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Comments on the Status and Future of Interfacial Polycondensation

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ABSTRACT

Interfacial polycondensation came into prominence in the 1950's with the work of Schnell on polycarbonates, Conix on polyesters, and Wittbecker, Morgan and co-workers on polyurethanes, polyamides and other polymer classes. There were a few earlier patent references. The method has several variations and is a highly effective procedure for the rapid preparation of many polymers on a small scale. It is particularly appropriate for polymers which are thermally unstable or unmeltable, for use with volatile or unstable intermediates and for polymers with reactive functional groups. Literally thousands of polymers have been made by this process. There are a number of short-comings to the process, most of which can be overcome by adjustment of the polymerization conditions. Polycarbonates and aromatic polyamides are reported to be prepared commercially by stirred interfacial processes. Another application is the encapsulation of pesticides, inks, and other materials. As to the future, the processes are a basic part of the chemist's tool kit and will continue to be used in the laboratory for rapid syntheses and for those polymers which are not obtained as readily by other means. The basic tests of commercial use of these processes, as with any other process, will be attainment of results not available by other routes, economic considerations, and safety and environmental factors.

INTRODUCTION

Interfacial polycondensation came into prominence as a major polymer-forming technique about 25 years ago with the work of

Schell (1) on polycarbonates at Bayer, Conix (2,3) on polyesters and polysulfonates at Gevaert, and Wittbecker, Morgan, and co-workers (4,5,6) on polyurethanes, polyamides, and other polymer classes at Du Pont. Scattered earlier reports were available in the patent literature as indicated in Table 1. (See introduction to reference 7 for greater detail on early literature.)

Interest in the polycarbonates as a new class of polymers for plastics was widespread. This interest was enhanced by the development of solution and melt methods for their preparation (8,9).

Polymer Film Formation by Interfacial Polycondensation

Perhaps a major contribution to the excitement and interest in interfacial polycondensation was the description of its broad applicability in 1958-1959 (4) and that fascinating experiment, the Nylon Rope Trick (6). In this experiment a film of aliphatic poly-

TABLE 1

Early Reports of Interfacial Condensation Polymerization

Authors	Type of Polymer	Date
I. G. Farbenindustrie	urethanes	1944,1945
Orthner, Schlack et al.	urethanes	1954,1955
Jones, McFarlane	amides, urethanes	1952
Kirby	amides	1953
Schnell, Bottenbruch, Krimm	carbonates	1954
Magat, Strachan	amides	1955
Wittbecker	urethanes	1956
Conix	aromatic esters	1957
Conix	aromatic sulfonates	1958
Wittbecker, Morgan et al.	amides and others	1958
Hill, Kwolek, Morgan	aromatic amides	1959
Morgan, Kwolek	nylon rope experiment	1959

amide is formed at the liquid-liquid interface and removed continuously as a small flexible rope.

This experiment has probably been done and viewed by more people than any other in polymer chemistry which is carried out solely for the experiment itself. By this condition we exclude such acts as the application of paints, cyanoacrylate glues, and epoxy cements. The Nylon Rope Trick has been done in technical lectures, school classrooms and polymer preparation courses, science fairs, World Fairs, and as part of sales pitches.

Many thousands of reprints have been distributed. The Eastman Kodak Co. pictured the Nylon Rope Trick in advertising for the intermediates (10) and Edmund Scientific Co., Rutherford, N.J., had kits available at one time.

The unstirred polymerization system never yielded an acceptable fine nylon fiber. The fibers were not compact enough for good strength. However, the film or rope of collapsed film can be shredded in a blender, or other device, to yield fibrous particles which will form tough paper or which can be used to bind other staple fibers into a paper (11).

The film-forming process has been used to form membranes which were examined for ion-exchange properties (12). It has been adapted for the encapsulation of inks, catalysts and insecticides (13a). Such encapsulated insecticides are being produced on a commercial scale (13b). Whitfield, Miller and Wasley (14) developed a process for coating wool fibers in fabric form with a thin film of interfacially formed polymer. The purpose was to prevent fabric shrinkage during ordinary laundering. The process reached pilot plant scale but eventually gave way to other procedures. Trubek Laboratories based an advertisement for diacid chlorides on the possible use of this process (15).

Chang (16) at McGill University and others have used interfacial polycondensation to form artificial cell-like capsules containing enzymes and other materials. These cells have possible applications in artificial kidneys, catalysis and in ion-exchange processes.

