

Condensation Polymers from Diisocyanates and Dioximes

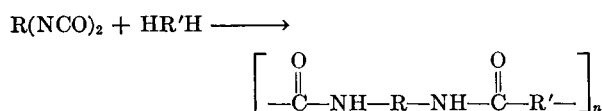
TOD W. CAMPBELL, VERONIKA S. FOLDI, and ROBERT G. PARRISH

*Pioneering Research Division, Textile Fibers Department, E. I. du Pont de Nemours & Company, Inc.,
Wilmington, Delaware*

The isocyanate group reacts quantitatively with a wide variety of active hydrogen compounds to give condensation products with the general structure shown in the equation:



If a diisocyanate and a symmetrical compound with two active hydrogen atoms is used, these reactions can at least theoretically lead to high polymers:



A number of such systems has been successfully exploited. Thus, simple glycols and diisocyanates have given polyurethanes.¹ Similarly, hydroxyl-terminated polyesters and polyethers have given segmented copolymers² with rubber-like properties. Reaction of certain diamines with diisocyanates has given polyureas,^{1c,3} while a combination of a host of other active hydrogen compounds with isocyanates has been suggested or described in the literature.⁴ The properties of such polymers as have been reported have ordinarily been outside of the range of usefulness for films or fibers. Thus, they are described as low molecular weight friable solids of limited solubility and thermal stability. It is the purpose of this communication to describe some condensation polymers made from diisocyanates and dioximes, which have high molecular weight and can be fabricated to tough films and fibers.

REACTION OF ISOCYANATES WITH OXIMES

There appears to be very little literature on the reaction of isocyanates with oximes. Thus, Goldschmidt⁵ reported that phenyl isocyanate reacted exothermically when mixed with benzaldoxime in

benzene solution. Evaporation of the solvent left a white mass of *O*-carbanilidobenzaldoxime ($\text{C}_6\text{H}_5\text{-NHCO}_2\text{N}=\text{CHC}_6\text{H}_5$). This substance was obtained as a crystalline product in unspecified yield. It decomposed vigorously at or above its melting point (135°) evolving carbon dioxide, and leaving a residue of diphenylurea and benzonitrile. Similar results were noted with other aldoximes. With ketoximes, the addition products reverted at the melting point to the oxime and the isocyanate. Petersen⁴ has studied diisocyanates with monoximes, and noted similar results. Hydroxylamine itself also reacts with phenyl isocyanate, preferentially at the amino group,⁶⁻⁸ then at the hydroxyl.

It would thus appear that oximes react predictably with isocyanates, and that the reaction of equimolar amounts of diisocyanate with a dioxime should lead to a linear high polymer.

POLYMERS FROM DIISOCYANATES AND DIOXIMES

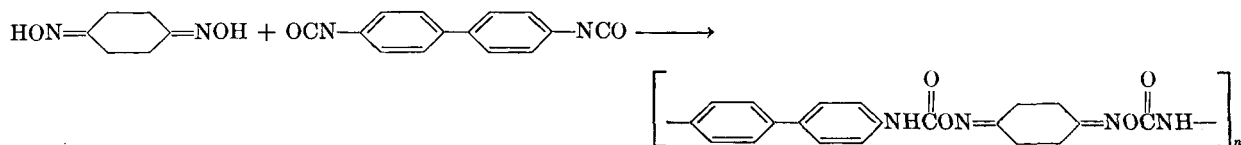
Four symmetrical dioximes, 1,4-cyclohexanedione dioxime, dimethylglyoxime, terephthaldehyde dioxime, and 2,6-pyridine dialdoxime have been polymerized with a variety of diisocyanates.

The usual method of polymerization consisted in mixing dimethyl sulfoxide solutions of the diisocyanate and the dioxime, and heating the resulting solution under nitrogen to $80\text{-}100^\circ$ for about 2 hr. The polymers were isolated by pouring the reaction mixture into water.

Of the three catalysts tried, triethylamine proved to be the most effective and general one. Copper dichloride which was reported to be an effective catalyst for reactions of isocyanates with alcohols⁹ was used successfully in the preparation of polymer from hexamethylene diisocyanate and dimethylglyoxime. Cobalt naphthenate, which is effective in catalyzing reactions of isocyanates with some active hydrogen-containing substances,¹⁰ did not act as a catalyst in the above system.

