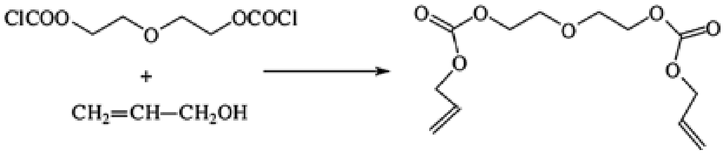
Kirk-Othmer Encyclopedia of Chemical Technology.

POLYCARBONATES

Polycarbonates are an unusual and extremely useful class of high heat polymers known for their toughness and clarity. The vast majority of polycarbonates are based on bisphenol A (BPA), and sold under the trade names Lexan (GE), Makrolon (Bayer), Caliber (Dow), Panlite (Teijin), and Iupilon (Mitsubishi). Many other producers and suppliers are available. BPA polycarbonates have glass-transition temperatures (T_g) in the range of 140–155°C, and are widely regarded for their optical clarity and exceptional impact resistance and ductility at or below room temperature. Other properties, such as modulus, dielectric strength, and tensile strength are comparable to other amorphous thermoplastics at similar temperatures below their respective T_g values. However, whereas most amorphous polymers are stiff and brittle below their T_g values, polycarbonates retain their ductility. Polycarbonates are prepared commercially by two completely different processes: Schotten–Baumann reaction of phosgene (qv) and an aromatic diol in an amine-catalyzed interfacial condensation reaction, or via base-catalyzed transesterification of a bisphenol with a monomeric carbonate such as diphenyl carbonate. Each process has its own inherent advantages and disadvantages. Many important products are also based on polycarbonate in blends with other materials, copolymers, branched resins, flame-retardant compositions, foams, and other materials. Polycarbonates are produced by more than a dozen companies, with global manufacture currently just over two million tons annually. Polycarbonate is also the object of academic research, due to its widespread utility and unusual properties. Research on polycarbonates has steadily increased over the past two decades, with over 5000 publications on the topic since 1995, and nearly 20,000 patents having appeared globally. More than 8000 have appeared since 1995. Japanese companies lead the number of patent holders, including Teijin Chemicals, Teijin Limited, Sekisui Chemical, Asahi Chemical, Idemitsu Petrochemical, Toray Ind., and Mitsubishi Gas Chemical Company. Other companies with significant patent portfolios include General Electric, Bayer AG, and Dow Chemical. Polycarbonate has been the subject of three monographs, once of them published in 2000 (1).

1. Historical Development

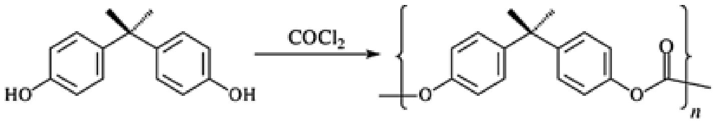
The first polycarbonates were prepared by Einhorn in the late 1890s via reaction of hydroquinone or resorcinol with phosgene using pyridine as solvent (2). Attempts to prepare the polycarbonate of catechol led only to the cyclic five-membered carbonate. A few years later, the same materials were prepared by Bischoff and von Hendenstioem via solventless transesterification using diphenyl carbonate (2). The hydroquinone polymer is brittle, crystalline, insoluble in most solvents, and melted at > 280°C. The polymer from resorcinol is glassy and brittle, although it crystallizes from solution, and melts at ∼ 190–200°C. Both of these polymers were apparently of low molecular weight and owing to difficulties of processing and characterization, were not developed further. In fact, no research on polycarbonates appeared in the literature for ∼ 30 years after their initial discovery. In the early 1930s, the preparation of aliphatic carbonates was studied during the investigation of the preparation and properties of polyesters by Carothers and co-workers (4). Because the reactions of aliphatic alcohols and phosgene proceed more slowly than those of phenols, two other methods were used to prepare the aliphatic polycarbonates: direct transesterification reactions, and ring-opening polymerization of low molecular weight cyclic polycarbonates prepared by a distillative transesterification-depolymerization. Further work was carried out in the 1940s. 1,6-Hexanediol polycarbonates were prepared via transesterification using dibutyl carbonate (5). The aliphatic polycarbonates had low melting points and did not prove interesting commercially. In 1941, the Pittsburgh Plate Glass Company (PPG) introduced a liquid casting resin designated as CR-39 (6). This material, formally a polycarbonate, was a cross-linked thermoset resin prepared by a peroxide-initiated radical polymerization of the bisallyl carbonate of diethylene glycol. The starting material was prepared from allyl alcohol and diethylene glycol bischloroformate (eq. **1**).



(1)

Once polymerized, CR-39 was a colorless, transparent, scratch-resistant plastic that was used in optical applications. These materials differ markedly from the current thermoplastic polycarbonates. Although its nature and chemical makeup are completely different from modern polycarbonates, CR-39 was the first commercially available polycarbonate.

A reexamination of aromatic polycarbonate chemistry was carried out ~ 50 years after the first polycarbonates of resorcinol and hydroquinone were discovered. In independent investigations by Schnell at Bayer AG and by Fox at General Electric, it was discovered that the polycarbonates of BPA could be prepared (eq. **2**).



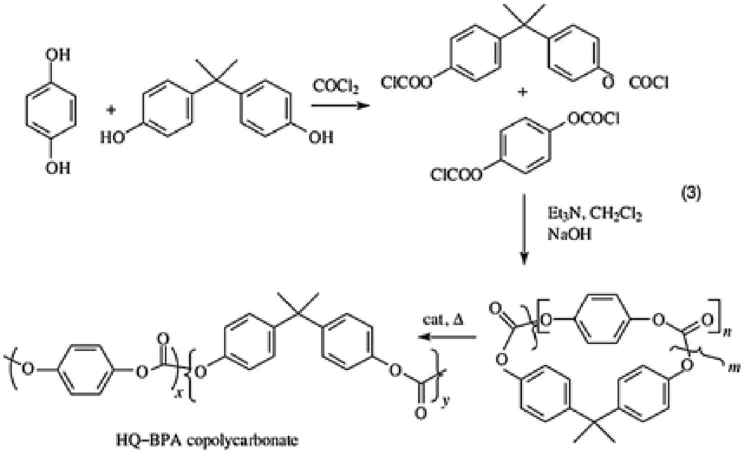
(2)

Unlike the aliphatic polycarbonates prepared earlier, which were either liquids or low melting solids, the aromatic polycarbonates were tough, amorphous solids having elevated T_g. Owing to the unusual properties of the BPA polycarbonate, ie, toughness, transparency, and thermal stability, each company began development programs. Bayer AG, the first to report the properties of a series of polycarbonates (7), had patents issuing as early as 1954 (8). Commercial production of polycarbonate by Bayer AG began in Germany in 1958, and in the United States in 1960. General Electric (GE) started U.S. commercial production in 1960. After a period of litigation, U.S. patents were issued to Bayer AG, which claimed an interfacial process for preparation of polycarbonates, and had multiple claims to various polycarbonates (9). The basic GE patent claimed the transesterification process and the polycarbonate product so formed (10). Since that time extensive research has been carried out on polycarbonates. Several manufacturers have developed many niches of new products, blends, or processes for production of these materials. Although GE and Bayer AG remain the principal producers, at least 50 companies have patented some aspect of polycarbonate chemistry. Over a dozen producers exist worldwide.

2. Properties

2.1. Solubility and Solvent Resistance

The majority of polycarbonates are prepared in methylene chloride solution. Other chlorinated solvents such as chloroform, *cis*-1,2-dichloroethylene, *sym*-tetrachloroethane, and methylene chloride are also good solvents for polycarbonates. The polymer is soluble in chlorobenzene or *o*-dichlorobenzene when warm, but crystallization may occur at lower temperatures. Methylene chloride is most commonly used because of the high solubility of the polymer (350 g/L at 25°C), and because this solvent has low flammability and toxicity. Nonhalogenated solvents include tetrahydrofuran (THF), dioxane, pyridine, and cresols. Hydrocarbons(qv) and aliphatic alcohols, esters, or ketones (qv) do not dissolve polycarbonates. Acetone (qv) promotes rapid crystallization of the normally amorphous polymer, and causes catastrophic failure of stressed polycarbonate parts. In general, polycarbonate resins have fair chemical resistance to aqueous solutions of acids or bases, as well as to fats and oils, although prolonged exposure to high or low pH conditions can lead to loss of molecular weight. Chemical attack by amines or ammonium hydroxide occurs readily and aliphatic and aromatic hydrocarbons promote crazing of stressed molded samples. For these reasons, care must be exercised in the choice of solvents for painting and coating operations. For sheet applications, polycarbonate is commonly coated with a silicone–silicate or acrylate hardcoat that provides abrasion resistance as well as increased solvent resistance. Coated films are also available. Certain blends and copolymers of polycarbonate demonstrate dramatically improved solvent resistance. The blend of polycarbonate and poly(butylene terephthalate), eg, Xenoy (GE) or Makroblend (Bayer), combines the toughness of polycarbonate with the solvent resistance of the semicrystalline polyester, and is used in automotive applications. Hydroquinone polycarbonates were reinvestigated in the late 1980s (11). Several binary and ternary copolycarbonates were prepared using monomers such as hydroquinone, biphenol, and substituted hydroquinones. No thermal transitions other than the T_g were noted, however, and the copolymer with hydroquinone had a very low molecular weight ($\eta_{\text{inh}} = 0.09 - 0.10$; inh = inherent). Difficulty in preparation of hydroquinone polycarbonates, owing to the insolubility of the oligomers, had been noted in the 1950s (12). Copolycarbonates of BPA and hydroquinone (HQ) can be prepared via the intermediacy of oligomeric cocyclics (eq. **3**) (13).



