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In Situ Formation and Incorporation of Additives into Polymers During Interfacial Polycondensation Reactions

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Synopsis

One of the objectives of the work was to attempt the in situ formation of inorganic fillers during interfacial polycondensation reactions. The complementary components of the filler were added separately to the organic and aqueous phases of the system so that they formed the insoluble filler at the interface simultaneously with the polymer. Since the polyamide plastics have good molding properties, nylon 610 was selected as the principal model, but some work was also carried out with a urethane polymer. Further, coloring of nylon 610 and of a polyurethane resin was investigated by lake formation at the interface with the help of 1,2-dihydroxyanthraquinone in the organic phase and a metal salt in the aqueous phase. In this way, red- and blue-colored polymers were prepared. Finally, by adding zinc ions to the aqueous and pentachlorophenol to the organic phase, zinc pentachlorophenate was incorporated into nylon 610 during its formation. The ignition point of the resultant product was significantly higher than that of a sample to which zinc pentachlorophenate had been added by mechanical mixing.

INTRODUCTION

Interfacial polycondensation is a widely applicable method for the preparation of many high molecular weight compounds,[1] including polyamides,[2] polyureas,[3] polyurethanes,[4] and polyesters.[5] The method makes use of a pair of immiscible liquids in each of which is dissolved a complementary reactant (or reactants) of a polymer-forming system. Polyamides comprise the largest group of polymers which have been synthesised by low-temperature polycondensation methods. One of the advantages of this method is that high molecular weight products may be obtained even in the absence of an exact stoichiometric relationship of the complementary reactant (or reactants) in the mixture. Most of the work during the course of this investigation was limited to poly(hexamethylene sebacamide), commonly known as nylon 610, and, to a lesser degree, to a polyurethane resin.

Commercial polymers usually require the presence of fillers, colorants, or other additives (e.g., light and heat stabilizers, lubricants, plasticizers,

flame retardants). Their incorporation into the polymer is generally carried out as a separate step, by mechanical blending or mixing procedures. Intimate dispersion of the additive is necessary to obtain its proper function, which may be enhanced by the establishment of additional bonding forces.[6]

In the case of colorants, flame retardants, or stabilizers, the function of the additive is obvious. The function of other additives, particularly when serving as reinforcements, can be complex and may require the formation of true chemical bonds.[7] In crystalline polymers, such as in nylon, where the mechanical properties depend on the size of the spherulites, the incorporation of fillers allows one to vary the spherulite size by controlling nucleation.[8]

It will be shown in the following sections that the interfacial polycondensation method can be used to prepare nylon 610 and a polyurethane in such a manner that the additives are formed in situ, that is, simultaneously with the polymer. A series of experiments were done on a laboratory scale with additives specifically falling into the category of fillers, colorants, and flame retardants. It is evident from these experiments that the formation of an additive in situ during the polymerization reaction not only obviates a separate step of mechanical blending or mixing procedure but also guarantees intimate dispersion of the additive in the polymer. The aspect of improvement in properties was experimentally demonstrated by incorporating a flame-retardant substance, namely, zinc pentachlorophenate, into the polymer.

BACKGROUND

All reactions commonly employed in the high-temperature polycondensation (melt) method are slow. While their rates may be increased by increases in temperature, changes in solvent polarity, and the presence of catalysts, they rarely approach those of interfacial polycondensation reactions. The condensation reaction best satisfying the requirements of mild conditions and fast rates is the Schotten-Bauman reaction of a dibasic acid halide or a bischloroformate with a difunctional complementary reactant containing at least two active hydrogen atoms, such as a diamine.

