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Regular Copolyamides. III.* Preparation and Characterization of Regular Aliphatic/Aromatic Copolyoxamides

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ABSTRACT

Regular aliphatic/aromatic copolyoxamides were prepared from diamine-oxamides and aromatic diacid chlorides by interfacial and solution polymerization. Solution polymerization in chloroform or dimethylacetamide is preferred for the preparation of large quantities of polymers but interfacial polymerization is most conveniently carried out for the preparation of polymers with high molecular weight. Aromatic diacid chlorides used included the diacid chlorides of terephthalic acid, isophthalic acid, 2,6-pyridinedicarboxylic acid, two isomeric naphthalene dicarboxylic acids, two cyclohexanedicarboxylic acid isomers, as well as 1,1-cyclobutanedicarboxylic acid. Copolymers of diamine-oxamides with mixtures of acid chlorides of isophthalic and pyridine dicarboxylic acid and isophthalic acid/tetrachloroterephthalic acid have also been prepared. Most polymers are film-forming

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*For the preceding paper in this series see Chang and Vogl [1].

and are soluble in concentrated sulfuric acid, trifluoroacetic acid, and dimethylacetamide (containing several per cent LiCl). A number of these polymers gave dense or asymmetric membranes, particularly the polymers from ethylene diamine as the aliphatic diamine, particularly poly(iminoethyleneiminooxalyliminoethyleneiminoisophthaloyl) (p-222I). Diamine oxamides with more than two amide groups in the molecules have been prepared, and in one case polymers with aromatic diacid chlorides have been prepared by interfacial polymerization. All regular aliphatic/aromatic copolyoxamides are high-melting and generally decompose above 350°C without melting. They can, however, be fabricated from solution into brittle fibers or into desalination membranes.

INTRODUCTION

A good method for the preparation of diamine-oxamides has been recently described, and these diamine polymer intermediates were used for the preparation of regular aliphatic copolyoxamides [1-5]. The diamine-oxamides could be readily obtained by adding slowly, under controlled conditions, an oxalate ester, usually diethyl or dimethyl oxalate, to a solution of an aliphatic diamine. A three- to fourfold excess of the diamine was used rather than the necessary twofold excess, which favored the formation of the diamine-oxamide over the polymer formation [Eq. (1)].

$$H_2N\text{—}(\text{—}CH_2\text{—})_n\text{—}NH_2 + ROOCCOOR \longrightarrow$$

$$H_2N\text{—}(\text{—}CH_2\text{—})_n\text{—}NH\text{–}COCO\text{–}NH\text{—}(\text{—}CH_2\text{—})_n\text{—}NH_2$$

$$+ \text{—}[\text{—}HN\text{—}(\text{—}CH_2\text{—})_n\text{—}NHCOCO\text{—}]\text{—} + 2nROH \qquad n = 2\text{-}6 \qquad (1)$$

The solubility of the aliphatic diamine in the reaction solvent and the rate of reaction in addition to the reaction temperature usually determined the maximal yield of diamine-oxamide. It has been found useful to select reaction conditions where the aliphatic diamines were only partially soluble in the reaction solvent, at least in the beginning of the reaction. If the concentration of diethyl oxalate during the reaction relative to the diamine was too high, polymer was formed rather than the desired diamine-oxamide.

By carefully selecting the proper reaction conditions, diamine-oxamide yields of up to 80-90% could be prepared reproducibly, in addition to a 5-10% yield of the corresponding polymer.

Diamine-oxamides whose diamine portion had less than five methylene groups were water-soluble but not soluble in dimethylacetamide. The solubility of the diamine-oxamide determined the preferred method for the preparation of high polymers. Water-soluble diamine-oxamides were more conveniently polymerized by interfacial polymerization with aliphatic diacid chlorides. Solution polymerization of water-soluble diamine-oxamides with aliphatic diacid chlorides, however, could still be carried out. Solution polymerization was the only method usable for diamine-oxamides which are soluble in organic solvents and have more than five methylene groups in the diamine portion of the molecule.

Regular aliphatic copolyoxamides from diamine-oxamides and aliphatic acid chlorides [Eq. (2)] gave regular copolymers of high molecular weight which were film forming, especially when the diacid chloride contained more than six carbon atoms [1]. Diacid chlorides with less than six carbon atoms tended to give

$$\begin{aligned}&H_2N{-}(CH_2)_n{-}NH{-}COCONH{-}(CH_2)_n{-}NH_2\\&\quad + ClOC{-}(CH_2)_n{-}COCl \longrightarrow\\&{-}[HN{-}(CH_2)_n{-}NH{-}COCONH{-}(CH_2)_n{-}NHCO{-}(CH_2)_n{-}CO]{-}\\&\quad + 2\ HCl\end{aligned} \tag{2}$$

cyclic products under solution polymerization conditions whose purification was sometimes difficult. As a consequence, the use of aliphatic diacid chlorides was limited to acid chlorides with more than six carbon atoms.

As the number of the methylene groups in the aliphatic diamine portion increased, the polymers became more hydrophobic and the melting point of the polymers decreased from an initial 350°C to nearly 200°C. Similarly, an increase in the methylene chain length of the diacid portion also decreased the melting point and increased the hydrophobicity of the polymers.

It was the objective of this work to prepare regular aliphatic/aromatic and aliphatic/alicyclic copolyoxamides [6]. These materials were to be investigated as membrane materials in reverse osmosis applications. It was expected that the aromatic part of the molecule would provide aromatic interchain interaction necessary for the high glass transition temperature needed to prevent creep of the membranes in use in the aqueous swollen state. It was furthermore expected that the oxamide part of the molecules and to some extent the aromatic amide portions would supply the hydrophilic units necessary to provide the proper conditions for water transport and facilitate the selective membrane permeability necessary for reverse osmosis use.

EXPERIMENTAL

Materials

Reactants

The synthesis of the four diamine-oxamides used, N,N'-bis(2-aminoethyl) oxamide (m-2-2-2), N,N'-bis(3-aminopropyl) oxamide (m-3-2-3), N,N'-bis(4-aminobutyl) oxamide (m-4-2-4), and N,N'-bis(6-aminohexyl)oxamide (m-6-2-6) was described previously [2]. For polymerization, these intermediates were recrystallized prior to their use.

Oxalic dihydrazide (Eastman Kodak Co., Rochester, N. Y.) was recrystallized from water and dried in a vacuum oven under nitrogen at 110°C for 2 days at 30 Torr.

m-Phenylenediamine (Aldrich Chemical Co., Metuchen, N. J.) was purified by distillation at 3 Torr, center-cut temperature of 130°C, before use; mp 63-64°C.

Ethylenediamine (Aldrich Chemical Co., Metuchen, N. J.) was stirred over BaO overnight, decanted, and then distilled under nitrogen at 117°C and stored over molecular sieves (3 Å) in the dark.

Diethyl oxalate (Aldrich Chemical Co., Metuchen, N. J.) was stored over molecular sieves (5 Å) before use and was given no further purification.

Isophthaloyl and terephthaloyl chlorides (Eastman Kodak Co., Rochester, N. Y.), 2,6-pyridinedicarboxylic acid chloride (Aldrich Chemical Co., Metuchen, N. J.), were recrystallized from n-hexane before use.

Tetrachloroterephthaloyl chloride (CT) (Diamond Shamrock, Painesville, Ohio) was recrystallized from a benzene-ethyl ether mixture and dried in vacuo.

4,6-Pyrimidinedicarboxylic acid chloride was purified by sublimation at 41°C/0.038 Torr. The acid itself was prepared by the oxidation of 4,6-dimethylpyrimidine (Aldrich Chemical Co., Metuchen, N. J.).

1,1-Cyclobutanedicarboxylic acid and 1,6-naphthalenedicarboxylic acid (Pfaltz and Bauer, Flushing, N. Y.), cis- and trans-1,4-cyclohexanedicarboxylic acid (Eastman Kodak Co., Rochester, N. Y.), 2,6-naphthalenedicarboxylic acid (Aldrich Chemical Co., Metuchen, N. J.), and 4,6-pyrimidinedicarboxylic acid were all converted into their respective acid chlorides by treatment with thionyl chloride [7]. Thionyl chloride was purified according to the procedure outlined in Fieser and Fieser [7] before use and stored at -20° C.

1,1-Cyclobutanedicarboxylic acid chloride was distilled at 59 Torr, bp 108° C, before use.

cis-1,4-Cyclohexanedicarboxylic acid chloride was distilled at 0.4 Torr, bp 86° C, before use.

Trans-1,4-cyclohexanedicarboxylic acid chloride and 1,6-naphthalenedicarboxylic acid chloride were recrystallized from n-hexane before use.

2,6-Naphthalenedicarboxylic acid chloride was recrystallized from 1,2-dichloroethane before use.

Solvents

n-Hexane (Fisher Chemical Co., Medford, Mass.) was distilled from freshly cut sodium.

Chloroform (Fisher Chemical Co., Medford, Mass.) was washed three times with equal volumes of distilled water and dried over calcium chloride.

1,2-Dichloroethane (Fisher Chemical Co., Medford, Mass.) was stored over NaOH pellets overnight, decanted, and distilled from P_2O_5 under nitrogen. It was kept over molecular sieves (3 Å) before use.

Tetrahydrofuran (THF) (Fisher Chemical Co., Medford, Mass.) was distilled from $LiAlH_4$.

Hexafluoroisopropanol (HFIP) (E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.) was used without further purification.

Skelly F, a petroleum ether fraction, bp 40-60° C (Fisher Chemical Co., Medford, Mass.) was used without further purification.

Dimethylacetamide (DMAc) (Aldrich Chemical Co., Metuchen, N. J.) was distilled from P_2O_5 at 85° C/30 Torr and stored over molecular sieves (3 Å).

Hexamethylphosphoric triamide (HMPA) (Eastman Kodak Co., Rochester, N. Y.) was distilled from CaH_2 and stored over molecular sieves (3 Å).

