

Polyurethane Analog of the Polyester, Polyethylene Terephthalate*

EMERSON L. WITTBECKER,† WILLIAM S. SPLIETHOFF,‡
and C. R. STINE,§ *Textile Fibers Department, Pioneering Research
Division, E. I. du Pont de Nemours & Company, Inc.,
Wilmington, Delaware*

Synopsis

Polyethylene piperazine-1,4-dicarboxylate, a polyurethane which structurally resembles the polyester, polyethylene terephthalate, was prepared by interfacial polymerization, and the properties of the two polymers, as well as the alternating copolymer of the two structures, are compared. Information on the molecular weight and molecular weight distribution of the polyurethane is presented, and a mechanism for the thermal decomposition observed is proposed. A series of copolymers of polyethylene piperazine-1,4-dicarboxylate with high melting polyamides was prepared by reacting piperazine with mixtures of ethylene bischloroformate with adipoyl, terephthaloyl, and bibenzoyl chlorides and data on crystalline melting points, solubility, and water absorption are given. It is concluded that the adipamide and terephthalamide copolymers with the polyethylene piperazine-1,4-dicarboxylate exhibited isomorphism.

INTRODUCTION

Polyurethanes as a class of condensation polymers have been known^{1,2} for over twenty years, but they have not reached the prominence of polyamides and polyesters to which they are structurally related. Of the different methods reported for their preparation, the diisocyanate-glycol reaction, as a solution polymerization in *o*-dichlorobenzene yielding a dispersed product or as a melt polymerization³, is most useful. The reaction of a diamine with the bischloroformate of a glycol in an aqueous emulsion is in an advanced laboratory stage² but is said to yield polymers with a broader molecular weight distribution than obtained from diisocyanates and glycols. In either case, polymers melting above about 200°C. are found to undergo decomposition and gelation, severely limiting the number of polymers that could be prepared by melt polymerization or processed by melt methods. At least one polyurethane from hexamethylene diisocyanate and tetramethylene glycol has been evaluated for commercial

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† Present address: E. I. du Pont de Nemours & Company, Waynesboro, Virginia.

‡ Present address: General Mills, Inc., Kankakee, Illinois.

§ Present address: E. I. du Pont de Nemours & Company, Martinsville, Virginia.

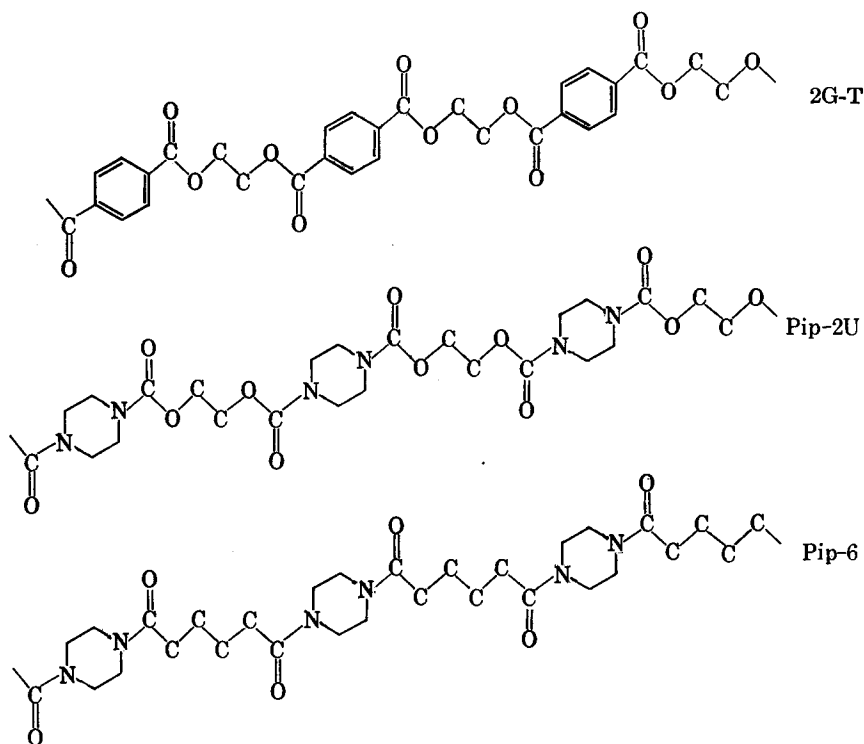


Fig. 1. Structure of 2G-T, Pip-2U, Pip-6.

