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Novel Preparations of Specialty Polyamides by Interfacial and Solution Methods

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ABSTRACT

A series of polyoxamide homopolymers and regular copolyoxamides was prepared by liquid-liquid interfacial, gas-liquid interfacial, and solution polycondensation techniques. Thus, poly(hexamethylene oxamide) {Nylon 62}, poly(ethylene oxamide) {Nylon 22}, and poly(p-phenylene oxamide) were prepared in moderate molecular weight by reacting gaseous oxalyl chloride with aqueous solutions of 1,6-hexanediamine, N,N'-bis(2-aminoethyl) oxamide, and p-phenylenediamine, respectively, using a gas-liquid interfacial technique developed for the continuous production of polyoxamides. A number of regular copolyoxamides were prepared by condensing various aliphatic diamine-diamides with both aliphatic and aromatic acid chlorides using both liquid-liquid interfacial and solution polymerization procedures. Both the yield and molecular weight of the polymers produced were found to be dependent on factors such as polymerization technique, monomer solubility, reaction temperature, reactant concentration, type of solvent, and type of acid acceptor.

INTRODUCTION

Polyamides have been prepared by a number of different techniques including the dehydration of ammonium salts, the condensation of amino acids, the ring opening polymerization of lactams, and the condensation of specific acid derivatives, particularly acid chlorides with diamines.[1] The high reactivity of acid chlorides has enabled these types of polymerization reactions to be carried out at low temperatures with a minimum of side reactions. Consequently, the use of the well known Schotten-Baumann reaction for the preparation of high molecular weight polyamides has become very important, particularly when sequential regularities in the polymer chain must be maintained. The reaction of acid chlorides and other reactive carboxylic acid derivatives with amines has been utilized in a variety of different techniques, most notably <u>interfacial</u> polymerization and <u>solution</u> polymerization in solvents of high dielectric constants.

<u>Liquid-Liquid Interfacial Polycondensation</u>: In an interfacial polycondensation, the reaction takes place at or near the interface between a pair of liquids with limited miscibilities, generally water and an organic solvent. The aqueous phase usually contains the diamine and an added acid acceptor while the organic phase generally contains the diacid chloride. Polymer formation has been shown to occur in the organic phase in that monofunctional reactants dissolved in the aqueous phase do not always decrease the molecular weight in the proportion to which they are used.[2] The primary function of the aqueous phase is to provide a solvent medium for the diamine and acid acceptor and to remove the byproduct acid from the polymerization zone. The controlled intro-

duction of the water soluble diamine into an excess of diacid chloride in the organic phase is carried out by the interface.

In order to maintain a rapid rate of reaction, an efficient transfer and neutralization of by-product hydrogen chloride is essential, which is generally done by adding an appropriate acid acceptor. In the absence of an acid acceptor, however, a portion of the reactant diamine reacts with the by-product acid to form the unreactive hydrochloride salt which consequently decreases both the yield and molecular weight of the resultant polymer due to the insufficient amount of diamine subsequently available for reaction. The amount and type of acid acceptor, therefore, has a great influence on both the yield and molecular weight of the polymer produced.

The major side reaction in interfacial polymerization reactions is the hydrolysis of the diacid chloride reactant. This is particularly prevalent with the more reactive lower aliphatic diacid chlorides.[3] It has been shown, for example, that terephthaloyl chloride undergoes only 1% hydrolysis in 10 minutes at pH 10 while 50% of adipoyl chloride hydrolyzes in 3 minutes, even at a pH value of 4.5.[4] Hydrolysis rates of aliphatic diacid chlorides were also shown to decrease with increasing chain length and increase with rising temperature.[5] Oligomers end-capped with acid chlorides are also susceptible to hydrolysis, which has frequently been found to occur when the polymer itself is substantially hydrophilic and/or where polymerization occurs close to the aqueous portion of the interface.