Most of the polymers obtained were of low molecular weight, gave only brittle films, and charred or decomposed at their melting points. The two exceptions were polymer from 4,4'-biphenylene diisocyanate and cyclohexanedione dioxime, and polymer from dimethylglyoxime and hexamethylene diisocyanate.

4,4'-Biphenylene diisocyanate reacted readily with cyclohexanedione dioxime when solutions of the reactants were mixed at 80–100°C.:



The dry polymer was easily soluble in dimethyl sulfoxide and had inherent viscosities of 0.81 to 1.26 in this solvent. This viscous polymer solution could be cast to clear, tough film, or wet-spun by extrusion into 50% aqueous dimethylformamide to give tough fibers.

The thermal and hydrolytic stability of the cast films was poor, e.g., a sample was completely destroyed in a few seconds at 225° in a Carver press, while samples of film decomposed rapidly in boiling alkali, acid, or water.

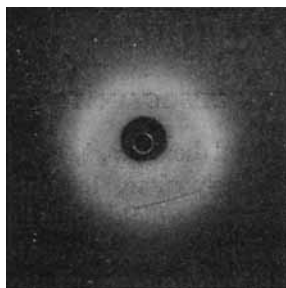
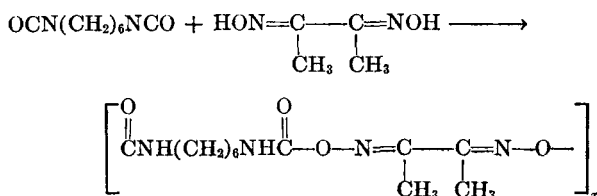


Fig. 1. X-ray fiber diagram of polymer from hexamethylene diisocyanate and dimethylglyoxime. Fiber stretched 600% at 125°C.

The reaction of dimethylglyoxime and hexamethylene diisocyanate was best carried out in dimethyl sulfoxide with triethylamine or copper chloride as catalyst. The resulting polymer



had inherent viscosities of 0.9 to 1.1 in dimethyl sulfoxide, and a polymer melt temperature of 160°. Tough, clear film was cast from the polymerization solutions. They were also wet-spun into aqueous 50% ethylene glycol to give fairly tough fibers. Both film and fiber could be stretched over a hot surface. The drawn and undrawn samples were amorphous, but the stretched yarn had a very high orientation (Fig. 1).

EXPERIMENTAL

(All melting points determined on Kofler Hot Stage with polarizing microscope.)

Cyclohexanedione Dioxime

A mixture of 39 g. of cyclohexanedione, 50 g. of hydroxylamine hydrochloride, 200 ml. of pyridine, and 200 ml. of absolute alcohol was refluxed for 4 hr. The resulting homogeneous solution was poured into a crystallizing dish and the solvents allowed to evaporate in a stream of air. Four hundred milliliters of water was added and the slightly greenish solid was filtered. It was recrystallized from 90% ethanol giving a pure white crystalline solid melting at 201–202°. (Piloty and Steinbock¹¹ give 188°.) We noted a phase transformation, but no melting in this range.

Anal. calc'd. for $\text{C}_6\text{H}_{10}\text{O}_2\text{N}_2$: N, 19.7. Found: N, 19.7, 19.9.

Terephthalaldehyde Dioxime

A mixture of 25 g. of terephthalaldehyde, 29 g. of hydroxylamine hydrochloride, 150 ml. of pyridine, and 150 ml. of absolute alcohol was refluxed for 4 hr. then evaporated in a crystallizing dish. The next day the mixture was treated with water and the solid was filtered and recrystallized from absolute alcohol two times. The colorless crystalline product had a crystalline melting point of 226°. (Westenberger¹² reports a melting point of 200°, and Rosenmund¹³ gives a value of 198°C.)

Anal. calc'd. for $\text{C}_8\text{H}_6\text{O}_2\text{N}_2$: N, 16.4. Found: N, 16.6, 16.4.