In the interfacial polycondensation method, use is made of a pair of immiscible liquids in which fast-reacting complementary reactants are dissolved. When the two phases are brought in contact, with or without stirring, in the presence of an acceptor for any by-product formed during the reaction, polycondensation proceeds at ambient temperature at high rate, at or near the interface. Table I shows a comparison between high- and low-temperature polycondensation methods.[1]

GENERAL PROCEDURE

When the complementary phases of a polycondensation system are brought together without stirring the system, that is, by layering one upon

the other, and if the organic liquid does not dissolve the polymer, a thin film of polymer forms at the interface. Under specific conditions, this polymer film is coherent and tough and has a high molecular weight. When the film is grasped and pulled out from the area of the interface, more polymer forms at the interface, and a collapsed sheet or tube of polymer may be withdrawn continuosuly[9] until the system becomes exhausted of either or both of the components.

When the complementary phases are brought together with stirring, preferably at high speed and in the presence of a detergent, the same media may be used as in the unstirred system and the same chemical reactions take place. However, stirred-batch systems do not form a coherent poly-

TABLE I
Comparison of Low-Temperature and Melt Polycondensation Methods[a]

	Low-temperature methods	Melt method
Intermediates		
Purity	moderate to high	high
Stoichiometric equivalence	often tolerant of wide deviations	necessary
Stability to heat	unnecessary	necessary
Structure	wide range but limited by reactivity requirement	limited by thermal stability and a lower reactivity requirement
Polymerization Conditions		
Time	several minutes	1 to 24 hr
Temperature	0° to 40°C	higher than 200°C
Pressure	atmospheric	high and low
Equipment	simple, open	special, often sealed
Products		
Yield	low to high	high
Structure	extremely wide range	limited by stability to heat and fusibility
By-products	salt	water or volatile organic compounds

[a] From ref. 1, p. 12.

mer film, and the product may be granular, powdery, or even dissolved. This allows for a wider choice of useful solvents and permits the preparation of a wider range of polymers. Rapid addition of the diacid chloride solution to the stirred diamine solution has given the best results.[10]

A variety of acid acceptors (diamines, sodium hydroxide, sodium carbonate) may be used, but an excess of strong acceptors is known to cause a decrease in both yield and viscosity of the polymer, attributed to an increase in hydrolysis of the acid chlorides.

Both stirred and unstirred systems allow one to incorporate additives into the polymer by adding, to each of the two phases, ions or molecules which will form the additive with a reaction rate the same or higher than that of the components of the condensation polymer. Under these condi-

tions, the additive is formed in situ and is incorporated progressively into the polymer in a finely divided and evenly dispersed state.

EXPERIMENTAL

The sources of the materials used were as follows: sebacyl chloride, Eastman Organic Chemicals Company; hexamethylenediamine, Aldrich Chemical Company; ethylene bischloroformate, Chemetron Chemicals Company; Duponol ME detergent (sodium lauryl sulfate), E.I. du Pont de Nemours and Company; alizarin, American Cyanamid Company; pentachlorophenol (technical), Reichhold Chemical Company.

During the course of this investigation, nylon 610 was used as the principal polymer model, while some studies were done with a polyurethane resin. The chemical reactions involved in these systems are given below:

Nylon 610:

$$\underset{\text{hexamethyldenediamine}}{H_2N{-}(CH_2)_6{-}NH_2} + \underset{\text{sebacyl chloride}}{Cl{-}CO{-}(CH_2)_8{-}CO{-}Cl} \rightarrow$$

$$+HN{-}(CH_2)_6{-}NH{-}CO{-}(CH_2)_8{-}CO+_x + HCl$$

Polyurethane:

$$\underset{\text{hexamethylenediamine}}{H_2N{-}(CH_2)_6{-}NH_2} + \underset{\text{ethylene bischloroformate}}{Cl{-}CO{-}O{-}(CH_2)_2{-}O{-}CO{-}Cl} \rightarrow$$

$$+HN{-}(CH_2)_6{-}NH{-}CO{-}O{-}(CH_2)_2{-}O{-}CO+_x + HCl$$

The choice of the additives was made on the basis of their ability to form precipitates, in the absence of a polymer, on the interfaces between the two solutions in which their components were dissolved. For example, when an aqueous solution of barium hydroxide was layered upon solutions of sulfuric acid or of alizarin in carbon tetrachloride, a white or a blue precipitate had formed on the interfaces.

