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Polymer Report: Polycarbonates Abound

Polycarbonates have found their way into both high- and low-tech applications because of the unique array of properties that make them suitable for entirely new applications *and* equally ideal as substitutes for existing materials that are becoming less preferred for many applications as a result. The growth areas for polycarbonates are primarily in applications that use their strength against impact damage or their optical transparency and ability to bend, or refract, light—properties shared by the commercially manufactured polycarbonates, which in the late nineties were increasing market share at the expense of acrylic (acrylonitrile polymers) and polyester resins, among other materials (Kogler, 3).

Of the two versions of polycarbonate that are commercially successful today, one is an amorphous, unbranched thermoplastic that is manufactured as pellets and reformed by injection molding, or composited with glass. GE Chemical's *Lexan* is the most ubiquitous example, most commonly used as a substitute for high-performance and safety plate glass. The second category of carbonates is comprised of resins that form thermoset plastics, abbreviated CR by the air force in the 1950s. Some trade names are Bayer's *Makrolon*, which is common to 21 billion CDs and DVDs, and Pittsburg Plate Glass' *CR-39*, dating back to the 40s, which is still the preferred material for plastic prescription eyeglass lenses.

1) What are the monomers?

Early manufacturing methods used in the first half of the 20th century directly combined **phosgene**, used as a weapon in the First World War, with phenol. This resulted in a **diphenyl carbonate** monomer that could undergo transesterification reactions with certain glycols, particularly **bis-phenol A (BPA)**—so named because it is formed by reaction of two equivalents phenol with acetone. Like other glycols, BPA has multiple alcohol groups, and each can exchange places with one of the two sp² single-bonded oxygens on a carbon in a carbonate group. The original reaction would occur when diphenyl carbonate was boiled at high temperatures to react in the gas phase with phosgene, very literally a condensation reaction, which yielded an alternating copolymer of carbonate and BPA groups. The product is called poly-(bis-phenol A carbonate) and is one and the same with GE's *Lexan*, still one of the most common polycarbonates around.

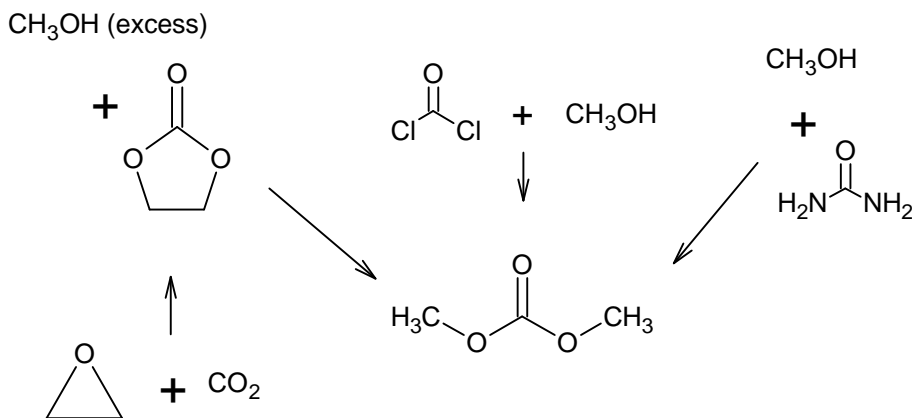
Transesterification is usually the outcome of an alcohol added in excess that loses a proton and replaces the alkoxide group of an ester, or in the case of a carbonate, *both* alkoxide groups. The hydroxy hydrogens of phenol and, likewise, Bis-phenol A, are particularly acidic because the negative formal charge on oxygen that result with loss of their proton are stabilized by resonance donation into the phenyl cloud of conjugated pi-bonding electrons. This makes them an ideal comonomer for phosgene.