Because of the nature of interfacial polymerization reactions, the presence of an equivalence of reactants is less critical than in other methods, however, it has been shown that a 12% excess of diacid chloride in the preparation of Nylon 610 decreases the inherent viscosity by 15% while the same excess of diamine decreases the viscosity by 25%.[6] The method of addition of the reactants as well as the stirring have also been shown to have a profound effect on the polymerization reaction as both yield and solution viscosity are effected.[7] Although interfacial polymerization reactions can tolerate some impurities in the reaction media, some monofunctional species such as the ethanol stabilizer in chloroform, and/or certain slow reacting difunctional materials will decrease the molecular weight of the polymer formed.[8]

Gas-Liquid Interfacial Polycondensation: In a gas-liquid interfacial polycondensation, an acid chloride diluted with an inert gas is bubbled through a hot aqueous solution of diamine. Although the subsequent reaction is interfacial in nature, it differs in several respects from typical liquid-liquid interfacial reactions.[9] In the first place, the reaction cannot take place in the organic phase as this phase is absent. Secondly, one of the phases is a gas which in turn alters many of the characteristics of the reaction itself. In normal liquid-liquid interfacial techniques, for example, the use of highly reactive acid chlorides such as oxalyl chloride leads to a significant amount of hydrolysis and a subsequent low molecular weight product,[2] whereas the limited solubility of gaseous oxalyl chloride at the elevated temperatures employed in the gas-liquid interfacial technique reduces hydrolysis and favors polymerization.[9-12] Consequently, polyamides that are prepared from highly reactive and volatile acid chlorides can be obtained in high yield and with high molecular weights.

In addition, gas-liquid interfacial polymerization techniques have a number of advantages over conventional methods of producing condensation polymers. A variety of otherwise difficult to utilize monomers may be employed, particularly the lower dicarboxylic acids, such as oxalyl chloride, phosgene, thiophosgene, and perfluoroadipic acid dichloride, as well as the relatively inflexible aromatic diamines such as p-phenylenediamine.[9] The method is rapid, and the need for organic solvents, high temperatures, and vacuum equipment is eliminated. The procedure can also be easily adapted for the production of polymer in a continuous manner.

Solution Polycondensation: In solution polycondensations, the polymerization reaction is carried out in a single liquid phase. The liquid may consist of a single solvent or a mixture or solvents inert to the reactants employed. Solution processes include not only systems where both reactants and products are soluble, but also systems where one or both of the reactants are undissolved in the early stages of the reaction, but dissolve as the reaction proceeds as well as systems where the polymer product precipitates during the course of the reaction.[2] In contrast to interfacial polymerization techniques, polymerization in solution avoids the possibility of acid chloride hydrolysis. The major disadvantage of solution techniques, however, is the necessity of utilizing systems with low levels of impurities.

The solvent used in solution polymerization reactions must be not only unreactive towards both the diamine and diacid chloride, but it must also be a good solvent for both reactants and polymer. It has, in fact, been shown that the molecular weight of a polyamide can be controlled through the use of good or poor solvents for the polymer.[13] As in interfacial procedures, an acid acceptor is usually necessary for most solution polymerization reactions involving diamines and diacid chlorides, although they are sometimes unnecessary when amide solvents such as DMAc are used. The major side reaction in solution polymerization is the destruction of the diacid chloride either by impurities or by the acid acceptor. Consequently, a high purity of reactants must be maintained as most reactive impurities will decrease the molecular weight of the polymer produced. A majority of side reactions can be avoided, however, by carrying out the reaction at low temperatures. An equivalence of reactants is also important in solution polymerization reactions as this method is more sensitive to reactant balance than are interfacial methods.