Preparation of Polymers

Example 1 (nylon 610, unstirred system, no additive). Sebacyl chloride (1.0 ml, 0.0043 mole) was added to 50 ml carbon tetrachloride (CCl_4) in a 250-ml beaker. A solution of hexamethylenediamine (HMDA) (2.2 g, 0.019 mole) in 50 ml water was then introduced carefully into the beaker containing acid chloride solution. The polymer film forming at the interface was grasped with a tweezer, and the resultant rope was rolled onto a glass rod being rotated horizontally until no more polymer formed at the interface. The fibrous polymer was broken up in ethyl alcohol, filtered, then washed with carbon tetrachloride, followed by another alcohol wash, then washed with water, and allowed to dry at room conditions.

Example 2 (nylon 610, stirred system, no additive). Following Morgan and Kwolek,[11] a solution of hexamethylenediamine (5.12 g, 0.044 mole) in 220 ml water was placed in a Waring blender. The blender was turned

on to medium speed. Over a period of 10 sec, a solution of sebacyl chloride (4.72 ml) in 380 ml carbon tetrachloride was added under stirring. After about 3 min of stirring, polymer was collected by filtration. The granular polymer was washed with water and then dried for 30 hr in an oven at 55 ± 5°C at a pressure of 120–130 mm Hg. It could be molded by compression (182°C, 70 kg/cm², 10 min) into discs (30-mm diameter, 11-mm thickness) of good color and appearance.

Example 3 (polyurethane, unstirred system, no additive). Following Wittbecker and Katz,[12] a solution of hexamethylenediamine (3.0 g, 0.0258 mole), sodium carbonate (5.0 g, 0.047 mole), and Duponol ME detergent (0.75 g) in 75 ml water was cooled to 5°C. In another beaker, a solution of ethylene bischloroformate (4.85 g, 0.0258 mole) in 63 ml benzene was cooled to 10°C. The organic phase was then carefully layered upon the aqueous solution. The resultant polymer film was removed continuously from the interface in the form of rope as described in example 1. The polymer was then washed with alcohol, water, and again with alcohol, and finally dried at room conditions.

Example 4 (polyurethane, stirred system, no additive). Following again Wittbecker and Katz,[12] a solution of hexamethylenediamine (3.0 g, 0.0258 mole), sodium carbonate (5.0 g, 0.047 mole) and Duponol ME (0.75 g) in 75 ml water was cooled to 5°C and placed in a Waring blender. A solution of ethylene bischloroformate (4.85 g, 0.0258 mole) in 63 ml benzene was cooled to 10°C and added rapidly while stirring. After about 5 min of stirring, the polymer was isolated by filtration and purified by successive washing with alcohol, water, and alcohol. The polyurethane was obtained as a white powder and was dried at ambient room conditions.

Incorporation of Fillers

A filler may be described as an inert material added to a polymer composition, physically or chemically, to modify its properties and/or reduce its cost. Fillers are employed to some extent in almost all plastics, both thermoplastic and thermoset, and their number is quite large.

The use of fillers of special types for purely functional reasons has been growing in importance. Some examples are fiber glass reinforcement for polyesters, carbon black for rubbers, barium ferrite as a magnetizable filler, molybdenum disulfide for lubrication in bearings, or metallic powders for electrical and thermal conductivity in plastics. The fundamental aspects of polymer–filler interaction have been studied in a number of polymers,[13] and the mechanical properties of a polymer were found to depend on the intimacy of additive dispersion and on the size of the filler particles.

It will be shown in the following experiments that condensation polymers can be prepared in one step at room conditions by applying the interfacial polycondensation method in such a manner that the fillers are formed in situ, that is, simultaneously with the polymer.

