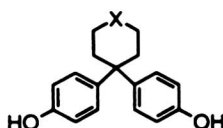
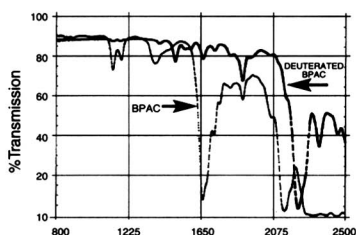
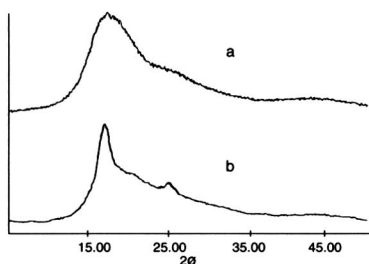


HANDBOOK OF POLYCARBONATE SCIENCE AND TECHNOLOGY



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HANDBOOK OF POLYCARBONATE SCIENCE AND TECHNOLOGY

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edited by

DONALD G. LEGRAND

*General Electric Company
Schenectady, New York*

JOHN T. BENDLER

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MARCEL DEKKER, INC.

NEW YORK • BASEL

Transferred to Digital Printing 2010

ISBN: 0-8247-9915-1

Headquarters

Marcel Dekker, Inc.
270 Madison Avenue, New York, NY 10016
tel: 212-696-9000; fax: 212-685-4540

Eastern Hemisphere Distribution

Marcel Dekker AG
Hutgasse 4, Postfach 812, CH-4001 Basel, Switzerland
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World Wide Web

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10 9 8 7 6 5 4 3 2 1

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The publisher has gone to great lengths to ensure the quality of this reprint but points out that some imperfections in the original may be apparent.

To our wives, Kathryn and Julie, for their patience and understanding



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Preface

The idea of producing a book on polycarbonates was inspired by three independent events. The first was an interview with Joe Hogan of GE Plastics that was published in *R&D* magazine; the second, a reference in the *R&D* article to one of the coeditors; and the last, a telephone call from Russell Dekker to propose editing such a book. A preliminary survey of the literature showed that considerable research on almost every aspect of polycarbonates had been carried out and that a large number of patents had been issued. As a result, the need became apparent for a book that addresses and summarizes both the methods of syntheses and the physical properties of polycarbonate resins, and that also illustrates current methods of fabrication and significant applications.

It has been almost 40 years since two—now classic and out-of-print—books were written on this subject. During this time, there has been progress in several different areas pertaining to the syntheses of the material. A significant amount of research has been carried out in an effort to understand polycarbonate properties utilizing novel experimental, theoretical, and modeling techniques, and much of this work has been discussed at technical meetings and published. Many new applications, formulations, and methods of fabrication have also been discovered and patented. The scope of the present book has been limited by a desire to cover in detail the topics that are the best understood, and that would likely be useful in future studies of properties and applications of polycarbonates.

The book begins with Chapter 1 on historical background. Chapter 2 describes various methods of syntheses, followed by Chapter 3 on molecular modeling. Chapter 4 describes NMR studies that have helped to elucidate some of the molecular motions that occur. Chapter 5 describes other polycarbonates such as the spirobis-indanes.

Chapters 6, 7, 8, and 9 deal with the physical properties of these materials. The focus is on mechanical, optical, thermal and rheological properties.

Chapters 10, 11, 12, and 13 address physical and chemical aging and degradation of polycarbonates. Crystallization is included in this section because it can be induced by long-term thermal aging or chemical degradation.

Chapters 14, 15, and 16 describe formulations of commercial products, fabrication methods, and secondary finishing operations.

Finally, Chapter 17 addresses more recent polycarbonate applications.

We wish to express our thanks to Russell Dekker, who approached us about writing this book, to Joe Hogan and Patricia Keenan for their support, and to Ray Naar, Niles Rosenquist, YeeGang Lin, Wie Pan, and many others who helped by reviewing the chapters. Of course, thanks are due the contributors to the book who made it a reality, to Connie Vanbockern who helped us with the typing, and to our production editor, Kathleen Baldonado, without whose perseverance the book would not have been completed.

Donald G. LeGrand

John T. Bendler

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HANDBOOK OF POLYCARBONATE SCIENCE AND TECHNOLOGY



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1

Introduction and Historical Background

E. E. Bostick

General Electric Plastics, Mt. Vernon, Indiana

I. INTRODUCTION

The discovery, invention, and development of aromatic polycarbonates has closely followed and been stimulated by developments in aromatic polyesters such as polyethylene terephthalate [1–4]. As will be stated later, there was a span of 50 years between early published findings and the actual discovery of useful thermoplastic aromatic polycarbonates. There were many factors possible to account for the low level of activity such as lack of perceived need for high-temperature resistance in applications, shortage of suitable commercially feasible monomers, and absence of process technology to fabricate useful parts. As it turned out, all of these factors were converging when D. W. Fox and H. Schnell, who were working independently toward different goals, discovered the polycarbonate of bisphenol A and both recognized the unique properties of this most interesting polymer [4,5].

II. EARLY CHEMISTRY

A. Aliphatic Polyesters and Polycarbonates

Aliphatic polyesters were first published by Lourenco [6] in 1863. Reaction products from succinic acid and ethylene glycol were described. Thirty years later Vorlander [7] prepared polyesters from fumaric and maleic acid and ethylene glycol. Hofmann [8] prepared and introduced polymers from adipic acid or

methyl adipic acid and ethylene glycol or 1,2-propanediol in 1917 as substitutes for natural fats and waxes. The intended use gives an idea that these materials were low molecular weight and possessed no structural properties. These polyesters later found use in coatings and polyurethanes by O. Bayer [9] but have never found use as load-bearing materials.

Some years later, W. H. Carothers and his colleagues [10–12] conducted an extensive study on aliphatic and aliphatic aromatic polyesters. Polyesters of malonic acid, succinic acid, adipic acid, sebacic acid, maleic acid, fumaric acid, and phthalic acid were obtained when reacted with ethylene glycol, 1,3-propanediol, 1,6-hexanediol, and/or 1,10-decanediol. Most of these products were low-melting, viscous liquids or microcrystalline wax-like solids with melting points below 100°C.

This group also prepared so-called superpolyesters and superpolycarbonates that were film and fiber formers, but once again the melting points and thermal resistance were low. None of these polyesters or corollary polycarbonates has become a standalone, commercially significant thermoplastic.