Despite these well known advances in polycondensation procedures, certain novel polyamides with unusually rigid backbone structures have remained difficult to prepare except under the most exacting conditions. These include the aromatic polyamides such as poly(p-phenylene terephthalamide),[14-18] poly(p-benzamide),[19-21] and poly(m-phenylene isophthalamide),[2,14] as well as the aliphatic polyamides based on the oxamide linkage. Neither polyoxamide homopolymers or copolymers have ever reached commercial importance in spite of their potential as high temperature nylons[22] or as materials for efficient desalination membranes.[23-29] This is due, in part, to difficulties involved in their production and fabrication. Standard methods of preparing polyamides have been found to be of limited use for the preparation of polyoxamide homopolymers due to a number of factors among which are their high melting point and limited solubility.

Polyoxamide homopolymers generally cannot be prepared directly from oxalic acid salts of aliphatic diamines, for example, as the oxalate salts tend to decompose to CO and CO_2 at the high temperatures necessary for melt polycondensations. The ring opening polymerization of oxalic acid lactams, on the other hand, have been shown to give polyamides, although under melt polymerization conditions some loss of CO and CO_2 again takes place, thus limiting the molecular weights obtainable.[30-32] Furthermore, the relative insolubility of most polyoxamides prevents the formation of high molecular weight polymer when using conventional solution techniques, whereas the use of typical liquid-liquid interfacial polycondensation procedures is limited due to the rapid hydrolysis of the oxalyl chloride starting material. Polymerization at a gas-liquid interface, on the other hand, is a polymerization technique initially developed by Sokolov[10-12] for the preparation of polymers based on acid chlorides that are both reactive and volatile. On the other hand, certain solution and liquid-liquid interfacial techniques can be used for the preparation of many regular copolyoxamides.[23]

EXPERIMENTAL

Poly(hexamethylene oxamide) {Nylon 62}

Using a procedure similar to that described earlier,[33] a solution of hexamethylene diamine (465g, 4.00 moles) and sodium carbonate (848g, 8.00 moles) in 20 liters of water was added slowly to a reactor which was equipped so as to allow continuous addition of fresh diamine solution while maintaining a constant volume of solution. The apparatus also allowed for the continuous removal of polymer. The aqueous diamine solution was preheated to 95°C by passing it through a heating coil prior to introducing it into the reactor. The polymerization was carried out by dispersing a gaseous mixture of oxalyl chloride and dry nitrogen in the hot diamine solution with a 70 µm to 100 µm fritted glass filter. Polymer formation was almost immediate, and a white foam consisting of small microballoons of poly(hexamethylene oxamide) could be seen floating on top of the diamine solution within a few minutes. The reaction was carried out for several hours while about 100g of oxalyl chloride was passed through the solution. The resultant moist polymer foam was washed repeatedly with water in a one-gallon Waring blender. The white fibrous material was then washed twice with methanol and dried at room temperature for 48 hr at 20 mm. The polymer yield was 28g (31% based on oxalyl chloride) and the inherent viscosity (0.5% in trifluoroacetic acid) was 0.65 dL/g.

Poly(ethylene oxamide) {Nylon 22}

Nylon 22 with an inherent viscosity (0.5% in trifluoroacetic acid) of about 0.4 dL/g was prepared from N,N'-bis(2-aminoethyl) oxamide[7] in a manner similar to that used for the preparation of Nylon 62.

Poly(p-phenylene oxamide)

p-Phenylene diamine was recrystallized and sublimed immediately prior to use. Poly(p-phenylene oxamide) was prepared in a manner similar to that described above. The reaction was carried out in the absence of oxygen in order to obtain a nearly colorless polymer of reasonable molecular weight. Polymers with an inherent viscosity (0.5% in H_2SO_4) of 0.8 to 1.1 dL/g were obtained.

Polymerization of N,N'-bis(6-aminohexyl)oxamide (m-6-2-6) with Sebacyl Chloride: (p-6-2-6-10)

(1) Interfacial Polymerization.

