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Regular Copolyamides. IX.* Some Aliphatic Aromatic Copolyoxamides

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ABSTRACT

Aromatic/aliphatic regular copolyoxamides were prepared from aromatic diamine-oxamides and aliphatic diacid chlorides of various lengths of methylene groups by solution polymerization. The aromatic diamine oxamides, N,N'-bis(4-aminophenyl)oxamide and N,N'-bis(3-aminophenyl)oxamide were prepared and both were reacted with adipoyl chloride, suberoyl chloride, and sebacoyl chloride to form six new regular copolyoxamides. The polymers formed were soluble in sulfuric acid and also in some polar amide solvents. All copolyoxamides were high melting, with the meta-phenylene copolyoxamides melting from 346 to 373°C with decreasing length of the aliphatic diacid chloride, and the para-phenylene copolyoxamides decomposing prior to melting at near 400°C. The new polymers were characterized by UV spectrophotometry, differential scanning calorimetry, and thermal gravitational analysis.

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*Part VIII: D. Tirrell, S. Grossman, and O. Vogl, ACS Symp. Ser., 127 (S. P. Rowland, ed.), 21, 361 (1980).

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INTRODUCTION

The preparation and polymerization of oxamides to form copolyoxamide polymers has been of interest to this research group for some time. Early work was concerned with the preparation and polymerization of cyclic oxamides [1, 2]. Further work concentrated on the preparation of α,ω-diamine oxamides with aliphatic spacer groups [3] and the polymerization of these aliphatic oxamides by solution and interfacial methods to form regular aliphatic copolyoxamides [4]. It was discovered that aliphatic/aromatic copolyoxamides [5], particularly those utilizing the isophthaloyl chloride comonomer with N,N'-bis(2-aminoethyl) oxamide, were excellent candidates for desalination membranes by reverse osmosis [6]. These regular aliphatic/aromatic copolyoxamides were further developed and investigated for use in membrane technology [7, 8].

Wholly aromatic para-phenylene oxamides have been investigated for various uses. It has been reported that diphenyl oxamide and various derivatives thereof have shown considerable utility as UV stabilizers [9-11]. Other work has concentrated on fiber preparation and characterization of regular, wholly aromatic polyoxamides. Fibers made from the reaction of aromatic diamine-oxamides [12-15] and diacid chloride-oxamides [16] with aromatic diacids and aromatic diamines have resulted in fibers with high modulus and anisotropic solution properties. These efforts have concentrated on the attempt to make wholly para-phenylene aromatic, stable, lyotropic liquid crystalline polymers similar to the well-known aromatic polyamides [17]. However, the oxamide link has been shown to be less thermally and chemically stable.

The objective of this work was to synthesize regular aromatic/aliphatic copolyoxamides. Both N,N'-bis(3-aminophenyl)oxamide (m-3p,2,3p) and N,N'-bis(4-aminophenyl)oxamide (m-4p,2,4p) as described previously [3] were to be copolymerized with adipoyl, suberoyl, and sebacoyl chloride to form new regular copolyoxamides. The new polymers were then characterized by UV spectrophotometry, differential scanning calorimetry, and thermal gravitational analysis.

EXPERIMENTAL PART

Materials

Reactants

Diethyl oxalate (DEO) (Aldrich Chemical Co.) was distilled under nitrogen at 6 mmHg and stored over 3A molecular sieves.

p-Phenylene diamine (PPD) (Fischer Chemical Co., mp 140.7-141.2°C) and m-phenylene diamine (MPD) (Aldrich Chemical Co.), were used as received.

Sebacoyl chloride (SEB) (Aldrich Chemical Co.), adipoyl chloride (ADC) (Aldrich Chemical Co.), and suberoyl chloride (SUC) (Aldrich Chemical Co.) were distilled under nitrogen at reduced pressure and then stored over fresh anhydrous magnesium sulfate in an inert atmosphere.

Solvents

Dimethylacetamide (DMAc) (Aldrich Chemical Co.) was stirred over anhydrous barium oxide for several days followed by a 1-h reflux under nitrogen and finally distillation under nitrogen at reduced pressure (5 mmHg). The product was stored in an inert atmosphere over 4A molecular sieves.

Pyridine (Py) (Eastman Kodak Co.) was heated to reflux under nitrogen at ambient pressure over anhydrous barium oxide for 20 h followed by distillation under nitrogen. It was stored in an inert atmosphere over fresh barium oxide.

