

# Precipitative Polymerization for Polycarbonate: A Simultaneous Reaction–Precipitation Technique

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## Synopsis

A novel phenomenon, termed precipitative polymerization, is described. In it, the BPA–phosgene reaction is conducted with simultaneous precipitation of polycarbonate granules. Very low organic-to-aqueous phase ratio and high pH medium are primarily required to cause this *in-situ* precipitation.

## INTRODUCTION

Bisphenol A-polycarbonate is usually produced by reacting bisphenol A and phosgene ( $\text{COCl}_2$ ) at the interface between an aqueous alkaline BPA solution and an inert organic solvent in the presence of a catalyst, typically triethylamine. The polymer which forms in this aqueous–organic heterophase mixture remains soluble in the organic solvent such as methylene chloride.<sup>1–3</sup> The polymer is isolated from the organic solution by means of steam, methanol, or some other antisolvent.

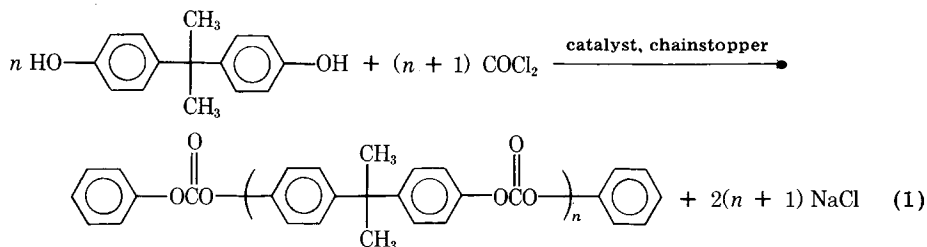
In contrast to this conventional technique, precipitative polymerization can be described as an interfacial polymerization technique whereby the polymer is precipitated in the reaction mixture itself as fine granules. The polymer precipitate can then be simply filtered off and washed free of the alkaline mother liquor. The *in situ* precipitation of polycarbonate in this technique is made possible by greatly reducing the organic loading of the reaction mixture so that the polymer cannot remain in solution.

The precipitative polymerization for polycarbonate described in this paper is a novel phenomenon not described in the literature before. The technique features total isolation of hard granular polymer particles. There have, however, been attempts to precipitate polycarbonates *in-situ*. For example, Schnell, Bottenbruch, and Khimm<sup>3</sup> described an *in situ* precipitation of polycarbonate in which xylene was used as the organic phase. In their scheme, the polymer precipitated in the form of white, xylene-swollen particles. The polymer granules had a low molecular weight interior and a high molecular weight skin, thus yielding a bimodal distribution. An alternate means of *in situ* precipitation of polycarbonate powder<sup>4</sup> is to use an organic medium containing a mixture of the solvent, such as methylene chloride, and a partial solvent such as isopropanol. The mechanism of precipitation in this case is the limitation of solubility for various polymer chains. As a result, the lower oligomers remain in solution yielding a fractionated polymer. One can narrow the molecular weight distribution in this fashion. In the extreme case when no solvent was used, Robertson, Cook, and Gregory<sup>5</sup> found upon phosgenation of BPA a low molecular weight

oligomer ( $\bar{M}_w = 1000$ ) precipitating in the reaction mixture. The precipitative polymerization described in this report, as will be apparent, is quite distinct from the examples mentioned above.

### Conditions Conducive to Precipitative Polymerization

The reaction between BPA and phosgene is believed to take place in two steps at the aqueous-organic interface. First, BPA-chloroformates are formed. The chloroformate then reacts either with itself or with more BPA to propagate the polymer chain. A monofunctional chainstopper such as phenol is used to regulate the chain length, i.e., the average molecular weight. An alkaline medium is necessary for obtaining high molecular weight. The overall stoichiometry of the polymerization reaction is the following:



Strictly speaking, the catalyst is not essential for this reaction. For technical reasons of obtaining high molecular weights and higher reaction rates, catalysts are always used.

The same chemistry as outlined above is harnessed in the case of precipitative polymerization also. However, the following reaction conditions have to be satisfied:

- (1) low organic-to-aqueous phase ratio, in the neighborhood of 0.1;
- (2) high initial pH of the reaction mixture, i.e., higher than 12.