N,N'-Bis(6-aminohexyl)oxamide (0.86g, 0.003 mole) and sodium carbonate (0.64g, 0.006 mole) was dissolved in 300 ml of distilled water. The organic solution was prepared by mixing sebacyl chloride (0.72g, 0.003 mole) with tetrachloroethylene (300 ml) in a 500 ml Erlenmeyer flask. To a one-quart Waring blender containing the aqueous diamine solution, was poured the organic solution while the blender was stirring at high speed. The blending was continued for 4 min., the mixture was filtered through a 600 ml sintered glass filter funnel and the solid polymer was washed with acetone (300 ml), water (400 ml), and acetone (100 ml). The residue was extracted in a Soxhlet extractor for 3 hrs. with tetrahydrofuran and dried for 20 hrs. at 80°C/1 mm. The polymer weighed 0.86g (63% yield), had a m.p. of 257°C (by DSC) and decomposed at 360°C (by TGA). The inherent viscosity (0.5% H_2SO_4 solution) of this polymer was 1.10 dL/g. Anal. Calcd. for $(C_{24}N_{44}O_4N_4)_n$: N, 12.4%; Found: N, 12.6%.

(2) Solution Polymerization.

To a 500 ml three-neck round bottom flask equipped with a mechanical stirrer, a condenser closed with a drying tube and a dropping funnel, was added m-6-2-6 (0.90g, 0.003 mole), and triethylamine (0.30g, 0.003 mole) in chloroform (40 ml). The flask was flushed with nitrogen and a slow flow of nitrogen was maintained during the reaction. The mixture was cooled to 10°C and sebacyl chloride (0.72g, 0.003 mole) in chloroform (10 ml) was added from a dropping funnel. Stirring was continued for 3 hrs., 300 ml of n-hexane was added and the suspension was filtered, washed consecutively with acetone (200 ml), water (400 ml) and acetone (200 ml), and dried at 60°C/1 mm for 20 hrs. The polymer weighed 0.85g (62% yield) and had an inherest viscosity (0.5% H_2SO_4 solution) of 0.45 dL/g.

<u>Polymerization of N,N'-Bis(2-aminoethyl)oxamide (m-2-2-2) with Isophthaloyl Chloride</u>: (p-2-2-2-I)

(1) Interfacial Polymerization.

N,N'-Bis(2-aminoethyl)oxamide (32.1g, 0.18 mole) and sodium carbonate (39.0g, 0.37 mole) in distilled water (1600 ml) were allowed to react with isophthaloyl chloride (37.4g, 0.18 mole) in chloroform (1000 ml). The reaction time was 3 min., and a polymer yield of 55.0g (99%) was obtained. The polymer had a m.p. of 367°C (by DSC), and decomposed above 370°C (by TGA). The polymer was soluble in sulfuric acid, trifluoroacetic acid and warm DMAc containing 3% LiCl. The inherent viscosity (0.5% H_2SO_4 solution) of this polymer was 1.32 dL/g. Anal. Calcd. for $(C_{14}H_{16}N_4O_4)_n$: N, 18.4%; Found: N, 18.4%.

(2) Solution Polymerization.

To a 2000-ml four-neck round-bottom flask was added N,N'-bis (2-aminoethyl)oxamide (57.0g, 0.33 mole), anhydrous triethylamine (100g, one equivalent excess), LiCl (48g), and anhydrous DMAc (120 ml). The mixture was warmed to 45°C until everything dissolved and isophthaloyl chloride (67.3g, 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 hrs. Triethylamine hydrochloride precipitated almost immediately. The warm mixture was poured into 1200 ml of ice water, the polymer precipitated and was filtered and washed with water, a water/acetone mixture and acetone, and dried at 40°C/20 mm for 48 hrs.; yield 82.0g (82%). The polymer decomposed above 355°C (by DSC). The inherent viscosity (0.5% H_2SO_4 solution) was 0.90 dL/g.

<u>Polymer of N,N'-Bis(4-aminobutyl)oxamide (m-4-2-4) with Isophthaloyl Chloride</u>: (p-4-2-4-I)

(1) Interfacial Polymerization.