(3)

Although hydroquinone linear oligomers having degrees of polymerization > 2 are insoluble in CH_2Cl_2, the cyclic analogues remain soluble when randomly cyclized with BPA. Polymerization of the hydroquinone–BPA cocyclics via anionically initiated, ring-opening polymerization leads to high molecular weight semicrystalline polymers. By using this methodology, hydroquinone can be incorporated into the polycarbonate in levels up to

60%. The copolycarbonates show dramatically increased solvent resistance, and are insoluble in all common polycarbonate solvents such as methylene chloride or THF. Furthermore, when molded bars of the polycarbonate are exposed to gasoline while under stress, impact properties are retained, whereas standard polycarbonate grades fail.

BPA polycarbonate has excellent resistance to hydrolysis. Prolonged contact with water at 60°C or moderate-term (months) contact at 100°C has little effect on polycarbonate, but extended contact can lead eventually to embrittlement. For example, exposure of polycarbonate film to steam at 101 kPa (1 atm) at 100 and 150°C showed failure of the film after 700 and 200 h, respectively (14). Additives can accelerate the degradation by catalyzing hydrolysis. Although acids have little effect, aqueous base can lead to etching. Hydrolysis occurs at the surface. The hydrolytic stability can be attributed to the low water solubility in the resin ($\sim 0.3\%$), which leads to essentially no swelling, and to the high T_g of the resin. Heating at elevated temperatures, eg, during molding, however, can lead to degradation owing to hydrolysis. Drying of all grades of polycarbonate is recommended prior to molding to avoid hydrolysis to lower molecular weight materials. Hydrolysis of polycarbonate has been extensively studied (15).

2.2. Molecular Weight and Viscosity

BPA polycarbonates are commercially available in a wide range of molecular weights. As the molecular weight increases, melt and solution viscosities increase proportionally. Molecular weights may be determined or inferred by several means, including gel-permeation chromatography, light-scattering size-exclusion chromatography, measurement of intrinsic or inherent viscosity, and measurements of melt viscosity and flow. Correlation of intrinsic viscosity (IV), or inherent viscosity $[\eta_{\text{inh}}]$, with weight-average molecular weight (M_w) has been carried out on carefully characterized polycarbonate samples (16). The following relationship exists when $[\eta_{\text{inh}}]$ is in mL/g.

$$[\eta] = 41.2 \times 10^{-3} M_w^{0.69}$$

For chemical studies, the chromatographic methods or solution viscosities are methods of preference, but for practical applications, melt flow is most important. Standard injection-molding grades of polycarbonate have intrinsic viscosities in the range of 0.50–0.55 dL/g in chloroform at 30°C, with $M_w = 35,000 - 70,000$ and number-average molecular weight (M_n) of 15,000–24,000, as determined by gel-permeation chromatography (gpc) using polystyrene standards, or $M_w = 18,000 - 30,000$ as determined by light scattering. The polydispersity ratio, M_w/M_n, of polycarbonate is $\sim$ 2.3–2.7. The range of molecular weights and viscosities available is shown in Table 1.

The mechanical properties of polycarbonate, eg, tensile strength, impact resistance, flexural strength, and elongation, improve dramatically with increasing polymer intrinsic viscosity up to a value of $\sim$ 0.45 dL/g. (Table 2). After that point, only slight increases in mechanical properties are seen with increasing molecular weight, but melt viscosity continues to climb. At IV values $>$ 0.6 dL/g, the melt viscosity becomes so high that processing is very difficult. Because some compromise between polymers having high molecular weight and good mechanical properties must balance the processibility of the resin, newer formulations having increased melt flow are being marketed. Lexan SP copolyestercarbonates (GE), eg, demonstrate enhanced flow rates as measured by melt flow index (10–22 g/min) compared to standard grades of resin (6–16 g/min), yet retain excellent impact resistance, eg, notched Izod of 642–910 J/m $(12 - 17\ \text{ftlb/in.})$. A variety of strategies have been used for improvement in the melt flow of polycarbonate, usually sacrificing thermal resistance (ie, lower T_g), while maintaining good impact strength. Ultrahigh molecular weight polycarbonates can be prepared via ring-opening polymerization of cyclic aromatic oligomeric carbonates. These materials, which are not commercially available, can lead to polycarbonates having intrinsic viscosities $>$ 1.0 dL/g, and molecular weights of 300,000–500,000 (17).

Table 1. Molecular Weight and Viscosity of Lexan Resins

Grade	Description	MFI[a]	IV*b*	M_w[c]	M_n[c]	PDI[d]	M_w[e]
131	ultrahigh viscosity	3.1	0.629	72,600	28,100	2.58	35,500
1881	very high viscosity	4.9	0.581	66,100	25,400	2.6	32,000
101	high viscosity	6.5	0.551	62,000	25,400	2.44	29,000
161	medium, high viscosity	7.4	0.538	60,600	24,400	2.48	27,900
141	medium viscosity	9.2	0.510	57,000	23,900	2.38	26,300
141L	medium low viscosity	11.2	0.493	54,500	22,700	2.40	27,400
121	low viscosity	16.2	0.454	49,800	20,400	2.44	21,200
HF1110	high flow	20.9	0.434	46,900	18,400	2.55	22,700
SP1110	superior flow	22	0.53	60,000	24,000	2.50	27,500
OQ1020	optical quality	78	0.35	35,800	13,900	2.57	16,600

[a] MFI = melt flow index
[b] IV = intrinsic viscosity in CH_2Cl_2 at 25°C
[c] From gel-permeation chromatography using polystyrene standards.
[d] PDI = polydispersivity ratio, M_w/M_n.
[e] Molecular weight from light scattering.

2.3. Structure and Crystallinity

The mechanical–optical properties of polycarbonates are those common to amorphous polymers. The polymer may be crystallized to some degree by prolonged heating at elevated temperature (8 d at 180°C) (18) or by immersion in acetone (qv). Recently, an extensive amount of work has appeared on solid-state polymerization of polycarbonate oligomers. The oligomers or low molecular weight polycarbonate can be crystallized by a variety of methods, typically treatment with an antisolvent vapor. Powdered amorphous powder appears to dissolve partially in acetone, initially becoming sticky, then hardening and becoming much less soluble as it crystallizes. Enhanced crystallization of polycarbonate can also be caused by the presence of sodium phenoxide end groups (19). Film or fibers derived from low molecular weight polymer tend to embrittle on immersion in acetone; those based on higher molecular weight polymer ($>$ 0.60 dLyg) become opaque, dilated, and elastomeric. When a dilated sample is stretched and dried, it retains orientation and is crystalline, exhibiting enhanced tensile strength. The tensile heat-distortion temperature of the crystalline file is increased by $\sim$ 20°C, and the gas permeability and resistance to solvent attack is increased.

Thermotropic polycarbonates have been prepared from mixtures of 4,4′-dihydroxybiphenyl and various diphenols (11). Nematic melts were found for copolycarbonates prepared from methylhydroquinone, chlorohydroquinone, 4,4′-dihydroxydiphenyl ether, and 4,4′-dihydroxybenzophenone. Slightly crystalline polycarbonates have been prepared from mixtures of hydroquinone and BPA (13) (T_g = 154°C, T_m = 313°C, ΔH_m = 11.0 J/g (2.63 cal/g)), and a highly crystalline, high heat polycarbonate has been prepared from methylhydroquinone (20) (T_g = 155°C, T_m = 289°C, ΔH_m = 31.0 J/g (7.41 cal/g)) Whereas the former (hydroquinone–BPA) copolymer has only been prepared via cyclic oligomers, the methylhydroquinone polycarbonate can be prepared via a melt process.

Experimental and theoretical studies on the structure of BPA polycarbonates have been the object of considerable interest since the work of Williams and Flory in the late 1960s (21). Because of the low conformational barriers to rotation, phenyl ring-flipping, and cis–trans isomerization about the carbonate group have been invoked as mechanisms for energy absorption providing polycarbonates with low temperature impact strength. Crystal structures of diphenyl carbonate, described in detail, have been published (22, 23). The crystal structures of a model carbonate (the bis-phenylcarbonate of BPA) has also appeared (24). All of the published structures indicate that the thermodynamically-preferred backbone conformation about the carbonate functionality is a trans–trans conformation. In this form, the dihedral angles of the aromatic rings with the carbonyl oxygen, C–O–C(=O, (174.8 and 176.5°) are nearly eclipsed, and as a consequence, the planes of the carbonyl groups are skewed from the planes of the aromatic rings by 59.1 and 53.2°. A cis–trans relationship about the carbonyl group was first seen in a complex of the bisphenyl carbonate of BPA with two molecules of a thiopyrilium salt (25). The cyclic dimer carbonate of BPA also shows only a cis–trans relationship of aromatic rings about the carbonyl (23). The crystal structure of the cyclic tetramer has also been described (23), showing two distinct types of aromatic conformations about the carbonyl. Several mathematical (26) and physical (27) methods have been used to analyze the conformational features of BPA polycarbonate. Estimations of the energy differences between conformations have been investigated by a variety of techniques, including *ab initio* calculations (28), nmr spectroscopy (29), and infrared (ir) spectroscopy (30). Molecular simulation studies on the conformation of cyclic oligomers have also appeared (31).