utility in filaments and plastics. When compared to some polyamides, it had better retention of properties when wet, greater stability to light, and better electrical properties.

An entirely different polyurethane structure, polyethylene piperazine-1,4-dicarboxylate (Pip-2U), was selected for this investigation because of its structural resemblance to the commercially important polyester, polyethylene terephthalate (2G-T) (see Fig. 1). Since there are no hydrogen atoms on the urethane linkages to give the strong intermolecular forces normally associated with polyamides and polyurethanes, a high melting point will depend on the piperazine ring reducing chain flexibility and giving a low entropy of fusion. This was known to be the case for a polyamide from piperazine and adipic acid (Pip-6, T_m 355°C.) which also resembles Pip-2U.

DISCUSSION OF RESULTS

Synthesis of Polyethylene Piperazine-1,4-Dicarboxylate (Pip-2U)

The diisocyanate-glycol reaction is not possible with secondary diamines, so it was necessary to use another polymerization method capable of giving high molecular weight Pip-2U. Since this polymer is a polyester of a

biscarbamic acid, an alcoholysis similar to that used for polyesters was tried first. However, melt polymerization of diethyl piperazine-1,4-dicarboxylate with ethylene glycol with the use of catalysts such as litharge or zinc borate showed the carbamate ester to be very unreactive. *N,N*-Disubstituted carbamates have been reported⁴ to be uniformly very stable to reaction with alcohols in the presence of acid catalysts.

A low temperature interfacial polycondensation has been shown⁵ to be a versatile method for the preparation of polyurethanes, and the polymerization of piperazine and ethylene bischloroformate readily yielded high molecular weight Pip-2U. The alternating polyurethane ester (Pip-2U-2G-T) was prepared similarly from the bischloroformate of bis(2-hydroxyethyl) terephthalate, where the ester linkages were preformed prior to the urethane polymerization. Structures of this type, where the repeat unit of two polymers alternate regularly along the macromolecular chain, are readily made because of the mild reaction conditions of interfacial polycondensation.

Molecular Weight and Molecular Weight Distribution

While weight-average to number-average molecular weight ratios (\bar{M}_w/\bar{M}_n) greater than the normal 2/1 equilibrium distribution of melt polycondensation have been obtained occasionally by the irreversible interfacial method (as reported² earlier), appreciably more homogeneous molecular weight distributions (with \bar{M}_w/\bar{M}_n below 2/1) were achieved when pure intermediates were reacted under proper conditions. Data obtained from ultracentrifuge sedimentation velocity experiments were used to characterize Pip-2U samples prepared in various ways. One important factor affecting molecular weight and molecular weight distribution was the polymer solubility limit in the organic solvent used in the two phase polymerization. Chloroform, which is a solvent for the polymer, gave a broader \bar{M}_w/\bar{M}_n of 3/1, than did a nonsolvent mixture (80/20 weight) of benzene and chloroform, which gave a \bar{M}_w/\bar{M}_n of 1.35/1. The type of mixing used in the extremely rapid polymerization was also important, but for small batch preparations a home blender was found to be quite adequate for obtaining uniform polymers.