Under such pH conditions, in a typical batch phosgenation, the BPA is totally soluble in the aqueous caustic soda.

### EXPERIMENTAL

The experiments were carried out in a 3-L jacketed glass reactor. Two 3 in. dia/six-bladed flat turbines were held by a Teflon-coated stainless steel shaft driven by a 0.25 hp Bodine variable speed motor (B&B Motor and Controls, New York). Four symmetrical vertical baffles made by indenting the inner wall of the jacketed reactor were used for reducing vortices. Figure 1 is a sketch of the laboratory reactor.

In addition to the center port of the flanged reactor top which was used for the stirrer shaft, there were other ports for phosgene and caustic soda addition, pH and thermocouple probes, and a condenser. The heat of reaction was removed in the condenser by the refluxing of methylene chloride. A temperature-controlled circulation bath provided another method of removing heat of reaction. The bath was employed to control any desired temperature in the jacket below 40°C, the refluxing temperature for methylene chloride. The bottom part, fitted with a stop cock, was used for sampling and product withdrawal.

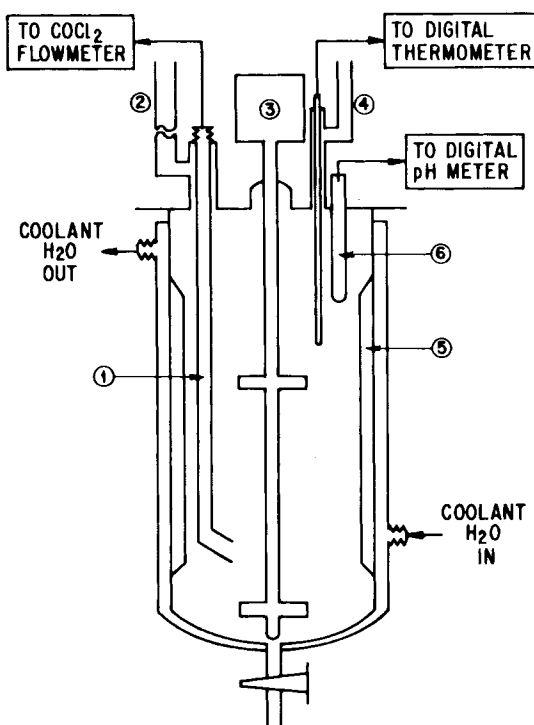


Fig. 1. Schematic of laboratory reactor: ① phosgene dip tube ② condenser; ③ stirrer motor; ④ caustic addition tube; ⑤ baffles; ⑥ pH meter probe.

In a typical experiment, 228 g (1 mol) of BPA was stirred at 800 rpm stirrer speed in a mixture consisting of 1400 mL of water, 160 mL of 50% NaOH (3.1 mol NaOH), 135 mL of methylene chloride, 0.21 g of triethylamine catalyst, and 3 g of phenol (0.03 mol), until all BPA dissolved resulting in a two-phase mixture. The organic loading, expressed as volume of methylene chloride per unit volume of aqueous phase, was 0.09. Because of methylene chloride solubility in the aqueous phase, the phase ratio  $\phi$  was somewhat less than 0.09. A temperature of 10°C was maintained by circulating cooling water through the jacket.

Phosgene was passed through the reaction mixture for 0.5 h at a rate such that 115% of the stoichiometric requirement shown by eq. (1) was introduced. Additional caustic soda was added to maintain a high pH of 12–13. The polymer granules appeared within 10 min; more formed as phosgenation continued. The product mixture had the consistency of a low-viscosity slurry.

At the conclusion of the reaction, the product granules were isolated by merely filtering the product slurry. The granules were washed with a 3% HCl solution to remove the catalyst and with water to remove HCl and NaCl. The granules were then dried in a vacuum oven at 80°C overnight.

Intermediate time samples were collected to follow the progress of the polymerization. The granular product was dissolved in methylene chloride and reprecipitated with methanol for measuring intrinsic viscosity and molecular weight distribution (the latter by gel permeation chromatography).