Interfacial Polycondensation with Stirring

Polymerization with stirring offered the greatest versatility in polymer making. Polymers could be prepared in a few minutes at room temperature which took hours or days to form by melt or solid-state polymerizations. Furthermore, non-melting polymers and thermally unstable polymers could be made. Thermally unstable intermediates could be used. Thousands of new polymers were prepared and examined over the first several years.

In the Pioneering Research Laboratory of the Du Pont Textile Fibers Department the search for high-temperature stable, non-melting polymers became a goal. This eventually led to the aromatic polyamides now manufactured and sold under the tradename, Nomex® aramid fibers and papers (17).

The first general interfacial procedure employed a solution of diacid chloride dissolved in a water-immiscible solvent combined with an aqueous solution of the complementary intermediate and an inorganic base. Sometimes authors report that they have used a "standard method", perhaps meaning the above process. The writer has been guilty of this statement on at least one occasion. Such a statement overlooks the fact that there are several major variations and there are so many important variables that no one set of polymerization conditions can be considered standard or broadly applicable for optimum results.

Let us review several variations of interfacial polycondensation and in doing so illustrate the point that by experimentation one can optimize the molecular weight and yield and thereby obtain better polymer samples for characterization and evaluation.

Phase Transfer Agents

During the last ten years there has been much excitement about phase transfer agents in chemical synthesis. These agents are compounds, such as quaternary ammonium salts, which when added to a two-phase system promote the reaction by transferring one of the intermediates across the interfacial boundary into the presence of the second intermediate. At least two books have appeared on the subject (18).

Upon casual examination of the literature, it was surprising to find that in general the use of these agents is treated as being a very recent discovery, whereas in fact Schnell and co-workers (1, 8) were using phase transfer agents for polycarbonate preparation by interfacial polycondensation in the early 1950's. Since many of the recent papers have been in the field of small molecule synthesis, one gets the impression that organic chemists are not reading the polymer literature. One hopes the opposite is not true.

The many syntheses to which phase transfer catalysts are being applied open up routes to new or improved condensation polymers. Polymer chemists should take advantage of this expanding technology and make additional contributions of their own. Several papers at this Symposium point the way.

Schnell and his co-workers used tertiary amines and quaternary ammonium compounds to accelerate and improve the synthesis of both polycarbonates (1,8,19) and the monomer, diphenyl carbonate (20), from phenols and phosgene. The additives not only increase the polymerization rate but their use leads to higher molecular weight in the polymers.

Schnell and Bottenbruch proposed that the tertiary amines formed adducts with the acid chloride in the organic phase and thus provided a more reactive intermediate. This is possible but it is more likely they are phase transfer agents for the phenoxide. A few careful experiments would settle this question.

Conix (2) used quaternary ammonium, arsonium, phosphonium, and tertiary sulfonium compounds to accelerate and enhance the preparation of aromatic polyesters, polycarbonates from bischloroformates (Table 2) and polysulfonates from bisphenols and disulfonyl chlorides (22). The data indicate arsonium compounds are the most

TABLE 2

Effect of Quaternary Compounds as Accelerators in the Preparation of the Polycarbonate from 2,2-Bis(4-hydroxyphenyl)propane and Its Bischloroformate by Interfacial Polycondensation[a]

Accelerator	Variation of intrinsic viscosity of the product with amount of accelerator and reaction time, dl./g.[b]			
	0.05%[c]		2.0%[c]	
	5 min.[d]	30 min.[d]	5 min.[d]	30 min.[d]
Triethylbenzylammonium chloride	-	0.26	0.10	0.70
Methyltriphenyl-arsonium iodide	-	0.68	0.96	1.65
Methyltriphenyl-phosphonium iodide	0.40	0.80	0.90	1.24
Benzyltriphenyl-phosphonium chloride	0.41	0.90	0.90	1.36
p-Xylylene-α,α'-bis(di-hydroxyethyl)sulfonium bromide	-	0.28	0.38	0.76

[a] From Conix (21).

[b] [η] measured in sym-tetrachloroethane at 25°C.

[c] By weight based on the theoretical weight of polymer

[d] Counted from point of complete addition of acid chloride (5 min.).

effective accelerators (Table 2; 21, 23). However, the additives are not strictly comparable in terms of substituents. Increased amounts of an accelerator gave higher viscosity numbers for the product (increased molecular weight) at the same reaction times.