B. Aromatic Polyesters and Polycarbonates

The earliest significant report of the synthesis of aromatic polycarbonates was by Einhorn [13] who reacted hydroquinone, resorcinol, and catechol with phosgene in pyridine solution to obtain linear polymers from hydroquinone and resorcinol and a cyclic carbonate from catechol. Hydroquinone yielded an insoluble crystalline powder that melted above 280°C. Resorcinol polycarbonate resin was an amorphous material that melted with decomposition at 190–200°C. Later, in 1902, Bischoff and Hedenstroem [14] reported the synthesis of these same polymers by transesterification with diphenyl carbonate.

Nothing was reported in connection with aromatic polycarbonates for the next 50 years.

Activity in aromatic acid aliphatic diol or polyol polyesters did proceed. The most significant report was that of the Whinfield and Dickinson invention of polyethylene terephthalate [3]. In fact, D. W. Fox [1] was looking for a more hydrolytically stable alternate to polyethylene terephthalate for use as a magnet wire insulation varnish when he discovered bisphenol A polycarbonate (BPA-PC). H. Schnell [15] reported a definite goal in achieving properties similar to polyethylene terephthalate while leading the research at Farben Fabricken Bayer. It is certainly interesting that they were actively conducting independent research in this field at the same time and discovered the same polymer. It is even more interesting that the unique and commercially valuable properties of this polymer have not been offset by any other feasible aromatic diol. The foundation of the polycarbonate engineering thermoplastic resin industry rests on BPA-PC.

III. BISPHENOL A CHEMISTRY AND DEVELOPMENT

Access to a high-quality purified monomer feedstock such as BPA has been and continues to be critical to the development and continued growth of polycarbonate resins as premier engineering thermoplastic resins of choice. Therefore, it is appropriate to briefly cover BPA research and commercial development during the same time frame. A. Baeyer [16] reported results of acid-catalyzed condensation of phenol with aldehydes and ketones in 1872. Later, in 1891, Dianin [17] condensed phenol with acetone to make BPA. Almost 60 years later, J. E. Janson [18] was granted a patent on the use of an ionizable sulfur compound as a promoter and accelerator with acid catalysis. This acceleration was very important during the commercialization of BPA.

BPA prepared for use in the manufacture of linear polycarbonates must be of highest purity to achieve the highest quality polycarbonate with respect to color and performance. In this connection, Kissinger and Wynn [19] have been allowed a process patent for fractional crystallization of crude BPA to yield a product of the highest purity without the use of water, organic solvents, extraction, or distillation. This innovation, along with acidic ion exchange resins in fixed or fluid beds, has advanced the commercial manufacture of BPA to a very accessible position.

IV. PROCESS HISTORY

A. Polymerization

The original discovery of BPA-PC was by transesterification of BPA monomer with diphenyl carbonate [4,5]. However, equipment limitations at that time prevented scale-up and commercialization of resin from melt processes. The first solvent system scaled up was pyridine as both solvent and acid acceptor in a system reaction of BPA with phosgene and a monofunctional phenol as molecular weight regulator [20]. Supply and economics of pyridine as a reaction solvent limited its growth.

Reaction of BPA, phosgene, and monohydric phenols in methylene chloride solution in contact with an aqueous solution of sodium hydroxide became the process of choice by one of the major producers early on [21]. Triethylamine was the catalyst of choice. An alternate process employing lime as the acid acceptor has been used extensively [22].

Processes for manufacture of BPA-PC resin have evolved and been modernized extensively during the past 35 years that significant production has been carried out. Both batch and continuous polymerization systems are now utilized. As it turns out, the original melt polymerization process is receiving attention and development facilitated by modern melt polymerization equipment and the

need to reduce or eliminate volatile organic chemical emission into the environment.

B. Polymer Recovery

The original solution polymerization processes yielded a resin solution of varying degrees of purity and quality. One of the first resin isolation processes was to simply add a nonsolvent until the polymer precipitated partially or entirely. Different purification schemes such as filtration through beds or columns of natural or synthetic zeolites, charcoal, activated carbons, silica gels, or other adsorbents have been used. Washing in plate columns or centrifuges has been extensively used in purification of polycarbonate resin solutions prior to nonsolvent precipitation, gelling and crushing, or steam precipitation. Resins are also recovered from these purified solutions by vacuum extrusion in devolatilizing extruders. All of these processes have one common goal—the attainment of a very pure water-white resin so as to receive maximum properties and performance from the resin.

V. PRODUCT COMMERCIALIZATION AND HISTORY

Polycarbonates derived from BPA and terminated with monofunctional phenols are essentially linear polymers. The properties that differentiate these thermoplastic resins are inherent toughness, transparency, broad temperature resistance, good electrical properties, high index of refraction, ease of colorability and compounding, and general structural properties suitable for engineering and durable goods applications. A very large, diverse, and important market has been developed for these materials. Every person on earth is affected by some or many applications of BPA-PC resins produced by several major firms on a global basis. Markets range from architectural to automotive, digital recording, electrical, electronic, and safety. The markets have been built in large part by replacing conventional wood, metal, glass, and other materials of less capability.

BPA polycarbonates are typical aromatic polyesters with respect to flame resistance. In order to enhance flame resistance early on, copolymers with tetrabromo BPA/BPA were introduced [23]. Although other more sophisticated systems have been discovered, these copolymers are still in use.

Although linear polymers of various molecular weights and with various monofunctional phenol end-groups predominate in the products offered to the marketplace, there are needs for resins with non-Newtonian, shear-dependent, viscoelastic flow properties. This is particularly true for extrusion and extrusion blow-molding processes.

Low-level copolymers with trifunctional and tetrafunctional monomers and BPA provide the desired flow characteristics. Incorporation of these monomers began over 30 years ago [24] and has evolved to meet product application needs, particularly in parts requiring extrusion blow molding, i.e., water bottles and large hollow shapes [25].

In order to achieve even higher levels of heat resistance, much work has been done to copolymerize difunctional aromatic carboxylic acids with BPA [26,27]. Increased heat resistance with retention of clarity and practical toughness has been obtained. Other approaches to include different structures of biphenols have been and are in development. Details of these activities are beyond the scope of this chapter and will be properly addressed elsewhere.

For a material development that many felt would not be commercially feasible in the early stages, BPA-PC has been extremely successful. From a very modest beginning of a market and capacity of less than 10 million pounds in 1960, steady growth has developed to more than 2.5 billion pounds of capacity and demand worldwide. Over the years many have estimated that the polycarbonate market is mature. On the contrary, there are major new opportunities appearing now with no valid evidence of a slowdown.