An explanation for the unusual homogeneity of some samples of Pip-2U can be obtained from the mechanism^{6,7} of the interfacial polycondensation. The initial reaction occurs at the interface, and the polymer which forms acts as a quasistatic barrier between the organic and aqueous phases. Under these conditions, the growing polymer chains are more accessible to the reactants than the reactants are to each other, and it is probable that further reaction will form high polymer from existing low polymer rather than form new low molecular weight polymer chains. When the growing polymer chains become insoluble in the organic phase, they agglomerate, precipitate, and are no longer accessible for further polymerization. The probability that a growing polymer chain will achieve a given molecular weight and then become incapable of further reaction can result in a nar-

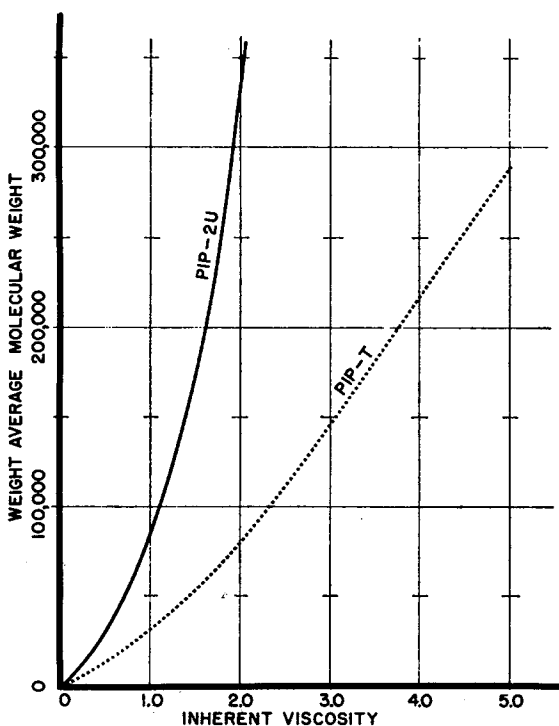


Fig. 2. Inherent viscosity (*m*-cresol) vs. molecular weight.

rower molecular weight distribution than that from a homogeneous polymerization where there is no inactivation of high polymer by precipitation. Thus when the organic phase is a solvent for the polymer, high molecular weight polymer will not become inaccessible by precipitation and a broadened distribution is favored.

In spite of the precipitation factor in interfacial polymerization, the rapid rate of reaction permits the preparation of polymers with molecular weights which are unusually high for condensation polymers. The speed can be estimated from the rate constant for the reaction of the second amine group in piperazine with ethyl chlorocarbonate in water at 20°C. (3×10^2 l./mole sec.). At 1*M* initial concentrations, 0.3 sec. would give 99% reaction. By using very pure intermediates and optimum polymerization conditions, Pip-2U with weight-average molecular weights as high as 500,000 has been prepared. A sample with an inherent viscosity of 1.5 (*m*-cresol) will have an \bar{M}_w of 200,000. Inherent viscosities as high as 4.4 have been obtained. The relationship between inherent viscosity (*m*-cresol) and weight-average molecular weight (by light scattering) is shown in Figure 2 along with that of the polyamide from piperazine and terephthaloyl chloride (Pip-T). The effect of chain flexibility on viscosity is marked with the more rigid polymer having a much higher inherent viscosity for a given \bar{M}_w .

Polymer Properties

It is significant that the clear tough films of Pip-2U had a density (1.35) close to but slightly lower than 2G-T (Table I). The crystalline melting

TABLE I
Polymer Properties

	Pip-2U	2G-T	Pip-2U-2G-T
T_m , °C.	243	265	220
T_g , °C.	60	80	53
Density, g./cc.	1.35	1.37	1.32
Solubility (CH ₂ Cl ₂)	+	—	+
Water absorption, %	12.5	1	3.5

point (T_m , 243°C.) and the glass transition temperature (T_g , 60°C.) were also lower by about 20°C. The T_m , T_g , and density of the alternating copolymer of the two, Pip-2U-2G-T, were lower than those for either of the homopolymers, perhaps because of the length of the chemical repeat unit.