## RESULTS AND DISCUSSION

Successful *in situ* precipitation of polycarbonate primarily depended on low phase ratio ( $\phi$ ) and high initial caustic to BPA ratio (or pH). Three possibilities exist depending on the relative values of phase ratio and NaOH/BPA ratios:

(1) for high NaOH/BPA ratio, viz., higher than 2.0 and low  $\phi$ , viz.,  $< 0.15$ , polymer precipitates *in situ*;

(2) for intermediate values of  $\phi$ , for example,  $\phi > 0.15$ , large sticky globs form in the reactor for all values of NaOH/BPA ratio and

(3) for  $\phi > 0.75$ , the polymer remains in solution in the organic phase.

This situation is qualitatively illustrated in Figure 2. Thus, the *in situ* precipitation takes place in a narrow region outlined by phase ratio and initial NaOH/BPA ratio. Though low values of  $\phi$  were important for the polymer of high molecular weight ( $\bar{M}_w > 10,000$ ),  $\phi$  did not influence the values of the intrinsic viscosity or the molecular weight. That is, other conditions remaining the same, one can get comparable molecular weight products irrespective of whether the polymer is precipitated as granules, sticky globs, or remained in solution as the phase ratio was increased from very low to very high values. Molecular weight was chiefly controlled by the amount of chainstopper used.

High intrinsic viscosities (0.4 and higher) were obtained for high values ( $> 2$ ) of NaOH/BPA ratio (causing a pH of over 12 or 13). Lower pH's, for example 10–11, yielded low-IV polymers (IV 0.1–0.3). It was found to be difficult to avoid glob formation at such low pH's also.

The two variables used to characterize both organic and aqueous phases are NaOH/BPA and phase ratios. At a certain phase ratio, NaOH/BPA determined the BPA solubility in the aqueous phase and appeared to control the precipitation process. For example, values of NaOH/BPA higher than 2.0 favored granular precipitates. The choice of NaOH/BPA as a parameter was because of a buffer action due to NaOH and sodium salts of BPA. The buffer made the aqueous phase pH inadequately sensitive to changes in NaOH concentration. The phase ratio, the other variable, describes the extent of the two phases, and in addition defines a polymer/solvent ratio for a constant batch production rate. It is obvious that polymer precipitation should take place at low phase ratios (or high

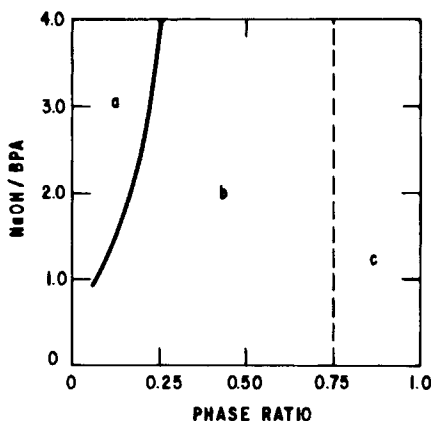


Fig. 2. Conditions causing (a) precipitative, (b) sticky globs, and (c) polymer in solution.

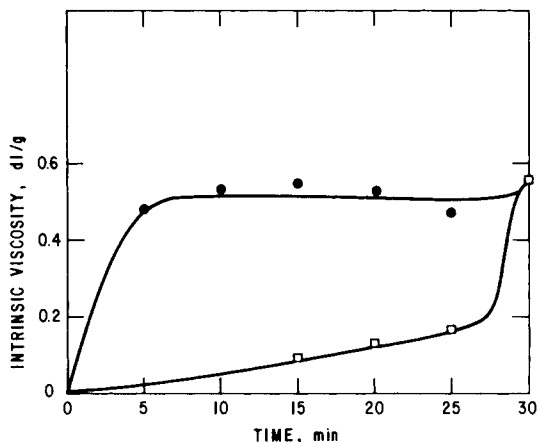


Fig. 3. Intrinsic viscosity vs. time: (●) typical precipitative polymerization; (□) typical conventional interfacial polymerization.

polymer/solvent ratios), but the fact that granular precipitates of high molecular weight form in high yield at lower phase ratios makes the technique intriguing.