Phosgene is an acyl dichloride. The formation of a tetrahedral “chloroformate” intermediate with almost any nucleophile tends to expel chlorine—twice per phosgene molecule—making it rather reactive, as is chlorine itself. A practical result is that most manufacturing of phosgene—and consequently, most carbonate manufacturing—is done near oceans, where chlorine is collected by the electrolysis of sodium chloride from sea salt. In fact, 72 percent of the US chlorine supply is produced on the Gulf Coast, primarily in Louisiana and Texas (Kirk-Othmer Encyclopedia of Chemical Technology, ctd. on CSA Website).

The fact that a substitution may occur twice consecutively is what makes phosgene a very effective monomer, although manufacturing processes must thoroughly contain it and prevent exposure of workers or release into the atmosphere, where contact with humidity decomposes the gas into carbon dioxide and hydrochloric acid. EPA data indicate that the effectiveness of containment from the environment had not been thoroughly studied as recently as 1997 (EPA Website, 11). Gas that has to be vented is burned in the presence of soda lime, yielding sodium chloride, and requiring remanufacture of chlorine from the thermodynamically unfavorable electrolysis of the salt. The loss of chlorine and constant high demand for polycarbonate have kept its price somewhat higher than other plastics.

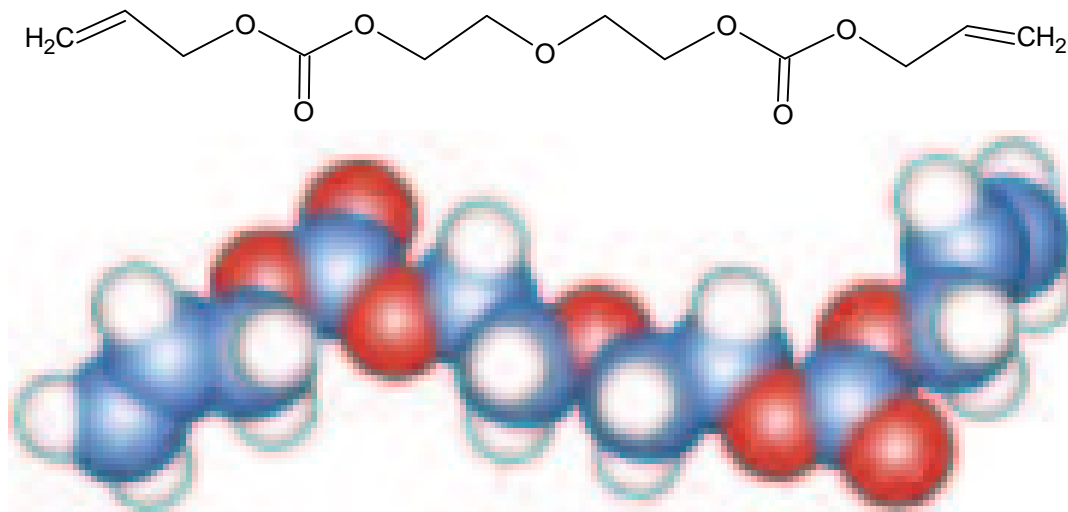
Because of the safety and cost concerns associated with phosgene, alternative monomers are being phased into production by industry and encouraged by government today. The EPA and our own Dr. Baretto have suggested that carbon dioxide be sequestered into solid form to reduce the greenhouse effect in the future. **Ethylene epoxide** and **carbon dioxide** form **ethylene carbonate**, which can in turn undergo transesterification with **methanol** to yield the monomer **dimethyl carbonate**. But because methanol and the target product are azeotropes, their distillation together gives no better than a ninety percent yield.

With the use of strong reducing agents, even **urea** can be reacted with methanol to give dimethyl carbonate at better than 98 percent yields. Other synthetic routes in the future may include nitrogen or carbon monoxide reacting with methanol (Chem Systems Website, 1-2).



Alternative routes to the carbonate monomer used to make poly-(BPA carbonate).