The most striking differences between polyethylene terephthalate and its polyurethane analog were in solubility and water absorption. Pip-2U was soluble at room temperature in chlorinated and acidic solvents (Table II).

TABLE II
Solvents for Pip-2U

Methylene chloride	Formic acid
Chloroform	Acetic acid
1,1,2-Trichloroethane	Chloroform/methanol (88/12)
Ethylene chlorohydrin	Chloroform/formic acid (85/15)
Tetrafluoropropanol	Trichloroethane/formic acid (70/30)
<i>m</i> -Cresol	

Films soaked in water absorbed much more than 2G-T (12.5 versus 1%). The alternating copolymer exhibited solubility more like the polyurethane but absorbed considerably less water (3.5%).

Thermal Degradation of Pip-2U

Since Pip-2U has no hydrogen atoms on the urethane linkage and cannot degrade and undergo gelation by the mechanism proposed for polyurethanes from diisocyanates and glycols, it should be more stable thermally. It can be melted for the short length of time (<1 min.) necessary to press a film, but is severely degraded when held for longer periods (Table III). Since traces of ionic impurities might catalyze the decomposition and would be difficult to remove from the granular polymer by normal washing techniques, a sample was purified by deionization of a solution

TABLE III
Thermal Degradation of Pip-2U^a

Time, min.	η_{inh}
0	1.58
5	1.33
30	0.41
150	0.26

^a Heated at 255°C. in evacuated sealed tubes.

with resins. Degradation was markedly less, and the η_{inh} was still 0.94 after heating at 255°C. for 7 hr. (original η_{inh} was 1.73). Among the volatile degradation products, carbon dioxide, ethylene oxide, and acetaldehyde were identified by gas chromatography in ratio of 25-27:-1.2:1. Plotting the amount of carbon dioxide released versus time (Fig. 3) shows that the rate of degradation of the deionized sample was about one-third that of the impure polymer, indicating that the degradation reactions were catalyzed by ionic impurities. This was confirmed by treating the deionized sample with an aqueous sodium hydroxide solution and drying in vacuum at 70°C. before testing. The rate of decomposition was increased to a level about twice as high as that of the original polymer.

The mechanism of the thermal degradation of 2G-T and related compounds has been studied⁸⁻¹³ in detail and because of the structural similar-

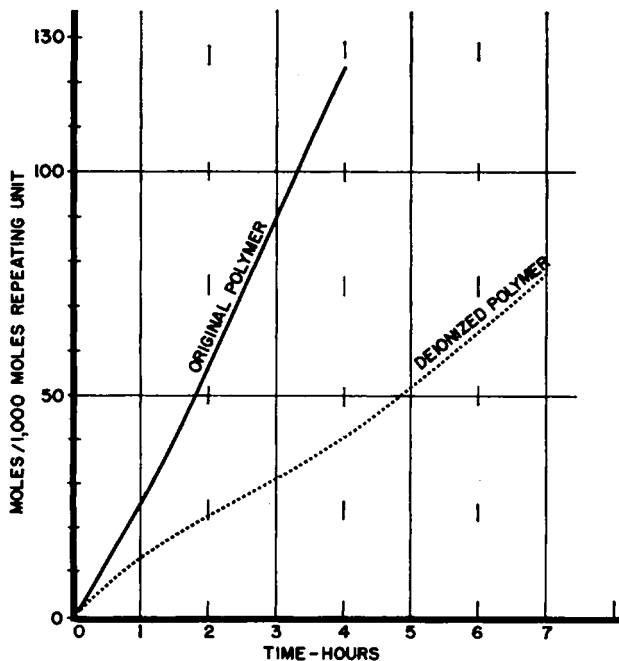


Fig. 3. Rate of formation of CO₂ from Pip-2U at 255°C.