N,N'-Bis(4-aminobutyl)oxamide (2.3g, 0.01 mole) and sodium carbonate (2.1g, 0.2 mole) in 300 ml of distilled water were allowed to react with isophthaloyl chloride (2.0g, 0.01 mole) in 200 ml of chloroform; reaction time 5 min.; polymer yield 3.0g (84%); m.p. 302°C (by DSC). The polymer decomposed above 350°C (by TGA). The inherent viscosity of a 0.5% solution of this polymer was 1.6 dL/g. Anal. Calcd. for $(C_{18}H_{24}N_4O_4)n$: N, 15.5%. Found: N, 15.6%.

(2) Solution Polymerization.

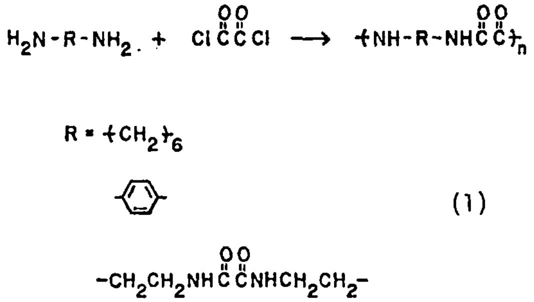
To a 250 ml three-neck round-bottom flask was added DMAc (50 ml) containing 5% LiCl, triethylamine (4.0g, 0.04 mole), and m-4-2-4 (4.5g, 0.02 mole). The mixture was warmed slightly until everything was dissolved. Isophthaloyl chloride (4.1g, 0.02 mole) in 50 ml of DMAc was added slowly at 0°C over a period of 1 hr. After 2 hrs. the mixture was allowed to warm to 25°C, stirred for 10 hrs., and poured into 500 ml of water. The suspension was filtered, and the solid was washed with water (200 ml), then acetone, and dried; polymer yield 5.8g (81%); m.p. 287°C (by DSC). The polymer decomposed above 350°C (by TGA). The inherent viscosity of a 0.5% solution of the polymer in DMAc containing 3% LiCl was 0.9 dL/g.

RESULTS AND DISCUSSION

Polymerization at a gas-liquid interface has been shown to be an effective method for the preparation of high molecular weight polyoxamide homopolymers.[10-12] The method of Sokolov was modified as described earlier[8] to provide for higher yields and continuous operation.

During a gas-liquid interfacial polymerization, both the molecular weight and yield increase rapidly as the temperature increases beyond 80°C. Polymerization at a gas-liquid interface must, therefore, be carried out at high temperatures in order to be effective. One would normally expect high temperatures to cause a rapid hydrolysis of oxalyl chloride in the basic media, however, the solubility of the gaseous monomer in the aqueous media is minimal at high temperatures, thus, the rate of acid chloride hydrolysis is reduced. As in the original method, the concentration of gaseous oxalyl chloride in nitrogen and the concentration of the diamine in the aqueous phase also influence the polymerization to a great degree, as does the basicity of both the diamine used and the reaction media itself.

Using this technique, several polyoxamides were produced using various diamines with oxalyl chloride (Equation 1).

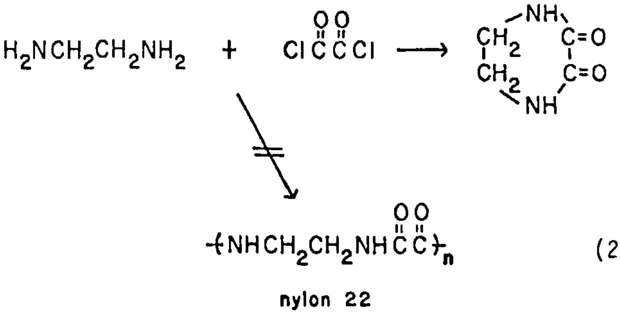


(1)