Hexamethylphosphoric triamide (HMPA) (Eastman Kodak Co.) was stirred over anhydrous barium oxide for 20 h, heated to reflux at 4 mmHg over barium oxide for 3 h, and then distilled under nitrogen at 4 mmHg. The middle fraction was then distilled from sodium metal under nitrogen at 1 mmHg and stored over 4A molecular sieves in an inert atmosphere.

1-Methyl-2-pyrollidone (MP) (Aldrich Chemical Co.) was distilled at 5 mmHg under nitrogen with benzene to remove water as a benzene azeotrope, and then stored over 4A molecular sieves in an inert atmosphere.

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

Measurements

Ultraviolet spectra were recorded on a Beckman MVI spectrophotometer. The m-3p,2,3p, m-4p,2,4p, and polymer samples were measured in solutions of 3.0×10^{-3} M based on total oxamide monomer in MP, HMPA, and sulfuric acid, respectively.

Differential scanning calorimetry was performed on a Perkin-Elmer DSC-II.

Thermal gravitational analysis was performed on a Perkin-Elmer TGS-II.

Polymer inherent viscosities were measured in sulfuric acid solutions (0.5% by weight) in an Ubbelohde viscometer at 30°C.

Microanalyses (C, H, N) were done at the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

Preparations

Monomers

N,N'-Bis(3-aminophenyl)oxamide (m-3p,2,3p). m-3p,2,3p was synthesized by an improved method first described by Chang and Vogl [3]. MPD (64.5 g, 0.60 mol) was placed in a three-neck, 250 mL flask which was heated under nitrogen to 110°C. DEO (15.0 g, 0.10 mol) diluted with 6 mL of Skelly F was added dropwise with vigorous stirring. The temperature was then raised to 120°C for 1.5 h as the Dean Stark trap filled with condensate. After filtration of the precipitate through an "E" fritted glass filter, the product was washed three times with 50 mL portions of methanol and then dried under a vacuum of 0.05 mmHg (72% yield, mp 233°C). The compound was then purified by heating it with benzene to reflux; a white powder was obtained which was used for polymerizations.

N,N'-Bis(4-aminophenyl)oxamide (m-4p,2,4p). m-4p,2,4p was synthesized by an improved method of Chang and Vogl [3] which gave an off-white product. PPD (46.2 g, 0.43 mol) was added to a 500-mL, three-neck flask which was heated under nitrogen to 150°C. The PPD was allowed to sublime to the top of the reaction vessel so that the DEO from the drop funnel would contact the purest, white crystals initially upon the start of the reaction. Then DEO (10.3 g, 0.070 mol) diluted with 19.5 mL of Skelly F was added dropwise. The temperature was then kept at 150°C for 45 min, after which the precipitated product was collected on an "E" fritted glass filter. It was washed twice with 50 mL portions of methanol and twice with 50 mL portions of acetone. After vacuum drying (0.05 mmHg) the product was an off-white powder (82% yield, mp 280°C). The monomer was heated to reflux with acetone under nitrogen to further purify it prior to its use for polymerizations.

Polymerizations

Poly(imino p-Phenyleneiminooxalylimino p-Phenyleneiminoadipoyl) (p-4p,2,4p,6). m-4p,2,4p (2.69 g, 0.010 mol) was dissolved in 70 mL HMPA and 30 mL MP. Adipoyl chloride (1.83 g, 0.010 mol), diluted with 10 mL MP and 10 mL HMPA, was added dropwise to the m-4p,2,4p solution and allowed to react under nitrogen for 20 h at room temperature. The polymer was precipitated with 100 mL of methanol, collected, washed with methanol and acetone, extracted in a Soxhlet extractor for 2 d each with secondary-butyl alcohol and acetone, and dried under vacuum (0.05 mmHg). It gave 3.65 g (96% yield) of inherent viscosity 0.36 dL/g.

Analysis: Calculated for $(C_{20}H_{20}N_4O_4)_n$: C, 63.1%; H, 5.3%; N, 14.7%. Found: C, 61.4%; H, 5.6%; N, 14.0%.