Example 5 (nylon 610, unstirred system, incorporated barium sulfate). In a beaker, a solution of hexamethylenediamine (2.2 g) and barium hydroxide (0.75 g) in 50 ml water was prepared. This solution was carefully layered upon a solution of sebacyl chloride (2.0 ml) and sulfuric acid (10 ml) in 50 ml carbon tetrachloride. The resultant polymer film was grasped and pulled out with tweezers in the form of a rope. The fibrous polymer was washed with alcohol, carbon tetrachloride, again with alcohol, and finally with water. It was then dried at ambient room conditions. The resultant polymer was tested qualitatively and quantitatively for barium sulfate. The qualitative test was done by means of the platinum wire method, in which the color of the flame changes to green, and quantitatively by ashing and weighing of the residue. The barium sulfate content was found to be 12%.

Example 6 (nylon 610, stirred system, incorporated silver bromide). A solution of hexamethylenediamine (3.0 g) and silver nitrate (0.8 g) in 75 ml water was placed in a Waring blender which was turned on to medium speed. Over a period of 15 sec, a solution of sebacyl chloride (3.0 ml) and ethylene bromide (5.0 ml) in 50 ml carbon tetrachloride was added. After stirring for 3 min, the polymer was isolated by filtration and washed and dried as described in example 2.

Originally white, the polymer turned dark on exposure to sunlight. The sample was found to contain 3% silver.

Example 7 (incorporation of silica filler). Hydrated forms of silica (SiO_2) are common reinforcing fillers in polymers. It was found that an interface of silica gel can be formed between water and carbon tetrachloride by adding sodium silicate to the water and sulfuric acid to carbon tetrachloride. Hydrochloric acid formed by the hydrolysis of sebacyl chloride will have the same effect if the latter is present in carbon tetrachloride. The reaction at the interface proceeds as follows:

$$Na_2SiO_3 + 2HCl \rightarrow 2NaCl + SiO_2 + H_2O$$

No attempt was made to incorporate silica into a polymer in the course of an interfacial polycondensation reaction.

Incorporation of Colorants

Colorants are substances capable of imparting color to a matrix by solution, adsorption, or dispersion. Pigments are fine, colored, solid particles substantially insoluble in their carrier. Lakes are very light-fast pigments consisting of an organic dye precipitated on, or bonded to, an inorganic carrier such as hydrated alumina.

In general, dyes containing the anthraquinone and related nuclei show high tinctorial strength, good brightness, and very good fastness to washing, crocking, chlorine, perspiration, light, and weather.[14] Among the anthraquinone dyes, the simplest is based on alizarin (1,2-dihydroxyanthraquinone).

With metal salts, this colorless compound gives highly colored lakes, e.g., red with aluminum salts, blue with barium salts. It was demonstrated that by incorporation of the metal salt in the aqueous phase and of the alizarin in the organic solvent phase, lakes can be precipitated in the interface simultaneously with the polymer, which thus becomes colored.

Example 8 (nylon 610, unstirred system, blue colored). A solution of hexamethylenediamine (10.0 ml) and barium hydroxide (1.0 g) in 50 ml water was carefully layered upon a solution of alizarin (0.5 g) and sebacyl chloride (3.0 ml) in 65 ml carbon tetrachloride. From the interface, nylon rope was pulled out. The resultant polymer was colored purple-blue. It was washed and dried as described in example 1.

Example 9 (nylon 610, stirred system, blue colored). A solution of hexamethylenediamine (10.0 ml) and barium hydroxide (1.0 g) in 70 ml water was placed in a Waring blender. The blender was turned on to medium speed. Over a period of 15 sec, a solution of sebacyl chloride (2 ml) and alizarin (0.5 g) in 50 ml carbon tetrachloride was added under stirring. After about 3 min of stirring, the polymer was collected by filtration. The resultant polymer was purple-blue. It was washed and dried as described in example 2.