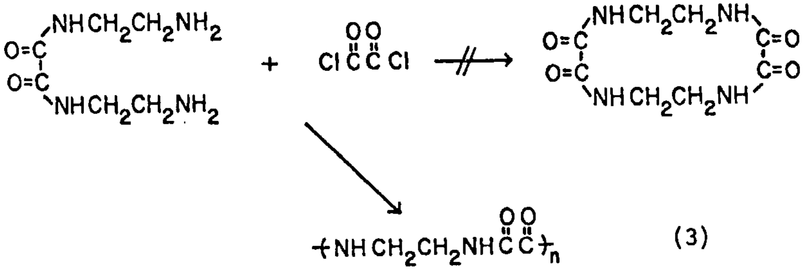
Nylon 62 prepared from hexamethylenediamine and oxalyl chloride was obtained in about 40% yield with an inherent viscosity of 0.6 to 0.8 dL/g. The highest molecular weight material was obtained when the concentration of the diamine was approximately 0.2 mole/liter. Nylon 62 prepared by gas-liquid interfacial polymerization was obtained in the form of microballoons of relatively tough polymer with an oriented structure.[33] The microballoons were formed of very thin films of the polymer, consequently the bulk density of the material obtained by this technique was quite low.

Nylon 22 cannot be made directly by the condensation of oxalyl chloride with ethylene diamine, as piperidine-2,3-dione is the normal reaction product (Equation 2). We have, however, succeeded in preparing nylon 22 from N,N'-bis(2-aminoethyl)oxamide (m-222) (Equation 3) in yields of 30% to 50% but with rather low inherent viscosity. Cyclo-condensation of m-222 and oxalyl chloride would give a 12-membered ring which apparently does not occur to a significant extent. The polymer obtained remains suspended in the polymerization mixture and, unlike nylon 62, does not form microspheres. The inherent viscosity and yield depend on the diamine and diacid chloride concentration in much the same manner as described for nylon 62.[10] Nylon 22 forms brittle films, however, as would be expected from the less flexible backbone structure.

Poly(p-phenylene oxamide) has been obtained in 20% to 50% yield with inherent viscosities of up to 1.1 dL/g. High molecular weight material can be produced over a much narrower range of diamine concentrations than is possible with nylon 62 or nylon 22, however. The inherent viscosity of the polymer decreases significantly when concentrations of diamine greater or less than 0.02 to 0.05 mole/liter are used. As with nylon 22, poly(p-phenylene oxamide) is formed as a suspended solid in the aqueous reaction mixture. This is presumably due to the brittle nature of these polymers preventing the formation of intact microballoons of polymer film.



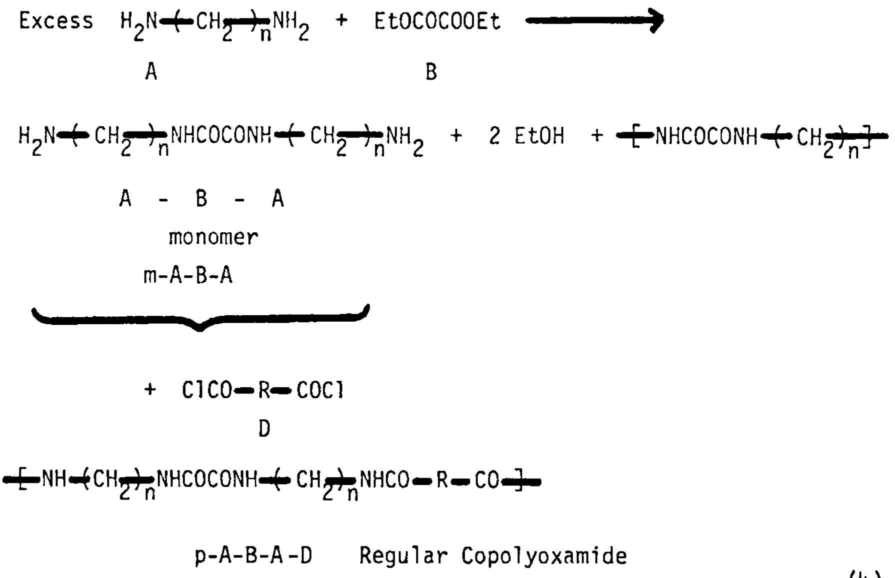
(2)