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2

Synthesis of Polycarbonates

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I. HISTORICAL EVOLUTION

The development of polycarbonate thermoplastic resins evolved as a subset of general polyester chemistry. Since Einhorn's initial solution preparation of resorcinol- and hydroquinone-derived polycarbonates in 1898 [1], research has focused on efficient resin preparation and material properties. This seminal synthetic work used phosgene in a pyridine solution. Einhorn's phosgene procedure was followed in 1902, by the development of a melt transesterification method. Using diphenyl carbonate (DPC) as a phosgene synthon, Bischoff and v. Hedens-troem produced the same materials obtained by Einhorn [2]. Due to the poor solubility of these early resins, the general difficulty in their manipulation (processing), and the limited methods of material characterization available, interest in aromatic polycarbonates waned.

By the early 1930s, interest in general polycarbonates was renewed. Carothers and van Natta demonstrated the preparation of low-melting, low molecular weight microcrystalline aliphatic polycarbonates using two synthetic approaches [3]: (a) transesterification of aliphatic dihydroxylic compounds with diethyl carbonate and (b) ring opening polymerization of cyclic carbonates of aliphatic dihydroxylic compounds. The transesterification work was extended by Peterson to make low-melting, high molecular weight films and fibers using 1,6-hexanediol and dibutyl carbonate [4]. By 1941, the first commercially viable polycarbonate was introduced by the Pittsburgh Plate Glass Company (PPG); this material was a liquid casting resin intended for use as a surface coating in fiber or optical applications. This crosslinkable resin—designated CR-39—is derived from the allyl ester of diethylene glycol carbonate; peroxide-initiated reaction produces a scratch-resistant, colorless (transparent) plastic.

The evolution of the field continued with the reexamination of the aromatic derivatives. Following in the footsteps of Whinfield and Dickson's work with aromatic polyesters in 1946 [5], Schnell et al. [6] prepared linear, high-melting, high molecular weight aromatic polycarbonates derived from 4,4'-dihydroxydiphenylalkane monomers in 1954. These aromatic polycarbonates could be prepared by either a two-phase interfacial method—a modified Schotten-Baumann reaction—or via a melt (monomers as solvent) transesterification process using diphenyl carbonate [7]. In contrast to the aliphatic polycarbonates, these aromatic polycarbonates were unique in that they could be made into transparent (colorless) structures exhibiting excellent long-term mechanical properties.

Prior to the Whinfield and Schnell disclosures, polyesters and polycarbonates were commonly believed to be either liquids or low-melting solids. However, major differences exist between these two types of materials. Whinfield's aromatic polyesters exhibited limited solubility in common organic solvents. They tended to crystallize, becoming translucent and brittle with a concomitant loss of mechanical properties. In contrast, the aromatic polycarbonate resins exhibited good solubility in organic solvents. Furthermore, the polycarbonates retained their amorphous internal structure, transparency, and long-term mechanical properties after molding.

The excellent properties of the aromatic polycarbonates—particularly for those derived from 2,2-bis(4-hydroxyphenyl)propane (bisphenol A or BPA)—precipitated a large amount of research into these materials. By 1959, Fox of the General Electric Company (GE) had initiated studies similar to those in progress at the Bayer AG laboratories in Uerdingen [8]. These concurrent efforts resulted in the commercialization of BPA-derived polycarbonate processes by Farbenfabriken Bayer AG (Uerdingen, Germany) in the fall of 1958, Mobay Chemical Company (New Martinsville, West Virginia; now Bayer America) in early 1960, and GE (Mt. Vernon, Indiana) by late 1960.

Due to the large number of concurrent research efforts oriented to commercialization of BPA-based amorphous polycarbonates, a number of technology infringement disputes arose. After protracted litigation, Farbenfabriken Bayer AG was awarded the initial U.S. patent on these materials [9]; their basic process claimed an interfacial method. Bayer AG's initial U.S. issue was followed shortly by GE's basic coverage of the melt transesterification process [10].

In the mid 1960s, GE reexamined and piloted both a DPC-based transesterification process and the phosgene-based interfacial method. This work led GE to abandon its initial homogeneous phosgene-pyridine "lime" process in favor of the interfacial technology. A similar pilot evaluation by Farbenfabriken Bayer AG indicated that the interfacial process produced better quality material than their current transesterification technology. By the 1970s, all commercial BPA polycarbonate homopolymer (BPA-PC) was produced via an interfacial technology.

The industrial predisposition toward the interfacial production of commercial BPA-PC persists today with three notable exceptions. Since the early 1980s, the Chinese government has operated a commercial transesterification (melt) process in Shanghai; their material suffers a number of the earlier melt process deficiencies, most notably poor resin color. The second is a new, high-technology transesterification process developed by GE Plastics Japan, a joint venture of the General Electric Company, Mitsui Petrochemical Industries, and Nagase. The GE Plastics Japan 35,000 ton/year capacity process went on-line in Chiba, Japan in the spring of 1993. The new melt process produces a virgin BPA polycarbonate resin with lower residual inorganic contaminant levels and inherently better melt stability than the traditional interfacial processes [11]. This new melt resin exhibits superior transparency and color ($YI < 1$) than the early melt materials while retaining all of the desirable BPA-PC mechanical properties. The third is a 150,000 ton/year melt plant in Cartagena, Spain run by G.E. Plastics. It went into operation in the spring of 1999. The Spain plant is based on the Chiba experience.

Given the long history and extensive work involved in the evolution of the field of polycarbonates, the purpose of this chapter is not to review all aspects of the properties, synthesis, and methods of characterization related to resin production. A number of excellent reviews already address these subjects. Most notably, the reader should be aware of the reviews by Schnell [12], Vernaleken [13], Fox [14], Lapp [15], Serini [16], Clagett and Shafer [17], and Freitag [18]. Although major efforts for polycarbonate copolymer production exist, only a few specific systems will be mentioned. The focus of the present section is to outline and critique a few of the synthetic trends in engineering thermoplastics related to aryl polycarbonates with particular emphasis on the BPA-PC homopolymer. Copolymer production generated by reactive blending, coextrusion, and/or compatibilizing materials (e.g., grafting) will not be discussed; a historical overview of commercial alloys and blends may be found in a recent work by Utracki [19].