2.4. Glass-Transition Temperature and Melt Behavior

The T_g of BPA polycarbonate is $\sim 150°C$, which is unusually high compared to other thermoplastics such as polystyrene (100°C), poly(ethylene terephthalate) (69°C), nylon-6,6 (45°C), or polyethylene ($-45°C$). The high T_g can be attributed to the bulky structure of the polymer, which restricts conformational changes, and to the fact that the monomer has a higher molecular weight than the monomer of most polymers. The high T_g is important for the utility of polycarbonate in many applications, because, as the point, which marks the onset of molecular mobility, it determines many of the polymer's properties such as dimensional stability, resistance to creep, modulus, and ultimate use temperature. Polycarbonates of different structures may have significantly higher or lower T_g (see Table 3).

Table 2. Bisphenol A Polycarbonate Properties

Property	Lexan 141	Lexan 3414[a]	ASTM method
	Physical properties		
specific gravity	1.52	1.20	D792
water absorption, 23°C, %			
24 h	0.15	0.12	D570
equil	0.35	0.23	D570
melt flow rate, 300°C, 1.2 kgf, g/10 min	10.5		D1238
mold shrinkage, 3.2-mm part, %	0.1–0.2	0.5–0.7	D955
light transmittance, 550 nm, %	86–89		D1003
haze, %	1–1.5		D1003
refractive index	1.586		
	Mechanical properties		
tensile strength, Type I, MPa[b]			
yield	60		D638
break	70	160	D638
tensile elongation, break, Type I, %	130	3.0	D638
flexural strength, MPa[b]	97	190	D790
flexural modulus, MPa[b]	2,300	9,600	D790
compressive strength, MPa[b]	86	140	D695
compressive modulus, MPa[b]	2,400	10,300	D695
shear strength, MPa[b]			
yield	41	75	D732
break	695		D732
shear modulus, MPa[b]	785	2,200	D732
hardness, Rockwell R	118	119	D785
fatigue limit, 2.5×10^6 cycles, MPa[b]	6.9	50	D671
deformation under load, 27 MPa[b], %			
at 23°C	0.2	0.1	D621
at 70°C	0.5	0.2	D621
	Impact properties		
Izod impact, J/m[c]			

Table 2. *Continued*

Property	Lexan 141	Lexan 3414[a]	ASTM method
notched	801	133	D256
unnotched	no break	1,300	D256
tensile impact, Type S, kJ/m^{2c}	578	67	D1822
	Thermal properties		
softening temperature, Vicat, °C	154	166	D1525
heat deflection, °C			
at 0.45 MPa[b]	138	154	D648
at 1.8 MPa[b]	134	146	D648
specific heat, J/(g·°C)[c]	1.25	1.0	C351
coefficient of thermal expansion, −40 to 95°C, %	6.75×10^{-3}	1.67×10^{-3}	E831
thermal conductivity, W/(m·°C) °C	0.19	0.22	C177
brittle temperature, °C	−129		D746
continuous use temperature, °C	121		
	Electrical properties		
dielectrical strength, mV/m	15	17.7	D149
dielectric constant			
60 Hz	3.17	3.53	D150
1 MHz	2.96	3.48	D150
dissipation factor			
60 Hz	0.0009	0.0013	D150
1 MHz	0.010	0.0067	D150
	Flame classifications		
100 Series 94, mm			
V-0 rating	6.10	3.05	UL 94
V-2 rating	1.14		UL 94
oxygen index, %	26	30	D2863

[a] This polycarbonate is 40% glass reinforced.
[b] To convert MPa to psi, multiply by 145.
[c] To convert J to cal, divide by 4.184.

BPA polycarbonate becomes plastic at temperatures of ~ 220°C. The viscosity decreases as the temperature increases, exhibiting Newtonian behavior, with the melt viscosity essentially independent of the shear rate. At the normal injection molding temperature of 270–315°C, the melt viscosity drops from 1100 to 360Pas (11,000–3600 P), which is about five times the viscosity of poly(ethylene terephthalate) of similar molecular weight over the same temperature range. Because the viscosity of polycarbonate can only be reduced by increasing the temperature, the ultimate limit on molecular weight is controlled by the processing conditions and the thermal stability of the polymer. Branched polycarbonates can be prepared by incorporation of small amounts of tri- or tetrafunctional phenols or carboxylic acids. The rheological properties of the branched resin are different from those of linear resins. The branched resins demonstrate non-Newtonian behavior, and viscosity depends on shear rate. The melt viscosity of branched resins decreases with increasing shear, allowing extrusion at lower temperatures of materials with exceptional melt strength for blow molding applications (Fig. 1). Polycarbonate melt rheology has recently been summarized in a review (53).

2.5. Thermal, Flame-Retardant, and Hydrolytic Behavior

BPA polycarbonate exhibits excellent thermal stability, especially in the absence of oxygen and water. The dry polymer may be heated to 320°C for several hours or, for short times, as high as 330–350°C with only minimal degradation. At these high temperatures, thermal–oxidative degradation leads to slight yellowing, requiring color stabilization. Low levels (usually < 5000 ppm) of stabilizers (phosphites, phosphonites, phosphines, epoxide compounds, and organosilicon compounds) are usually added during processing. At temperatures > 400°C,

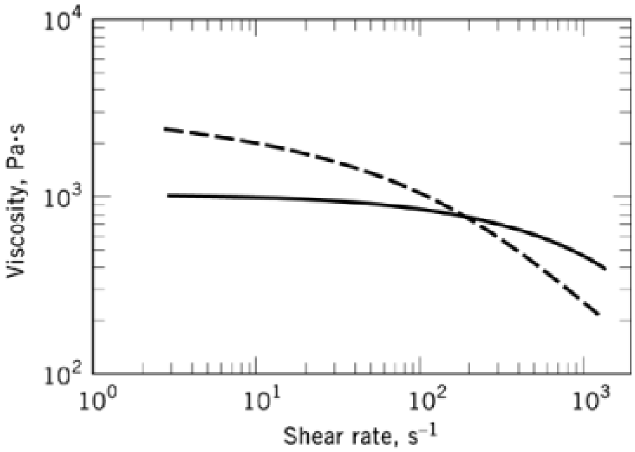


Fig. 1. Melt viscosity as a function of shear rate for (—) linear BPA polycarbonate and (- - -) branched polycarbonate. To convert Pa·s to poise, multiply by 10.

rapid decomposition and cracking occur. BPA has an oxygen index of 26 according to ASTM D2863-70, indicating that under test conditions, an atmosphere of 26% oxygen is required to sustain combustion. Owing to thermal–oxidative stability, polycarbonate has some inherent flame resistant properties and can be classified as V-2 according to UL94 of the Underwriters Laboratory. Several polycarbonate grades include additives to increase the flame-retardant properties, and to decrease smoke. Flame-retardant agents include brominated oligomers or polymer from tetrabromo-BPA, alkali metal salts, usually alkali sulfonates, and polytetrafluoroethylene (PTFE). The flame-retardant grades are classed as V-0 according to UL94 testing procedures, using a wall thickness of 3.2 mm Recently, several so-called Eco-FR grades have appeared, which contain no halogenated or phosphorus additives, yet which still retain the V-0 rating.

Because of the low solubility of water in the resin, BPA polycarbonates are inherently resistant to aqueous acid and base, although strong nucleophilic bases can catalyze hydrolysis. Prolonged contact with water at 100°C can lead to reduced impact strength as a result of microcrack formation. In autoclave testing under steam pressure, water can be forced into the resin, forming pockets that eventually lead to haze, microcracks, and loss of properties. The formation of water-filled pockets has been confirmed experimentally (54). Although many additives have a deleterious effect on hydrolytic stability by acting as hydrolysis catalysts, some stabilizers, especially epoxides, can increase the hydrolytic stability. Polycarbonate should always be dried prior to melt processing, because even the low levels of water present in the resin at equilibrium can lead to partial hydrolysis and lowering of the molecular weight of the molded parts. The equilibrium water content at 60% relative humidity is 0.26% by weight at ambient temperature, and 0.9% at 100°C in water.

2.6. Optical Properties

Polycarbonate is a transparent, nearly colorless polymer, making it attractive as a glass replacement. Visible light transmission is ∼ 90%, and haze is only (1–2%) in typical commercial products. Absorption in the ultraviolet (uv) regions, accounted for by the aromatic structure reaches a maximum at ∼ 255 nm. Polycarbonate has a high refractive index (1.588) and lower density than glass (1.52 g/mL), making it an attractive material for eyewear. Exposure of non-uv stabilized polycarbonate to strong uv or outdoor sunlight conditions can lead to photoyellowing of the surface. The uv screens can be combined with hard coats to protect the surface of polycarbonate, and also to provide resistance to chemical attack in sheet products used for glazing applications. Polycarbonate eyewear is usually available with a scratch-resistant coating.

Special polycarbonate grades have been developed for the rapidly growing optical information storage markets. Compact disks (CDs) utilize the transparency, low birefringence, mechanical and dynamic stability and good heat distortion properties of polycarbonate. Polycarbonate prepared by the melt technique can be made especially free of contamination, and with a controlled low molecular weight, and is the preferred substrate. The use of *p*-alkyl phenols with branched alkyl groups containing 8 or 9 carbon atoms result in extremely high melt flow polycarbonates having sustained impact strength. A number of other agents for increasing melt flow have also been patented. Typically, polycarbonate as molded is highly anisotropic, and exhibits birefringence. Although the birefringence can be minimized using the appropriate processing conditions, only modification of the backbone can be used to reduce birefringence to zero. Use of high flow resins leads to lower birefringence in the molded parts, and also decreases the molding cycle times to only a few seconds. New polycarbonates with inherently lower birefringence have also been studied recently. A number of polymers with the phenyl rings out of the plane of the PC backbone are effective at reducing birefringence; the spirobiindane bisphenol (SBI) is a notable example. A copolymer of BPA with SBI can lead to zero orientational birefringence. This work has been reviewed (55).

