutions of some of these polymers are relatively unstable at elevated temperatures, the polymer apparently reverting to starting materials. Attempts to stabilize the solutions were unsuccessful.

Résumé

Les diisocyanates condensant facilement avec l'hydrazine et l'hydrate d'hydrazine pour former des polyuréylènes avec la structure



De façon semblable, les dihydrazides ($NH_2NH-COR'-CONHNH_2$) condensent avec les diisocyanates pour former les polymères de structure



On peut en obtenir par les techniques habituelles de films durs et des fibres. Les solutions de certains de ces polymères sont relativement instables à température élevée, les polymères retournant apparemment au matériel de départ. Des essais de stabilisation de ces solutions ont été vanis.

Zusammenfassung

Dissocyanate kondensieren leicht mit Hydrazin oder Hydrazinhydrat unter Bildung von Polymeren mit der Struktur:



In ähnlicher Weise kondensieren Dihydrazide (NH_2NH-

$COR'CONHNH_2$) mit Diisocyanaten unter Bildung von Polymeren mit der Struktur



Aus diesen Polymeren können durch konventionelle Methoden zähe Filme und Fasern dargestellt werden. Die Lösungen einiger dieser Polymerer sind bei höheren Temperaturen verhältnismässig instabil, wobei offenbar die Ausgangsmaterialien aus den Polymeren rückgebildet werden. Versuche, die Lösungen zu stabilisieren, blieben ohne Erfolg.

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