In the case of carbonate resins, the monomers are often difunctional. The CR-39 prepolymer is the product of an ether, diethylene glycol and an allylic ester. This is **diethylene glycol bis-(allyl carbonate)**.

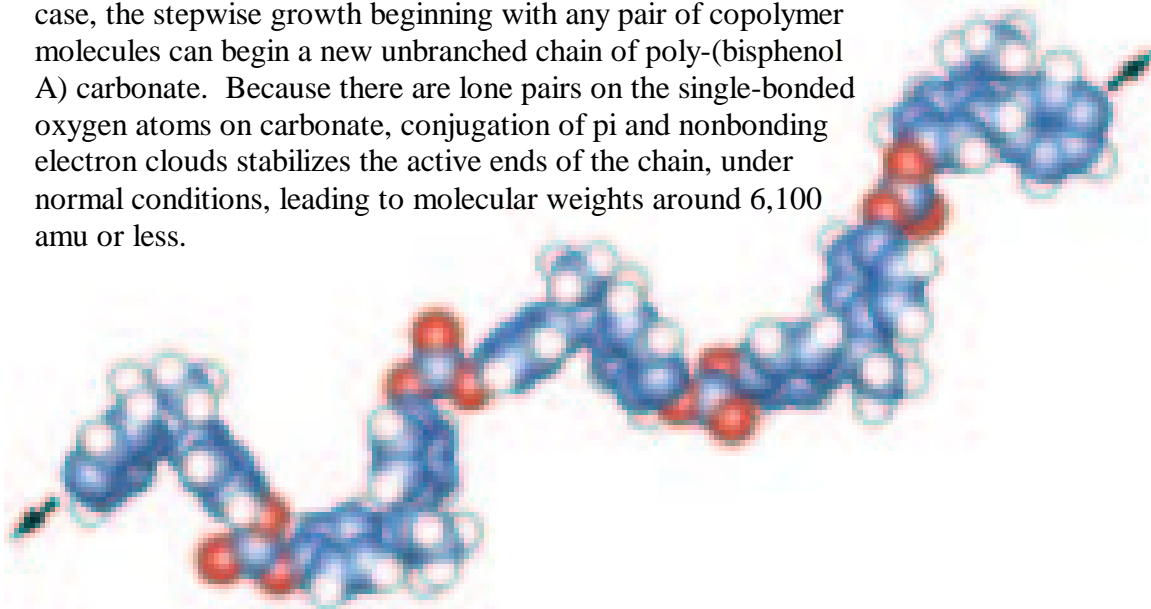


CR-39 prepolymer, also known as **allyl diglycol carbonate**. It is usually shipped in this form as a liquid and remains so until it is thoroughly polymerized in the slow, catalyzed thermal molding of the finished plastic. In contrast, thermoplastic polycarbonates are fully polymerized at the chemical plant and shipped as dry pellets or grains for high-speed injection molding.