Dimethyl sulfoxide (DMSO) (Eastman Kodak Co., Rochester, N. Y.) was distilled at 54° C/2 Torr and stored over molecular sieves (3 Å).

Other Materials

Triethylamine (Eastman Kodak Co., Rochester, N. Y.) was distilled from freshly cut sodium under a dry nitrogen atmosphere and stored in the dark over molecular sieves (3 Å).

Lithium chloride (Fisher Chemical Co., Medford, Mass.) was dried under vacuum at 140° C.

Molecular sieves (MC/B Manufacturing Chemists, Norwood, Ohio) (3 Å) were activated at 300° C in a column under a slow nitrogen stream.

Preparation of Individual Polymers

Most polymers were prepared several times but only one representative experiment is described. Interfacial polymerizations were carried out either in 1-qt or 1-gal Waring Blendors.

Poly(diiminooxalyldiiminoisophthaloyl) (p-0-2-0-I)

By Interfacial Polymerization. An aqueous solution of oxalic dihydrazide (7.00 g, 0.059 mole) and sodium carbonate (12.72 g, 0.12 mole) in 400 ml of distilled water was placed into a 1-qt Waring Blendor, and the proper blending speed was obtained at a 100 V setting on a 140 V Variac. The solution of isophthaloyl chloride (11.97 g, 0.059 mole) in 275 ml of chloroform was added at once. White polymer was formed as soon as the organic solution was added and blending was continued for 5 min. The resulting white mass was filtered, rinsed with 300 ml of acetone, 600 ml of water, 300 ml of acetone again, and finally dried at 60° C/30 Torr for 12 hr.

The polymer weighed 11.80 g (81% yield), and started to decompose at 295° C (DSC). The infrared spectrum (KBr disk) showed absorptions at 3200 cm^{-1} (NHCO stretching), 3000-2900 cm^{-1} (asym. and sym. stretching of CH_2), 1650 cm^{-1} (CO stretching), 1520-1470 cm^{-1} (irresolvable; NH bending and CN stretching), and 730 cm^{-1} (NH out-of-plane bending). The polymer was insoluble in CF_3COOH. The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.23 dl/g.

Analysis. Calcd for $(C_{10}H_8N_4O_4)_n$: N, 22.58%. Found: N, 22.52%.

By Solution Polymerization. To a 1000-ml three-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, and a nitrogen inlet and exit tube was added oxalic dihydrazide (5.45 g, 0.046 mole), triethylamine (8.40 g, 1 eq. excess), LiCl (12 g), and 300 ml of anhydrous DMAc. The temperature was raised to 45° C, and isophthaloyl chloride (9.35 g, 0.046 mole) dissolved in 100 ml of DMAc was added in 10-ml portions. After each addition the temperature rose spontaneously to 55° C and a precipitate formed. After the final addition was made, the temperature was maintained at 55° C for 18 hr. The reaction mixture, which was light yellow but clear, was cooled and poured into 500 ml of an ice-water bath while stirring in the blender. White polymer precipitated; it was filtered and washed several times in the blender with water, acetone, and ether, and was then dried in a vacuum oven at 50° C/30.0 Torr; polymer yield, 10.70 g (86%); decomposed > 295° C (DSC). The spectral characteristics of this sample were identical with those of the earlier samples. The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.44 dl/g.

Poly(iminoethyleneiminooxalyliminoethyleneiminoisophthaloyl) (p-2-2-2-I)

By Interfacial Polymerization. N,N'-Bis(2-aminoethyl) oxamide (32.05 g, 0.18 mole) and Na_2CO_3 (39.01 g, 0.37 mole) in 1600 ml of distilled water were reacted with isophthaloyl chloride (37.36 g, 0.18 mole) in 1000 ml of chloroform; reaction time 3 min; polymer yield 55.0 g (99%); mp 367° C; (decomposed > 370° C) (DSC). The polymer was soluble in sulfuric acid, CF_3COOH, and warm DMAc containing 3% LiCl. IR spectrum (film): 3290 cm^{-1} (NHCO stretching), 2940 cm^{-1} (asym. stretching of CH_2), 2880 cm^{-1} (sym. stretching of CH_2), 1665 cm^{-1} (CO stretching), 1518 cm^{-1} (NH bending), 1440 cm^{-1} (CN stretching), and 728 and 708 cm^{-1} (NH out of plane bending). The PMR (CF_3COOH) showed δ: 8.85 (NHCOCO, 2), 8.38 to 7.60 (irresolvable; aromatic H, 4 and NHCO, 2), and 3.86 (CH_2, 8). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 1.32 dl/g.

Analysis. Calcd for $(C_{14}H_{16}N_4O_4)_n$: N, 18.40%. Found: N, 18.41%.

By Solution Polymerization. To a 2000-ml four-necked round-bottomed flask was added N,N'-bis(2-aminoethyl) oxamide (57.00 g, 0.33 mole), anhydrous triethylamine (100 g, 1 eq. excess), LiCl (48 g), and 120 ml of anhydrous DMAc. The mixture was warmed to 45° C until everything dissolved. Isophthaloyl chloride (67.30 g, 0.33 mole) in 300 ml of DMAc was added over a 1-hr period. The temperature rose spontaneously to 55° C, where it was maintained for 18 hr. A precipitate (triethylamine hydrochloride) formed almost immediately. The warm mixture was poured into 1200 ml of ice water. The white polymer was filtered and washed in a Waring Blendor twice each with water, 1:1 acetone: water and acetone, and dried at 40° C/20.0 Torr for 48 hr; polymer yield 82.0 g (82%); decomposed > 355° C (DSC). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.90 dl/g.

Poly(iminoethyleneiminooxalyliminoethyleneiminoterephthaloyl) (p-2-2-2-T) by Interfacial Polymerization

N,N'-Bis(2-aminoethyl) oxamide (5.00 g, 0.029 mole) and Na_2CO_3 (6.08 g, 0.057 mole) in 340 ml of distilled water were reacted with terephthaloyl chloride (5.83 g, 0.029 mole) in 200 ml of chloroform; reaction time 5 min; polymer yield 7.90 g (91%); decomposed > 400° C (DSC). IR spectrum (film): 3270 cm^{-1} (NHCO stretching), 2945 cm^{-1} (asym. stretching of CH_2), 2860 cm^{-1} (sym. stretching of CH_2), 1650 cm^{-1} (CO stretching), 1520 cm^{-1} (NH bending), 1425 cm^{-1} (CN stretching), and 710 cm^{-1} (NH out of plane bending). The PMR (CF_3COOH) showed δ: 8.90 (NHCOCO, 2), 8.30 to 7.64 (aromatic H, 4; and NHCO, 2), and 3.89 (CH_2, 8). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.63 dl/g.

Analysis. Calcd for $(C_{14}H_{16}N_4O_4)_n$: N, 18.41%. Found: N, 18.08%.

Poly[iminoethyleneiminooxalyliminoethyleneimino-(20% tetrachloroterephthaloyl/80% isophthaloyl)] [p-2-2-2-(CT 20/I 80)] by Interfacial Polymerization

N,N'- Bis(2-aminoethyl) oxamide (13.59 g, 0.078 mole) and Na_2CO_3 (16.54 g, 0.16 mole) in 650 ml of distilled water were reacted with tetrachloroterephthaloyl chloride (5.32 g, 0.016 mole) and isophthaloyl chloride (12.48 g, 0.062 mole) in 400 ml of chloroform; reaction time 5 min; polymer yield 20.40 g (80%); mp 367° C, (decomposed > 370° C) (DSC). IR spectrum (film): 3290 cm^{-1} (NHCO stretching), 2950 cm^{-1} (asym. stretching of CH_2), 2880 cm^{-1} (sym. stretching of CH_2), 1660 cm^{-1} (CO stretching), 1518 cm^{-1} (NH bending), 1440 cm^{-1} (CN stretching), 1045 cm^{-1} (C-Cl stretching), and 725 and 708 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 8.94 (NHCOCO), 8.47 to 7.37 (irresolvable; aromatic H, and NHCO), and 3.89 (CH_2). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 1.32 dl/g.

Analysis. Calcd for $(C_{14}H_{15.2}Cl_{0.8}N_4O_4)_n$: N, 16.84. Found: N, 16.70%.

Poly(2,6-pyridinediylcarbonyliminoethyleneiminooxalyliminoethyleneiminocarbonyl) (p-2-2-2-P)

By Interfacial Polymerization. N,N'-Bis(2-aminoethyl) oxamide (8.71 g, 0.050 mole) and Na_2CO_3 (10.60 g, 0.10 mole) in 450 ml of distilled water were reacted with 2,6-pyridinedicarboxylic acid chloride (10.20 g, 0.050 mole) in 250 ml of chloroform; reaction time 4 min; polymer yield 14.00 g (94%); decomposed > 340°C (DSC). IR spectrum (film): 3290 cm^{-1} (NHCO stretching), 2945 cm^{-1} (asym. stretching of CH_2), 2880 cm^{-1} (sym. stretching of CH_2), 1660 cm^{-1} (CO stretching), 1525 cm^{-1} (NH bending), 1450 cm^{-1} (CN stretching), and 708 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 8.92 to 8.48 (irresolvable; NHCOCO, 2, and aromatic H, 3, and NHCO, 2), and 3.85 (CH_2, 8). The inherent viscosity of a 0.5% H_2SO_4 solution of the polymer was 0.30 dl/g.

Analysis. Calcd for $(C_{13}H_{15}N_5O_4)_n$: N, 22.94%. Found: N, 22.42%.

By Solution Polymerization. To a 100-ml three-necked round-bottomed flask was added N,N'-bis(2-aminoethyl) oxamide (5.69 g, 0.033 mole), triethylamine (9.91 g, 1 eq. excess), LiCl (16 g), and 400 ml of DMAc. The temperature was raised to 45°C, and 2,6-pyridinedicarboxylic acid chloride (6.67 g, 0.033 mole) was added in portions. After 1 hr the addition was completed and the reaction was stirred for an additional 18 hr at 55°C. The mixture was poured into 800 ml of ice water, the precipitate was filtered, washed in a blender with acetone, and dried. The polymer yield was 2.33 g (23%); decomposed > 370°C (DSC). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.34 dl/g.