Example 10 (nylon 610, unstirred system, red-colored). A solution of hexamethylenediamine (15 ml) and aluminum sulfate (1.5 g) in 50 ml water was carefully layered upon a solution of sebacyl chloride (10 ml) and alizarin (0.5 g) in 65 ml carbon tetrachloride. The polymer was pulled from the interface in the form of a rope. It was washed and dried as described in example 1. The resultant polymer was rose-red in color.

Example 11 (nylon 610, stirred system, red-colored). A solution of hexamethylenediamine (15 ml) and aluminum sulfate (1.0 g) in 50 ml water was placed in the Waring blender. The blender was turned on to medium speed. Over a period of 15 sec, a solution of sebacyl chloride (10 ml) and alizarin (0.5 g) in 65 ml carbon tetrachloride was added. After about 3 min of stirring, the polymer was collected by filtration. It was washed and dried as described in example 2. The resultant polymer was rose-red in color.

Example 12 (polyurethane, stirred system, red colored). A solution of hexamethylenediamine (15 ml), aluminum sulfate (1.5 g), sodium carbonate (5.0 g, 0.047 mole), and Duponol ME (0.75 g) in 75 ml water was cooled to 5°C and placed in the Waring blender. A solution of ethylene bischloroformate (5 ml) and alizarin (1.0 g) in 60 ml benzene was cooled to 10°C and added rapidly under stirring. After about 5 min, the polymer was isolated by filtration. It was washed and dried as described in example 4. The resultant polymer was rose-red in color.

Incorporation of Flame Retardants

Safety requirements make it necessary to continuously increase the flame resistance of polymers. The following examples show how fire-retarding

additives may be incorporated in situ during the interfacial polycondensation.

Example 13 (nylon 610, unstirred system, incorporated zinc phosphate). A solution of zinc chloride (0.9 g) and hexamethylenediamine (2.2 g) in 50 ml water was carefully layered upon a solution of sebacyl chloride (2.5 ml) and concentrated phosphoric acid (5 ml) in 50 ml carbon tetrachloride. The polymer forming at the interface was pulled out in the form of a rope. It was then washed and dried as described in example 1. The dried polymer contained 4% zinc, corresponding to about 8% zinc phosphate.

Example 14 (nylon 610, unstirred system, incorporated zinc pentachlorophenate). A solution of hexamethylenediamine (6.0 g) and zinc chloride (0.9 g) in 50 ml water was carefully layered onto a solution of sebacyl chloride (3.0 ml) and pentachlorophenol (1.5 g) in 50 ml carbon tetrachloride. Polymer forming at the interface was pulled out in the form of a rope. It was then dried as described in example 1. For the purpose of analysis, a portion of the polymer was then digested with hydrochloric acid, dried in a vacuum oven at 50°C under a pressure of 120 mm Hg, and extracted with *n*-hexane for about 20 hr. At the end of extraction, the solvent was removed in a rotary evaporator and the residue was dissolved in acetone. After removal of the acetone, the sample was analyzed. Pentachlorophenol was positively identified and the polymer was found to contain 3% zinc, corresponding to about 30% zinc pentachlorophenate.

Example 15 (nylon 610, stirred system, incorporated zinc pentachlorophenate). A solution of hexamethylenediamine (14 g) and zinc chloride (1.5 g) in 220 ml water was placed in a Waring blender. The blender was turned on to medium speed. Over a period of 10 sec, a solution of sebacyl chloride (4.72 ml) and pentachlorophenol (0.5 g) in 380 ml carbon tetrachloride was added to the blender under stirring. After about 3 min of stirring, the polymer was collected by filtration, washed, and dried as described in example 2. The polymer was found to contain 3.9% zinc, corresponding to about 39% pentachlorophenate.