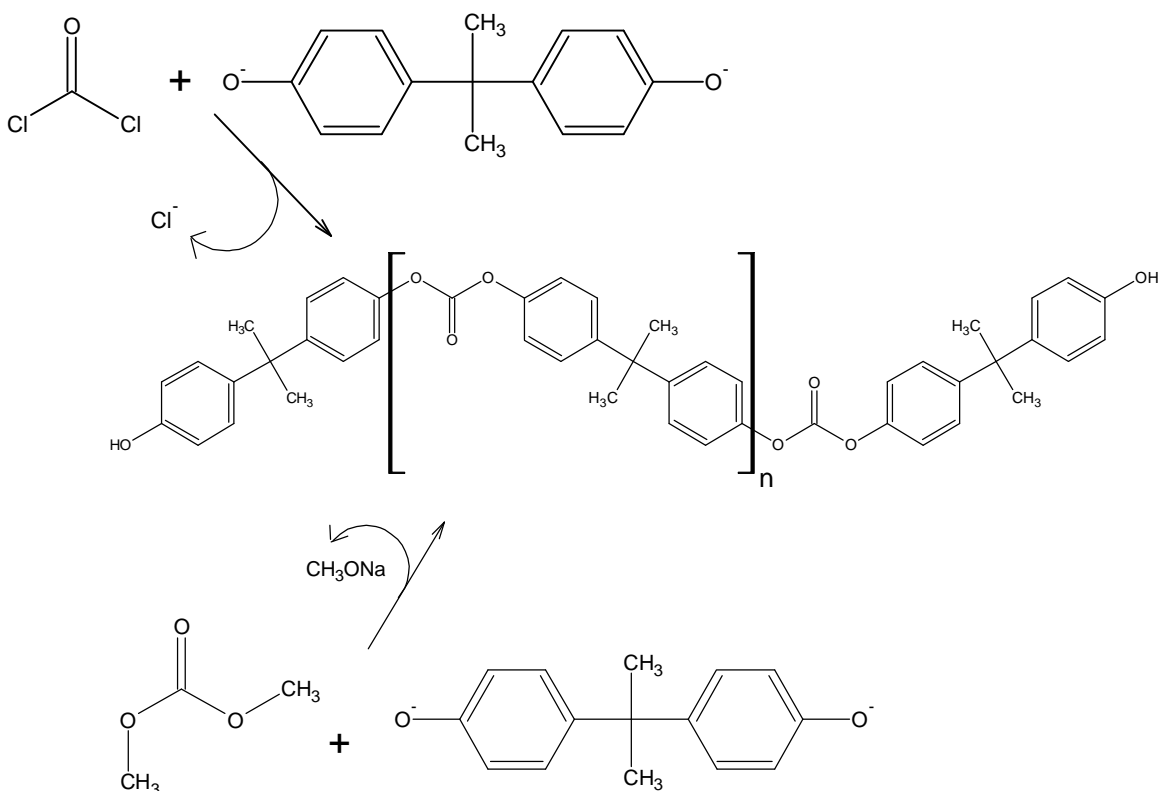
2 & 3) What reactions produce polycarbonates? What are the resulting structures?

The reaction used to produce poly-BPA carbonate and other thermoplastic polycarbonates is a step-growth reaction. As in the production of epoxides that use bisphenol, in this process, BPA is reacted with sodium hydroxide to give a solution of the conjugate base. Phosgene gas undergoes acyl substitution with the base at the boundary between the solution and gas phases. The polycarbonate precipitates out and is removed. Like the formation of nylon, which occurs between two liquid phases, this characterizes the process as *interfacial polymerization*.

The new facilities that use dimethyl carbonate instead of phosgene, in contrast, use transesterification to disproportionate methanol with excess bisphenol. In either case, the stepwise growth beginning with any pair of copolymer molecules can begin a new unbranched chain of poly-(bisphenol A) carbonate. Because there are lone pairs on the single-bonded oxygen atoms on carbonate, conjugation of pi and nonbonding electron clouds stabilizes the active ends of the chain, under normal conditions, leading to molecular weights around 6,100 amu or less.