Poly[iminoethyleneiminooxalyliminoethyleneimino-(50% isophthaloyl/50% carbonyl-2,6-pyridinediylcarbonyl)] [p-2-2-2-(I50/P50)] by Interfacial Polymerization:

N,N'-Bis(2-aminoethyl) oxamide (5.70 g, 0.033 mole) and Na_2CO_3 (6.95 g, 0.066 mole) in 350 ml of distilled water were reacted with isophthaloyl chloride (3.32 g, 0.016 mole) and 2,6-pyridinedicarboxylic acid chloride (3.23 g, 0.016 mole) in 250 ml of chloroform; reaction time 30 min; polymer yield 7.86 g (79%); mp 302°C, (decomposed > 355°C) (DSC). IR spectrum (KBr pellet): 3300 cm^{-1} (NHCO stretching) 2910 cm^{-1} (asym. stretching of CH_2), 2860 cm^{-1} (sym. stretching of CH_2), 1650 cm^{-1} (CO stretching), 1520 cm^{-1} (NH bending), 1455 cm^{-1} (CN stretching), and 720 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 9.30 to 7.40 (NHCOCO, aromatic H, and NHCO) and 3.91 (CH_2). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.33 dl/g. Analysis for this polymer was N, 19.75%. For a 1:1 ratio of isophthaloyl to pyridinediyl units the N analysis is 20.69%.

Poly(4,6-pyrimidinediylcarbonyliminoethyleneiminooxalyliminoethyleneiminocarbonyl) (p-2-2-2-4,6-Pm) by Interfacial Polymerization

N,N'-Bis(2-aminoethyl) oxamide (1.70 g, 0.0098 mole) and Na_2CO_3 (2.04 g, 0.019 mole) in 250 ml of water were reacted with 4,6-pyrimidine dicarboxylic acid chloride (2.00 g, 0.0098 mole) in 200 ml of chloroform; reaction time several minutes; polymer yield 2.01 g (66%); decomposed > 345°C (DSC). IR spectrum (film): 3290 cm^{-1} (NHCO stretching), 2950 cm^{-1} (asym. stretching of CH_2), 2880 cm^{-1} (sym. stretching of CH_2), 1660 cm^{-1} (CO stretching), 1530 cm^{-1} (NH bending), 1455 cm^{-1} (CN stretching), and 715 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 9.70 to 8.60 (aromatic H, 2; NHCOCO, 2; and NHCO, 2) and 3.91 (CH_2, 8). The inherent viscosity of a 0.5% CF_3COOH solution of this polymer was 0.25 dl/g (30°C).

Analysis. Calcd for $(C_{12}H_{14}N_6O_4)_n$: N, 27.44%. Found: N, 25.44%.

Poly(iminoethyleneiminooxalyliminoethyleneiminocarbonyl-1,6-naphthylenecarbonyl) (p-2-2-2-1,6-N) by Interfacial Polymerization

N,N'-Bis(2-aminoethyl) oxamide (0.82 g, 0.0047 mole) and Na_2CO_3 (1.00 g, 0.0094 mole) in 56 ml of distilled water were reacted with 1,6-naphthalenedicarboxylic acid chloride (1.19 g, 0047 mole) in 34 ml of chloroform; reaction time 5 min; polymer yield 1.38 g (83%); decomposed > 370°C (DSC). IR spectrum (film): 3300 cm^{-1} (NHCO stretching), 2948 to 2865 cm^{-1} (asym. and sym. stretching of CH_2), 1670 cm^{-1} (CO stretching), 1520 cm^{-1} (NH bending), 1428 cm^{-1} (CN stretching), and 730 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 8.86 (NHCOCO, 2), 8.30 to 7.60 (broad, NHCO, 2 and aromatic H, 6), and 3.87 (CH_2, 8). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.78 dl/g.

Analysis. Calcd for $(C_{18}H_{18}N_4O_4)_n$: N, 15.81%. Found: N, 15.24%.

Poly(iminoethyleneiminooxalyliminoethyleneiminocarbonyl-2,6-naphthylenecarbonyl) (p-2-2-2-2,6-N) by Interfacial Polymerization

N,N'-Bis(2-aminoethyl) oxamide (2.06 g, 0.012 mole) and Na_2CO_3 (2.52 g, 0.024 mole) in 350 ml of distilled water were reacted 2,6-naphthalenedicarboxylic acid chloride (3.00 g, 0.012 mole) in 210 ml of chloroform; reaction time 5 min; polymer yield 4.24 g (100%); decomposed > 370°C (DSC). IR spectrum (film): 3300 cm^{-1} (NHCO stretching), 2950 cm^{-1} (asym. stretching of CH_2), 2880 cm^{-1} (sym. stretching of CH_2), 1660 cm^{-1} (CO stretching), 1520 cm^{-1} (NH bending), 1440 cm^{-1} (CN stretching), and 717 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 8.91 (NHCOCO, 2), 8.36 (aromatic H, 6), 7.94 (NHCO, 2), and 3.94 (CH_2, 8). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.58 dl/g.

Analysis. Calcd for $(C_{18}H_{18}N_4O_4)_n$: N, 15.81%. Found: N, 15.51%.

Poly(iminoethyleneiminooxalyliminoethyleneiminocarbonyl-1,1-cyclobutylenecarbonyl) (p-2-2-2-1,1-cyclobut.) by Interfacial Polymerization

N,N;-Bis(2-aminoethyl) oxamide (2.47 g, 0.014 mole) and Na_2CO_3 (3.02 g, 0.028 mole) in 168 ml of distilled water were reacted with 1,1-cyclobutanedicarboxylic acid chloride (2.57 g, 0.014 mole) in 100 ml of chloroform; reaction time 5 min; polymer yield 3.39 g (85%); mp 286°C (DSC). IR spectrum (film): 3300 cm^{-1} (NHCO stretching), 2950 cm^{-1} (asym. stretching of CH_2), 2880 cm^{-1} (sym. stretching of CH_2), 1650 cm^{-1} (CO stretching), 1520 cm^{-1} (NH bending), 1440 cm^{-1} (CN stretching), and 710 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 8.71 (NHCOCO, 2), 7.82 (NHCO, 2), 3.71 (acyclic CH_2, 8), and 2.67 to 2.09 (broad, cyclic CH_2, 6). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.50 dl/g.

Analysis. Calcd for $(C_{12}H_{18}N_4O_4)_n$: N, 19.85%; Found: N, 19.13%.

Poly(iminoethyleneiminooxalyliminoethyleneiminocarbonylcis-1,4-cyclohexylenecarbonyl) (p-2-2-2-cis-1,4) by Interfacial Polymerization

N,N'-Bis(2-aminoethyl) oxamide (9.55 g, 0.055 mole) and Na_2CO_3 (11.62 g, 0.11 mole) in 650 ml of distilled water were reacted with cis-1,4-cyclohexanedicarboxylic acid chloride (11.46 g, 0.555 mole) in 390 ml of chloroform; reaction time 5 min; polymer yield 12.90 g (76%); decomposed > 370°C (DSC). IR spectrum (film): 3280 cm^{-1} (NHCO stretching), 2940 cm^{-1} (asym. stretching of CH_2), 2870 cm^{-1} (sym. stretching of CH_2), 1645 cm^{-1} (CO stretching), 1527 cm^{-1} (NH bending), 1447 cm^{-1} (CN stretching), and 716 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 8.71 (NHCOCO, 2), 7.85 (NHCO, 2), 3.69 (acyclic CH_2, 8), and 2.75 to 1.98 (broad, cyclic CH and CH_2, 10). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.48 dl/g.

Analysis. Calcd for $(C_{14}H_{22}N_4O_4)_n$: N, 18.05%. Found: N, 17.59%.

Poly(iminoethyleneiminooxalyliminoethyleneiminocarbonyltrans-1,4-cyclohexylenecarbonyl) (p-2-2-2-trans-1,4) by Interfacial Polymerization

N,N'-Bis(2-aminoethyl) oxamide (9.17 g, 0.053 mole) and Na_2CO_3 (11.15 g, 0.11 mole) in 625 ml of distilled water were reacted with trans-1,4-cyclohexanedicarboxylic acid chloride (11.00 g, 0.053 mole) in 375 ml of chloroform; reaction time 5 min; polymer yield 12.00 g (74%); decomposed > 370°C (DSC). IR spectrum (film): 3280 cm^{-1} (N$\underline{H}$CO stretching), 2935 cm^{-1} (asym. stretching of CH_2), 2860 cm^{-1} (sym. stretching of CH_2), 1654 cm^{-1} (CO stretching), 1524 cm^{-1} (NH bending), 1448 cm^{-1} (CN stretching), and 717 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 8.87 (NHCOCO, 2), 7.84 (NHCO, 2), 3.68 (acyclic CH_2, 8), and 2.55 to 1.60 (broad, cyclic CH and CH_2, 10). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.51 dl/g.

Analysis. Calcd for $(C_{14}H_{22}N_4O_4)_n$: N, 18.05%. Found: N, 17.94%.

Bis(ethoxyoxalylimino) ethane

To a 1000-ml three-necked round-bottomed flask equipped with a mechanical stirrer at the center neck, a Claisen adapter on a side neck with a thermometer and a Liebig condenser, and a 250-ml pressure equalizing addition funnel on the remaining neck, were added, under dry nitrogen, diethyl oxalate (140.40 g, 0.96 mole) and 650 ml of anhydrous diethyl ether. The addition funnel contained ethylenediamine (14.40 g, 0.24 mole) in 115 ml of anhydrous diethyl ether. The three-necked flask was cooled to keep the temperature below 15°C by means of an ice-water bath. The ethylenediamine solution was slowly added over a period of 4 hr and the reaction mixture which consisted of a white solid was filtered through a Buchner funnel, washed in a 1-gal blender with ether, and filtered. The material was dried in a vacuum oven overnight at room temperature; yield 57.80 g (93%).