Morgan (5,24) called phase transfer agents accelerators and explained their function in accord with current thought; i.e. that they act to transfer the aqueous reactant (phenoxide in the case of phenols) into the organic phase and make it available for reaction there. Experiments with acid chlorides and phenols plus quaternary ammonium salts in single organic solvents had shown no catalytic effect on the condensation reaction. The formation of aromatic polyester films in an unstirred interfacial polycondensation was shown to take place in the organic phase and the addition of tetraethylammonium chloride to the aqueous phase greatly accelerated the rate of film formation (25,26).

Lower alkyl substituted quaternary ammonium compounds, such as tetramethyl and tetraethyl ammonium salts, have been reported to be ineffective as phase transfer agents for some interfacial condensation reactions. Morgan (27) found that tetraethylammonium chloride was quite effective in the preparation of aromatic polyesters. Relatively large amounts of the salt were required for short reaction times of ten minutes or less and a maximum degree of polymerization (Figure 1). With higher concentrations of salt the degree of polymerization dropped. This could be due in part to impurities in the salt.

Brzozowski, Dubczynski and Petrus (28) have recently found tetrabutylammonium hydroxide effective in polycondensation of 2,2-bis(4-hydroxyphenyl)-1,1-dichloroethane with isophthaloyl chloride and have examined the mechanism.

The interfacial polycondensation of phenolphthalein and terephthaloyl chloride proceeds fairly well without a phase transfer agent. However, with tetraethylammonium chloride much higher inherent viscosities are obtained (29) and the small scale, stirred reactions have been completed in less than 2.5 minutes. Polyesters based on phenolphthalein have been developed for plastics applications at the Russian Academy of Sciences.

Polymerization in Water-Miscible Solvents

An important variation of interfacial polycondensation is the use of wholly or partially water-miscible solvents (30-32). The procedure is applicable to several classes of polymers such as polyesters, polyamides, polyurethanes, and polysulfonamides, and in particular to systems wherein the diacid chloride component has relatively high hydrolytic stability. Hydrolysis is further reduced by use of weakly alkaline acid acceptors.

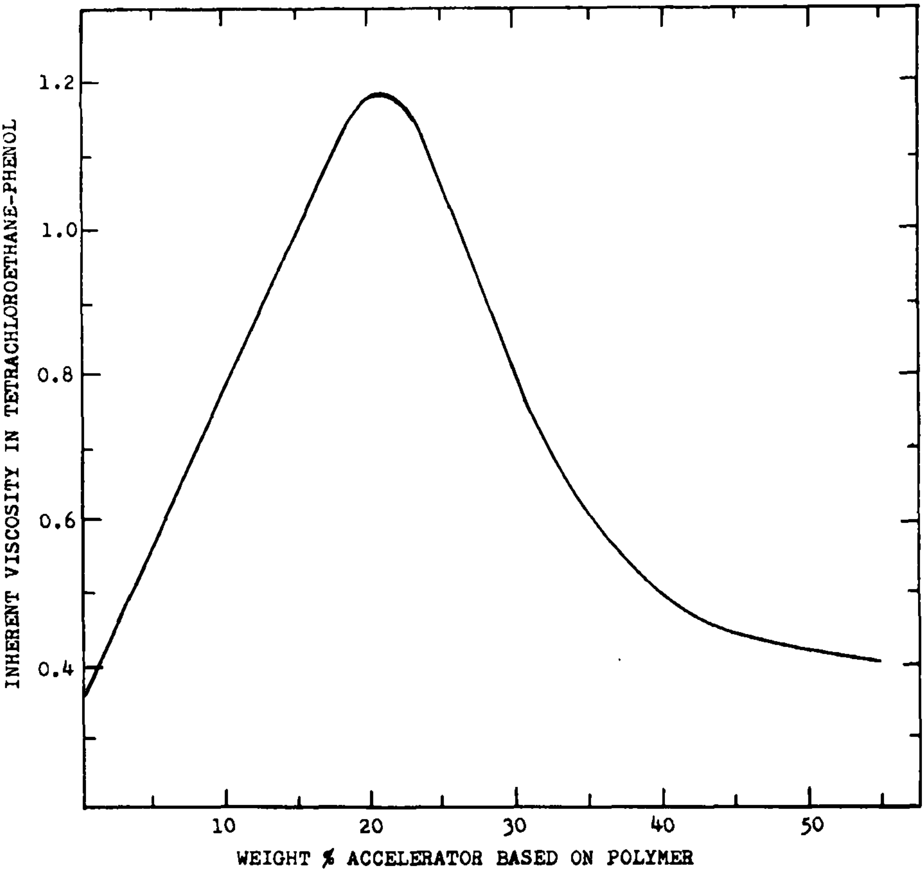

Fig. 1. Variation in inherent viscosity of the polyester from 2,2-bis(4-hydroxyphenyl)propane and terephthaloyl chloride with amount of tetraethylammonium chloride in an interfacial polycondensation system. Procedure: 0.02 mole reactants in 1,1,2-trichloroethane-water (60/130 by vol.) and 0.04 mole sodium hydroxide with stirring for 10 min. (27).