II. COMMERCIAL POLYCARBONATE PRODUCTION

To date, only two commercial production methods have been demonstrated to produce high-quality resin and remain economically viable. These processes are the two-phase interfacial (phosgene) and the melt transesterification (DPC) processes mentioned previously. All other potentially useful methods are merely direct variations on or simple combinations of these two main procedures. The spin-off process technologies include (a) the simple oligomer approach (Asahi Chemical Industries Co. Ltd., Bayer AG., Daicel Chemical Industries Ltd., Idemitsu Petrochemical Co. Ltd., Nippon GE Plastics K.K., Mitsui Petrochemical Industries K.K., and Teijin Ltd.); (b) the "crystalline" oligomer approach (Asahi

Chemical Industries Co. Ltd., Daicel Chemical Industries Ltd., and Teijin Ltd.); and (c) the “cyclic oligomer” polymerization process (GE Plastics, Bayer AG/Miles Inc. or Bayer America). These newer oligomer approaches all require multiple condensation reaction stages in order to produce high molecular weight materials. This multistep polymerization requirement, coupled usually with an intermediate isolation step, makes these oligomeric processes inherently more expensive.

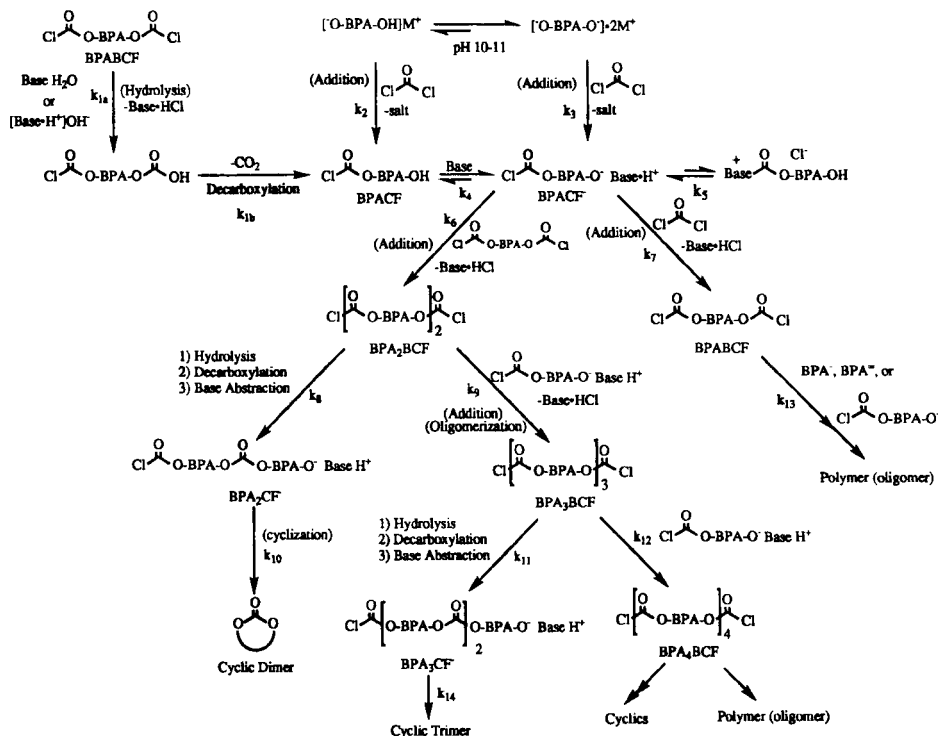
Although empirically well understood, both of the principal synthetic approaches and their process derivatives continue to be areas of active research. Much of the work is oriented towards computational modeling for process simulation. Toward this end, a number of studies have developed accurate mathematical derivations of the incremental kinetic expressions and process parameter dependencies in simplified model systems. The following summaries update the earlier reviews on these commercial processes [18,20].

A. Interfacial Technology

The basic process is outlined in Scheme 1. The BPA is initially introduced into the reactor in methylene chloride along with a monohydroxylic phenol (end-capper) to control the polymer molecular weight. Phosgene is added as a gas-liquid (bp 4°C) into this solution. Concomitant with the phosgene addition, aqueous sodium hydroxide (caustic) is added to scavenge the HCl produced; this aqueous caustic addition generates a two-phase liquid-liquid system. At high pH (9–12), low organic phase volume, and high BPA concentration, the system also contains a third (solid) phase consisting of the mono/dianion of BPA ($pK_{a1} = 9.59$; $pK_{a2} = 10.2$; 40°C) [21]. After reaction is complete, the organic phase is washed a number of times with aqueous acid and water to remove the residual base and salts. The polycarbonate resin is collected via solvent exchange (e.g., chlorobenzene) followed by evaporation of the solvent, by direct steam precipitation, or by its precipitation from antisolvent addition (e.g., MeOH), followed by filtration and drying.

Due to the low reaction temperature of this synthetic procedure (40°C), the average molecular weight of the polymer is the result of a kinetic distribution. This type of nonequilibrium distribution necessitates the final material to be completely passivated by end-capping (~100%) and melt-stabilized. These precautions are necessary to prevent a lowering of molecular weight as indicated by changes in gel permeation chromatography (GPC), melt flow index (MFI), and intrinsic viscosity (IV) on processing or extrusion; once in the neat, molten state, an unstabilized resin tends to redistribute itself towards a thermodynamic product.

Since the early work of Schnell [12], the mechanistic assumption has been that the reaction takes place at the liquid-liquid interface and involves the addi-



Scheme 1 General BPA polycarbonate (BPA-PC) formation steps in interfacial synthesis.

tion of BPA or its corresponding anion to an acylammonium species. Due to the complexity of this multiphase system, accurate experimental confirmation of the mechanism for each of the incremental steps is still wanting. Model systems and computer reaction simulations are currently attempting to confirm the dominant mechanistic contributions and pathways. King and Bryant [22,23] have prepared a variety of model acylammonium compounds in order to facilitate study of the putative condensation reaction steps. Their analysis of the triethylammonium carbophenoxy model salt indicates it to be quite stable. Its x-ray data indicate the carbonyl moiety to be sterically unencumbered, i.e., open toward nucleophilic addition, and of normal bond length (1.180 Å) compared to either BPA bischloroformate (1.177 Å) or phosgene (1.180 Å). These putative condensation reaction intermediates also contribute to the unwanted carbamate end-group formation. Modeling of this carbamate side reaction indicates it to follow first-order reaction

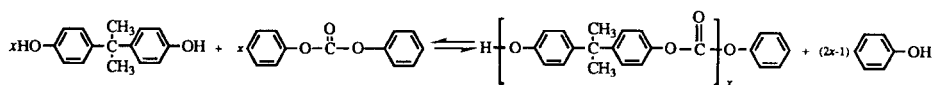
kinetics based on the intermediate acylammonium salt concentration [24]. Studies are underway to determine the bimolecular rate constants for the addition to these acylammonium species [25].