Poly(imino m-Phenyleneiminooxalylimino m-Phenyleneiminoadipoyl) (p-3p,2,3p,6). m-3p,2,3p (2.69 g, 0.010 mol) was dissolved into 50 mL HMPA and 20 mL MP. Adipoyl chloride (1.83 g, 0.010 mol), diluted with 10 mL HMPA and 10 mL MP, was added dropwise to the m-3p,2,3p solution and allowed to react under nitrogen for 20 h at room temperature. The polymer was precipitated with 100 mL of methanol, collected, washed with methanol and acetone, extracted in a Soxhlet extractor for 2 d each with secondary-butyl alcohol and acetone, and dried under vacuum (0.05 mmHg). It gave 3.51 g (93% yield) of inherent viscosity 0.22 dL/g.

Analysis: Calculated for $(C_{20}H_{20}N_4O_4)_n$: C, 63.1%; H, 5.3%; N, 14.7%. Found: C, 61.6%; H, 5.6%; N, 14.2%.

Poly(imino p-Phenyleneiminooxalyl p-Phenyleneiminosuberoyl) (p-4p,2,4p,8). m-4p,2,4p (2.63 g, 0.0098 mol) was dissolved in 60 mL HMPA and 25 mL MP. Suberoyl chloride (2.07 g, 0.0098 mol), diluted with 10 mL HMPA and 10 mL MP, was added dropwise to the m-4p,2,4p solution and allowed to react under nitrogen for 20 h at room temperature. The polymer was precipitated with methanol, collected, washed with methanol and acetone, extracted in a Soxhlet extractor for 2 d each with secondary-butyl alcohol and acetone, and dried under vacuum. It gave 3.80 g (95% yield) of inherent viscosity 0.48 dL/g.

Analysis: Calculated for $(C_{22}H_{24}N_4O_4)_n$: C, 64.7%; H, 5.9%; N, 13.7%. Found: C, 63.6%; H, 6.3%; N, 12.6%.

Poly(imino m-Phenyleneiminooxalylimino m-Phenyleneiminosuberoyl) (p-3p,2,3p). m-3p,2,3p (2.68 g, 0.010 mol) was dissolved in 60 mL HMPA and 25 mL MP. Suberoyl chloride (2.09 g, 0.010 mol), diluted with 10 mL HMPA and 10 mL MP, was added dropwise to the m-3p,2,3p solution and allowed to react under nitrogen for 20 h at room temperature. The polymer was precipitated with methanol, collected, washed with methanol and acetone, extracted in a Soxhlet extractor for 2 d each with secondary-butyl alcohol and acetone, and dried under vacuum. It gave 2.73 g (63% yield, some polymer was lost in handling) of inherent viscosity 0.25 dL/g.

Analysis: Calculated for $(C_{22}H_{24}N_4O_4)_n$: C, 64.7%; H, 5.9%; N, 13.7%. Found: C, 63.2%; H, 6.0%; N, 13.3%.

Poly(imino p-Phenyleneiminooxalylimino p-Phenyleneiminosebacoyl) (p-4p,2,4p). m-4p,2,4p (4.16 g, 0.015 mol) was dissolved in 40 mL HMPA and 15 mL MP. Sebacoyl chloride (3.64 g, 0.015 mol), diluted with 10 mL HMPA and 10 mL MP, was added dropwise to the m-4p,2,4p solution and allowed to react under nitrogen at room temperature for 2 h. The polymer, which precipitated from solution as a hard mass, was further precipitated by methanol, collected, washed with methanol and acetone, extracted in a Soxhlet extractor for 2 d each with secondary-butyl alcohol and acetone, and dried under vacuum (0.05 mmHg). It gave 6.46 g (97% yield) of inherent viscosity 0.98 dL/g.

Analysis: Calculated for $(C_{24}H_{28}N_4O_4)_n$: C, 66.0%; H, 6.5%; N, 12.8%. Found: C, 63.7%; H, 6.2%; N, 12.4%.

Poly(imino m-Phenyleneiminooxalylimino m-Phenyleneiminosebacoyl) (p-3p,2,3p). m-3p,2,3p (2.70 g, 0.010 mol) was dissolved in 80 mL DMAc and 30 mL pyridine. Sebacoyl chloride (2.10 g, 0.010 mol), diluted by 10 mL DMAc, was added dropwise to the m-3p,2,3p solution and allowed to react under nitrogen at room temperature for 4 h. The polymer, which precipitated from the solution within 15 min, was further precipitated with methanol, washed twice with methanol and acetone, and dried under vacuum (0.05 mmHg). It gave 4.00 g (90% yield) of inherent viscosity 0.25 dL/g.