(3)

Both liquid-liquid interfacial and solution polycondensation procedures were used to prepare a variety of regular copolyoxamides[23-29] as shown in Equation 4, where m and p designate the diamine-diamide monomer used and the resultant polymer, respectively, and where A represents the number of carbon atoms in the diamine portion, B represents the number of carbon atoms in the diacid portion, and D represents the diacid chloride comonomer portion.

Among other factors, both solubility and reaction time were important considerations in the selection of the polymerization technique used with the solubility of the diamine reactant the most important factor. Hydrophilic diamine-diamides such as m-2-2-2 to m-6-2-6 were found to be water soluble and as such were suitable for standard liquid-liquid interfacial polycondensations.[24] Diamine-diamides with longer aliphatic groups in the diamine portion could only be used effectively in solution polycondensations, however.



$$\text{Excess}\ \underset{A}{H_2N\left(CH_2\right)_nNH_2} + \underset{B}{EtOCOCOOEt} \longrightarrow$$

$$\underbrace{\underset{\substack{A\ -\ B\ -\ A\\ \text{monomer}\\ \text{m-A-B-A}}}{H_2N\left(CH_2\right)_nNHCOCONH\left(CH_2\right)_nNH_2}} + 2\ EtOH + \left[NHCOCONH\left(CH_2\right)_n\right]$$

$$+\ \underset{D}{ClCO-R-COCl}$$

$$\left[NH\left(CH_2\right)_nNHCOCONH\left(CH_2\right)_nNHCO-R-CO\right]$$

p-A-B-A-D Regular Copolyoxamide

(4)

The polymer p-6-2-6-10 was the material that received the greatest attention as its preparation was used as a model for a study of procedures suitable for the synthesis of regular copolyoxamides by both interfacial and solution methods.[25] The diamine monomer used, m-6-2-6, was found to be only moderately soluble in water (0.8 g/dL at 25°C), hence interfacial polymerizations had to be carried out either in dilute solution at room temperature or in higher concentrations at elevated temperatures. Sebacyl chloride was found to be suitable under these conditions due to its reduced rate of hydrolysis.

Interfacial polycondensations were carried out using tetrachloroethylene, chloroform, or carbon tetrachloride as the organic solvent. Copolyoxamides containing the more hydrophilic segments tended to swell in the solvents used for the polymerizations which made their isolation difficult. Monomer concentrations were generally kept at about 1% as higher concentrations caused the formation of a thick polymer gel which tended to affect the blending efficiency.

The nature of the acid acceptor utilized was shown to have a pronounced effect on the molecular weight of the polymer produced as evidenced by their inherent viscosities.[25] Sodium bicarbonate, for example, was found to be an inefficient acid acceptor, as was sodium hydroxide. Utilizing sodium carbonate as an acid acceptor, on the other hand, gave p-4-2-2-10 with an inherent viscosity of 1.03 dL/g from m-4-2-4 and sebacyl chloride while sodium hydroxide yielded polymer with an inherent viscosity of only 0.54 dL/g. Similarly inherent viscosities of 1.09 and 0.67 dL/g were obtained when sodium carbonate and sodium hydroxide respectively were used with m-6-2-6 and sebacyl chloride for the preparation of p-6-2-6-10. The amount of acid acceptor used was also found to be critical as the inherent viscosity decreased by 50% when the quantity of acid acceptor was reduced by 20%.