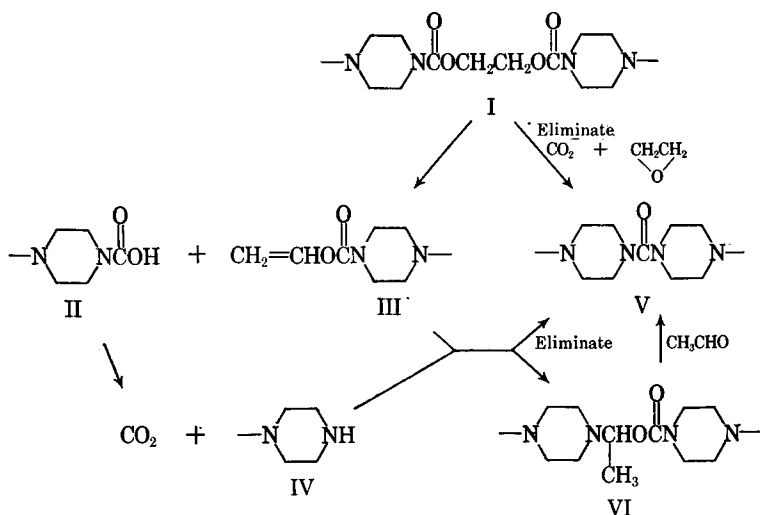


Fig. 4. Mechanism of thermal decomposition.

ity of Pip-2U, this work was relied on heavily in proposing a mechanism for the thermal degradation (Fig. 4). The major reaction which accounts for the chain scission and rapid lowering of molecular weight is a β -hydrogen elimination to yield a carbamic acid (II) and the vinyl ester of a carbamic acid (III). Because of its instability, II would immediately decompose to a secondary amine (IV) and the major volatile product, carbon dioxide. The small amount of ethylene oxide along with some additional CO_2 , might be formed through a disproportionation of the polyurethane (I) to a polyurea (V). The minor amount of acetaldehyde could be formed by direct reaction of the vinyl ester (III) with the amine (IV) to give a urea (V) or by first forming an adduct (VI) which disproportionates to (V) by eliminating acetaldehyde.

Structure Measurements by X-Ray Diffraction

X-ray diffraction patterns of oriented and crystalline samples of Pip-2U, 2G-T and the alternating copolymer of the two were obtained and the dimensions were compared (Table IV). The lateral spacings of the polymers containing urethane linkages were larger and the identity period shorter than comparable dimensions of polyethylene terephthalate, reflecting less favorable packing of the piperazine rings than the planar benzene rings.

It must be concluded from the data that Pip-2U and 2GT are not a perfect isomorphous pair. However, the identity period of the alternating copolymer is approximately one-half of the length of the chemical repeating unit, indicating that the urethane and ester segments can fit the same crystal lattice.

TABLE IV
X-Ray Data

	Pip-2U	2GT	Pip-2U-2G-T
Lateral spacings, A.	5.57	5.04	
	4.75	3.92	4.62
	3.95	3.43	3.62
Identity period, A.	10.4	10.8	9.2

Polyurethane-Polyamide Copolymers

Since Pip-2U bears an even closer structural relationship to the polyamide from piperazine and adipic acid (Pip-6), it was of interest to determine whether they were isomorphous. A series of copolymers was prepared by polymerizing piperazine with mixtures of ethylene bischloroformate with adipoyl chloride as well as with two cyclic diacid chlorides, terephthaloyl chloride and bibenzoyl chloride. Completely random copolymers were probably not obtained because of the difference in reactivity between chloroformates and acid chlorides. The degree of order developed in the copolymerization of ethylene bischloroformate and terephthaloyl chloride with 2,5-dimethylpiperazine has been postulated¹⁴ from the probable reaction mechanism. For this study, it was assumed that the amount