Recently, detailed computational kinetic rate analyses of the interfacial process have appeared. The published work relates to the production of polymer in both batch and semibatch/semicontinuous processes [26,27]. The dominant variables that influence the resin composition are the linear velocity, liquid–liquid volume ratio, aqueous pH, and phosgene/BPA ratio. Modeling of a Stockmayer distribution of BPA-PC oligomers based on a Monte Carlo method has received some attention [28]. Although the continuous production of the BPA-PC homopolymer is known, no process rate work has been published [29].

B. Transesterification (Melt or Solventless) Process

The process involves the base-catalyzed condensation polymerization of DPC (bp 312°C/760 torr) with BPA (bp 208°C/2 torr, 250°C/12.8 torr, or 287°C/50 mm Hg). The general reaction is shown in Scheme 2. The reaction is run at sufficiently high temperature (150–350°C) such that the starting monomers, oligomers, and final polymer remain molten throughout the course of the reaction. The reactor pressure is staged throughout the course of the reaction to allow the efficient removal of phenol (bp 180°C); the pressure ranges from 150–200 torr initially to 0.1–1 torr in the later stages of conversion. Using this methodology, the BPA-PC resin is prepared without any additional solvent, drying step, or phosgene. When the process is properly designed and engineered, the quality of the final resin is directly related to the quality of the starting monomers. Thus, the amount of residual contaminants in the final resin is highly controllable.

Based on experimental observation, the tacit mechanistic assumption is that a simple phenoxy anion addition to a carbonate linkage is involved in the oligomer/polymer production steps. Once the phenoxy-based anion adds to a carbonate group (e.g., DPC) a phenoxide anion is liberated. Phenol distills from the melt after the liberated phenoxide anion exchanges a proton with another hydroxy end-group or BPA; proton exchange is extremely rapid and the equilibrium constant for the reaction of phenoxide with BPA is roughly unity. The conversion of the monomers to BPA-PC is driven by the constant removal of phenol from the melt. This removal of phenol from the reaction solution is mandatory



Scheme 2 General “melt” BPAPC synthesis.

for the production of high molecular weight polymer. Based on evaluation of the published data (and patent claims), this simple base-catalyzed condensation process is the most effective and commonly used approach. The catalyst loading necessary to effect efficient conversion to polymer is in the 10–250 ppb range [11].

Detailed mechanistic examinations of both the batch [30] and semibatch [31] processes have been published by Choi et al. Both works are substantial improvements over the earlier efforts of Losev et al. [32]. The model condensation steps are predicated on base-catalyzed reactions. Choi's more recent process model accounts for the evaporative loss of DPC during each phase of the multistage polycondensation in the melt process [31]. The earlier work assumed that only phenol was removed from solution during the transesterification reaction; this leads to inaccurate rate expressions due to a poor control of the DPC/BPA ratio and improper mass balance at each stage of the reaction. His work indicates that efficient condensation polymerization requires the proper maintenance of the ratio of reactive end-groups. This end-group dependence becomes particularly important during the later stages of the semibatch process. Furthermore, in order to compensate for the loss of DPC from solution during the low-pressure polycondensation stages, their results indicate that the addition of a slight excess of DPC is beneficial; the advantage of using an excess of DPC has been known since the early 1960s [10,12,14].

With the advent of high-quality, high molecular weight BPA-PC melt resin a commercial reality, current research focus has been directed to catalyst improvement. Catalyst systems other than alkali metal hydroxides (e.g., NaOH) have been investigated; they range from fluoride [33], carboxylate [34], and phosphonium [35] salts to neutral amines [36], phosphite [37], and guanidine [38] systems. However, except in very special circumstances or applications, alkali metal hydroxides (e.g., NaOH) are still the catalysts of choice.

The principal product advantage of the melt transesterification approach is its production of a resin having a most probable ("thermodynamic") molecular weight distribution. Thus, under normal processing conditions, the anhydrous resin exhibits no tendency toward redistribution (i.e., a change in molecular weight, MFI, or IV). This distribution allows the resin to have extremely high OH end-group concentrations, which allow easy copolymer elaboration. Furthermore, the process yields a final resin that is contaminated neither with residual solvent (plasticization) nor with high salt concentrations (e.g., NaCl). Because the process is solventless, monomers of limited or no appreciable solution solubility and thermotropic liquid crystalline polycarbonates [39] can easily be prepared or incorporated into resins via a melt route. This thermodynamic material distribution coupled with the solventless, nonphosgene nature of the process makes the melt approach highly desirable from both a processing and an environmental viewpoint [40].

C. General Redistribution Method

The general redistribution method is merely the opposite path from the melt synthetic process mentioned previously. Various lower molecular weight polycarbonate resins can be produced from existing higher polycarbonate materials via incorporation of monomeric or oligomeric materials [41]. This process is amenable to both extrusion and melt equilibration reactors, e.g., in a Helicone. Since the material is equilibrated, the final molecular weight of the resin is determined by the numerical weight average (wt%) of the added components plus that of the initial polycarbonate resin. A catalyst is necessary for efficient (rapid) redistribution. During a redistribution process, the number and type of end-groups present within the system are conserved. The extreme of this methodology is the complete reversion of the initial polycarbonate back to monomeric materials; this latter process is the basis of a number of resin recycling efforts [42].

D. Simple Oligomer or Multistage Method

BPA-PC oligomers are produced by a melt transesterification or an interfacial process [43]; the interfacial method usually requires a large amount of end-capper (e.g., phenol or *p*-substituted phenols) to keep the chains short. The oligomer molecular weights produced in this process range from 800 to 12,000 (M_w). These oligomers can be used as a blend stock for alloying and copolymer production or polymerized/copolymerized in the melt to produce higher molecular weight polycarbonate materials.

The potential advantages of such oligomeric materials are their (marginally) improved miscibility with a variety of resins relative to a high molecular weight polycarbonate, lower melt viscosity, ease of preparation, and (possibly) added flexibility in end-capping % (e.g., % hydroxyl end-group) for copolymer alloying.