Analysis: Calculated for $(C_{24}H_{28}N_4O_4)$: C, 66.0%; H, 6.5%; N, 12.8%. Found: C, 64.5%; H, 6.4%; N, 12.3%.

RESULTS AND DISCUSSION

Two general methods to synthesize m-4p,2,4p have been reported. Biland [18] reported a method involving the reaction of oxalyl chloride with p-nitroaniline followed by reduction of the nitro group. Silver [13] reported a melting point of an off-white, similarly synthesized m-4p,-2,4p of 276-277°C with an overall yield for the two-step synthesis of 68%. Chang and Vogl [3] reported the synthesis of m-4p,2,4p in one step by reacting DEO to a sixfold excess of p-phenylene diamine and obtained a 73% yield of a bluish-grey solid that balckened but did not melt. In this work, special care was taken to improve the one-step synthesis of m-4p,2,4p to give an 82% yield of off-white product with a melting point of 280°C. The special care involved using p-phenylene diamine from a freshly opened bottle of higher purity, and then allowing the diamine to sublime to high purity white crystals at the top of the reaction flask so that the DEO from the addition flask contacted the highest grade diamine. This method provides for a quicker, higher yield synthesis of m-4p,2,4p than previously reported from the polymerization of lower grade material.

The solution polymerizations of the aromatic-diamine oxamides (see Fig. 1) with the several aliphatic diacid chlorides involved the usual precautions and inert atmosphere combined with the problem of keeping the polymer in solution during the entire polymerization. The reaction of the meta isomer, m-3p,2,3p, with sebacoyl chloride used a combination of DMAc and pyridine as cosolvents. These cosolvents did not keep the polymer in solution during the reaction, as the polymer precipitated within 15 min. The five other solution polymerizations in this work utilized in HMPA/MP (2:1 by volume) cosolvent system. It

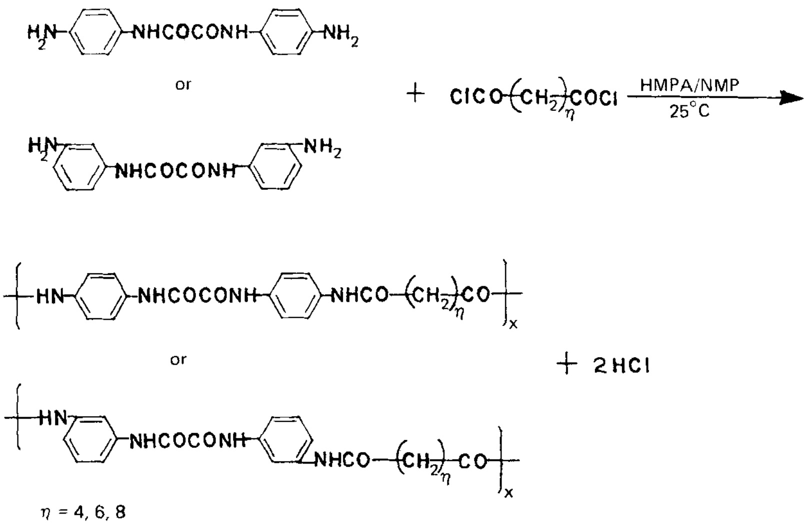

FIGURE 1.

has been reported [19, 20] that amide solvents, like DMAc and potentially HMPA, can be involved in side reactions at room temperature in polycondensations. Side reactions of the solvents with the initial diacid chlorides do not decrease the yield of the polymerization, but the molecular weight, expressed by the inherent viscosity, is reduced. To decrease these side reactions, polyamide formation between diacid chlorides and diamines is frequently performed at lower temperature (-10 to -40°C) and the overall concentration of the reactants are kept higher. Data reported by Bair [20] showed that with increasing weight percent of each reactant, up to a point of 0.3 mol/L, the inherent viscosity of aromatic polyamides increased.

In this work it was not possible to lower the temperature of the reaction below room temperature due to the difficulty of keeping the aromatic diamine oxamides in solution. However, the concentration of the comonomers was varied in an attempt to observe the effect upon molecular weight. The three polymerizations involving m-4p,2,4p with the three diacid chlorides did show an increased inherent viscosity with increasing percentage of comonomers in solution. The weight percent of reactants and inherent viscosities of the corresponding polymers are included in Table 1; a clear correlation of concentration on polymer molecular weight is observed. To further increase the molecular weight in these solution polymerizations, a better optimization of comonomer concentration and comonomer purity should be investigated.