Some specific polymers which have been made in high molecular weight are:

Poly(hexamethylene sebacamide)

Poly(terephthaloyl trans-2,5-dimethylpiperazine)

Poly(m-phenylene isophthalamide)

Poly(1,4-phenylenedioxycarbonylpiperazine)

Poly(hexamethylene 1,3-phenylenedisulfonamide)

Poly(terephthaloyl oxalamidrazone) (33)

Examples of useful organic solvents are tetrahydrofuran, acetone, cyclohexanone, and 2,4-dimethyltetramethylene sulfone. Advantages are accelerated reaction rates, enhanced polymer swelling and ease of polymer recovery. Although the solvents by themselves may be highly water-miscible, this miscibility is greatly reduced by the presence of salt, base, intermediates and polymer.

As with other polycondensation systems, there is considerable sensitivity to variables such as solvent ratio, concentration of intermediates and manner of mixing and therefore the optimum combinations must be sought for highest molecular weight and yield. This is illustrated by the effect of tetrahydrofuran-water ratio (Figure 2)

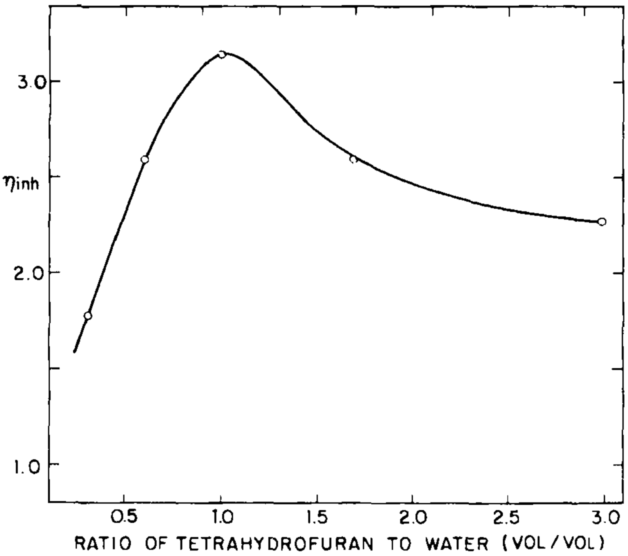

Fig. 2. Inherent viscosity versus the ratio of tetrahydrofuran to water in the preparation of poly(terephthaloyl trans-2,5-dimethylpiperazine). Total liquid volume, 200 ml.; 0.02 mole of terephthaloyl chloride, 0.02 mole of diamine, and 0.04 mole of sodium carbonate; stirred for 5 min. Yields 84-90%. Inherent viscosity in tetrachloroethane-phenol (40-60 by wt.).

and intermediates concentration (Figure 3) for the preparation of poly(terephthaloyl trans-2,5-dimethylpiperazine) (32).

Interfacial polycondensation in water-miscible solvents is being used in Japan on a large scale to prepare aromatic polyamides. The process has been much studied in Russia by Sokolov and co-workers (34).

Chemists at Glanzstoff A. G. studied the preparation of poly(terephthaloyl oxalamidrazone) in tetrahydrofuran-water quite extensively (33). A variation of the procedure, also used by Sokolov (35), is to decrease or modify the phase miscibility by the addition of salts such as sodium and lithium chlorides and sulfates.