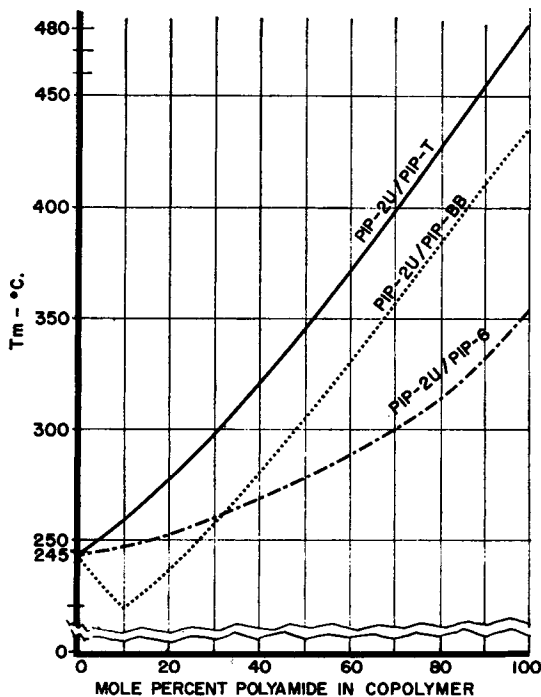


Fig. 5. Crystalline melting points of copolyurethaneamides.

TABLE V
Copolymers of Pip-2U and Their Properties

Polymer	Reactant ratio	Copolymer composition ^a	Yield, %	η_{inh}	Cryst. m.p., °C.	Water absorption, %	Relative solubility
Pip-2U	—	—	94	1.52	245 ± 5	12.5	43 ^b
Pip-2U/6	0.75/0.25	0.65/0.35	70	2.00	265 ± 5	14.0	34
Pip-2U/6	0.5/0.5	0.4/0.6	71	1.73	290 ± 10	18.9	26
Pip-2U/6	0.25/0.75	0.3/0.7	72	1.99	300 ± 5	26.4	25
Pip-6	—	—	—	2.2	355 ± 5	47.2	18
Pip-2U/T	0.8/0.2	0.65/0.35	87	1.94	310 ± 5	7.3	28
Pip-2U/T	0.5/0.5	0.43/0.57	87	1.73	365 ± 3	15.8	22
Pip-2U/T	0.25/0.75	0.25/0.75	89	1.12	415 ± 5	26.0	19
Pip-T	—	—	—	1.85	>420 ± 5	31.7	8
Pip-2U/BB	0.9/0.1	0.9/0.1	95	2.8	218 ± 5	26.3	39
Pip-2U/BB	0.5/0.5	0.43/0.57	82	1.27	320 ± 5	10.1	24
Pip-2U/BB	0.25/0.75	0.22/0.78	100	1.32	385 ± 2	11.1	21
Pip-BB	—	—	—	1.74	>425	13.9	14

^a As determined by infrared analysis.

^b The higher the number (arbitrary units), the higher the solubility.

of order obtained might reduce but not eliminate the usual copolymer effects from nonisomorphous polymers.

The crystalline melting points, solubility, and water absorption of the series of copolymers were measured. The effects of isomorphism on copolyamide properties have been explored extensively by Cramer and Beaman.¹⁵

The crystalline melting points for the Pip-2U/Pip-6 and Pip-2U/Pip-T systems are given in Table V and plotted in Figure 5. The nearly linear increase in melting point from the 245°C. of Pip-2U to 355°C. for Pip-6 and 420°C. for Pip-T is strong evidence that these copolymers exhibit isomorphism. This is not too surprising, since copolyamides from adipic and terephthalic acids have also been observed¹⁶ to be isomorphous. Pip-2U/Pip-BB copolymers, however, would not be expected to be isomorphous, and this was confirmed by the presence of a minimum in the T_m /composition plot. (Pip-BB stands for the polyamide from piperazine and bibenzoic acid.)

The amount of crystallinity in each copolymer was measured by x-ray diffraction. Determination of lateral and longitudinal order indicated that the Pip-2U/Pip-6 copolymers are isomorphous in both lateral directions as well as longitudinally. Pip-T is isomorphous with Pip-2U longitudinally and in one of the two lateral directions. The Pip-2U/Pip-BB system is not isomorphous, and there was a distinct minimum in the amount of crystallinity which was not observed in the other two systems where all of the copolymers exhibited intermediate to high crystallinity.