Polymer from 1,4-Cyclohexanedione Dioxime and Biphenylene Diisocyanate

A solution of 2.93 g. of biphenylene diisocyanate in 15 ml. of dimethylformamide was mixed with 1.76 g. of cyclohexanedione dioxime in 10 ml. of dimethylformamide at about 80–100°C. An immediate reaction was noted and the solution rapidly became viscous. After approximately 1/2 hr., the solution, which had become somewhat cloudy, was poured into water and the polymer was isolated by filtration. It was ground up, washed thoroughly with water, and dried in a high vacuum. The yield was 4.35 g. The infrared spectrum was consistent with the proposed structure of the polymer.

Anal. calc'd. for $(C_{20}H_{18}O_4N_4)_n$: N, 14.8. Found: N, 14.4, 14.4.

The dry polymer was easily soluble in dimethyl sulfoxide. It had an inherent viscosity of 0.81 in this solvent and could be cast to clear, tough film. In other preparations, inherent viscosities as high as 1.26 were obtained. A solution of polymer prepared as above was extruded from a mechanically driven syringe into 50% aqueous dimethylformamide contained in a long steel trough. Fiber was wound up easily on a mechanical windup. The yarn was amorphous, but was fairly tough after stretching.

Thermal and Hydrolytic Stability

Small samples of cast film were boiled with 10% sodium hydroxide, 10% sulfuric acid, and water. The sodium hydroxide treated film was nearly completely dissolved after 30 min. The sulfuric acid treated film was black and too brittle to handle after 30 min. The film treated with boiling water showed very little change during the first hour. However, after 2 hr. it had darkened and was too brittle to handle. The film was completely destroyed in a few seconds at 225° in a Carver press.

Polymer from Cyclohexanedione Dioxime and Methylene Bis(4-Phenyl Isocyanate)

To a solution of 2.13 g. (0.015 mole) cyclohexanedione dioxime in 15 ml. of dimethyl sulfoxide was added 3.75 g. of diisocyanate in 15 ml. of dimethyl sulfoxide followed by 2 ml. triethylamine. The resulting solution was heated with stirring under nitrogen to 100° for about 2 hr. After this period, a clear, coherent film was cast from the solution. The solid polymer was isolated and worked up as previously. The yield was 5.2 g. (88%) of a light

tan powder, PMT,*¹⁴ = 210°, η_i = 0.08 (dimethylformamide).

Anal. calc'd. for $(C_{21}H_{18}N_4O_4)_n$: N, 14.1. Found: N, 13.85, 13.83.

Polymer from 1,4-Cyclohexanedione Dioxime and 3,3'-Dimethoxy-4,4'-Biphenylene Diisocyanate

To a solution of 2.13 g. (0.015 mole) of cyclohexanedione dioxime in 15 ml. of dimethyl sulfoxide was added a solution of 4.44 g. (0.015 mole) 3,3'-dimethoxy-4,4'-biphenylene diisocyanate in 15 ml. of dimethyl sulfoxide, followed by 2 ml. of triethylamine. The resulting solution was heated with stirring under nitrogen to 110°; in about 20 min. the solution turned cloudy. After one and a half hours heating, the polymer was isolated as previously. The yield was 5.5 g. (84%) of a light brown solid, with PMT of 220° with charring.

Anal. calc'd. for $(C_{22}H_{22}N_4O_6)_n$: N, 12.8. Found: N, 12.06, 12.15.

Polymer from 1,4-Cyclohexanedione Dioxime and Hexamethylene Diisocyanate

To a solution of 5.04 g. (0.03 mole) hexamethylene diisocyanate in 25 ml. of dimethyl sulfoxide was added with stirring 4.26 g. (0.03 mole) cyclohexanedione dioxime dissolved in 25 ml. of dimethyl sulfoxide. The resulting clear, colorless solution was stirred at 100–120°. After 10–15 min., the solution became somewhat viscous and cloudy. Stirring and heating were continued for 1 1/2 hr., the suspension was then poured into 300 ml. water. A filterable precipitate settled out overnight, it was washed twice with water in a home mixer and dried in a vacuum oven at 110°. Yield: 7.0 g. (75%) of a light tan powder, with PMT of 240° (with charring).

Anal. calc'd. for $(C_{14}H_{22}N_4O_4)_z$: N, 18.0. Found: N, 17.98, 17.91.