The solid was extracted in a Soxhlet extractor with anhydrous tetrahydrofuran. After cooling a white solid deposited from the extract which was filtered and dried. It melted at 128-129°C (capillary). It was soluble in o-dichlorobenzene, hexafluoroisopropanol, and water. The infrared spectrum (KBr disk) showed absorption at: 3290 cm^{-1} (N$\underline{H}$CO stretching), 2965 cm^{-1} (asym. stretching of CH_2), 2925 cm^{-1} (sym. stretching of CH_2), 1717 cm^{-1} (ester stretching), 1655 cm^{-1} (CO stretching), 1547 cm^{-1} (NH bending), 1465 cm^{-1} (CN stretching), and 722 cm^{-1} (NH out-of-plane bending). The PMR (DMSO) spectra showed δ: 8.89 (NHCOCO, 2), 4.25 (CH_3-C$\underline{H}_2$, 4), 3.28 (N-CH_2, 4), and 1.29 (CH_3, 6).

Analysis. Calcd for $C_{10}H_{16}N_2O_6$: C, 46.15%; H. 6.20%; N, 10.76%. Found: C, 46.31%; H, 6.41%; N, 10.65%.

Bis(2-aminoethyliminooxalylimino)ethane (m-2-2-2-2-2)

To a 1000-ml three-necked round-bottomed flask were added ethylenediamine (23.10 g, 0.38 mole) and 300 ml of THF. Bis(2-ethoxyoxalylimino)ethane (5.00 g, 0.019 mole) was dissolved in 200 ml of hot THF. The reaction was run under a slow nitrogen flow while the flask contents were kept boiling (4 hr). The white precipitate was filtered through a coarse glass sintered funnel and dried in a vacuum oven overnight at room temperature; yield 5.30 g (96%; decomposed >250°C (DSC). It was soluble in trifluoroacetic acid and boiling water. IR spectrum (KBr disk): 3300 cm^{-1} (N$\underline{H}$CO stretching), 2950 cm^{-1} (asym. stretching of CH_2), 2870 cm^{-1} (sym. stretching of CH_2), 1655 cm^{-1} (CO stretching), 1530 cm^{-1} (NH bending), 1460 cm^{-1} (CN stretching), and 780 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) spectra showed δ: 8.22 (NHCOCO, 4) 6.75 (^+H_3N, 6), and 3.29 (CH_2, 12).

Analysis. Calcd for $C_{10}H_{20}N_6O_4$: C, 41.66%; H. 6.99%; N, 29.15%. Found: C, 41.76%; H, 7.03%; N, 29.00%.

Bis(2-aminoethyliminooxalylimino) ethane dihydrochloride salt [m-2-2-2-2-2-(2 HCl)]

m-2-2-2-2-2 was dissolved in boiling water and a large excess of concentrated hydrochloric acid was quickly added, whereupon the salt precipitated out immediately. The solution was cooled rapidly, filtered and dried. The white powder decomposed > 290°C (DSC). IR spectrum (KBr disk): 3300 cm^{-1} (N$\underline{H}$CO stretching), 2970 to 2900 cm^{-1} (asym. and sym. stretching of CH_2), 1648 cm^{-1} (CO stretching), 1595 cm^{-1} (amine salt bending), 1521 cm^{-1} (NH bending), 1455 cm^{-1} (CN stretching), and 742 cm^{-1} (NH out-of-plane bending).

Analysis. Calcd for $C_{10}H_{22}N_6O_4Cl_2$: C, 33.25%; H, 6.14%. Found: C, 33.42%; H, 6.35%.

Poly(iminoethyleneiminooxalyliminoethyleneiminooxalyliminoethyleneiminoisophthaloyl) (p-2-2-2-2-2-I) by Interfacial Polymerization

Bis(2-aminoethyliminooxalylimino)ethane dihydrochloride salt (1.78 g, 0.0049 mole) and Na_2CO_3 (1.57 g, 0.015 mole) dissolved in 90 ml of hot (85°C) distilled water were reacted with isophthaloyl chloride (1.00 g, 0.0049 mole) in 75 ml of chloroform in a warm blender (65°C); reaction time 5 min; polymer yield 1.89 g (92%); decomposes > 370°C (DSC). IR spectrum (film): 3300 cm^{-1} (N$\underline{H}$CO stretching), 3080 cm^{-1} (asym. stretching of CH_2), 2960 cm^{-1} (sym. stretching of CH_2), 1655 cm^{-1} (CO stretching), 1525 cm^{-1} (NH bending), 1440 cm^{-1} (CN bending), and 710 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 8.74 (NHCOCO, 2), 8.40 to 7.60 (broad, aromatic H, 4 and

NHCO, 2), and 3.79 (CH_2, 2). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.45 dl/g.

Analysis. Calcd for $(C_{18}H_{22}N_6O_6)_n$: N, 20.09%. Found: N, 18.96%.

Poly(2,6-pyridinediylcarbonylaminoethyleneiminooxalyliminoethyleneiminooxalyliminoethyleneiminocarbonyl) (p-2-2-2-2-2-P) by Interfacial Polymerization

m-2-2-2-2-2 (1.52 g, 0.00053 mole) and Na_2CO_3 (0.78 g, 0.0074 mole) in 300 ml of distilled water were reacted with 2,6-pyridinedicarboxylic acid chloride (1.08 g, 0.00053 mole) in 100 ml of chloroform plus 20 ml of dimethyl sulfoxide; reaction time 10 min; polymer yield 0.22 g (10%); decomposed > 400°C (DSC). IR spectrum (film): 3270 cm^{-1} (NHCO stretching), 2950 to 2880 cm^{-1} (asym. and sym. stretching of CH_2), 1665 cm^{-1} (CO stretching), 1515 cm^{-1} (NH bending), 1450 cm^{-1} (CN stretching), and 725 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 8.89 (NHCOCO, 4), 7.18 (aromatic H, 3; NHCO, 2), and 3.75 (CH_2, 12). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.25 dl/g.

Analysis. Calcd for $(C_{17}H_{21}N_7O_6)_n$: N, 23.38%. Found: N, 24.13%.

N,N'-Bis(ethoxyoxalyliminoethylene) oxamide

To a 2000-ml three-necked round-bottomed flask was added diethyl oxalate (83.90 g, 0.57 mole) in 400 ml THF. N,N'-Bis(2-aminoethyl) oxamide (5.00 g, 0.029 mole) was dissolved in 1000 ml of hot THF and added during a period of 6 hr to the boiling solution of diethyl oxalate. The precipitate was filtered and dried at 1 Torr overnight at room temperature; yield 9.21 g (86%). The white powder is soluble only in hexafluoroisopropanol; mp 249°C (DSC). IR spectrum (KBr disk): 3300 cm^{-1} (NHCO stretching), 2950 cm^{-1} (asym. stretching of CH_2), 2870 cm^{-1} (sym. stretching of CH_2), 1740-1655 cm^{-1} (broad, ester and CO stretching), 1540 cm^{-1} (NH bending), 1450 cm^{-1} (CN stretching), and 740 cm^{-1} (NH out-of-plane bending). The PMR (HFIP) spectra showed δ: 8.84 (NHCOCO, 4), 4.23 (CH_3-CH_2, 4), 3.26 (N-CH_2, 8), and 1.35 (CH_3,6).

Analysis. Calcd for $C_{14}H_{22}N_4O_8$: C, 44.92%; H, 5.92%. Found: C, 44.93%; H, 5.99%.

N,N'-Bis(2-aminoethyliminooxalyliminoethylene) oxamide dihydrochloride salt [m-2-2-2-2-2-2-2 (2 HCl)]

To a 50-ml three-necked round-bottomed flask were added ethylenediamine (1.61 g, 0.027 mole) and 15 ml of hexafluoroisopropanol.

N,N'-Bis(2-ethoxyoxalyliminoethylene) oxamide (2.00 g, 0.0053 mole) was dissolved in 24 ml of hexafluoroisopropanol, gravity-filtered from undissolved material, and added over a period of 6 hr to ethylenediamine while the solution was refluxing. The mixture was chilled overnight and the precipitate was suction-filtered, washed, and dried at 100°C/4 Torr overnight; yield 1.11 g (51%). The compound had very low solubility and could only be purified through the dihydrochloric acid salt which decomposed > 270°C (DSC). IR spectrum (KBr disk): 3300 cm^{-1} (NHCO stretching), 3000-2900 cm^{-1} (asym. and sym. stretching of CH_2), 1657 cm^{-1} (CO stretching), 1600 cm^{-1} (amine salt bending, weak), 1505 cm^{-1} (NH bending), 1457 cm^{-1} (CN stretching), and 750 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) spectra showed δ: 8.34 (NHCOCO, 6), 6.79 (^+H_3N, 6), and 3.32 (CH_2, 16).

Analysis. Calcd for $C_{14}H_{28}N_8O_6Cl_2$: C, 35.38%; H, 5.94%. Found: C, 35.12%; H, 5.94%.

Poly(iminotrimethyleneiminooxalyliminotrimethyleneiminoisophthaloyl) (p-3-2-3-I) by Interfacial Polymerization

N,N'-Bis(3-aminopropyl) oxamide (7.68 g, 0.038 mole) and Na_2CO_3 (8.05 g, 0.076 mole) in 350 ml of distilled water were reacted with isophthaloyl chloride (7.71 g, 0.038 mole) in 250 ml of chloroform; reaction time 5 min; polymer yield 11.20 g (90%); decomposed > 345°C (DSC). The polymer was soluble in H_2SO_4, CF_3COOH, and DMAc containing 3% LiCl and partially soluble in hot DMSO. IR spectrum (film): 3300 cm^{-1} (NHCO stretching), 2940 cm^{-1} (asym. stretching of CH_2), 2875 cm^{-1} (sym. stretching of CH_2), 1655 cm^{-1} (CO stretching), 1525 cm^{-1} (NH bending), 1440 cm^{-1} (CN stretching), and 728 and 707 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 9.00 to 7.40 (irresolvable; NHCOCO, 2, and aromatic H, 4, and NHCO, 2), 3.78 (N-CH_2, 8), and 2.22 (C-CH_2-C, 4). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 1.90 dl/g.