All diamine oxamides and the polymers prepared from them were investigated as to their UV spectra between 600 and 200 nM. This was performed to investigate claims that aromatic diamine oxamide deriva-

TABLE 1. Diamine Oxamide, Diacid Chloride, Weight Percent Monomers in Solvent, Inherent Viscosity, Yield, and Elemental Analysis for the Solution Polymerizations of Regular Aromatic/Aliphatic Copolyoxamides

					Elemental analysis					
					Theoretical			Found		
Diamine oxamide	Diacid chloride	Weight percent monomers in solvent	Inherent viscosity (dL/g)	Yield (%)	C	H	N	C	H	N
m,4p,2,4p	ADC	3.2	0.36	96	63.1	5.3	14.7	61.4	5.6	14.0
m-3p,2,3p	ADC	4.2	0.22	93	63.1	5.3	14.7	61.6	5.6	14.2
m-4p,2,4p	SUC	3.8	0.48	95	64.7	5.9	13.7	63.6	6.3	12.6
m-3p,2,3p	SUC	3.8	0.25	63	64.7	5.9	13.7	63.2	6.0	13.3
m-4p,2,4p	SEB	9.1	0.98	97	66.0	6.5	12.8	63.7	6.2	12.4
m-3p,2,3p	SEB	-	0.25	90	66.0	6.5	12.8	64.5	6.4	12.3

tives were useful UV stabilizers for polyethylene and polyvinyl chloride [9-11]. The diamine oxamide monomers or the corresponding polymers did not absorb in the UV range. This result, however, is clouded by the problem that the solvents utilized to dissolve these difficultly soluble materials absorbed heavily in the 200-250 nM range, thus masking any potential absorption of the oxamides in that range. Additionally, lack of absorption in this range could have been due to shifts in the absorbing wavelength caused by interaction of bound chromophores as reported by Bolotsvetvov [21].

The regular aromatic/aliphatic copolyoxamides made were also investigated by DSC and optical microscopy as to their possible thermotropic liquid crystalline behavior. It was thought that the rigid aromatic oxamide in the backbone could result in some liquid crystalline behavior in these polymers. Lyotropic liquid crystalline behavior, as previously mentioned, has been reported for full aromatic para aromatic copolyoxamides [12-16]. The insertion of flexible aliphatic units into rigid aromatic polyesters has succeeded in reducing the melting point of these compounds below their decomposition point and has yielded thermotropic liquid crystalline polyesters [22]. Attempts to reduce the melting point of rigid aromatic polyamides by introducing flexible spacers into the backbone has been successful in maintaining lyotropic liquid crystalline behavior if the length and percentage of aliphatic flexible units have been held to a very low amount. However, such work has never yielded thermotropic liquid crystalline polyamides [23-25] since the melting points and decomposition points have been too close. The polymers synthesized in this work also had decomposition points for the polymers with 4p,2,4p linkages rather than melting points (see Table 2); consequently, thermotropic liquid crystal behavior was not observed.

The melting points and degradation behavior of the regular aromatic/aliphatic copolyoxamides are reported in Table 2. As can readily be seen, the regular aromatic/aliphatic copolyoxamides with the 4p,2,4p linkage and shorter aliphatic flexible groups had the higher melting behavior. The general rule of about a 10°C drop in the melting point per increase of one methylene unit in the chain seems to hold. The degradation behavior also indicates that the para-polymers are more stable by some 10 to 20°C. The meta-polymers have a melting point rather than a decomposition point.

This work has described the synthesis of six new regular aromatic/aliphatic copolyoxamides by solution polymerization. The improved one-step synthesis of m-4p,2,4p has also been described. The melting and degradation behavior of these six new polymers has also been discussed. No indication of UV absorption of thermotropic liquid crystalline behavior was found in either the monomers or polymers.

TABLE 2. Melting Points and Degradation (10% weight loss) Behavior for Diamine Oxamide Monomers and Regular Aromatic/Aliphatic Copolyoxamides

Material[a]	Melting point (°C)	10% Weight loss (°C)
m-4p,2,4p	280	-
m-3p,2,3p	233	-
p-4p,2,4p,6	Decomposed	390
p-3p,2,3p,6	373	388
p-4p,2,4p,8	Decomposed	400
p-3p,2,3p,8	355	370
p-4p,2,4p,10	Decomposed	397
p-3p,2,3p,20	346	394

[a] All measurements done at 20°C heating rate.

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