The above polymer was produced on a pilot plant scale by Akzo Research and Engineering N.V. and in chelated form promoted

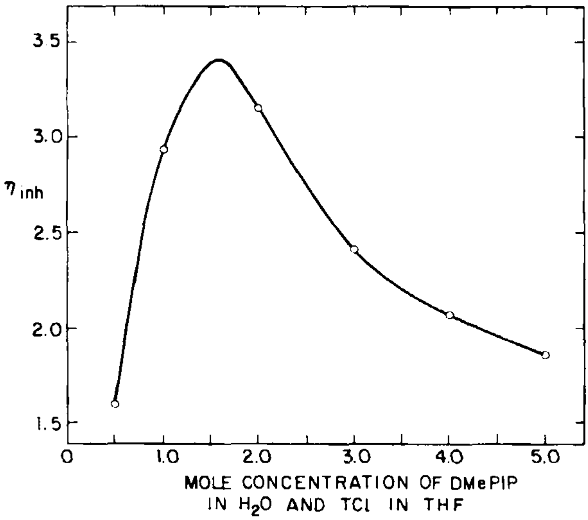

Fig. 3. Inherent viscosity versus mole concentration of intermediates in preparation of poly(terephthaloyl trans-2,5-dimethylpiperazine). 100 ml. of tetrahydrofuran and of water; 2 moles of sodium carbonate for each mole of diamine; stirred 5 min. Yields 86-94%. Inherent viscosity in tetrachloroethane-phenol (40-60 by wt.).

as a highly flame resistant fiber (36). For this program the polymer was prepared in hexane-water.

Aromatic polyesters based on 2,2-bis(4-hydroxyphenyl)propane and iso- and terephthaloyl chlorides are produced in Russia by the water-miscible solvent interfacial process for use in plastics (35,37). The procedure has been called emulsion polycondensation by Sokolov.

Gas-Liquid Interfacial Polycondensation

The final topic is a variation of interfacial synthesis which we have recently applied to polyoxamide preparation (38). Polyoxamides have been traditionally difficult to prepare because of thermal instability and/or low solubility.

In 1960 Sokolov and his co-workers (39) introduced a new gas-liquid process which yielded good molecular weight ranges for polyoxamides from a variety of diamines but the polymer yields were about 60% at best. The process employs an aqueous solution of the diamine and oxalyl chloride vapor in an inert gaseous diluent. In the course of their extensive studies they prepared the polyoxamides from hexamethylenediamine, 1,4-phenylenediamine, and benzidine with intrinsic viscosity/percent yield as follows: 1.1/58, 1.44/66, 1.62/56. Sokolov and Astakhova (40) examined the use of inert organic liquids as the solvent for hexamethylenediamine in the gas-liquid process, but obtained lower intrinsic viscosities and yield than when water was used.

We have found that much higher yields of polymer result when both water and a water-immiscible organic solvent are used and polymers with high viscosities can be obtained.

The reactions were carried out in a small resin kettle equipped with a 2000-rpm disk stirrer. Equal volumes of water and organic solvent phases were used with the diamine and any alkali dissolved in the mixed phases. Oxalyl chloride at 5-20 mole % excess (based on diamine) was warmed in a generator and carried by means of a flow of dry nitrogen such that a gas mixture of 25% by volume of acid chloride passed over the surface of the stirred liquids at a rate of 2 liter/hr.

Several variables were studied in a limited way with 2,2'-dimethyl-4,4'-diaminobiphenyl as the diamine. Variables were the concentration of diamine, the proportion of inorganic base, the organic solvent, and the reaction temperature. Figure 4 shows the effect of diamine concentration on yield and inherent viscosity. Table 3 gives the inherent viscosities (0.5 g./100 ml. of solution in 98% sulfuric acid at 30°C.) and yields for a number of aromatic polyoxamides.

In addition to the goal of a method of synthesis, an objective was to determine whether these presumably stiff-chain polyamides would yield liquid crystalline (anisotropic) solutions. The oxamides from 2,2'-dimethyl-4,4'-diaminobiphenyl and chloro-1,4-phenylenediamine were soluble enough and of sufficient molecular weight to yield anisotropic solutions.

While the application of the gas-liquid interfacial process has been newly applied to advantage for the preparation of polyoxamides, the process is old in that it was used early by Schnell (1,8) and others in the preparation of polycarbonates.

Future of Interfacial Polycondensation

Interfacial polycondensation and its modifications are valuable tools for the polymer researcher. They provide advantages of simplicity and speed for obtaining samples of polymer in high molecular weight and in an easily isolated form. Because of their complexity, they also offer a challenge to kineticists and others who would better understand the effects of the many variables.