Analysis. Calcd for $(C_{16}H_{20}N_4O_4)_n$: N, 16.87%. Found: N, 16.65%.

Poly[iminotrimethyleneiminooxalyliminotrimethyleneimino-(20% tetrachloroterephthaloyl/80% isophthaloyl)] [p-3-2-3-(CT 20/I 80)] by Interfacial Polymerization

N,N'-Bis(3-aminopropyl) oxamide (13.08 g, 0.065 mole) and Na_2CO_3 (13.67 g, 0.13 mole) in 650 ml of distilled water were reacted with tetrachloroterephthaloyl chloride (4.33 g, 0.013 mole) and isophthaloyl chloride (10.55 g, 0.052 mole) in 400 ml of chloroform; reaction time 5 min; polymer yield 17.50 g (76%; mp 367°C, (decomposed > 370°C) (DSC). IR spectrum (film): 3290 cm^{-1} (NHCO stretching), 2940 cm^{-1} (asym. stretching of CH_2), 2875 cm^{-1} (sym. stretching of CH_2), 1640 cm^{-1} (CO stretching), 1530 cm^{-1} (NH bending), 1442 cm^{-1} (CN stretching), 1040 cm^{-1} (C-Cl stretching), and 738 and 708 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 9.03 to 8.60 (irresolvable; NHCOCO, aromatic H, NHCO), 3.79 (N-CH_2), and 2.22 (C-CH_2-C). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 1.90 dl/g.

Analysis. Calcd for $(C_{16}H_{19.2}Cl_{0.8}N_4O_4)_n$: N, 15.57%. Found: N, 15.93%.

Poly(2,6-pyridinediylcarbonyliminotrimethyleneiminooxalyliminotrimethylenecarbonyl) (p-3-2-3-P) by Interfacial Polymerization

N,N'-Bis(3-aminopropyl) oxamide (9.90 g, 0.049 mole) and Na_2CO_3 (10.38 g, 0.098 mole) in 450 ml of distilled water were reacted with 2,6-pyridinedicarboxylic acid chloride (10.0 g, 0.049 mole) in 250 ml of chloroform; reaction time 4 min; polymer yield 12.80 g (79%); decomposed > 330°C (DSC). IR spectrum (film): 3300 cm^{-1} (NHCO stretching), 2940 cm^{-1} (asym. stretching of CH_2), 2875 cm^{-1} (sym. stretching of CH_2), 1660 cm^{-1} (CO stretching), 1520 cm^{-1} (NH bending), 1455 cm^{-1} (CN stretching), and 720 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 9.34 to 8.00 (irresolvable; NHCOCO, 2, and aromatic H, 3, and NHCO, 2), 3.80 (N-CH_2, 8), and 2.20 (C-CH_2-C, 4). The inherent viscosity of a 0.5% solution of the polymer in DMAc containing 3% LiCl was 0.36 dl/g.

Analysis. Calcd for $(C_{15}H_{19}N_5O_4)_n$: N, 21.02%. Found: N, 20.72%.

Poly(iminotetramethyleneiminooxalyliminotetramethyleneiminoisophthaloyl) (p-4-2-4-I)

By Interfacial Polymerization. N,N'-Bis(4-aminobutyl) oxamide (2.26 g, 0.010 mole) and Na_2CO_3 (2.12 g, 0.020 mole) in 300 ml of distilled water were reacted with isophthaloyl chloride (2.03 g, 0.010 mole) in 210 ml of chloroform; reaction time 5 min; polymer yield 3.00 g (84%); mp 302°C, (decomposed > 350°C) (DSC). IR spectrum (film): 3290 cm^{-1} (NHCO stretching), 2940 cm^{-1} (asym. stretching of CH_2), 2870 cm^{-1} (sym. stretching of CH_2), 1660 cm^{-1} (CO stretching), 1520 cm^{-1} (NH bending), 1442 cm^{-1} (CN stretching), and 728 and 708 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 8.80 to 7.65 (irresolvable; NHCOCO, 2, and aromatic H, 4, and NHCO, 2), 3.70 (N-CH_2, 8), and 1.91 (C-CH_2-C, 8). The inherent viscosity of a 0.5% solution of this polymer was 1.57 dl/g.

Analysis. Calcd for $(C_{18}H_{24}N_4O_4)_n$: N, 15.55%. Found: N, 15.58%.

By Solution Polymerization. To a 250-ml three-necked, round-bottomed flask was added DMAc (50 ml) containing 5% LiCl, triethylamine (4.04 g, 0.040 mole), and N,N'-bis(4-aminobutyl) oxamide (4.52 g, 0.020 mole). The mixture was warmed slightly until everything was dissolved. Isophthaloyl chloride (4.06 g, 0.020 mole) in 50 ml of DMAc was added slowly at 0°C over a period of 1 hr. After 2 hr the mixture was allowed to warm to 25°C, stirred for 10 hr, and poured into 500 ml of water. The suspension was filtered, and the solid was washed with 200 ml of water, then acetone, and dried; polymer yield 5.80 g (81%); mp 287°C (decomposed > 350°C) (DSC). The inherent viscosity of a 0.5% solution of the polymer in DMAc containing 3% LiCl was 0.88 dl/g.

Poly(iminotetramethyleneiminooxalyliminotetramethyleneimino-(20% tetrachloroterephthaloyl/80% isophthaloyl) [p-4-2-4-(CT 20/I 80)] by Interfacial Polymerization

N,N'-Bis(4-aminobutyl) oxamide (8.75 g, 0.038 mole) and Na_2CO_3 (8.06 g, 0.076 mole) in 350 ml of distilled water were reacted with tetrachloroterephthaloyl chloride (2.59 g, 0.0076 mole) and isophthaloyl chloride (6.17 g, 0.030 mole) in 250 ml of chloroform; reaction time 5 min; polymer yield 11.80 g (82%); decomposed > 390°C (DSC). IR spectrum (film): 3290 cm^{-1} (N$\underline{H}$CO stretching), 2940 cm^{-1} (asym. stretching of CH_2), 2870 cm^{-1} (sym. stretching of CH_2), 1660 cm^{-1} (CO stretching), 1520 cm^{-1} (NH bending), 1441 cm^{-1} (CN stretching), 1045 cm^{-1} (C-Cl stretching), and 730 and 708 cm^{-1} (NH out-of-plane bending). The PMR (CH_3COOH) showed δ: 8.80 to 7.65 (irresolvable; NHCOCO, 2, and aromatic H, 3.75, and NHCO, 2), 3.68 (N-CH_2, 8), and 1.91 (C-CH_2-C, 8). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 1.60 dl/g.

Analysis. Calcd for $(C_{18}H_{23.2}Cl_{0.8}N_4O_4)_n$: N, 14.56%. Found: N, 14.50%.

Poly(2,6-pyridinediylcarbonyliminotetramethyleneiminooxalyliminotetramethyleneiminocarbonyl) (p-4-2-4-P) by Interfacial Polymerization

N,N'-Bis(4-aminobutyl) oxamide (9.82 g, 0.044 mole) and Na_2CO_3 (9.20 g, 0.087 mole) in 450 ml of distilled water were reacted with 2.6-pyridinedicarboxylic acid chloride (8.85 g, 0.044 mole) in 250 ml of chloroform; reaction time 4 min; polymer yield 14.80 g (97%); decomposed > 340°C (DSC). IR spectrum (film): 3290 cm^{-1} (N$\underline{H}$CO stretching), 2940 cm^{-1} (asym. stretching of CH_2), 2870 cm^{-1} (sym.

stretching of CH_2), 1660 cm^{-1} (CO stretching), 1523 cm^{-1} (NH bending), 1444 cm^{-1} (CN stretching), and 731 and 718 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 8.85 to 8.10 (irresolvable; NHCOCO, 2, and aromatic H, 4, and NHCO, 2), 3.66 (N-CH_2, 8), and 1.87 (C-CH_2-C, 8). The inherent viscosity of a 0.5% solution of the polymer in DMAc containing 3% LiCl was 0.88 dl/g.

Analysis. Calcd for $(C_{17}H_{23}N_5O_4)_n$: N, 19.39%. Found: N, 18.75%.

Poly(iminohexamethyleneiminooxalyliminohexamethyleneiminoisophthaloyl) (p-6-2-6-I) by Interfacial Polymerization

N,N'-Bis(6-aminohexyl) oxamide (2.86 g, 0.010 mole) and Na_2CO_3 (2.12 g, 0.020 mole) in 320 ml of distilled water were reacted with isophthaloyl chloride (2.03 g, 0.010 mole) in 210 ml of chloroform; reaction time 5 min; polymer yield 3.30 g (79%); mp 254°C (decomposed > 285°C) (DSC). IR spectrum (film): 3290 cm^{-1} (NHCO stretching), 2940 cm^{-1} (asym. stretching of CH_2), 2870 cm^{-1} (sym. stretching of CH_2), 1660 cm^{-1} (CO stretching), 1530 cm^{-1} (NH bending), 1443 cm^{-1} (CN stretching), and 738 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 8.75 to 7.65 (irresolvable; NHCOCO, 2, and aromatic H, 4, and NHCO, 2), 3.60 (N-CH_2, 8), and 1.70 (C-CH_2-C, 16). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.80 dl/g.

Analysis. Calcd for $(C_{22}H_{32}N_4O_4)_n$: N, 13.45%. Found: N, 12.58%.