2.7. Mechanical Properties

Mechanical and other properties of BPA polycarbonate are listed in Table 2. The room temperature modulus and tensile strength are similar to those of other amorphous thermoplastics, but the impact strength and ductility are unusually high. Whereas most amorphous polymers are glass-like and brittle below their T_g, polycarbonate remains ductile to about -10°C. The stress–strain curve in uniaxial tension (Fig. 2) is typical of ductile materials, having an initial Hookean region, followed by shear-induced yielding and plastic deformation. Breakage occurs at $\sim 120\%$ elongation. The area under the stress–strain curve is a measure of energy absorption per unit volume, and is ~ 65 J/m^3 (15.5 cal/m^3). That value is ~ 8.5 times higher than the energy absorption of cast aluminum, and 60% that of carbon steel, placing polycarbonate in an ideal position for use as a metal replacement. Weight savings as a metal replacement are substantial, because polycarbonate is only 44% as dense as aluminum and one-sixth as dense as steel.

Impact strength can be measured by a variety of methods, including notched Izod, tensile impact, and falling dart impact. The notched Izod test is most widely used to measure the toughness of a resin. This test involves measuring the energy absorption under impact conditions on a sample in which a notch has been cut to serve as a stress concentrator. Polycarbonates are among the highest rated engineering polymers for impact resistance, and are the toughest transparent materials known. Under high strain rate conditions (impact), polycarbonates are sensitive to the nature of the stress concentrator, and different results can be obtained depending on how the notch is cut and the thickness of the sample. At room temperature, decreasing the radius of the notch tip from 0.038 to 0.020 mm reduces the notched impact strength from 960 to 130 J/m (230–31 cal/m). A similar transition is noted when samples are tested over a range of temperatures, showing a transition from ductile to brittle behavior at temperatures around -20°C. As the thickness of the specimen is increased from 3.18 to 6.35 mm, a similar transition occurs, with brittle failure of thicker samples. The critical thickness phenomenon, as well as the low temperature embrittlement, can be alleviated by use of copolymers or blends.

Glass-reinforced polycarbonates are sold as high modulus materials having properties approaching those of metals while retaining the basic plastic attributes of low cost processing, dielectric character, resistance to corrosion, light weight, and inherent color. As the level of glass is increased, tensile and flexural strength and modulus increase to almost double their original values. Compressive strength increases by $\sim 65\%$. Fatigue endurance increases dramatically to seven times the value of the neat resin; deformation under load drops to 0.1% under 27 MPa (6800 psi) at 23°C. Both the coefficient of thermal expansion and mold shrinkage drop in glass reinforced resins. As expected for a stiffer resin, the impact properties drop as well, to a notched Izod

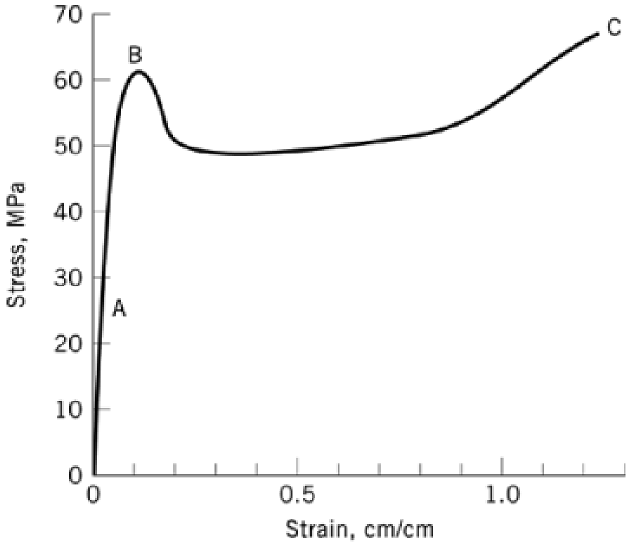
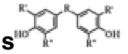


Fig. 2. Stress–strain curve for standard polycarbonate resin at 23°C where the points A, B, and C correspond to the proportional limit (27.6 MPa), the yield point (62 MPa), and the ultimate strength (65.5 MPa), respectively. To convert MPa to psi, multiply by 145.

impact value of 133 J/m (32 cal/m). Properties of a 40% glass-reinforced resin are compared to a standard injection molding resin in Table 2.

Table 3. Aromatic Polycarbonates Derived from Bisphenols 

Monomer (common name)	Monomer mp, °C	T^g, °C	Melt range	References
R' = R'' = H; R =				
 (methylenediphenol)	163	147	>300	7, 32, 33
 (oxydiphenol)	161	145	230–235	7, 32, 33
 (thiodiphenol, SDA)	152	113	220–240	7, 32, 33
 (sulfonyldiphenol)	249		200–210	7, 23

Table 3. ***Continued***

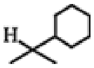
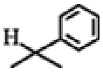
Monomer (common name)	Monomer mp, °C	T^g, °C	Melt range	References
 (dihydroxybenzophenone)	213–215			35
 (BPC)	214–215	168	230–260	36, 37
	122	130	185–195	7, 32, 33
	129	123	150–170	7, 32, 33
	155	149	170–180	7, 32, 33
	224	190		38
	161	121	200–215	38
 (bisphenol A, BPA)	157	149	215–230	7, 32, 33
	149	137	200–220	7, 32, 33
	188	176	210–230	7, 32, 33

Table 3. ***Continued***

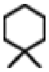
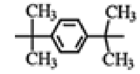
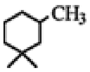
Monomer (common name)	Monomer mp, °C	T^g, °C	Melt range	References
	295	220	240	7, 32, 33
 (6F-DA)	161	149		39
	170	200		40
	147	186		40
	190	179	250–260	7, 32, 33
	157	167	240–250	7, 32, 33
	224	275	390	41, 42
	239	239		43
	304	228		44
	207			45

Table 3. ***Continued***

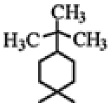
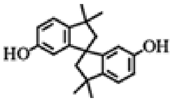
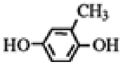
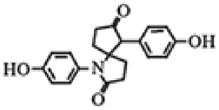
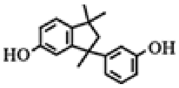
Monomer (common name)	Monomer mp, °C	T^g, °C	Melt range	References
	221			36
	229			47
$R = C(CH_3)_2$; $R' = R'' = CH_3$	165	207		
$R = C(CH_3)_2$; $R' = R'' = Br$	178–80	265		32, 33
 (SBI)			230	49
 (methyl-HQ)	128–130	155		13
	223			50
				51

Table 3. ***Continued***

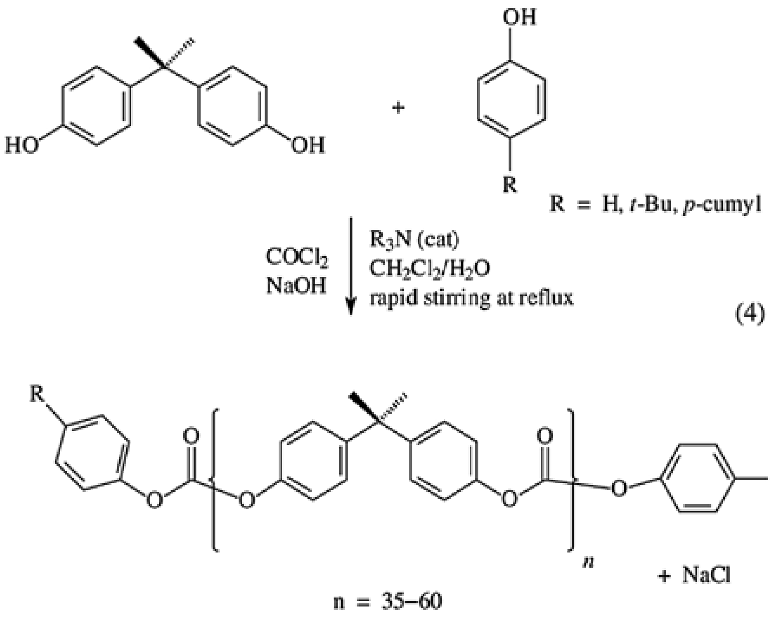
Monomer (common name)	Monomer mp, °C	T^g, °C	Melt range	References
	243			52

3. Preparation

The historical direct reaction route, which utilized phosgenation of a solution of BPA in pyridine proved inefficient commercially because of the need for massive pyridine recycle. Calcium hydroxide was used as an HCl scavenger for a brief period of time, but again, recycle was an issue. Although both solution and melt processes were piloted through the early and mid-1960s, the industry settled on an amine-catalyzed interfacial phosgenation process. In this process, the BPA is phosgenated in a solvent such as CH_2Cl_2 using a tertiary amine catalyst, while maintaining pH via the addition of NaOH. The by-product NaCl is then recycled back to chlorine (used to make phosgene in combination with carbon monoxide) and NaOH. The melt transesterification process simply involves base-catalyzed reaction of BPA with diphenyl carbonate. After sporadic work on the melt process over many years, GE Plastics first commercialized this technology in a joint venture with Mitsui Petrochemical Industries, now called GE Plastics Japan. The small plant (35,000 t/yr) validated the technology and led to large scale commercialization of the melt process in a full scale plant (150,000 t/yr) in Cartagena, Spain.