Example 16 (Polyurethane, unstirred system, incorporated zinc pentachlorophenate). A solution of ethylene bischloroformate (4.0 ml) and pentachlorophenol (1.0 g) in 60 ml benzene was gently layered upon a solution of hexamethylenediamine (15 ml), sodium carbonate (5.0 g), and zinc chloride (1.5 g) in 75 ml water. The polymer forming at the interface was pulled out in the form of a rope. It was then washed and dried as described in example 3. The polymer was found to contain 2.5% zinc, corresponding to about 25% zinc pentachlorophenate.

Comparative Evaluation of Flame Retardant

In order to investigate whether there is a real advantage in incorporating a flame-retarding agent during the interfacial condensation reaction, the burning properties of three sample were compared, viz., (a) nylon 610 made by interfacial polycondensation without an additive, made according to

example 2; (b) nylon 610 made as in (a), but blended with 40% zinc pentachlorophenate; and (c) nylon 610 made by interfacial polycondensation with 40% zinc pentachlorophenate incorporated in situ during the reaction, made according to example 15.

The zinc pentachlorophenate used in sample b was prepared as follows[15]: 5.28 g pentachlorophenol was dissolved in 250 ml water containing 0.88 g sodium hydroxide. To this was added, drop by drop and under stirring, 6 ml very dilute nitric acid until a slight precipitate formed, which was then filtered. To the clear solution, a solution of 2.70 g zinc chloride in 200 ml water was gently added. The precipitate of zinc pentachlorophenate was isolated by filtration, washed with water, and then dried in a vacuum oven for 25 hr at 50°C and under a pressure of 125 mm Hg. Laboratory analysis showed 10% zinc in the sample, while the infrared spectrum confirmed the presence of pentachlorophenate. Theoretically, a pure sample of zinc pentachlorophenate should contain 10.67% zinc. Allowing for experimental errors, the sample was assumed to be sufficiently pure for further use.

TABLE II
Effect of Fire Retardant on Ignition Points of Samples of Nylon 610

Temp., °C	Sample a (without additive)		Sample b (blended with Zn pentachlorophenate)		Sample c (Zn pentachlorophenate formed during reaction)	
	Change	In sec	Change	In sec	Change	In sec
350	none	361	none	364	none	406
400	none	400	none	422	none	445
450	ignites	134	none	422	none	408
500	ignites	89	ignites	98	none	420
550	ignites	56	ignites	58	ignites	54

In the flammability test, equal amounts of samples a, b, and c, ground and dried, were put in porcelain crucibles. The crucibles were then placed into a muffle furnace preheated to the temperature at which the test was conducted. The time taken by each sample from the moment it was put in the furnace until it caught fire was recorded. Since the presence of moisture in the sample influences its ignition point, all samples were tested at the same room conditions, i.e., 40% relative humidity and 25°C.

As shown in Table II, the ignition temperature of untreated nylon 610 (sample a) lies between 400° to 450°C (Hauck[16] reports the ignition temperature of nylon as 420°C). An increase of 50°C in ignition point is attained when nylon 610 is mechanically blended with 40% zinc pentachlorophenate (sample b). However, incorporation of the same amount of zinc pentachlorophenate during the interfacial polycondensation reaction (sample c) caused the ignition point to increase by 100°C.

ADVANTAGES AND POTENTIAL SCOPE OF METHOD

The primary advantage of incorporating an additive from its reactive components into a polymer in the course of an interfacial polycondensation reaction lies in the fact that this additive will become dispersed in the polymer, equally and in a very fine form. This is the most desirable condition for obtaining maximum efficiency, as was shown earlier in the case of a flame-retardant compound. There further exists the possibility that the in situ formation and incorporation of additives may promote the formation of chemical bonds between the additive and the polymer, giving further improvement in the desired properties, viz., strength in the case of reinforcing fillers, greater permanency in the case of coloration, increased flame resistance, and stability toward elution by solvents.