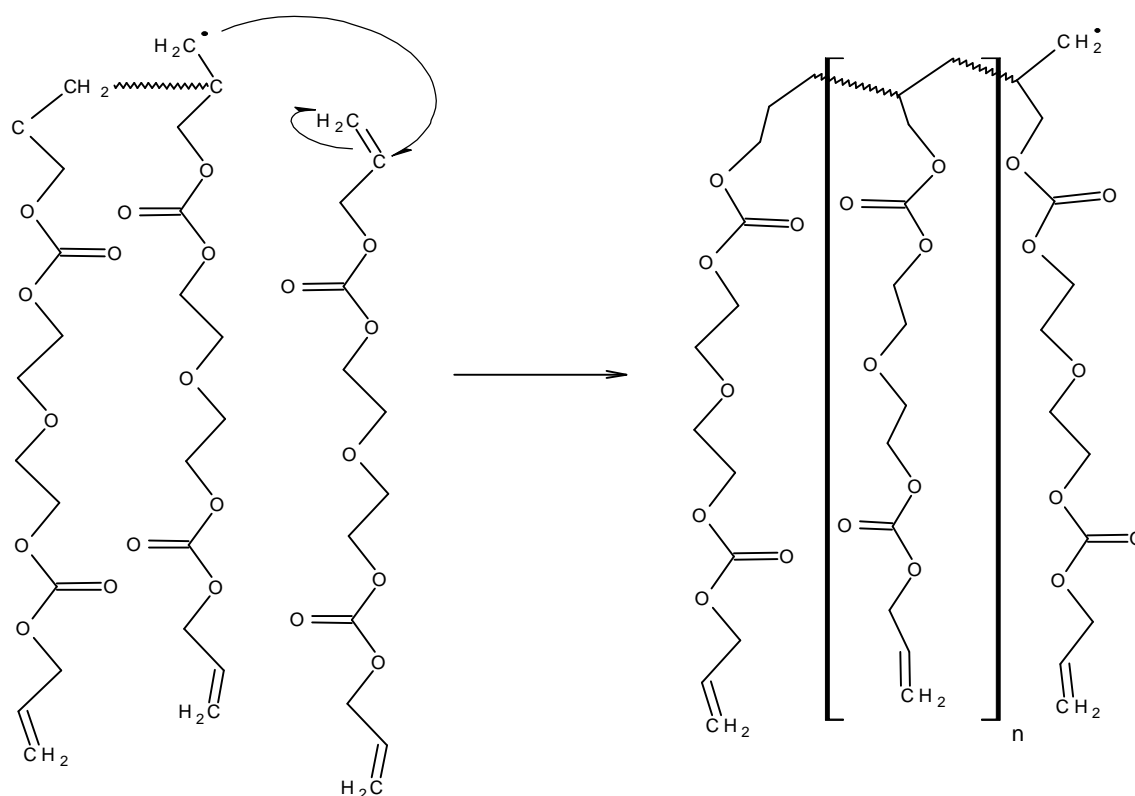
Acyl chloride substitution with conjugate base of bis-phenol A,