Poly(iminohexamethyleneiminooxalyliminohexamethyleneiminoterephthaloyl) (p-6-2-6-T) by Interfacial Polymerization

N,N;-Bis(6-aminohexyl) oxamide (7.15 g, 0.025 mole) and Na_2CO_3 (5.30 g, 0.050 mole) in 350 ml of distilled water were reacted with terephthaloyl chloride (5.07 g, 0.025 mole) in 200 ml of chloroform; reaction time 5 min; polymer yield 9.00 g (89%); decomposed > 395°C (DSC). IR spectrum (film): 3290 cm^{-1} (NHCO stretching), 2940 cm^{-1} (asym. stretching of CH_2), 2870 cm^{-1} (sym. stretching of CH_2), 1650 cm^{-1} (CO stretching), 1550 and 1518 cm^{-1} (NH bending), 1441 cm^{-1} (CN stretching), and 730 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 8.65 to 7.65 (irresolvable; NHCOCO, 2, and aromatic H, 4, and NHCO, 2), 3.63 (N-CH_2, 8), and 1.70 (C-CH_2-C, 16). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 0.66 dl/g.

Analysis. Calcd for $(C_{22}H_{32}N_4O_4)_n$: N, 13.45%. Found: N, 12.66%.

Poly(2,6-pyridinediylcarbonyliminohexamethyleneiminooxalyliminohexamethyleneiminocarbonyl) (p-6-2-6-P) by Interfacial Polymerization

N,N'-Bis(6-aminohexyl) oxamide (12.31 g, 0.043 mole) and Na$_2$CO$_3$ (9.20 g, 0.087 mole) in 800 ml of distilled water were reacted with 2,6-pyridinedicarboxylic acid chloride (8.85 g, 0.043 mole) in 400 ml of chloroform; reaction time 5 min; polymer yield 10.00 g (56%); decomposed > 340°C (DSC). IR spectrum (film): 3290 cm^{-1} (N$\underline{H}$CO stretching), 2940 cm^{-1} (asym. stretching of CH$_2$), 2860 cm^{-1} (sym. stretching of CH$_2$), 1660 cm^{-1} (CO stretching), 1530 cm^{-1} (NH bending), 1443 cm^{-1} (CN stretching), and 732 and 720 cm^{-1} (NH out-of-plane bending). The PMR (CF$_3$COOH) showed δ: 9.10 to 8.10 (irresolvable; NHCOCO, 2, and aromatic H, 3 and NHCO, 2), 3.60 (N-CH$_2$, 8), and 1.70 (C-CH$_2$-C, 16). The inherent viscosity of a 0.5% H$_2$SO$_4$ solution of this polymer was 0.80 dl/g.

Analysis. Calcd for (C$_{21}$H$_{31}$N$_5$O$_4$)$_n$: N, 16.78%. Found: N, 16.12%.

Synthesis of N,N'-Bis(2-aminoethyl)succinamide (m-2-4-2)

To a 500-ml three-necked round-bottomed flask was added ethylenediamine (27.76 g, 0.46 mole) in 150 ml petroleum ether, bp 40-60°C. Diethyl succinate (23.40 g, 0.13 mole) in 300 ml of petroleum ether was added dropwise over a 1-hr period. The temperature of the reaction mixture was kept below 0-10°C. The solid was isolated and extracted in a Soxhlet extractor with THF; monomer yield 12.00 g (48%); mp 130.5-132°C (capillary). IR spectrum (KBr): 3275 cm^{-1} (N$\underline{H}$CO stretching), 2920 cm^{-1} (asym. stretching of CH$_2$), 2870 cm^{-1} (sym. stretching of CH$_2$), 1625 cm^{-1} (CO stretching), 1545 cm^{-1} (NH bending), 1465 cm^{-1} (CN stretching), and 730 cm^{-1} (NH out-of-plane bending). The PMR (CF$_3$COOH) showed δ: 8.36 (N$\underline{H}$CO, 2), 7.26 ($^+$NH$_3$, 6), 3.92 (CONH-C$\underline{H}_2$, 4), 3.62 ($^+$H$_3$N-C$\underline{H}_2$, 4), and 3.01 (CO-CH$_2$, 4).

Analysis. Calcd for C$_8$H$_{18}$N$_4$O$_2$: N, 27.20%. Found: N, 27.18%.

Poly(iminoethyleneiminosuccinyliminoethyleneiminoisophthaloyl) (p-2-4-2-I) by Interfacial Polymerization

N,N'-Bis(2-aminoethyl) succinamide (2.85 g, 0.017 mole) and Na$_2$CO$_3$ (3.48 g, 0.032 mole) in 200 ml of distilled water were reacted with isophthaloyl chloride (3.34 g, 0.017 mole) in 125 ml of chloroform; an extra 50 ml of chloroform was added after 1-2 min; total reaction time 5 min; polymer yield 2.70 g (54%); mp 267°C (decomposed > 345°C) (DSC). IR spectrum (film): 3290 cm^{-1} (N$\underline{H}$CO stretching), 3065 cm^{-1} (asym. stretching of CH_2), 2940 cm^{-1} (sym. stretching of CH_2), 1645 cm^{-1} (CO stretching), 1540 cm^{-1} (NH bending), 1435 cm^{-1} (CN stretching), and 740 to 705 cm^{-1} (NH out-of-plane bending). The PMR (CF_3COOH) showed δ: 8.50 to 7.83 (irresolvable; aromatic H, 4, and NHCO, 2), 3.90 (N-CH_2, 8), and 3.03 (-CO-CH_2, 4). The inherent viscosity of a 0.5% H_2SO_4 solution of this polymer was 2.50 dl/g.

Analysis. Calcd for $(C_{16}H_{20}N_4O_4)_n$: N, 16.86%. Found: N, 16.34%.

Poly(imino-1,3-phenyleneiminooxalylimino-1,3-phenyleneiminoisophthaloyl) (p-MPD-2-MPD-I) by Solution Polymerization

N,N'-Bis(3-aminophenyl) oxamide (7.70 g, 0.028 mole) [2] and DMAc containing 4% LiCl (100 ml) were reacted with isophthaloyl chloride (5.68 g, 0.028 mole); reaction temperature 0°C; reaction time 10 hr; polymer yield 11.20 g (100%); decomposed > 385°C (DSC). IR spectrum (film): 3280 cm^{-1} (NHCO stretching), 3100 to 2850 cm^{-1} (asym. and sym. stretching of CH_2), 1655 cm^{-1} (CO stretching), 1515 cm^{-1} (NH bending), 1418 cm^{-1} (CN stretching), and 730 cm^{-1} (NH out-of-plane bending). The PMR (4% LiCl/DMAc) showed δ: 9.74 (NHCOCO, 2), 9.04 (NHCO, 2), and 8.42 to 7.36 (aromatic H, 8). The inherent viscosity of a 0.5% solution of this polymer in 3% LiCl/DMAc was 0.76 dl/g.

Analysis. Calcd for $(C_{22}H_{16}N_4O_4)_n$: N, 14.00%. Found: N, 13.52%.

Measurements

Elemental analyses were performed by Instranal Laboratories, Inc., Rensselaer, N. Y., and by the Microanalysis Laboratories of the University of Massachusetts in Amherst, Massachusetts. The melting points were determined in a few cases in a capillary tube in a Mel-Temp apparatus. All polymer melting and decomposition points, including the melting behavior and some degradation studies, were determined on a Perkin-Elmer DSC-1B differential scanning calorimeter at a heating rate of 20°C/min under nitrogen.

The infrared spectra were determined on a Beckman IR-10 or a Perkin-Elmer IR-727 spectrometer. Where possible, spectra of the polymers were measured on films cast on KBr disks from 5 w% polymer solutions in CF_3COOH. Otherwise, spectra were measured by the standard KBr technique.

PMR spectra were measured on a Hitachi Perkin-Elmer R-24 NMR spectrometer (60 MHz) and a Perkin-Elmer R-32 NMR spectrometer (90 MHz) of 5-10% polymer solutions in CF_3COOH (except where noted otherwise).

The viscosities of the polymers were measured on 5 w% solutions of polymer in sulfuric acid (or LiCl/DMAc or CF_3COOH where noted otherwise) in a Cannon-Fenske viscometer at a temperature of 30°C.

RESULTS AND DISCUSSION

Synthesis of Regular Aliphatic/Aromatic Copolyoxamides:

Regular copolyoxamides of the general formula $(A\text{-}2\text{-}A\text{-}D)_n$, where A is an alkylenediamine from 2 to 6 carbon atoms and D is an aromatic or alicyclic dicarboxylic acid group, were prepared by interfacial or solution polymerization. The diamine-oxamides (m-2-2-2) to (m-6-2-6) were sufficiently soluble in water such that an interfacial polymerization could be carried out, sometimes at elevated temperature. The interfacial polymerization had the advantage that molar equivalency of the diamine and diacid chloride was not critical and the reaction was completed in less than 5 min. Much of the work in this paper is concerned with the use of m-2-2-2 as the diamine component.

$$H_2N\text{-}(CH_2)_n\text{-}NH\text{-}COCO\text{-}NH\text{-}(CH_2)_n\text{-}NH_2 + ClOC\text{-}R\text{-}COCl$$

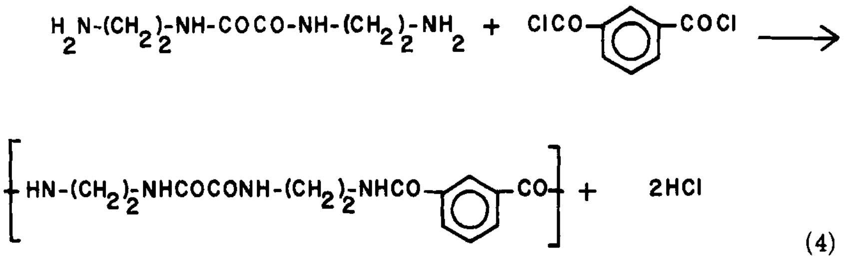
$$\longrightarrow \text{-}[HN\text{-}(CH_2)_n\text{-}NH\text{-}COCO\text{-}NH\text{-}(CH_2)_n\text{-}NHCO\text{-}R\text{-}CO]\text{-}$$

$$+ 2\ HCl \qquad (3)$$

It was substantially water-soluble and consequently interfacial polymerization usually was preferred. The synthesis of regular aliphatic/aromatic copolyoxamide by interfacial polymerization gave polymers with an inherent viscosity of 0.30-0.80 dl/g in high yields. In many cases these polymers formed brittle films and an inherent viscosity of higher than 1.00 dl/g was generally necessary to obtain films sufficiently tough to be suitable for preparation of asymmetric membranes.