3.1. Interfacial Polymerization

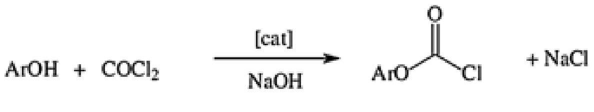
Most BPA polycarbonate is produced by an interfacial polymerization process utilizing phosgene. The interfacial process for polycarbonate preparation involves stirring a slurry or solution of BPA and 1–5% of a chain stopper such as phenol, *p*-*tert*-butylphenol, or *p*-cumylphenol, in a mixture of methylene chloride and water, while adding phosgene in the presence of a small amount (0.1–3%) of a tertiary amine catalyst (eq. **4**).



(4)

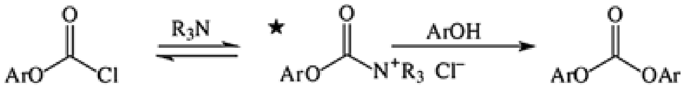
Sodium hydroxide solution is added concurrently to maintain the appropriate reaction pH (typically 10–12). Efficient mixing is important, to ensure contact between the four phases present [solid BPA, gaseous phosgene, methylene chloride (into which the polymer dissolves)], and the aqueous phase, in which the by-product sodium chloride becomes concentrated. Phosgene addition is continued until the presence of free phenolic groups can no longer be detected. Interfacial reactions are often overphosgenated, to ensure complete reaction, and the excess phosgene becomes hydrolyzed, sometimes forming significant amounts of sodium carbonate. When the reaction is complete, and after the brine phase has been separated, the methylene chloride solution of polymer is washed first with acid to remove residual base and amine, then with water. Many variations of this basic interfacial process have been patented, including continuous or semicontinuous processes, various workup procedures, many types of catalysts, including phase-transfer catalysts and bifunctional catalysts, methods that rely on the intermediacy of bischloroformate oligomers, and various schemes to control the formation of low molecular weight oligomeric species or cyclics.

Studies on the mechanism of interfacial polycarbonate formation are complicated by its interfacial nature, involving four phases. In addition, effects such as stirring rate, interfacial volume, and acid–base equilibria of BPA with NaOH are involved. Although some authors still believe that the tertiary amine acts solely as a base (56) (and hence as a phase-transfer agent, with $R_3N{-}H^+$ as the cationic species), other experimental kinetic evidence supports the importance of formation and reaction of acyl ammonium salts as intermediates (57). Assuming that acyl ammonium salts are formed, the sequence of reactions shown in eqs. **5–7** would occur. In the first step, the bisphenol reacts with phosgene to form a chloroformate (eq. **5**, Ar = aryl group).



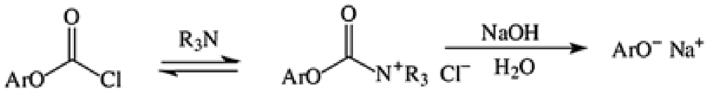
(5)

Although this reaction can proceed in the absence of catalyst, it is accelerated both by phase transfer and by nucleophilic catalysts. The reaction occurs quickly enough to compete effectively with phosgene hydrolysis, even at the reaction pH of 10–12. Reaction of a chloroformate functionality with a phenol to form a carbonate functionality requires a catalyst to proceed effectively (eq. **6**).



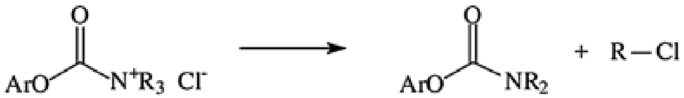
(6)

In the absence of catalyst, the reaction takes several hours even at high pH (57). Tertiary amines provide a substantial rate acceleration, but phase-transfer catalysts (such as Bu_4NOH or Bu_3NMeOH) are also very effective (58). The amines function by nucleophilic catalysis, forming an acyl ammonium salt in an equilibrium reaction with chloroformate, which is more susceptible toward attack by a phenol. Brittain, and co-workers studied the effects of tertiary amines on the formation and reactions of aryl chloroformates using model compounds (57). These studies, which used stop flow Fourine transform infrared (ftir) techniques to measure kinetics clearly showed that very slight changes in the nature of the tertiary amine structure can lead to dramatic changes in both the rate at which equilibrium is achieved and the position of equilibrium; both the rate and position of equilibrium can be affected by a factor of 4000–5000, simply by changing the amine from triethylamine to diethylmethylamine. Other investigators have shown that those changes effectively account for dramatic changes in product formation (59). Less hindered amines such as methyldiethylamine afford very fast reactions, but significant hydrolysis of chloroformate, while more hindered amines, such as tributyl amine afford less hydrolysis, but also slower rates. Phase-transfer catalysts cannot involve intermediacy of an acyl ammonium salt, yet also provide fast rates. These catalysts function by solubilizing the phenoxide anion, making reaction in the organic phase more facile. Phase-transfer catalysts also provide the advantage that hydrolysis of both phosgene and chloroformates is greatly reduced. In highly phosgene-efficient cases, however, a small amount of tertiary amine is required to catalyze chloroformate hydrolysis (60). It is believed that the main route to hydrolysis, a largely undesired reaction, is via the acyl ammonium salt, which as it becomes less lipophilic enters the water-rich interfacial region. Normally, polycarbonate reactions are overphosgenated to ensure complete conversion of bisphenol to product, forming slight stoichiometric excesses of chloroformate. Some hydrolysis of the chloroformate so-formed is then necessary to complete the reaction, by converting the chloroformate to a phenoxide so that condensation to a carbonate can occur (eq. **7**).



(7)

The use of bifunctional catalysts containing both a tertiary amine and a quaternary ammonium salt on the same molecule for polycarbonate synthesis has recently been patented (61). A side reaction that can also occur during interfacial phosgenation is formation of urethanes. Under conditions of long reaction time or high amine level, acyl ammonium salts undergo a first-order reaction to form dialkyl urethanes (eq. **8**) (62).

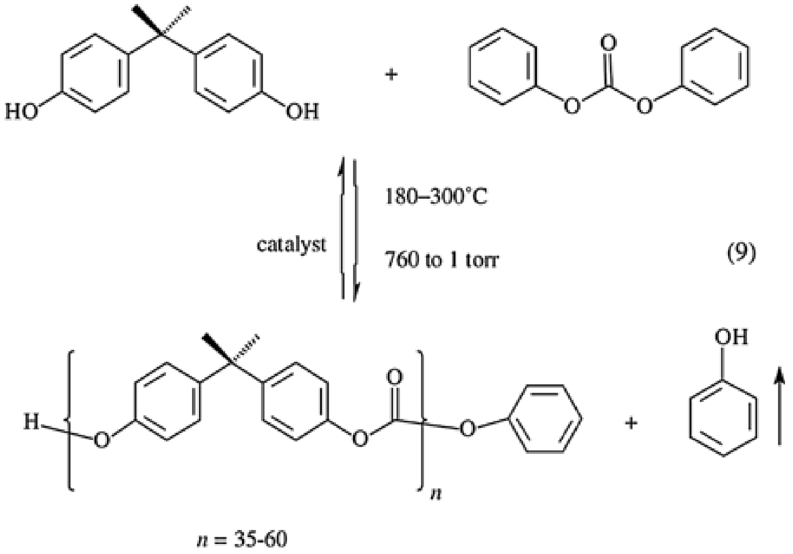


(8)

Methods for isolation of the product polycarbonate remain trade secrets. Feasible methods for polymer isolation include antisolvent precipitation, removal of solvent in boiling water, spray drying, and melt devolatilization using a wiped film evaporator or similar equipment. Regardless of the technique, the polymer must be dried, to avoid hydrolysis, and essentially devoid of methylene chloride. Most polycarbonate, whether isolated as pellets or powder is extruded, at which point stabilizers, additives, and colors may be formulated.

3.2. Transesterification or Melt Process

There has recently been much renewed interest in the transesterification process for the preparation of polycarbonate because of the desire to transition technology to environmentally friendly processes. There are 350 patents that have appeared since 1995 on the melt process. The transesterification or melt process utilizes no solvent during polymerization, producing neat polymer directly, and so chlorinated solvents may be entirely eliminated. GE Plastics operates two melt polycarbonate plants, in Chiba, Japan, and in Cartagena, Spain. The melt polymerization process involves the base-catalyzed transesterification reaction of a bisphenol with a source of carbonate functionality, such as diphenyl carbonate. During the reaction, by product phenol is removed, and polycarbonate forms directly. In the first stage of the reaction, diphenyl carbonate and BPA are combined with small amounts (usually $< 0.01\%$ M) of basic catalysts (Na, Li, K, tetraalkylammonium, or tatraalkylphosphonium hydroxides or carbonates) in a melt reactor. Phenol is liberated in an equilibrium reaction shown in (eq. **9**).

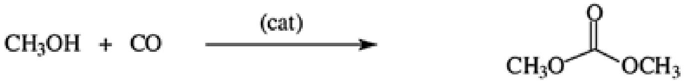


(9)

As the raw materials pass through the stages of reaction, the reaction temperature is increased, and higher vacuum is provided, to facilitate removal of the phenol, driving the equilibrium toward polycarbonate. In the later stages of reaction, the polymer melt becomes very viscous, and specialized equipment such as wiped film evaporators, helicone reactors, or multiply vacuum-vented extruders are necessary to expedite mass transfer of by product phenol via good surface renewal of the melt.