E. "Crystalline" Oligomer Approach

BPA-PC oligomers are generated via either an interfacial or a transesterification process and subsequently injected into a solvent to induce precipitation; injection into a solvent (e.g., acetone) results in their partial crystallization upon oligomer precipitation. After their isolation and drying, these oligomers can be further polymerized to produce high molecular weight BPA-PC via a melt transesterification process or solid state polymerization. This process is essentially the same as the simple oligomer approach but with a change in the oligomer isolation procedure.

Since all low molecular weight BPA-PC oligomeric materials ($IV < \sim 0.35$ dL/g) are known to produce a crystalline precipitate under the process conditions

(e.g. [14]), it is not surprising that the isolated powders are found to exhibit high crystallinity [12]. These isolated materials are intermediate between the starting monomers and traditional polycarbonate resin grades in terms of ease of manipulation and processing.

The crystalline oligomers would be used for the same applications as the noncrystalline (simple) oligomeric materials. Their principal use would be as a feedstock for melt polycarbonate or copolymer production; a secondary use would be as a low molecular weight blending or compounding resin. Any advantage due to the crystalline nature of these oligomers (e.g., hydrolytic stability and solvent resistance) will be lost on processing since the materials will revert to an amorphous, glassy structure on melting. As with the multistaged approach mentioned previously, except for the crystalline oligomer's unique application to solid state polymerization, the principal use of this technology is to skirt existing process patents.

An inverted variant of this "crystalline" approach is the *solid state polymerization* method (e.g., Iyer et al. [44,45]). Using this approach, one first prepares the low molecular weight linear oligomers (IVs; $\eta = 0.26\text{--}0.35\text{ dL/g}$; $T_g = 120\text{--}135^\circ\text{C}$) using a melt process. After isolation, a basic catalyst (e.g., an alkali hydroxide, phenoxide, or BPA dialkali salt) is blended into this "prepolymer." After thermal/vacuum conditioning, the prepolymer is heated to $210\text{--}250^\circ\text{C}$ in stages while under vacuum ($<1\text{ torr}$); this temperature range is above the T_g but below the T_m , hence the name "solid state" polymerization. After prolonged heating (4–8 h) high molecular weight polymer (IVs; $\eta = 0.44\text{--}0.81\text{ dL/g}$; $T_g = 151\text{--}159^\circ\text{C}$; $T_m = 254\text{--}271^\circ\text{C}$) with high crystallinity (26–43%) is obtained. The initial crystallinity of the starting oligomer is assumed to contribute to or induce further crystallinity in the product [44]. Bayer AG has been active in this area as well [46].

The solid state polymerization stage suffers the same kinetic limitations (mass transport) as the later stages of the traditional melt technology. A high concentration of hydroxylic end-groups (many as their anion) are required to undergo reasonable polymer build and exchange rates. However, this process has none of the transport/surface renewal advantages of the traditional melt process. Due to the static nature of the prepolymer glass during the final polymerization stage, encounter group problems (diffusion limitations) and phenol-DPC removal rates are much lower than in a melt. This procedure generates a "living" resin since the catalyst is unquenched in the final product. Due to the long heated residence time with high catalyst loading (up to 300 ppm wt%), the potential for base-induced crosslinking (due to Fries product, branched or gel formation) and degradation is quite high. Due to the crystallinity, the materials are translucent to opaque and densification occurs. Color-body formation may be an occasional problem.

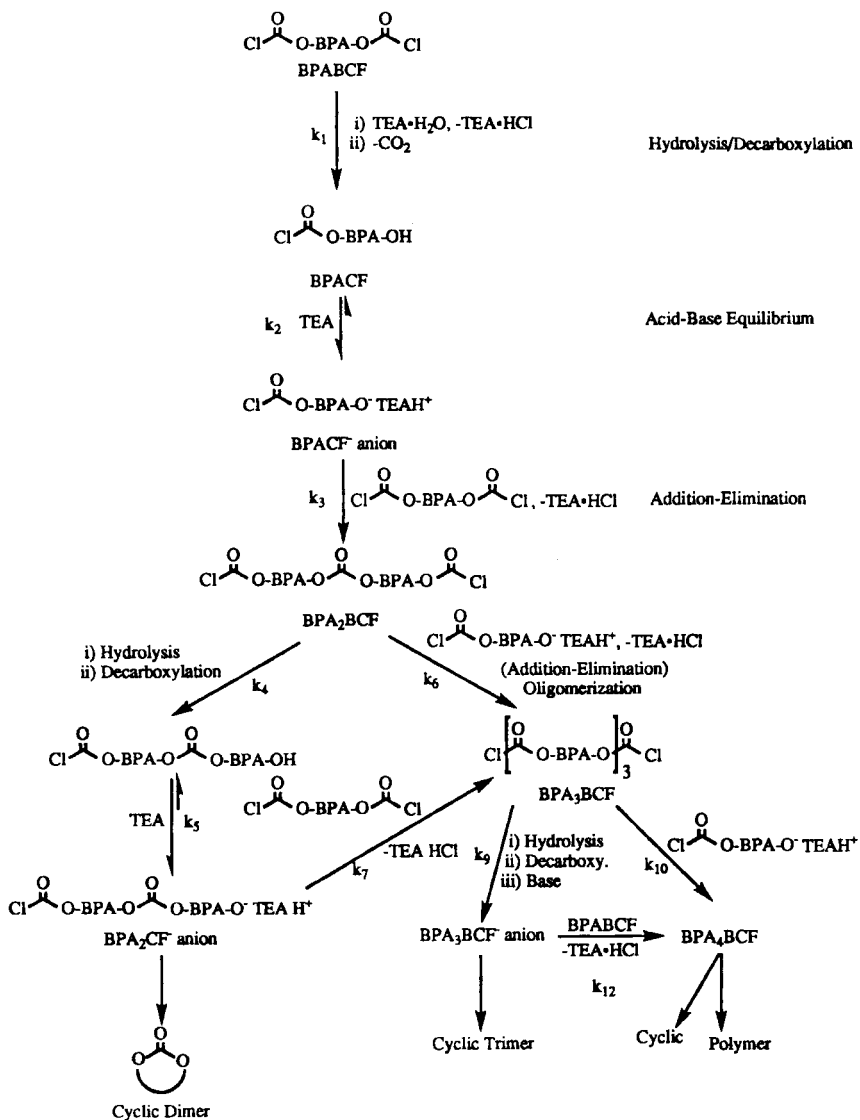
During solid state polymerization high crystallinity in the product would