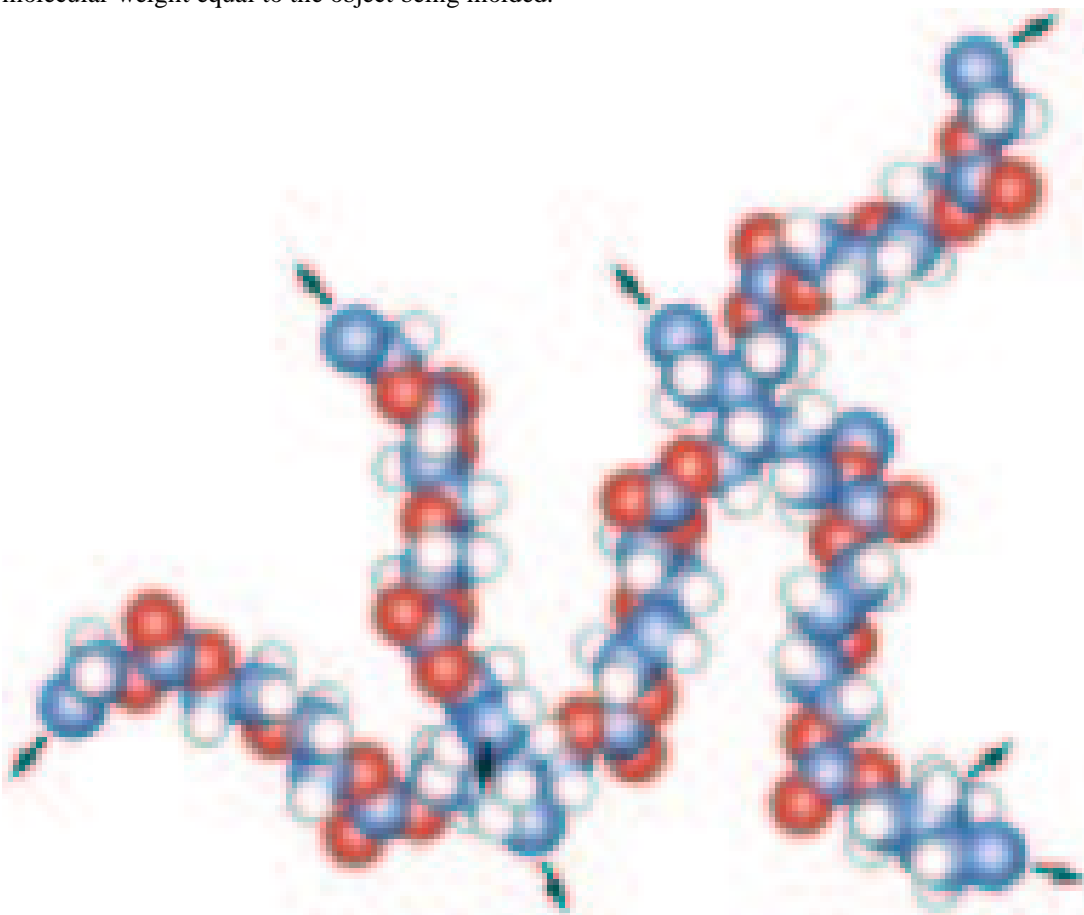
...or transesterification of bis-phenol A both form the same alternating copolymer through step-growth that relies on the well-understood acyl substitution mechanism. No initiator is required.

When the polymer chains stop encountering additional carbonate monomer, or molecular weight takes the living chain from the solution-phosgene interface, the terminal oxygen is capped with sodium or a proton, neither changing the properties of the polymer overall. Usually excess BPA is used so that phosgene is completely reacted. Then, excess BPA salt in the solution can be recycled. The accumulating product is removed and purified into dry granules.

Carbonate resins, unlike Lexan, can form bonds through radical chain reaction and do not require a copolymer. The process in which the prepolymer forms a three-dimensional network of covalent bonds is called *reticulation*. In particular, CR-39 is not usually a copolymer, because it bonds at the vinylic carbons on either end of the molecule. As the density of monomer chains around the relatively stationary active site increases, the reaction tends to undergo chain transfer. The densely packed chains in these areas are the crystallites in lightweight polycarbonate prescription lenses that give them optical properties similar to glass, but with even greater refraction, or the ability to bend light that is characteristic of such crystalline substances. Recent studies show that the amount of crosslinking, and consequential density of the resulting plastic can be controlled by fractionally adding similar monomers with only one unsaturated site (Dlubek, Alam).



Partial Polymerization of CR-39 occurring at an isolated active site. The opposite ends would likely bond to various different active sites that result in strongly crosslinked crystallites. As an active site reaches the maximum chain packing density, the radical is transferred to a new monomer that can initiate the reaction at a new active site. The resulting polymer, poly-(diethylene glycol bis(allyl carbonate)), effectively has a molecular weight equal to the object being molded.



The radical mechanism that forms optical polycarbonate is not unique. Like crosslinked polymers, the extensive covalent bonding prevents reforming of the plastic after it is set. In practice, the resins are baked for up to 72 hours as the thermosetting takes place. UV light, in addition to a peroxide initiator, can lower this time down to an hour, at the expense of lower crystallinity.

4) How does the underlying molecular structure affect the function of the polymer?

Polycarbonates are often associated with their safety applications in bulletproof glass and airplane windows, and as you are now aware, CDs and eyeglasses. The plastic is far more ubiquitous, though. It is found in skylights, telephone booths and bus stops, visors, riot shields, safety glasses and low-temperature mechanical parts.