Solubilities of all copolymers (Table V) were lower than Pip-2U homopolymer. This was to be expected of the Pip-2U/Pip-6 and Pip-2U/Pip-T systems, but it was surprising to find no maximum in the nonisomorphous Pip-2U/Pip-BB system. A maximum has been observed in nonisomorphous copolyamides.¹⁷ This might be a result of some degree of order obtained in the interfacial polymerization.

Water absorption measurements on film (Table V) show that, in general, absorption increased with the amount of the more hydrophilic polyamide (Pip-6 or Pip-T) in the copolymer. In the Pip-2U/Pip-BB series the composition with the minimum T_m absorbed the most water. In a nonisomorphous copolyamide system, water absorption was found¹⁷ to be nearly a linear function of composition.

Fibers from Pip-2U

Pip-2U was dry-spun readily from essentially anhydrous formic acid to yield fibers with round cross sections, which did not require further extraction after leaving the dry-spinning cell. The fibers were drawable up to 6X, giving physical properties in the range of other synthetic fibers such as polyethylene terephthalate (Dacron) and nylon 66.

Fabrics from Pip-2U fibers exhibited some interesting properties. The handle was judged to be dry. Static in both fiber processing and garments was negligible. Whiteness retention after exposure to heat, base, bleaches,

ultraviolet light, and after soiling and washing, was very good. Dyeability was excellent with disperse, acid and selected vat dyes. Pip-2U fabrics had the ease-of-care (fast-drying, less wrinkling, etc.) normally associated with synthetic fibers.

EXPERIMENTAL

Intermediates

Bis(2-hydroxyethyl)terephthalate was prepared from dimethyl terephthalate (291 g., 1.5 moles) and ethylene glycol (1740 ml., 30 moles) with the use of 0.5 g. of calcium acetate as catalyst. This mixture was heated at 160–180°C. until no more methanol was evolved and was then cooled, diluted with twice its volume of acetone, and allowed to stand. The crystalline product was filtered, washed with cold water, and dried in a vacuum oven (yield 85%). After recrystallization from water, the melting point was 107–108°C.

The bischloroformate of bis(2-hydroxyethyl) terephthalate was prepared by adding a solution of 203 ml. of liquefied phosgene in 300 ml. of dioxane to a mixture of 68.6 g. (0.27 mole) of bis(2-hydroxyethyl) terephthalate and 700 ml. of dioxane in a 2-liter, three-necked flask equipped with a stirrer, Dry Ice condenser and a dropping funnel. After 1 hr. of stirring, a clear solution resulted. After 4 hr. at 40°C., the dioxane was removed by distillation under reduced pressure. The crystalline product was recrystallized from 900 ml. of cyclohexane and 150 ml. of benzene. The yield was 91.6 g. (90% of theoretical). The melting point was 101–104°C. A second recrystallization raised the melting point to 104°C. Cl analysis, calculated for $C_{14}H_{12}O^2Cl_2$ is 18.73%; found, 18.60% and 18.71%.

Ethylene bischloroformate was prepared by reported^{18–20} methods and was purified by distillation, b.p. 72°C. at 2.2 mm.

Bibenzoyl chloride was prepared as described by Beaman.²¹

Polymerization

Interfacial polymerizations were run as described⁵ in the literature. When benzene was used as the organic solvent, Pip-2U was obtained as a white, granular product. Methylene chloride and chloroform gave solutions of the polymer in the organic phase. It has also been found that high yields of high molecular weight Pip-2U can be prepared by using solvents which are miscible with water, for example, tetrahydrofuran. A typical polymerization is described.