be anticipated. The percent crystallinity usually tracks the catalyst loading, which functions as the nucleating agent [44,47]. Thermal annealing at these polymerization temperatures should induce quite rapid crystallization. The literature reports that polyarylcarbonates undergo crystallization at 180°C over 8 days [48]. If the crystallization rate can be approximated by a simple Arrhenius rate expression, then 8 days/180°C \approx 1–2 h/230–250°C. In fact, experimental work by Bailly et al. [49] and Gallez et al. [50] indicates that the rate of crystallization with phenoxide anions is on the order of tens of minutes at 230°C. The rate of BPAPC crystallization can also be accelerated by the presence of plasticizers [49–51]; smaller oligomers, phenol, and DPC might function in this capacity under the prepolymer conditioning. An additional contribution to the observed crystallinity might come from the oligomeric materials themselves. As produced, the prepolymer oligomers have high crystallinity (20–30%), which may increase in proportion to the catalyst loading or their conditioning, prior to polymerization; this conditioning stage is at 210°C (2–6 h). Since low molecular weight BPA-PC crystallizes more rapidly than higher molecular weight material, this latter rationale would explain the narrow crystalline composition range usually observed (26–38%).

The advantage of a high crystallinity BPA-PC material would be to increase the tensile heat distortion temperature and its solvent resistance while decreasing the gas permeability [14] and increasing embrittlement [52]. In order to retain these desirable properties, the solid state BPA-PC would have to be used like a thermoset resin. One would anticipate densification of the resin as crystallinity increases plus overall loss of material volume and mass due to the expulsion of phenol and DPC. Normal secondary melt processing such as injection molding and extrusion will convert these materials to the normal glassy polycarbonate resin.

F. “Cyclic” Oligomer Technology

Cyclic oligomers are synthesized using an initial interfacial preparation of the cyclic BPA-PC oligomers followed by their isolation (Scheme 3). Catalyst-initiated polymerization of the anhydrous cyclic oligomeric powder in the melt can then be used to produce high molecular weight resin. These materials were originally discovered by Schnell and Bottenbruch in 1962 [53]. Their work demonstrated that Lewis acid catalysts could be used effectively to produce very high molecular weight resin from a variety of tetrameric oligomers. This preliminary work was extended by Moody in 1964 [54] and Prochaska between 1965–1969 [55]. The basic interfacial technology for this process was further developed by Horbach [56] and Weirauch [57] at Bayer AG in the late 1970s. More recently, the application of the interfacial approach was developed as a commercial process



Scheme 3 General "cyclic" oligomer formation steps.

by the General Electric Company [58–60]. Work in this general area has resurfaced at Bayer AG recently [61].

In the current cyclics process, the oligomers are prepared interfacially at a lower pH (3–7) than the usual interfacial process (9–12); this minimizes any base-initiated ring opening hydrolysis resulting in linear oligomerization. Unlike the standard interfacial process, no end-capping agents are used because they would promote the formation of linear material. The cyclic oligomers range from 2 to 20 monomer units in length, the bulk of the composition usually being the dimer-heptamer cyclic oligomers. The molecular weight range is usually $M_w = 1300\text{--}1700$ with $M_w/M_n < 2$ (1.3–1.5).

Since an interfacial synthesis generates a kinetic distribution of products, the cyclic oligomers themselves represent a kinetically distributed material. Nested in this process is a second kinetically selective distribution process for the generation of cyclic oligomers vs. linear material. This latter selectivity is obtained by controlling the reaction conditions such that the *monomer* concentrations are in constant high dilution in the reaction phase; this original type of *Ziegler-Ruggli dilution* approach [12] was renamed the “pseudo-high dilution” method by Brunelle [59]. The traditional *Ziegler-Ruggli dilution* approach is quite effective for small cyclic oligomer synthesis; this is the result of the addition of the aryloxy anion monomers to either the chloroformate anions or linear oligomeric chloroformates being rate limiting. Thus, the intramolecular cyclization of aryloxy anion-chloroformate-derived species can be favored over intermolecular condensations by simple control of the monomer addition rates (concentrations), liquid phase ratios, added base, and temperature. Although quite high concentrations of the cyclic oligomers are present in solution by the end of the reaction (20–40 wt%), these oligomers are known to be stable to the reaction conditions. This kinetic stability results from the intermolecular rate of addition of an anionic species to the carbonate bond being $10^4\text{--}10^7$ times slower than the corresponding addition to a chloroformate-derived species.

To gain insight into the formation of cyclic oligomers, efforts have been made to simulate the existing experimental data [62]. This work has had limited success since the model can be parameterized to simulate any specific oligomer distribution but lacks any predictive value. The principal cause of this weakness is that to date accurate, experimentally derived rate data and kinetic expressions for cyclic oligomer formation are still lacking. As a result, the mechanism for the incremental condensation steps is simply assumed to be that of the traditional interfacial process [12]. Recently, Aquino et al. have endeavored to clarify a number of the reactions related to carbonate bond formation [25,63].

For the polymerization of cyclic oligomers, a variety of catalyst initiators work well in the melt. The most effective catalysts are simple bases. Their mechanism of initiation involves anionic (base) addition to the carbonate bond. The mechanism of propagation involves a phenolic anion (end-group) addition similar

to that indicated in the melt polymerization process; the addition of (acidic) melt stabilizers is often required to prevent premature polymerization in the melt. In general, the ring opening of the cyclic BPA oligomers generates a "living" polymer system with $M_w = 202,500$ and $M_n = 45,410$ [64]; molecular weights (M_w) as high as 700,000–1,000,000 can be obtained by using low initiator levels. The base-initiated activation energy for cyclics polymerization is roughly 12.5 kcal/mol [65]; this activation energy value is comparable to that observed in simple carbonate transesterification [66].

Although the overall reaction to form linear polycarbonates is only mildly exothermic (0.4 kcal/mol [64]), less than 0.5% cyclic material remains at the end of the polymerization. The polymerization (redistribution) to linear material is driven entropically, coupled to the small exothermicity of the cyclic dimer and trimer ring openings.