The polymer chemist should and will choose among the various synthetic methods available today and not be bound by a particular route. In part the choice will be determined by the polymer and the

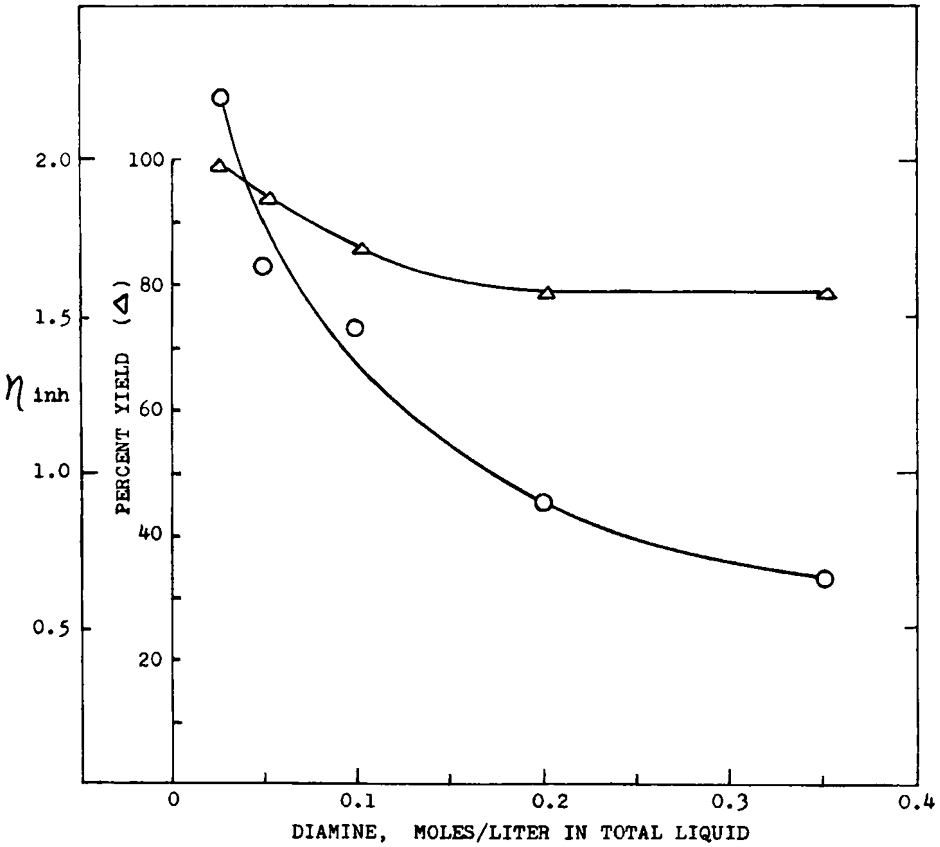

Fig. 4. Inherent viscosity and yield versus diamine concentration for the preparation of poly(2,2'-dimethyl-4,4'-biphenylene oxamide) in an oxalyl chloride vapor-chloroform-water system. Temperature, 55°C.; pH held between 6.8 and 7.2 by automatic titration.

applicability of the processes. On the other hand the type of sample and its expected use may be determining.

The industrial chemist may have other considerations to take into account. The politics of selling a product to management may determine that one process is more acceptable than another; for example, local prejudices or the goal of introducing a new product into existing facilities.

TABLE 3

Polyoxamides Prepared by Gas-Liquid Interfacial Polycondensation[a]

Diamine	Inherent viscosity (dl/g)	Yield[b] (%)
2,2'-Dimethyl-4,4'-diaminobiphenyl	2.20	99
Bis(4-aminophenyl)methane	1.64	97
1,4-Phenylenediamine	0.87	92
Chloro-1,4-phenylenediamine	0.97	92
trans-1,4-Cyclohexylenediamine	0.76	92

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[a] Polymerization in $CHCl_3$-H_2O (1/1 v/v) with diamine at 0.025M in the total volume, a temperature of 55°C, and pH 6.8-7.2.

[b] Based on diamine.

Toxicity of all materials is more of a problem today on all scales than a few years ago. This is proper but nevertheless presents problems in experimentation and achieving results. Benzene and chloroform may be "out". Hexane is "in" but is often a poor solvent choice. Methylene chloride is generally acceptable but is low boiling. For safety reasons, we now do the Nylon Rope Trick with a high-boiling chlorofluorocarbon solvent.

Some problems with large scale use of interfacial polycondensation in polymer preparation are:

Toxicity of solvents
Incomplete yields in some cases
High energy for stirring
Heat of reaction and stirring
Corrosion of equipment
Disposal of by-products

These problems can be overcome as is shown by the manufacture of polycarbonates in Europe and the U.S., aromatic polyamides in Japan, and a number of polyesters in Russia.

The continued interest in interfacial polycondensation and other interfacial syntheses is demonstrated by the range of topics presented and discussed at this Symposium.

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