A solution of 0.05 mole of ethylene bischloroformate in 30 ml. of tetrahydrofuran was added rapidly to a solution of 0.05 mole of piperazine and 0.1 mole of sodium carbonate in 100 ml. of water while agitating in a home blender. The polymer was isolated in a white granular form, yield 93%, η_{inh} , 1.12.

Polymer Characterization

In general, the polymers prepared were characterized by the scheme proposed by Beaman and Cramer.¹⁷ The polymeric nature of each polymer was determined in terms of inherent viscosity ($\eta_{inh} = [\ln\eta_{rel}]/C$) in *m*-cresol at a concentration of 0.5 g./100 ml. at 30.0°C. Films were obtained by either melt-pressing or solvent casting solutions of the white granular polymers.

Crystalline melting points were determined by standard techniques. Below 350°C. a hot stage (Kofler) polarizing microscope was used. The x-ray hot camera technique was used for melting points above 350°C. Differential thermal analysis was also useful in cases where decomposition occurred at the high temperatures needed for melting.

Solubilities of all copolymers were determined in twelve different solvents using the scheme described¹⁷ for characterizing isomorphous copolyamides.

Water absorption measurements were made by soaking films in water until constant weight was obtained and then drying in a vacuum oven to get the dry weight of the films. Values obtained are not always highly accurate, since the degree of crystallinity (which can change during the measurement) affects the amount of water absorbed.

Ultracentrifuge sedimentation velocity experiments were run using solutions of Pip-2U in glacial acetic acid in the Spinco Model E velocity ultracentrifuge (Specialized Instruments Corporation).

We are indebted to W. O. Statton for interpretation of x-ray diffraction patterns and Louise H. Jones for the calculation of molecular weight distributions from the ultracentrifuge sedimentation diagrams.

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Résumé

On a préparé par polymérisation interfaciale le polyéthylène pipérazine-1,4-dicarboxylate, un polyuréthane qui structurellement ressemble au polyester, le téréphtalate de polyéthylène, et on a comparé les propriétés de ces deux polymères ainsi que du copolymère contenant ces deux structures. On donne des renseignements au sujet du poids moléculaire et de la distribution du poids moléculaire du polyuréthane et on propose un mécanisme pour la décomposition thermique observée. Une série de copolymères de polyéthylène pipérazine-1,4-dicarboxylate avec des polyamides à point de fusion élevé a été préparée en faisant réagir la pipérazine avec des mélanges de bischloroformiate d'éthylène avec les chlorures d'adipoyle, de téréphtaloyle et de dibenzoyle et on présente des résultats sur les points de fusion cristallins, la solubilité et l'absorption d'eau. On peut conclure que les copolymères de l'amide adipique et du téréphtalamide avec le polyéthylène pipérazine 1,4-dicarboxylate sont isomorphes.

Zusammenfassung

Polyäthylenerpipérazin-1,4-dicarboxylat, ein dem Polyester Polyäthylenterephthalat strukturell ähnliches Polyurethan, wurde durch Grenzflächenpolymerisation dargestellt und die Eigenschaften beider Polymerer sowie des alternierenden Copolymeren der beiden Strukturen werden verglichen. Daten bezüglich des Molekulargewichts und der Molekulargewichtsverteilung des Polyurethans werden angegeben, und ein Mechanismus für die beobachtete thermische Zersetzung wird vorgeschlagen. Eine Reihe von Copolymeren von Polyäthylenerpipérazin-1,4-dicarboxylat mit hochschmelzenden Polyamiden wurde durch Reaktion des Piperazins mit einer Mischung von Äthylendichlorformiat mit Adipoyl-, Terephthaloyl- und Bibenzoylchloriden dargestellt, und Daten bezüglich des kristallinen Schmelzpunkts, der Löslichkeit und der Wasserabsorption werden angegeben. Es wird angenommen, dass die Adipamid- und Terephthalamidcopolymeren mit Polyäthylenerpipérazin-1,4-dicarboxylat isomorph sind.

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