The polymer is exposed to an extensive heat history in the melt process. Early work on transesterification technology was troubled by thermal–oxidative reactions of the polymer, especially in the presence of basic catalysts (eqs. **7–10**). Early polycarbonates prepared by Fox and others via the melt process had noticable brown colors. More recent work on catalyst systems, more reactive carbonates, and modified processes have improved the process to the point where formation of color and product decomposition can be effectively surpressed. Polymer with color at least as good as interfacially prepared materials can now be prepared commercially. One of the key requirements for the transesterification process is the use of clean starting materials. Methods for the purification of both BPA and diphenyl carbonate have been developed and patented. Activated carbonates that form high molecular weight polycarbonate at equilibrium in solution at or below room temperature have also been reported, although they are chiefly only of academic interest (63).

Initially, diphenyl carbonate to be used for the transesterification process was prepared by reaction with phosgene. The phosgenation can be carried out in CH_2Cl_3, or in water, which avoids the use of organic solvents in the polycarbonate process altogether (64). More recently other methods for the preparation of diphenyl carbonate have been devloped that avoid the use of phosgene. GE Plastics uses a process commercialized by Enichem for the preparation of diphenyl carbonate, utilizing a two-step process. In the first step (eq. **10**),

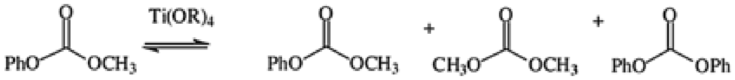


(10)

methanol is carbonylated using carbon monoxide in the presence of a catalyst to produce dimethyl carbonate. Reaction of dimethyl carbonate and phenol under specific transesterification conditions produces diphenyl carbonate. The by product is methanol, which can be recycled. Because the transesterification reaction from dimethyl to diphenyl carbonate is a thermodynamically unfavorable equilibrium process, the reaction is normally carried out in two stages: first, formation of a mixed carbonate (eq. **11**),

(11)

then disproportionation to dimethyl carbonate and diphenyl carbonate (eq. **12**).



(12)

An alternative method for formation of diphenyl carbonate is the direct carbonylation of phenol, using palladium catalysts (65). Although this latter chemistry works well for formation of diphenyl carbonate, it has not proved efficient enough for the formation of high molecular weight polycarbonate directly from BPA.

Preparation of polycarbonate via the melt process offers several processing advantages, including elimination of solvents and phosgene. The principal *product* advantage of melt-prepared polycarbonate is the fact that, as an equilibrium product, the resin is stable. No changes in polydispersivity, oligomers, etc, will be seen upon further processing (unless monomers are introduced). Additionally, the equilibrium levels of low molecular weight species (cyclic and linear oligomers, diaryl carbonates formed from chain stopper) are much lower than typically found in interfacially prepared polymer, and hence the polydispersivity (M_w/M_n) is narrower. Other impurities are also minimized, since there are no sources for contaminants such as solvent, amine, or NaCl to enter the process. One other major difference from interfacially prepared polycarbonate is the fact that the polymer is typically not completely end-capped; some level of phenol-terminated polymer will usually be present, which should be recognized in subsequent formulations.

Recent patent literature from Asahi describes novel polymerization processes that involve equipment with no moving parts, where the molten prepolymer is allowed to fall through holes and descend either freely or along a wire as a molten strand (66). The molten polymer from the bottom of the reactor is recycled to the top to reach the desired molecular weights. The setup provides a method to overcome mass transfer resistances and allows for removal of phenol from the system. Another process that has been an area of patent activity from GE and Asahi is in the area of solid-state polymerization of polycarbonate, wherein the prepolymer is converted to flakes/powder/particles and crystallized. The solids are then polymerized at a lower temperature than conventional melt polymerization. Both methods seem to be in the development stage.

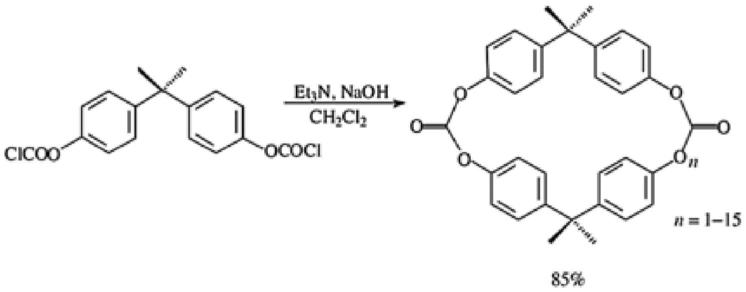
A spinoff of the melt process is "redistribution" technology, patented by GE (67). In the redistribution process, high molecular weight polycarbonate is extruded in the presence of a transesterification catalyst and, optionally, other monomeric or oligomeric materials. At the extrusion temperature, equilibrium transesterification occurs, leading to products similar to melt-prepared polycarbonate, even though the polymer may have originally been prepared by interfacial phosgenation. This technique is very useful for lowering the amounts of oligomers in interfacial resin, and for forming very low M_w polycarbonate or branched polycarbonates.

3.2.1. Other Polymerization Techniques

An analogue of the transesterification process has also been demonstrated, using the diacetate of BPA (68). Transesterification of the diacetate with dimethyl carbonate using a titanate catalyst produces polycarbonate with methyl acetate as the by product. Removal of the methyl acetate from the equilibrium drives the reaction to completion. Due to the problem of recycling methyl acetate back to BPA–diacetate, the process has not been commercialized.

Another technique for the preparation of polycarbonates that can lead to many novel applications is the ring-opening polymerization of cyclic oligomers. Although discrete cyclic oligomers of BPA and other bisphenols were isolated in the early 1960s, exploitation of this chemistry was not possible, owing to the difficulty of their preparation and purification (69). Furthermore, the cyclic tetramer of BPA, the most easily isolated, in ~ 25% yield, was a high melting, crystalline solid with a melting point of ~ 375°C making melt polymerization difficult.

A newer process for the preparation of mixtures of cyclic oligomers has been recently discovered (17,59). This process utilizes a triethylamine-catalyzed hydrolysis and condensation of BPA bischloroformate in a pseudo-dilution reaction. This reaction efficiently provides 85–95% of a mixture of cyclic oligomers having a degree of polymerization of 2 to ~ 12, with good productivity [10–20% solids reactions (eq. **13**)].



(13)

Three important features distinguish this work from the previous preparation of cyclic tetramer. First, the reaction is extremely selective toward formation of cyclic oligomers: < 0.01% linear oligomers are formed. Because any linear oligomers that might be present would reincorporate into the polymer via chain-transfer reactions during ring-opening polymerization, their presence would limit ultimate molecular weight, so it is important to limit their level. Second, a mixture of cyclics is formed. The fact that a broad mixture of cyclics is formed results in depression of the melting point of the cyclics, allowing a clear melt to form at 200–210°C from BPA carbonate cyclic oligomers. The melting point can be depressed further by the incorporation of long-chain bisphenols (70). Lastly, the reaction can be carried out at concentrations similar to conventional polycarbonate processes, rather than under very high dilution (eg, < 0.01 M) conditions, allowing good productivity in large scale equipment.

Melt polymerization of the cyclic oligomers can be achieved at 200–300°C, and solution polymerization is possible at ambient temperature (71). The ring-opening polymerization is driven almost entirely by entropy, in a reaction with almost no exotherm, leading to the highest molecular weight polycarbonates achievable by any process. Because the viscosity of the cyclic oligomers is $\sim 10^5$ times lower than the ultimate polymer, a variety of processing techniques become possible, including pultrusion, resin-transfer molding, and other techniques for the fabrication of fiber-reinforced composites. The use of cyclic oligomer technology also makes it possible to prepare polycarbonates that have been unattainable other by means, eg, hydroquinone–BPA copolymers. Although scaling to hundreds of kilograms has been carried out, this technology has not yet been commercialized.

Solid-state polymerization of BPA–polycarbonate oligomers has received much recent attention, with over 160 patents since 1995 (72). Typically, one prepares oligomeric or low molecuar weight polycarbonate ($\eta_{\text{inh}} =$ 0.2–0.3 dL/g, $T_g \sim$ 120–135°C) via a melt process. After isolation of the oligomer, and enhancing crystallization by various techniques, additional basic catalyst is blended. By using solid state polymerization techniques, the solid is then heated above its T_g, but below the melting point of crystalline polycarbonate, using a variety of techniques to remove the by product phenol. Vacuum and nitrogen purge conditions have been demonstrated, as well as methods involving supercritical or liquid carbon dioxide (73). After prolonged heating, the molecular weight increases to a useful range ($\eta_{\text{inh}} =$ 0.44–0.8 dL/g). The polycarbonate is then processed as usual, losing the crystallinity and leading to an amorphous product, as in conventional melt processes. Despite many patents, the process has not yet been commercialized.

3.3. Processing

Polycarbonates may be fabricated by all conventional thermoplastic processing operations, of which injection molding is the most common. Recommended operating conditions are stock temperatures of 275–325°C and molding pressures of 69–138 MPa (10,000–20,000 psi). Thorough predrying is necessary to prevent hydrolysis of the polymer by dissolved water at the high processing temperatures. Inadequate drying may lead to surface-streaked parts and loss of molecular weight. Extrusion produces film, sheet and stock shapes, and higher molecular weights but those used for injection molding are preferred. Temperatures for extrusion vary between 285 and 315°C.

Structural foam molding is also a valuable commercial technique. The molding compound is charged with an inert gas under pressure, and at the same time thermally plasticized in an extruder. Nitrogen gas may be pumped into the melt, or the molding compound may contain a chemical blowing agent that decomposes with gas generation at the plasticizing temperature. The pressurized plasticized melt is injected into a low pressure mold with a volume change taking place, causing the polymer to expand and fill the mold cavity. Very large parts having relatively low clamping pressures can be produced with this process.