Both the straight chain thermoplastic and the thermoset polymer are clear. However, a result of the alternating diphenyl section in Lexan is that it absorbs all UV light below 380 nm in length. The phenyl rings on this plastic also make it relatively unreactive, which make it tough to dye. On the bright side, Lexan is usually formed into thin sheets that act accept covalent bonds of other polymers that can be easily dyed. This also allows it to be coated with polyurethane layers that can further protect it against chemicals like acetone and sulfuric acid. Ususally, an impurity that disperses absorbed UV energy gives polycarbonate a longer life. This is the reason why CD makers advise that their discs be kept out of sunlight. The thermoset polymer is easily dyed, which allows for tinted prescription eyewear. But this version of polycarbonate is usually coated because it is not as resistant to scratching, that people used to glass take for granted. There does not seem to be a good technical reason why CDs shouldn't be coated, too.

The fact that Lexan can be reformed means that it needs to be kept below 120 to 150 degrees Centigrade. In this range and above, its most valuable physical properties—impact resistance and plasticity—begin to weaken, as do intermolecular Van der Waals forces. The reason that polycarbonates are impact resistant to the point where they are dubbed “bullet-proof” seems to be related to their chain packing, sometimes called molecular architecture. The straight chain has been shown to avoid any repeating pattern whatsoever, perhaps making it one of the most amorphous polymers. The random orientation of the chains' atoms makes it very resistant to fracturing (Schmidt-Rohr). Of course, everything has its limits. Many taillights on cars are polycarbonate. But be assured, if it breaks, there must have been between 9,000 and 20,000 pounds per square inch of force applied to the 1/8 inch thick barrier. Polystyrene is an example of polymer that tends to form interlocking, repeating units among different chains. Hence it is brittle.

Proof that the amorphous nature of the plastic isn't totally responsible for its strength is glass. Lexan is only about 20 percent more dense than water, while glass can be up to six times as dense. So, the hypothesis is that amorphous architecture in combination with long covalent chains including conjugated rings can disperse torsional strain. The evidence for this is that polycarbonate sheets can handle 40 percent more strain when they are flexed sideways.

But “filling” molded polycarbonate with 10 to 50 percent glass fiber can actually more than double the plastic's impact resistance. This is an example of how thin fibers of everyday substances and almost any polymer can composite the physical properties of both. Common “alloys” of plastic include BASF Ultradur, which includes polyester, in addition to glass. The addition of these enables polycarbonate to be used on oven handles and higher-temperature uses.

Because they have high resistivity, sometimes called dielectric strength, certain polycarbonates also are being used in electronic components and as electrical insulators.

Other novel uses in recent years take advantage of the chemical reactivity and weakness towards scratching in the thermoset polycarbonates. Samples are used as radiation detectors, absorbing gamma rays and neutrons that strain the molecular architecture. Crystallinity at these locations can be washed away with a solvent and the resulting pits and grooves can be counted. Such small micropores in very thin polycarbonate sheets are being used to study the physical properties of liposomes and cell components as small as 30 nm in diameter.

5) Are there any environmental concerns involved in the use of or manufacturing of the polymer?

Tests on polycarbonate by Underwriters Laboratories and the FDA indicate that polycarbonates are safe and are used in applications that have been questioned, but studied carefully, including baby bottles. (Biles, McNeal, Begley, Hollifield). One issue about the cited studies is that tests for bisphenol A, the monomer usually in excess during manufacture, use hydrophilic solvents, even though infant formula contains fats. The one test cited on the plastics interest website that involves fat solubility used synthetic coconut oil, which unlike most other fats and oils, has three identical fatty acid chains. Polycarbonate itself does not emit any toxic gasses when burned, though coatings and other layers might. The flash point of a sheet is high enough to exceed fire safety codes at 663 kelvin.

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