The principal advantages of the cyclic oligomers derives from their low viscosity in the melt ($T_g = 149^\circ\text{C}$; mp $\sim 200^\circ\text{C}$; 170 poise at 200°C ; 6 poise at 250°C) and their ability to rapidly form very high molecular weight resin without the evolution of volatile materials (e.g., phenol or DPC). The cyclic oligomers have potential use in applications where higher resin flow and surface wetting (lower surface tension/energy) are required in comparison to normal polycarbonate grades. Once applied, the cyclic materials can be command-cured in either the liquid or solid (glassy) state to form the final high molecular weight resin; this technology is similar to that used for epoxy resin and pre-preg applications. Furthermore, their direct use in injection molding applications where high flow and concomitant rapid polymerization were required would be an excellent fit for this technology.

III. DIRECT COPOLYMER PRODUCTION

Over the past 45 years during which interest in aryl polycarbonates was renewed, literally hundreds of monomer and copolymer systems have been evaluated. Only those materials will be discussed that have had a sustained research effort due to their current or potential commercial viability; a few of the commercial copolymers, such as the polyester carbonates and optical materials, will be dealt with in separate chapters. Within this framework, all of the reaction processes common to polycarbonate homopolymers (e.g., interfacial, melt, etc.) have been tried for most of the copolymer systems. In general, the most consistent preparative success has been in condensation polymerizations involving monomers of similar intrinsic reactivity (e.g., HO-Ar-OH with HO-Ar'-OH). Largely disparate monomer-monomer intrinsic reactivities lead to copolymer blockiness or low-to-variable copolymer production.

A. General Synthetic Preparation: Aryl-aryl Copolymers

A variety of aryl-aryl copolycarbonates have been prepared. These copolymers demonstrate either improved melt flow properties [67] or hydrolytic stability [68,69] as their primary goal. Resorcinol incorporation into the normal BPA-PC backbone greatly improves its overall flow properties [67]; a melt synthetic approach is preferred but interfacial or “cyclic” methods work just as well.

Polymer hydrolytic and solvent stability are usually important considerations in engineering thermoplastic applications. For BPA-PC, hydroquinone and its derivatives offer the potential for improved hydrolytic stability with minimum monomer expense [68,69]. The incorporation of the simple biphenols such as 4,4'-biphenol improve hydrolytic stability as well. As with the resorcinol above, a melt approach is preferred. This preference is a logical extension of what one is trying to achieve with a solvent-resistant material—limited or no solubility. A melt synthetic approach circumvents any monomer–polymer solubility problems.

B. Enhanced Weathering, Thermal Stability, and Flame Retardancy of Novel Copolymers

The addition of copolymers to polycarbonate for the simple improvement of its weatherability, thermal and photochemical stability are constantly being sought. Towards these goals, heteroatom incorporation into the polycarbonate backbone—particularly silicon and sulfur—is an area of active research. The direct substitution of these heteroatoms into BPA-PC structure generally improves both chemical resistance and flame retardancy (FR) of the resin. Due to their potential importance as substitutes for halogens and phosphorus-containing PC resins and copolymers, a few of these materials will be discussed briefly.

Copolymers of BPA-PC and polydimethylsiloxane (PDMS) have been examined intensively since their accidental discovery in the early 1960s by the General Electric Company; attempts to lower the melt viscosity of BPA-PC during extrusion led to the addition of silicone fluids as internal lubricants. The coextrusion of silicone fluids with BPAPC resulted in copolymer production. The improved FR, UV and hydrolytic stability of these materials has made them of interest. Newer methods of preparation include direct cocondensation between the respective monomers as well as via cyclic PC oligomers with dimethylsiloxane cyclic tetramer (D_4 [70]).

The solvent resistance and weatherability of these materials has been examined in detail. One simple indicator of a polymer's resistance to a given solvent is manifested by the liquid's ability to wet the resin surface. The surface wettability of BPA-PC-PDMS blends is similar to that of pure PDMS even at low concentrations of the block copolymer [71]. The wettability was shown to be insensitive

to PDMS block length when the block length was greater than 20 units. More recently, Chen et al. [72] studied multiblock copolymers of these materials in order to evaluate PDMS block size on surface segregation. Using an ESCA analysis of the surface (27 Å), Chen studied PDMS block lengths of 2–40 units and found that their surface concentrations of the PDMS greatly exceeded their bulk concentrations; ESCA depth profiling of each material indicated this effect as well. For a given bulk loading of PDMS, there was an increase in its surface concentration with increasing block length; this is similar to the earlier observations by LeGrand and Gaines [71]. In all cases, annealing enhanced the PDMS percentage at the surface of the resins.

Copolymer systems of BPA and bis(*p*-hydroxyphenyl)dimethylsilane (BPSi) have been prepared using an interfacial synthesis [73,74]. These materials exhibit increased flame resistance (increased oxygen index) and char residue with increasing BPSi monomer content vs. BPA homopolymer. These materials show great improvement in their weathering behavior (UV stability, yellowness index, and % haze) due to lower UV absorptivity, higher water repellency, and a lower number of side chain photooxidation reactions. Their general optical behavior has been examined [75]. A number of patents have been issued in this area; see, for example, Davis et al. [76], Evans and Carpenter [70], Lewis [77], Lewis and Bunelle [78], Lucarelli et al. [79], Yokoyama et al. [80], Umeda et al. [81], and Rich et al. [82].

Due to the possibility for enhanced chemical resistance and FR properties, substitution of the carbonate oxygen atoms by sulfur atoms has been investigated. Polythio-, polydithio-, and polytrithiocarbonate analogs of BPA-PC have been prepared and characterized. The polythiocarbonates from thiophosgene and BPA [83,84] and the polydithiocarbonate of phosgene plus 4,4'-isopropylidenedibenzeneethiol (BTA [85]), and polytrithiocarbonate from BTA with carbon disulfide [86] were originally prepared some time ago. However, extensive reexamination of these materials have recently been published [87–89]. These more current works report improved general (interfacial) syntheses and include better material characterization. Although high molecular weight polymers ($M_w = 40,000$ – $170,000$) are now easily produced, their thermogravimetric analyses indicated that the substitution of any of the oxygen atoms by sulfur atoms leads to a lower overall thermal stability than the parent BPAPC. These thio-containing polymers range in color from light yellow to dark orange. Thus, as is often the case, improvement in one desirable resin property with a change in monomer composition comes at the expense of another property. These thio-substituted materials did show better chemical resistance than the BPAPC homopolymer, but no new FR work was reported.

One other FR monomer has had a long and favored history in BPAPC chemistry. This monomer is tetrabromobisphenol A (TBBPA). At relatively low