Injection blow molding of polycarbonates produces an assortment of containers, from 20-L water bottles and 0.25-L milk bottles to outdoor lighting protective globes. The polymer normally contains a small amount of polyfunctional monomer that serves as a branching agent. Low level branching enhances the melt strength, as well as inducing non-Newtonian flow behavior (sensitivity of melt viscosity to shear).

Conventional thermoforming of sheet and film is applicable to the production of skylights, radomes, signs, curved windshields, body parts for automobiles, ski mobiles, boats, etc. Because BPA–polycarbonate is malleable, it can be cold formed like metal, and may be cold-rolled, stamped, or forged.

4. Economic Aspects

4.1. Production

Production of polycarbonate has steadily increased since the first commercial scale plants were built in the early 1960s. Current annual capacities are edging close to the 4.5 billion lb mark. Demand forecasts continue to be in the 8–12% range, with the Far East showing the greatest growth potential. A number of joint ventures have been announced over the last few years, namely, Dow/Sumitomo, Asahi/Chi Mei, Idemitsu/Formosa, to name a few. Plants have also opened in several countries and several more have been announced. Production of polycarbonate is approaching a fairly even split between the Americas, Europe, and Asia. Polycarbonate enjoys a comfortable niche between high priced specialty polymers and lower priced commodity resins.

GE Plastics is the largest polycarbonate producer, accounting for ~ 44% of the worldwide capacity (2 billion lb). Bayer AG has a worldwide capacity of ~ 900 million lb. Dow & the Dow/Sumitomo JV account for ~ 500 million lb of annual capacity. Other producers include Mitsubishi & associated JVs (475 MM lb), Teijin (200 MM lb), and Idemitsu (100 MM lb). Capacity announcements have been made for the near future by Teijin (in Singapore; ~ 150 MM lb), Asahi/Chi Mei (in Taiwan; ~ 100 MM lb), Idemitsu/Formosa (100 MM lb), and General Electric (in Spain and in the US). Normal grades of polycarbonate sold in 2000 for $1.40–1.50/lb ($3–3.30/kg). Many specialty grades demanded significantly higher prices. Over the last few years, growth of optical quality polycarbonate has been extremely strong.

5. Analytical Methods

5.1. Spectroscopy and Analysis

Polycarbonates have a strong C—O stretching band at $1770\ \mathrm{cm}^{-1}$, and strong C—O stretching bands at 1220 and $1235\ \mathrm{cm}^{-1}$, distinguishing them from polyesters. The amount of phenol end groups can be determined from the O—H absorption at $3595\ \mathrm{cm}^{-1}$. Proton nuclear magnetic resonance (H nmr) spectroscopy shows a symmetrical A_2B_2 aromatic pattern at 7.16 and 7.24 ppm, and absorption for the *gem*-dimethyl at 1.68 ppm, relative to $(CH_3)_4Si$. The ^{13}C nmr shows seven distinct absorptions: 152.1, attributable to C=O ; 148.9; 148.2; 127.9; 120.3; 42.5; and 30.9. X-ray spectroscopy shows a weak absorption at $725\ \mathrm{cm}^{-1}$, related to crystallinity, and a band at $917\ \mathrm{cm}^{-1}$, independent of crystallinity. Differential scanning calorimetry reveals a T_g temperature at $\sim 154°C$, shifting somewhat with the molecular weight or the level of branching. End group and impurity analysis is best revealed by hydrolysis of the polycarbonate using KOH–methanol in THF under nitrogen, followed by reversed-phase high-performance liquid chromatography (hplc) analysis or by spectroscopic techniques. Trace levels of impurities, such as methylene chloride, amine, chloride, and sodium, are determined by standard analytical techniques, eg, atomic absorption or titration.

6. Health and Safety Factors

BPA polycarbonate is an amorphous solid, supplied as extruded pellets averaging 2.5 mm in diameter and 3.2 mm long, or as a powder. Polycarbonate is considered a slight or nonexistent fire hazard. The ignition temperatures are quite high; flash ignition is at 449°C and autoignition is at 632°C, according to ASTM D1929. Odor and volatiles are negligible. Processing fumes, which include water, carbon dioxide, diphenyl carbonate, methylene chloride, and phenol are not formed in levels considered to be hazardous. Nonetheless, good housekeeping and industrial hygiene techniques should be followed. Polycarbonate has very low acute oral and dermal toxicity, is not a primary skin irritant, and does not cause systemic or local sensitization. In a finely divided form, polycarbonate is a mild eye irritant, consistent with the abrasive nature of the ground resin particle. Polycarbonate does not degrade during storage, and no heating or cooling requirements are necessary. For transportation purposes, polycarbonate is not classified as a hazardous material by U.S. Department of Transportation code, Title 49.

7. Uses

Extreme toughness, transparency, low color, resistance to burning, and maintenance of engineering properties over a wide thermal range are the outstanding properties of polycarbonate that make it useful for a variety of applications. Glazing and sheet are the largest markets for polycarbonate resins. In the United States ∼ 80,000 t are used in these markets annually, and 150,000-t worldwide. Clarity and an impact resistance 250 times greater than glass and 30 times greater than an acrylic sheet makes polycarbonate the natural choice for window replacement in areas where breakage is common. Windows in airplanes, trains, and schools commonly use polycarbonate. Exotic applications include military use, eg, in high speed aircraft canopies, where tests have shown polycarbonate to withstand impact with fowl at Mach 2. Polycarbonate is also used for security applications as laminates with glass or other materials. Polycarbonate offers unsurpassed projectile-stopping capability, as the material softens upon impact with a bullet, absorbing the projectile's energy. A large volume in laminated products also exists. The soft inner layer may be a urethane–, acrylic–, or siloxane–polycarbonate copolymer.

Automotive applications account for ∼ 150,000 t of worldwide consumption annually, with applications for various components including headlamp assemblies, interior instrument panels, bumpers, etc. Many automotive applications use blends of polycarbonate with acrylonitrile–butadiene–styrene (ABS) or with poly(butylene terephthalate) (PBT). A large effort is currently underway to commercialize automotive window glazing from coated polycarbonate. Both large and small appliances also account for large markets for polycarbonate. Consumption is ∼ 75,000 t annually. Polycarbonate is attractive to use in light appliances, including houseware items and power tools, because of its heat resistance and good electrical properties, combined with superior impact resistance and the ability to produce a wide variety of colors.

Packaging is a growing segment of the polycarbonate market, accounting for an ∼ 30,000-t consumption annually. Polycarbonate has been the preferred choice for large returnable, refillable 20-L water bottles because of its light weight and impact resistance. GE Plastics has also introduced returnable, refillable 0.25-L milk bottles for use in schools. These bottles, which can be refilled 50–100 times, are attractive alternatives to nonreusable paper milk cartons in communities that are concerned about waste.

Electrical, electronic, and technical applications use polycarbonates for a variety of purposes. The worldwide market is ∼ 160,000 t annually. Because of excellent electrical properties (dielectric strength, volume resistivity), and resistance to heat and humidity, polycarbonate is used for electrical connectors, telephone network devices, outlet boxes, etc. Polycarbonate had been popular for use in computer and business machine housings, but the use of neat resin was largely supplanted by blends of polycarbonate with ABS. However, new, highly colored and special effect resins (translucents, flip–flop colors, speckles, etc) have recaptured a significant portion of that market. A total of 25–30,000 t of resin is used annually. Polycarbonate also has many technical uses in instrument panels and devices, especially for membrane switches and insulators. Optical quality polycarbonate is the only suitable material for the compact disk market. Since their introduction in 1983, compact disks have shown explosive growth in the consumption of polycarbonate, with utility for audio, video, and computer applications, reaching ∼ 25,000 t of annual production.

Medical and health care related applications consume ∼ 30,000 t of polycarbonate annually. Polycarbonate is popular because of its clarity, impact strength, and low level of extractable impurities. Special grades have been developed to maintain clarity and resistance to yellowing upon gamma radiation sterilization processes. Leisure and safety applications are many and varied, accounting for ∼ 30,000 t of consumption annually. The largest markets are for protective headgear such as football and motorcycle helmets, and safety helmets for firefighters and construction workers. Protective eyewear also uses polycarbonate, because of its clarity and impact resistance.

8. Other Polycarbonates, Blends, and Copolymers

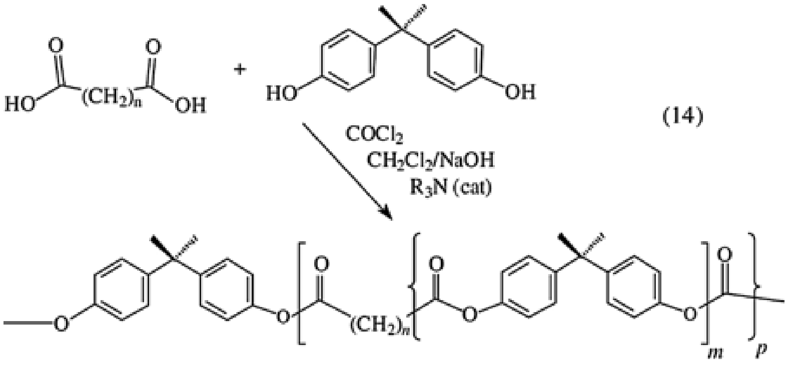
During the early development of polycarbonates, many bisphenols were investigated for potentially useful products. Some of these monomers and polymers are listed in Table 3. Despite this intensive research, however, no homopolycarbonates other than that of BPA have been produced commercially in any significant volume. Copolymers and blends, on the other hand, have been quite successful. Copolymer research constitutes a large portion of polycarbonate patents, with nearly 6000 patents since 1995. An excellent review of many types of polycarbonate homo- and copolymers arranged according to utility has recently appeared (74). Blends of polycarbonate with ABS and with PBT, in particular, have shown significant growth since the mid-1980s.