The mechanism of precipitative polymerization is not well understood. Presumably, it occurs because of rapid crystallization of the polymer from a highly concentrated polymer solution. The degree of crystallinity observed in

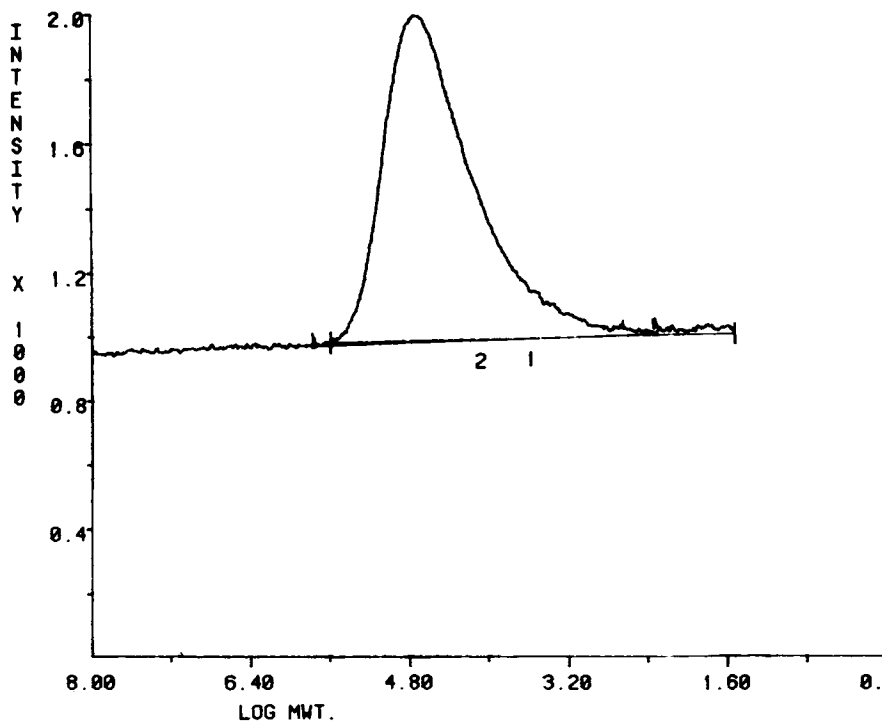


Fig. 4. Molecular weight distribution by GPC, in a typical run at  $t = 20$  min.

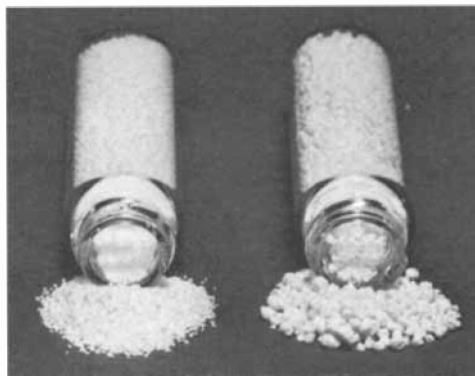


Fig. 5. Precipitative polymer particles.

these polymers is quite significant (20–25%) in comparison to almost no crystallinity in polycarbonate isolated by steam from a solution.

One unique feature of this polymerization is that the polymer attains a high molecular weight very early in the reaction. This is shown in Figure 3. Also shown is a typical intrinsic viscosity rise for a conventional batch polymerization utilizing a phase ratio of 1.0. The molecular weight distribution of the polymer is monomodal as shown in Figure 4, where a typical intermediate-time data point is shown. The molecular weight, within experimental error, did not change with time, thus showing the efficiency of the chainstopper utilization. In the absence of chainstopper very high intrinsic viscosity polymers ( $IV > 2$ ) were obtained. Typically, these polymers were difficult to redissolve in methylene chloride.

The precipitative polymer product varied in consistency between fine fluffy powder to hard spherical granules, 2 mm in diameter. Variables responsible for this variation were not identified in this study. Figure 5 shows photographs of precipitates obtained by this technique.

## CONCLUSION

A new technique of BPA–phosgene reaction with *in situ* precipitation of polycarbonate powder or granules is reported here. The *in situ* precipitation is caused by conditions of high NaOH/BPA ratio (or high pH) and low organic-to-aqueous phase ratio. The granules are nonsticky and easily filterable. The polymer is unimodal. The mechanism of granule formation in this technique, while not well understood, differs from an *in situ* precipitation which can be brought about by an antisolvent. The BPA–phosgene reaction behavior is similar to the more familiar interfacial polymerization.

The author expresses his gratitude to General Electric Research and Development for permission to publish this work.

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Received June 6, 1982

Accepted August 23, 1982