Conventionally, additives are incorporated into polymers by dry blending or by milling, which are expensive processes, sometimes even causing incipient degradation of the polymer. Elimination of this step would be of economic advantage, particularly since the possibility exists that interfacial polycondensations can be carried out as continuous processes.[1]

In situ formation and incorporation of additives is applicable to any condensation polymer capable of being formed by interfacial condensation, such as polyamides, polyesters, polyurethanes, polysulfonamides, polyphosphonamides, polyanhydrides, polyamines, polyethers, and polysulfides.

Virtually any additive capable of formation by the reaction of coreactants soluble or dispersible in the respective complementary phases of the interfacial polycondensation system may be incorporated by this method. Generally any filler, comprising a water-insoluble salt precipitable from its water-soluble ionic components, may be formed in the polymer. These include fillers such as metal silicates (Al, Ca, Mg), metal sulfates (Ca, Ba, Pb), metal phosphates (Ca, Ba, Mg, Zn), and metal halides (AgCl, AgBr). Silica gel may be incorporated in condensation-type polymers by including an alkali metal silicate and an acid in the respective complementary phases of the system.

There is also variation in the choice of colored pigments, resulting from the reaction of a lake former and a metallic salt. Lake formers are the anthraquinones containing two hydroxyl groups ortho to each other, such as alizarin, naphthazarin, and quinalizarin; and the so-called acid dyes, such as Alizarin Blue SAP (1,5-dihydroxy-4,8-diamino-2,6-anthraquinonedisulfonic acid) and Alizarin SAE (the corresponding monosulfonic acid). Suitable metallic salts include those of aluminim, chromium, iron, calcium, barium, and other multivalent metals.

Among flame-retardant additives, those may be considered which, by their chemical structure, are capable of forming metal salts. These include chlorendic anhydride (HET Anhydride, Hooker Chemical Corporation), tetrabromophthalic acid (Niagathal, Hooker Chemical Corporation), tetrabromobisphenol A (Firemaster BP4A, Michigan Chemical Corporation), and Chloran (UOP Chemical Company).

AREAS OF FUTURE STUDIES

Most of the work done in interfacial polycondensation reactions, as summarized up to 1965 in the book by Morgan[1] and available in numerous publications afterward, is dedicated to the study of the influence of the process variables on the product properties and to the establishment of optimum polymerization conditions. Different for unstirred and stirred systems, the effects of these variables also differ for the various classes of polymers involved.

The incorporation of additional reactants to such systems is bound to change their mechanisms and may interfere with the achievement of high molecular polymer weight, so that earlier established rules may no longer be fully applicable. Thus, optimum polymerization conditions will again have to be determined for changes made in some systems. In particular, methods have to be established which will allow to incorporate constant and predetermined amounts of a certain additive into a polymer.

Furthermore, as was done so far in the case of the in situ formation and addition of a flame-retardant additive, it will have to be shown in each case that the product resultant from the interfacial polycondensation method is superior to that obtained by conventional mixing and blending procedures.

Finally, whenever superiority in properties has been established, fundamental studies into the causes for this superiority (e.g., degree of dispersion, polymer grafting reactions) will become necessary for further development of the entire concept.

CONCLUSIONS

1. It has been demonstrated that additives (fillers, colorants, fire retardants) which can be formed in situ can be incorporated into polymers during interfacial polycondensation reactions, carried out with or without stirring.

2. In the case of the incorporation of a flame retardant into nylon 610, the product made by interfacial polycondensation had a significantly higher ignition point than one of the same composition prepared by mechanical blending. This is taken as an indication of the potential superior ity of the in situ method over conventional mixing processes.

3. The interfacial method of the incorporation of additives into condensation polymers has a broad scope, but requires additional studies for the establishment of optimum polymerization conditions and the development of techniques to be able to produce polymers with consistent and predetermined amounts of particular additives.

4. In cases where superiority of the in situ method is shown in terms of improved product properties, fundamental studies into the physical and/or molecular causes of this superiority are in order. This should open a broad field of basic research in the interface study area.

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