8.1. Copolymers

The copolymer of tetrabromo-BPA and BPA was one of the first commercially successful copolymers (75). Low levels of the brominated comonomer lead to increased flame resistance (V-0 rating by UL-94), while having little effect on other properties. The homopolymer of tetrabromo-BPA can also be prepred (76), but only the oligomeric version has been commercialized. The polycarbonate of bis(4-hydroxyphenyl)-1,1-dichloroethylene, prepared from chloral and phenol, followed by dehydrohalogenation, was investigated as another inherently flame-resistant polymer that retained good impact properties (78).

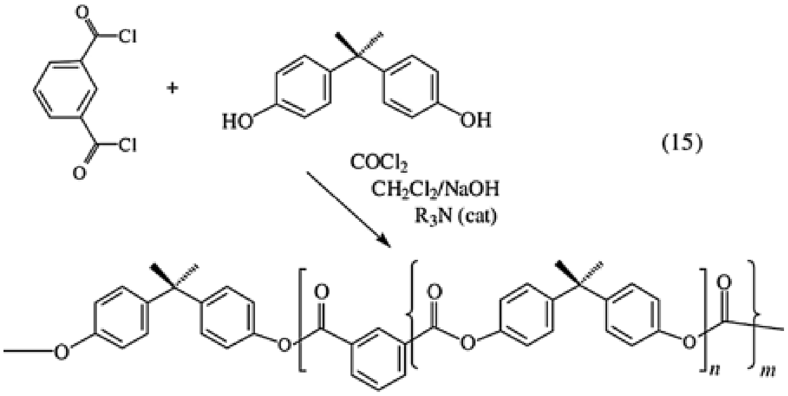
For utility in compact disks and other laser-readable and especially in read–write data storage systems, polycarbonates of low birefringence are advantageous. Birefringence can be reduced by using bulky polarizable side groups, or eliminated entirely in structures such as the spirobiindane bisphenol (76) (SBI) shown in Table 3. Efforts to reduce the birefringence of polycarbonate by modifying the bisphenol have been reviewed (55). Numerous alkyl-substituted bisphenols have also been used (79). Aliphatic groups do not contribute to birefringence, and also lead to less water absorption in the polymer. Birefringence can also be reduced by eliminated molded-in stresses via the use of high flow resins. Many techniques for achieving high-flow polycarbonates have been reported, including incorporation of aliphatic diesters into the backbone, modification of the bisphenol with aliphatic groups, changing the polymer end groups. Incorporation of aliphatic diacids to form aliphatic ester carbonates can provide nearly twice the melt flow with little sacrifice in ductility.

Polyester carbonates can be prepared by the copolymerization of BPA with diacyl chlorides such as iso- or terephthaloyl chloride (eq. **14**) (80).

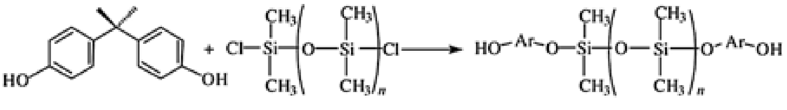


(14)

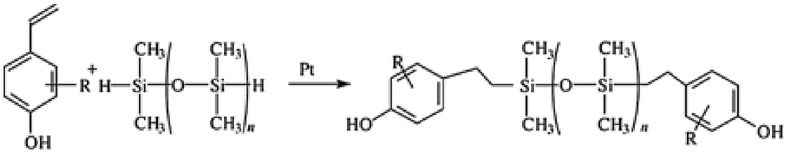
These polymers have been commercialized by Bayer AG, GE, Dow Chemical, and Mitsubishi Chemical, Ltd. Melt processes to prepare these materials have also been demonstrated. In some cases, a diacid can be used directly, because reaction with phosgene converts it into an acid chloride prior to reaction with the bisphenol. The polyester carbonates prepared using aromatic diacids are useful as high heat materials. Although the polyarylate esters are crystalline as homopolymers, copolymerization as copolyestercarbonates allows formation of amorphous resins that have impact strength similar to BPA polycarbonate, with the T_g elevated to ∼ 190°C. Incorporation of aliphatic esters into polycarbonate leads to elastomeric materials or copolymers with depressed T_g, but with dramatically increased melt flow (eq. **15**) (34).



(15)



(16)



(17)

Some of these block copolymers also have improved low temperature impact strength and higher stress-crack resistance than neat BPA polycarbonate.

A variety of methods have been developed for the preparation of polydimethylsiloxane-*co*-BPA polycarbonates (81). These polymers differ greatly from conventional polycarbonate, in that they have very low glass-transition temperatures ($T_g = -123$°C), yet that have excellent thermal stability and good weathering properties. Phosgenation of silanol-terminated siloxane oligomers in the presence of BPA, or reaction of BPA sodium salt with chlorosilane-stopped siloxane oligomers, followed by phosgenation with BPA are two of the described procedures (82). Hydrosilation methods are also used (83). Use of cyclic oligomers for the preparation of these copolymers has also been described (84). These materials display a wide range of properties, depending on the block length of the individual polymers and on the weight level of silicone present. Some of the block copolymers having low levels of silicone have outstanding low temperature impact strength; those having higher levels of silicone are thermoplastic elastomers. The enhanced ductility at low temperature was

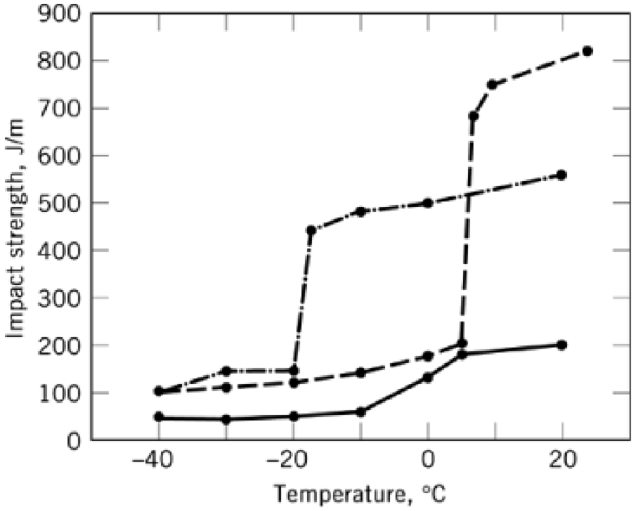


Fig. 3. Dependence of Izod impact strength on temperature for (- - -) polycarbonate, (—) ABS, and (-•-) polycarbonate–ABS blends. To convert J to cal, divide by 4.184.

reported in the 1970s; incorporating 25% silicone into BPA polycarbonate lowers the ductile-brittle transition temperature from ~ -15°C to -110°C (85).

In 1991, Bayer reported the preparation of a family of polycarbonates (Apec) using a monomer based on the condensation of a hydrogenated isophorone with phenol (86). Because the bulky structure leads to rigidity derived from hindered rotational freedom, the polycarbonate retains the low temperature loss modulus of BPA polycarbonate, which affords low temperature impact strength, yet has a high T_g. The homopolymer has a T_g of 239°C, and copolymers with BPA provide intermediate glass-transition temperatures. A variety of other monomers also provide high heat polycarbonates, but often at the expense of limited ductility (73).

8.2. Blends

The concept of blending two or more commercially available materials to create a new material having properties different from either starting material has generated a great deal of interest over the past few decades. One of the fastest growing market segments within the polycarbonate industry is this arena of blends. Polycarbonate blends are used to tailor performance and price to specific markets. Despite its strengths, polycarbonate suffers from shortcomings with regard to flow characteristics and solvent resistance. The two principal blends are produced to improve those characteristics. Polycarbonate–ABS blends (GE, Cycoloy; Bayer, Bayblend; Dow, PULSE; and Monsanto, Triax 2000) have improved flow and lower cost, and polycarbonate–polyesters that use either PBT or PET (GE, Xenoy; Bayer, Makroblend; Dow, Sabre; and Hoechst Celanese, Vandar) utilize semicrystalline polymers to improve chemical resistance, especially for automotive applications.

Fundamental studies of blends of polycarbonate with ABS indicate that the presence of ABS greatly decreases the melt viscosity in the blend, enhancing processibility. Even as little as 20% ABS provides a decrease in melt viscosity by a factor of 4–5 (87). A synergistic improvement of the notched impact strength at low temperature is also seen for polycarbonate–ABS blends (Fig. 3). About 35,000 t of these blends are produced annually, and significant growth in the market has been seen, with a yearly growth rate of 12–13%. More than half of the blends produced are used in the automotive market, mostly on instrument panels. The other large use for polycarbonate blends is in office and business machines, such as computer and printer housings.

Polycarbonate–polyester blends were introduced in 1980 and have steadily increased sales to a volume of ∼ 70,000 t. This blend, which is used on exterior parts for the automotive industry, accounting for 85% of the volume, combines the toughness and impact strength of the polycarbonate with the crystallinity and inherent solvent resistance of PBT, PET, and other polyesters. Although not quite miscible, polycarbonate and PBT form a fine-grained blend, which upon analysis shows the T_g of the polycarbonate and the T_m of the polyester.

Other blends of polycarbonate have limited markets so far. The most significant blends are with polyurethane, polyetherimides, acrylate–styrene–acrylonitrile (ASA), acrylonitrile–ethylene–styrene (AES), and styrene–maleic anhydride (SMA).

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