Regular Copolyoxamides with Aromatic Dicarboxylic Acid Chlorides

Regular aliphatic/aromatic copolyoxamides of m-2-2-2 with aromatic dicarboxylic acid chlorides were prepared according to the general formula expressed in Eq. (4), which describes the preparation of p-2-2-2-I, the most extensively studied polymer of this series.



(4)

This polymer was prepared from m-2-2-2 by interfacial polymerization with isophthaloyl chloride with sodium carbonate as the acid acceptor and chloroform as the organic phase. The polymer was obtained in almost quantitative yield and it melted at 367°C which is near its decomposition point. The infrared spectra and NMR spectra confirmed the structure of this polymer. Inherent viscosities of more than 1.30 and in some cases as high as 1.90 dl/g have been obtained. Solution polymerization in DMAc in the presence of some anhydrous triethylamine gave p-2-2-2-I of an inherent viscosity of 0.90 dl/g in good yield. It was not uncommon that the molecular weight of these regular copolyoxamides, as judged by the inherent viscosity, was slightly lower in the case of the solution polymerization. m-2-2-2 reacted with terephthaloyl chloride by interfacial polymerization to give a nearly quantitative yield of p-2-2-2-T of reasonable molecular weight. As expected, the melting point and decomposition point of this polymer were above 400°C. A high melting copolymer of 20% tetrachloroterephthaloyl chloride and 80% isophthaloyl chloride was obtained from a corresponding mixture of the diacid chlorides in an interfacial polymerization with m-2-2-2. This polymer was more soluble in organic solvents but was also more hydrophobic than the previous two polymers, and the water permeability was low.

p-2-2-2-P was prepared by interfacial polymerization and by solution polymerization. In both cases the polymer obtained had a relatively low inherent viscosity regardless of whether the polymer was prepared by interfacial polymerization or by solution polymerization (0.30 dl/g). As it will be indicated later, it is thought that this low molecular weight is not caused by an impurity in the diacid chloride but rather by insolubility of the polymer in the reaction medium in the case of the solution polymerization which prevented the formation of high molecular weight polymer. In the case of interfacial polymerization it is believed that oligomers and low molecular weight polymers having the reactive acid chloride group as an endgroup could be hydrolyzed readily because of the high hydrophilicity of the pyridine ring and consequently the formation of high molecular weight polymer was not possible. In the solution polymerization for the preparation of p-2-2-2-P, even in the presence of lithium chloride and triethylamine, the polymer precipitated early in the polymerization in a physical form which prevented the formation of high polymers. p-2-2-2-(I50/P50) was prepared in good yields from m-2-2-2 and a 50/50 solution of isophthaloyl chloride and 2,6-pyridinedicarboxylic acid chloride by interfacial polymerization. Also, in this case the inherent viscosity of the copolymer was low (0.30 dl/g). It appears that the hydrolysis of the acid chloride group adjacent to the pyridine ring limits molecular weight here as in the preparation of the p-2-2-2-P.

By interfacial polymerization the regular copolyoxamide of m-2-2-2 and 4,6-pyrimidinedicarboxylic acid chloride was prepared with chloroform as the organic phase. Again, the inherent viscosity of this polymer was only 0.25 dl/g.

Interfacial polymerizations of m-2-2-2 were also carried out with 1,6-naphthalenedicarboxylic acid chloride and 2,6-naphthalenedicarboxylic acid chloride. The polymers gave an inherent viscosity in sulfuric acid of 0.78 dl/g and 0.58 dl/g, respectively. Since the regular polymers were from m-2-2-2 and aromatic (not heteroaromatic) dicarboxylic acids, the molecular weight was high.

Polymers of m-2-2-2 with aromatic dicarboxylic acid chlorides are high melting and usually melt with decomposition above 350° C. The determination of the melting point was carried out by DSC but the melting points varied from preparation to preparation within a range of about 10° C.

The inherent viscosities of these polymers were measured either in CF_3COOH, H_2SO_4, or DMAc/LiCl (0.5% solutions) at room temperature and the infrared spectra were measured in film form. The PMR spectra of all these polymers agreed with the proposed structure and were measured in CF_3COOH or DMAc/LiCl. The δ values are recorded and described in the experimental part.

It was very difficult to obtain good elemental analyses of C, H, and N from all the polyamide samples. Consequently, in many cases the nitrogen analysis together with the PMR identification of the polymer sample were used to confirm the structure. Nitrogen analyses of different kinds were used for the analysis of the regular aliphatic/aromatic copolyoxamides. They included the normal Dumas method and also a variation of the method; combustion in oxygen. In the initial part of the combustion the polymers degraded as the temperature was increased and produced materials that were difficult to burn. As a consequence, all our nitrogen analyses were low, sometimes as much as 1-3%. Good analyses could only be obtained with careful individual attention to the combustion of the polymer samples. In no case was the observed nitrogen analysis higher than the theoretical.

It can be seen that the polymers produced from the heteroaromatic dicarboxylic acid chlorides, 2,6-pyridinedicarboxylic acid chloride and 4,6-pyrimidinedicarboxylic acid chloride, have substantially lowered inherent viscosities. As it was indicated before, the lower viscosity and consequently lower molecular weight seems to be caused by the ease of hydrolysis of the activated acid chloride group and does not appear to depend on the purity of the acid chloride.

The structural formula and abbreviations of the aromatic dicarboxylic acids used for the preparation of regular aliphatic/aromatic copolyoxamides are described in Table 1.

Copolyoxamides with Alicyclic Dicarboxylic Acid Chlorides

Regular aliphatic/alicyclic copolyoxamides from m-2-2-2 and the two stereoisomers of 1,4-cyclohexanedicarboxylic acid chloride as well as of 1,1-cyclobutanedicarboxylic acid chloride were prepared by interfacial polymerization. The inherent viscosity of these polymers in sulfuric acid solution was 0.5 dl/g and all polymers formed brittle films.

Regular polymers of m-2-2-2 with 1,4-cyclohexanedicarboxylic acid, both cis and trans isomer, melted with decomposition above 370°C, while the 1,1-cyclobutanedicarboxylic acid polymer melted at 286°C.

It was considered desirable to study the behavior and the characteristics of alicyclic copolyoxamides in order to determine if the aromatic ring influenced the behavior of the polymer and if alicyclic groups such as cyclobutane or cyclohexane rings could reduce sufficiently the mobility of the polymer chains, and the polymers would hence be of higher or more definable glass transition points. All polymers had molecular weights that were low and the films were

TABLE 1. Dicarboxylic Acids Used for the Preparation of Regular Aliphatic/Aromatic Copolyoxamides

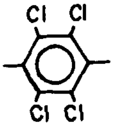
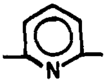
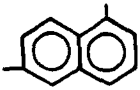
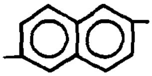
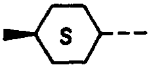
R	D = –OC–R–CO–
	Terephthalic acid (T)
	Isophthalic acid (I)
	Tetrachloroterephthalic acid (CT)
	2,6-Pyridinedicarboxylic acid (P)
	4,6-Pyrimidinedicarboxylic acid (Pm)
	1,6-Naphthalenedicarboxylic acid (1,6 N)
	2,6-Naphthalenedicarboxylic acid (2,6 N)

TABLE 2. Dicarboxylic Acids Used for the Preparation of Regular Aliphatic/Alicyclic Copolyoxamides

R	D = –OC–R–CO–
	1,4-trans-Cyclohexanedicarboxylic acid (trans-1,4)
	1,4-cis-Cyclohexanedicarboxylic acid (cis-1,4)
	1,1-Cyclobutanedicarboxylic acid (1,1-cyclobut.)

very brittle. The brittleness may have been caused by the low molecular weight of the polymer and/or by the lack of aromatic groups in the polymer which often increase the toughness of condensation polymers in spite of low molecular weight.

Table 2 lists the dicarboxylic acids used for the preparation of the regular aliphatic/alicyclic copolyoxamides.

Copolyoxamides with Several Oxamide Groups in the Aliphatic Diamine

m-2-2-2-2-2 and m-2-2-2-2-2-2-2 were synthesized from readily available starting materials. The preparation of m-2-2-2-2-2 was accomplished by the condensation of bis(ethoxyoxalylimino)ethane with two moles of ethylenediamine, as indicated in Eq. (5). This reaction was carried out in boiling tetrahydrofuran and gave the desired product in high yields. Bis(ethoxyoxalylimino) ethane was prepared in anhydrous ether by allowing ethylenediamine to react with diethyl oxalate in great excess below room temperature.

In principle, m-2-2-2-2-2 can be prepared from bis(ethoxyoxalylimino)ethane and ethylenediamine or by the reaction of ethyl

$$\mathrm{Et{-}OOC{-}CONH{+}CH_2{+}_2NHCO{-}COO{-}Et} + 2\ \mathrm{H_2N{+}CH_2{+}_2NH_2}$$

$$\longrightarrow \mathrm{H_2N{+}CH_2{+}_2NHCOCONH{+}CH_2{+}_2NHCOCONH{+}CH_2{+}_2NH_2}$$

$$+\ 2\mathrm{Et{-}OH} \qquad \text{m2-2-2-2-2} \qquad (5)$$

N-(2-aminoethyl) oxamate and ethylenediamine by involving symmetric intermediates. Several asymmetric reactions can be considered, for example, the reaction of m-2-2-2 with ethyl N-(2-aminoethyl)oxamate hydrochloride. We chose the first reaction which gave the desired product in excellent yield.

m-2-2-2-2-2 was soluble in trifluoroacetic acid and boiling water and could be reacted under interfacial polymerization conditions and at elevated temperatures with isophthaloyl chloride and 2,6-pyridinedicarboxylic acid chloride. An inherent viscosity of 0.45 dl/g in H_2SO_4 was measured for the polymeric product from isophthaloyl chloride which had the structure of p-2-2-2-2-2-I. The reaction of m-2-2-2-2-2 with 2,6-pyridinedicarboxylic acid chloride gave a polymer whose inherent viscosity was only 0.25 dl/g, an experience which parallels our earlier experience on the preparation of p-2-2-2-P and polymers which were prepared from other heteroaromatic diacid chlorides.