The use of standard liquid-liquid interfacial techniques was found to be unsuitable for the preparation of regular copolyoxamides derived from lower diacid chlorides (e.g., malonyl or succinyl chloride) as those intermediates were readily hydrolyzed. In fact, no polymers of useful molecular weights were obtained using liquid-liquid interfacial techniques when diacid chlorides lower than adipoyl chloride were used. This phenomenon was particularly noticeable when the diamine-diamides used were highly water soluble which caused the resultant polymers to be quite hydrophilic.[34]

Polycondensations performed in solution generally utilized chlorinated hydrocarbons as solvents, however, DMAc both with and without LiCl was used for the preparation of aliphatic/aromatic copolyoxamides.[26] In several cases, the molecular weight of the product prepared by solution techniques was found to be limited by premature precipitation, a problem commonly encountered in the synthesis of many homo and copolyoxamides. The acid acceptor most commonly used for solution polycondensations was triethylamine while the reaction temperature was generally held below 40°C in order to minimize side reactions. In addition, the concentration of polymer in solution polycondensations was generally kept below 2.5% as the starting materials often could not be kept in solution at higher concentrations.

In an effort to gain a better understanding of the factors involved in synthesizing copolyoxamides using solution polymerization procedures, the sequence of addition of the reactants was varied. The addition of the diamine-diamide to the diacid chloride was found to give the highest molecular weight material in the highest yield. By adding m-6-2-6 to sebacyl chloride, for example, p-6-2-2-10 with an inherent viscosity of 0.43 dL/g was produced in 62% yield, while the reverse order of addition afforded polymer with an inherent viscosity of only 0.13 dL/g in a 34% yield.[25]

Both standard liquid-liquid interfacial and solution polycondensation techniques were compared for the preparation of a series of copolyoxamides based on the condensation of a number of diamine-diamides with the same diacid chloride. Chloroform was used as the organic solvent in the interfacial polymerizations, while DMAc with LiCl was used as the solvent in the solution procedures. When m-0-2-0 was condensed with isophthaloyl chloride using interfacial techniques, an inherent viscosity of 0.23 dL/g was obtained while solution techniques gave polymer with an inherent viscosity of 0.44 dL/g. On the other hand, inherent viscosities of 1.3 and 0.90 dL/g respectively were obtained when m-2-2-2 was used. Similarly, interfacial polymerizations using m-4-2-4 as the diamine-diamide gave an inherent viscosity of 1.6 dL/g while a value of 0.88 dL/g was obtained using solution techniques. A number of copolyoxamides were also prepared by interfacial methods utilizing m-2-2-2 as the diamine-diamide. Inherent viscosities of 0.4 to 0.8 dL/g were routinely obtained. Most aromatic diacid chlorides gave copolyoxamides with inherent viscosities between 0.6 and 0.8 dL/g, however. When the diamine-diamide m-2-4-2, the only diamine-diamide without an oxamide linkage, was condensed with isophthaloyl chloride, on the other hand, a polymer with an inherent viscosity of 2.5 dL/g was readily obtained.[26]

From our studies comparing both gas-liquid and liquid-liquid interfacial techniques with solution techniques for the preparation of both aliphatic and aromatic polyoxamides and aliphatic/aliphatic and aliphatic/aromatic copolyoxamides, it was found that solubility and reactivity (i.e., hydrolyzability) were both essential factors for the preparation of high molecular weight materials. The purity and reactivity of the solvents employed was also found to be critical. The choice of solution versus interfacial polymerization techniques for preparing polymers was thus based on those factors. The gas-liquid interfacial technique was found to be far superior for the preparation of polyoxamide homopolymers, while solution techniques, although more difficult, were generally found to be most suitable for the preparation of regular copolyoxamides. Liquid-liquid interfacial techniques were found to be more readily carried out than either gas-liquid interfacial or solution techniques and thus were useful for the fast screening of reaction conditions and polymer properties.

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