Polymer from Terephthalaldehyde Dioxime and Hexamethylene Diisocyanate

To a solution of 1.64 g. (0.01 mole) terephthalaldehyde dioxime in 7 ml. of dimethyl sulfoxide was added with stirring 1.68 g. (0.01 mole) hexamethylene diisocyanate in 8 ml. of dimethyl sulfoxide. The resulting solution was heated with stirring under nitrogen at 120° for 2 1/2 hr. The solution turned cloudy on cooling; the suspended polymer could not be dissolved on reheating the suspension

* PMT = polymer melt temperature.

to 120°. The product was isolated and worked up as in the above experiments. Yield: 1.5 g. (45%), PMT: 110°.

Polymer from Terephthalaldehyde Dioxime and Methylene Bis(4-Phenyl Isocyanate)

To a solution of 1.64 g. (0.01 mole) terephthalaldehyde dioxime in 10 ml. of dimethyl sulfoxide was added 2.5 g. (0.01 mole) methylene bis(4-phenyl isocyanate) dissolved in 10 ml. of dimethyl sulfoxide and 1 ml. triethylamine. The resulting solution was heated at 110° with stirring and under nitrogen for 2 hr. After this period, a coherent but very brittle film was cast from the solution. The solid polymer was isolated and worked up as previously. Yield: 3.1 g. (75%) of a yellow solid. PMT: 170°, $\eta_i = 0.15$ (dimethylformamide).

Anal. calc'd. for $(C_{23}H_{18}N_4O)_x$: N, 13.5. Found: N, 13.64, 13.59.

Polymer from Pyridine-2,6-dialdoxime and Methylene Bis(4-Phenyl Isocyanate)

In a 3-necked flask equipped with a stirrer and outlet tube and a nitrogen inlet was placed 8.25 g. of pyridine-2,6-dialdoxime (Aldrich Chemical Company) followed by 50 ml. of dimethyl sulfoxide. A solution of 12.5 of methylene bis(4-phenyl isocyanate) in 50 ml. of dimethyl sulfoxide was then added with stirring. However no reaction occurred. One cubic centimeter of triethylamine was added and the solution became viscous. After 24 hr., the solution was poured into water and the solid polymer was filtered, washed, and dried. It was soluble in cold dimethyl sulfoxide and in cold *N*-methylpyrrolidone. It had inherent viscosity of 0.12 in *N*-methylpyrrolidone and a PMT above 320°C., with discoloration at about 260°C.

Polymer from Dimethylglyoxime and Hexamethylene Diisocyanate

To a solution of 5.80 g. (0.05 mole) of dimethylglyoxime in 30 ml. of dimethyl sulfoxide was added a solution of 8.40 g. (0.05 mole) hexamethylene diisocyanate in 30 ml. of dimethyl sulfoxide followed by 0.5 ml. of triethylamine. The resulting clear solution was heated under nitrogen with stirring at 80–90° for 1½ hr. After this period, a clear, tough, film was cast from one portion of the solution and dried in a forced draft oven at 80° for 1½ hr. Another portion of the solution was manually wet-spun into a 50/50 water-ethylene glycol precipitating bath, while the remaining por-

tion was precipitated in water, washed three times with water in a home mixer, and dried in a vacuum oven at 80° overnight. This sample had an inherent viscosity of 0.88 in dimethyl sulfoxide, and a polymer melt temperature of 160°.

The film was soaked in 100 ml. of water for 6 hr., it turned opaque but on drying in air became clear again. Thin strips of this film was drawn 3× at 90° on a hot surface. Both the drawn and undrawn films were amorphous and showed no orientation when submitted to x-ray analysis.

The wet spun yarn was extracted in water, dried in air, and was drawn 6× on a hot surface at 125°. The drawn yarn was amorphous and had very high orientation as determined by x-ray (see Fig. 1).

In another experiment 1.16 g. dimethylglyoxime was dissolved in 15 ml. of dimethyl sulfoxide and 1.68 g. of hexamethylene diisocyanate was added followed by two drops of triethylamine. An immediate exothermic reaction took place, the solution became increasingly viscous and turned to a gel in 20 min. A sample of the gel was dissolved in additional hot dimethyl sulfoxide. The remaining portion of the gel was worked up in water, washed with water and methanol, and dried in air. This product had an inherent viscosity of 0.98 (dimethyl sulfoxide).