N,N'-Bis(2-ethoxyoxalyliminoethylene) oxamide was obtained from N,N-bis(2-aminoethyl) oxamide and diethyl oxalate in high yields and it was then allowed to react with ethylenediamine.

$$\mathrm{H_2N{+}CH_2{+}_2NH\ COCONH{+}CH_2{+}_2NH_2} + 2\ \mathrm{Et{-}OOCCOO{-}Et} \longrightarrow$$

$$\mathrm{Et{-}OOCCONH{+}CH_2{+}_2NHCOCONH{+}CH_2{+}_2NHCOCOO{-}Et}$$

$$+\ 2\ \mathrm{Et{-}OH} \qquad (6)$$

Hexafluoroisopropanol was the only solvent in which preparation of m-2-2-2-2-2-2-2 could be effectively carried out. m-2-2-2-2-2-2-2 was obtained in 50% yield and purified via the dihydrochloric acid salt. The spectral identification and the elemental analysis confirmed the structure of this compound.

Unfortunately, m-2-2-2-2-2-2-2 was only slightly soluble in water and attempts to carry out interfacial polymerization with isophthaloyl chloride gave products which could not be identified as the desired regular copolyoxamide.

$$\mathrm{Et\text{-}OOCCONH\text{-}(CH_2)_2\text{-}NHCOCONH\text{-}(CH_2)_2\text{-}NHCOCOO\text{-}Et}$$

$$+\ 2\ \mathrm{H_2N\text{-}(CH_2)_2\text{-}NH_2} \longrightarrow$$

$$\mathrm{H_2N\text{-}(CH_2)_2\text{-}NHCOCONH\text{-}(CH_2)_2\text{-}NHCOCONH\text{-}(CH_2)_2\text{-}NHCOCONH\text{-}(CH_2)_2\text{-}NH}$$

$$+\ 2\ \mathrm{Et\text{-}OH} \qquad (7)$$

In principle, m-2-2-2-2-2-2-2 could be prepared from two moles of m-2-2-2 and 1 mole of diethyl oxalate or in the way which we indicated [Eq. (6)], i.e., with inverse m-2-2-2-2-2 where the end groups are oxalate ester groups with two moles of ethylenediamine [Eq. (7)], by use of symmetrical intermediates. However, the second reaction proved to be successful, and no further attempts to improve the methods of synthesis were undertaken.

Copolyoxamides with Various Aliphatic Diamines

In the previous sections we described the use of m-2-2-2 as the diamine-oxamide as well as diamine oligooxamides with more than one oxamide group in the molecule.

We also used m-0-2-0, m-3-2-3, m-4-2-4, and m-6-2-6 as the diamineoxamide intermediates for the polymerization with aromatic dicarboxylic acid chlorides.

m-0-2-0, oxalic dihydrazide, was allowed to react by interfacial and solution polymerization with isophthaloyl chloride. By interfacial polymerization, a polymer of low molecular weight having 0.23 dl/g in 0.5% H_2SO_4 solution was obtained, while the solution polymerization of oxalic dihydrazide and isophthaloyl chloride in DMAc in the presence of LiCl gave a polymer with an inherent viscosity of 0.44 dl/g and which decomposed over 295°C.

Interfacial polymerization of m-3-2-3 with (1) isophthaloyl chloride, (2) a 20/80 mole % mixture of CT and isophthaloyl chloride, and (3) 2,6-pyridinedicarboxylic acid chloride gave polymers whose inherent viscosity were 1.90 dl/g for the first two cases and 0.36 dl/g for the third. As it can be seen again, the 2,6-pyridinedicarboxylic acid chloride gave polymers of low molecular weight apparently caused by the ease of hydrolysis of the acid chloride group.

m-4-2-4 was also allowed to react by interfacial polymerization with isophthaloyl chloride, a 20/80 mole % mixture of CT and isophthaloyl chloride, and 2,6-pyridinedicarboxylic acid chloride.

Regular copolyoxamides were obtained with an inherent viscosity of 1.57 dl/g, 1.60 dl/g, and 0.88 dl/g, respectively. p-4-2-4-I was also obtained by solution polymerization in chloroform and had an inherent viscosity of 0.88 dl/g.

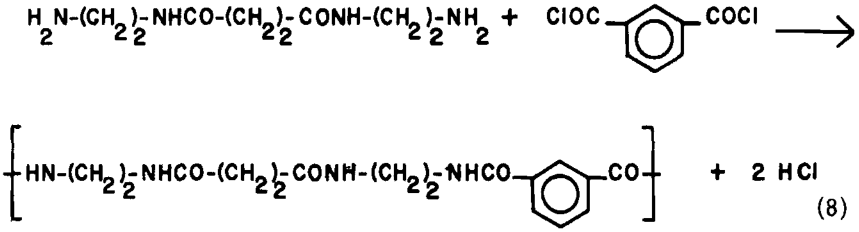
It should be pointed out that the interfacial polymerization of m-4-2-4 with 2,6-pyridinedicarboxylic acid chloride gave a substantially higher molecular weight as judged by the inherent viscosity than the polymers obtained from m-2-2-2 or m-3-2-3 and 2,6-pyridinedicarboxylic acid chloride. The increased viscosity and correspondingly higher molecular weight of the regular copolyoxamide apparently reflects the lower solubility of m-4-2-4 in the aqueous phase. This diamine diffuses to a greater extent into the organic part of the interface and the condensation reaction is consequently carried out more on the organic side, in turn preventing, to a considerable extent, the hydrolysis of the more active acid chloride.

By interfacial polymerization, m-6-2-6 was allowed to react with isophthaloyl chloride, terephthaloyl chloride, and 2,6-pyridinedicarboxylic acid chloride. The polymers were obtained in good to excellent yields from this reaction and the inherent viscosities of these polymers were satisfactory (0.70-0.80 dl/g).

The copolyoxamide p-6-2-6-P also had a reasonably good molecular weight, similar in inherent viscosity to p-4-2-4-P. Since in all cases the 2,6-pyridinedicarboxylic acid chloride used was the same sample and purified the same way, it can be concluded that the difference in the molecular weight involving polymers of 2,6-pyridinedicarboxylic acid chloride was not caused by a different level of impurities in the 2,6-pyridinedicarboxylic acid chloride but by the reactivity of the acid chloride end groups in the polymers.

It is known that interfacial polymerization proceeds in various places of the organic/aqueous interface. The more water soluble the individual diamineoxamides, the more will the reaction be carried out on the aqueous side of the interface and consequently in the case of highly reactive acid chlorides, will cause the formation of low molecular weight polymers as it was experienced with 2,6-pyridinedicarboxylic acid chloride and m-2-2-2 and m-3-2-3. In the cases of m-4-2-4 and m-6-2-6 the diamines are sufficiently soluble in the organic phase and the reaction was essentially carried out on the organic side of the interface.

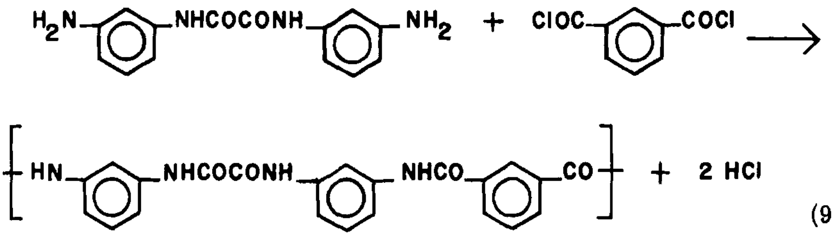
An additional example of our series on aliphatic/aromatic regular copolyamides, and not only copolyoxamides, was that N,N'-bis(2-aminoethyl)succinamide (m-2-4-2) was also prepared in the usual manner and in reasonable yield. m-2-4-2 was allowed to react by interfacial polymerization with isophthaloyl chloride with chloroform as the organic phase and gave in moderate yield polymer p-2-4-2-I with an inherent viscosity of 2.50 dl/g.



(8)

All polymers described in this section had melting points from 250°C to nearly 400°C. The lower melting materials usually contained a larger number of methylene groups in the polymer chain as exemplified by p-2-4-2-I, mp 267°C, or p-6-2-6-I, mp 254°C. Most copolyoxamides degraded above 250°C and some as high as 400°C at a substantial rate as judged by the results of the DSC scans.

One completely aromatic regular copolyoxamide was prepared from N,N'-bis(3-aminophenyl) oxamide and isophthaloyl chloride. This polymerization was carried out in DMAc containing 4% LiCl at 0°C. The polymer was obtained in 100% yield and an inherent viscosity of 0.76 dl/g in DMAc with 3% LiCl. The polymer decomposed without melting above 385°C.



(9)

The techniques which were developed in the past for the preparation of diamine-oxamides and for the polymerization of these diamine-oxamides with aliphatic diacid chlorides could be successfully applied for the preparation of regular aliphatic/aromatic or aliphatic/alicyclic copolyoxamides. These polymers could be prepared in good yields by interfacial and solution techniques and gave polymers, some of which have molecular weights such that they are suitable as membrane materials. Preparation of polymers from m-2-2-2-2-2 and m-2-2-2-2-2-2-2 was attempted in the hope of preparing polymers with larger sequences of hydrophilic groups to improve the water transport through membranes. The use of aromatic diacid chlorides, particularly condensed aromatic chlorides derived from naphthalene dicarboxylic acids, was considered important to increase the influence of groups which would contribute to a higher glass transition temperature of the polymer.

The work on the preparation of membranes from these aliphatic/aromatic copolyoxamides, their characterization and the description of their performance will be described elsewhere.

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