A similar experiment was carried out using about 0.05 g. of cupric chloride as catalyst. A viscous solution resulted which was stable for 2 hr.; however, after this period, solid particles started to separate out. At this point the polymerization solution was precipitated in water and the polymer worked up as above. This product had an inherent viscosity of 1.10 (in dimethyl sulfoxide).

Polymerization at room temperature in the absence of a catalyst was unsuccessful.

Polymer from Dimethylglyoxime and Methylene Bis(4-Phenyl Isocyanate)

To a solution of 2.90 g. (0.05 mole) dimethylglyoxime in 25 ml. of dimethyl sulfoxide was added 6.25 g. (0.025 mole) methylene bis(4-phenyl isocyanate) in 25 ml. of dimethyl sulfoxide followed by 2 ml. of triethylamine. Immediately on addition of the amine, the solution turned viscous. The solution was heated with stirring under nitrogen at 110° for 1 hr.; after this period, a clear, coherent film was cast. The solid polymer was isolated and worked up as previously. The yield was 8.1 g. (88%) of a light tan powder with PMT of 190°.

Polymer from Dimethylglyoxime and 3,3'-Dimethoxy-4,4'-Biphenylene Diisocyanate

To a solution of 2.90 g. (0.025 mole) of dimethylglyoxime in 25 ml. of dimethyl sulfoxide was added a solution of 7.40 g. of 3,3'-dimethoxy-4,4'-biphenylene diisocyanate in 30 ml. of dimethyl sulfoxide followed by 2 ml. triethylamine. On addition of the amine, the solution turned very cloudy and the suspension did not clear up on heating to 110° with stirring under nitrogen. After 1½ hr. heating, the suspension was poured into 200 ml. water and a solid separated which was worked up as previously, yield: 7.7 g. (75%) of a light tan substance that turned dark brown on standing in air. It decomposed at about 260° without melting.

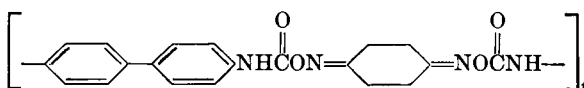
Anal. calc'd. for $(C_{20}H_{20}N_4O_6)_x$: N, 13.5. Found: N, 12.86, 12.85.

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Synopsis

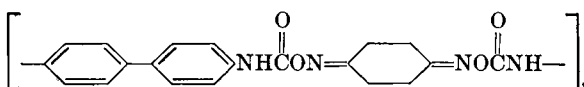
Diisocyanates condense readily with the two active hydrogen atoms in dioximes to give high molecular weight linear condensation polymers. In several cases these polymers, such as the one from cyclohexanedione dioxime and 4,4'-biphenylene diisocyanate,



may be converted to tough films or fibers. Thermal, hydrolytic, and light stability of these polymers were in general poor.

Résumé

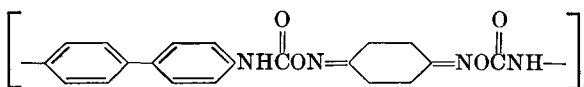
Les diisocyanates condensent facilement avec les deux atomes d'hydrogène actifs des dioximes et forment des polycondensats linéaires de haut poids moléculaire. Dans pe nombreux cas ces polymères, tels celui de la dioxime de la cyclohexanedione et du 4,4'-diisocyanate de biphenylène



peuvent être transformées en films durs ou fibres. En général la stabilité thermique, hydrolytique et la stabilité à la lumière étaient faibles.

Zusammenfassung

Diisocyanate können leicht mit den beiden aktiven Wasserstoffatomen von Dioximen unter Bildung hochmolekularer linearer Kondensationspolymerer kondensiert werden. In einigen Fällen können diese Polymeren, wie z.B. das aus Cyclohexandiondioxim und 4,4'-Biphenylendiisocyanat,



zu zähen Filmen oder Fasern verarbeitet werden. Im allgemeinen war die thermische und hydrolytische Beständigkeit sowie die Lichtbeständigkeit dieser Polymeren nur gering.

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