

The Use of Ultrasound to Initiate Ring-Opening Polymerization

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SYNOPSIS

It has been discovered that a combination of heat and high-power ultrasound can be used to initiate ring-opening polymerization in cyclic bisphenol A polycarbonate oligomers. The polymerization can be conducted with or without the use of added chemical initiators. The use of ultrasound was extended to prepare glass-filled composites. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Ultrasound's utility for polymerization has been limited to two areas. The ability to superagitate is the first area, and it has been used many times.¹ An interesting example is the sonication of 4,4'-dihalo-biphenyls and Li wire in hexanes or xylenes to produce high molecular weight poly(*p*-phenylene).² The interfacial polymerization of chloroformates and phenols to form polycarbonates is claimed to have enhanced yields when sonicated.³ Ultrasound has also been used to initiate free radical polymerizations;⁴ for example, unsaturated polyesters and epoxies were cured with ultrasound to form self-adhesive films for circuit boards,⁵ bond two metal parts to form a car door,⁶ and to form composites with carbon and glass fibers.⁷ No reports of ionic, that is, nonradical, polymerization initiated by ultrasound have been seen.

Processibility of aromatic polycarbonates can be improved through the use of cyclic oligomeric precursors.^{8,9} The cyclic oligomers are prepared from *o*-chloroformates of bisphenol A under pseudo-high dilution conditions, and are mixtures of oligomers (Fig. 1) that have a melting range of 150–200°C. The cyclics have melt-flow viscosities of 10 (250°C) versus 10,000 poise (250°C) for the linear high polymer. The low viscosity allows for low molding pressures to be used for part fabrications that in turn lessens tooling costs, and more complicated parts can be molded than with the high molecular

weight polycarbonate. The lower viscosity of the cyclics also allows for better wetting of a reinforcement in a composite structure than could be achieved with high molecular weight polymer. After fabrication, the cyclics are converted to the mechanically superior linear high polymers by polymerization initiators that open the carbonate rings.

Polymerization of cyclic carbonates is generally chemically initiated. The most common initiators are nucleophiles capable of cleaving a carbonate group or bases that can abstract protons from any free phenol end group present in the cyclics. Both processes result in formation of a phenoxide ion. The true propagating agent of polymerization is the phenoxide ion at the end of the growing chain. Remarkably low concentrations of initiator (less than 0.1%) can cause virtually complete conversion of the cyclics to polymer.⁸ The presence of a chemical initiator in the cyclic mixtures means polymerization has started during the fabrication of the part. Preliminary resin transfer molding experiments with polycarbonate cyclics and initiators were conducted to establish processing conditions.⁹ If a trial was unsuccessful, three types of failure were observed: incomplete mold filling, uneven mold filling, and fiber wash. Each failure is associated with premature polymerization (too rapid rate of viscosity build).⁹ The current chemical initiators do not always provide sufficient control of the initiation process to prevent premature polymerization at the desired molding conditions.

It has been found that high-power ultrasound will polymerize molten BPA cyclics either neat or in a glass-filled composite. This is a new method of ring-opening polymerization that is particularly ame-

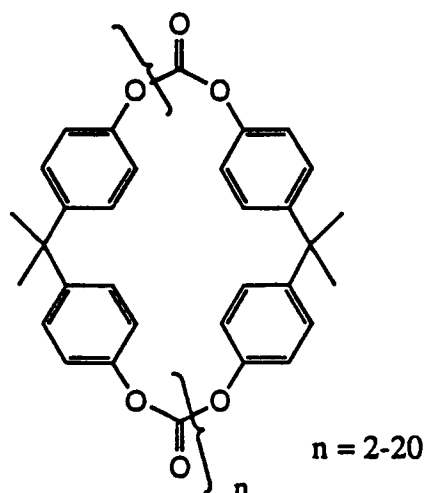


Figure 1 Cyclic oligomeric bisphenol A polycarbonates.

nable for fabrication and processing of polymer composites. No solvents are used in the process, reactive residues are not left in the polycarbonate resin, and polymerization does not occur until the sonic field is applied.

RESULTS AND DISCUSSION

A 20 kHz, 1" diameter titanium carbide-tipped Branson 184V probe generator (capable of 860 W of sonic output) was used to generate the sonic field. Typically, 2 g of BPA-cyclics were placed in a steel die (1.003" or 1.034" in diameter) that had been heated to 250°C. When the cyclics had melted, the tip was placed in the die in contact with the molten cyclics, and the sonic field applied. When the narrower diameter die was used, a pressure of at least 7 psi could be generated by allowing the probe to

stand freely on the molten cyclics. The wider diameter die did not allow any pressure to be applied as the material was forced out past the probe's tip when the sonic field was applied.

The results are outlined in Table I. In trials where some pressure could be applied to the molten cyclics, ultrasound alone effected polymerization of resin cyclics (entry 1). Very good molecular weights ($M_w = 88,000$) and high conversions to polymer were obtained. In the absence of applied pressure, polymerization did not occur. The polymerization also occurred in glass-filled preregs (entry 2), again leading to high conversions and high molecular weight.

To be certain that the ultrasound was responsible for polymerization, several control experiments were carried out. Treating the cyclics in an identical manner, without applying the ultrasound, did not cause polymerization of neat cyclics (entry 7). Some polymerization (34%) was observed in the glass-filled control (entry 8), and the polymer formed in the control case was of much lower molecular weight than when ultrasound was used. Glass is known to cause polymerization of cyclics without added initiator, but the extent of polymerization in the control demonstrates that the glass surface was not the primary initiator in the ultrasound experiment. Control experiments in acid-washed glassware or where the tungsten carbide tip of horn does not touch the molten cyclics show that ultrasonication is necessary for polymerization, and cyclics polymerization is not occurring because of contact with metal or carbide surfaces.

Inclusion of a chemical initiator in ultrasound-mediated polymerizations gave reaction rates significantly higher than those observed when the reaction was carried out with chemical initiators alone.

Table I Results of Ultrasound Polymerization^a

No.	Sample	P (psi)	t (min) ^b	M_w	M_{peak}	Polymer (%)
1	Cyclics	7	5	87700	84900	95
2	50% Cyclics/glass ^c	7	5	86600	84900	95
3	Cyclics/Li salicylate ^d	—	2	98100	95400	100
4	0.2 mol % Li sal/cyclics ^e	—	2	76300	83500	89
5	LiO ₂ CC ₆ H ₅ (Me ₂)OH/cyclics ^d	—	2	55000	52700	70
6	LiCl/cyclics ^d	—	2	48800	46500	52
7	Cyclics	7	0	—	—	0
8	50% Cyclics/glass ^c	7	0	42400	37500	34

^a Performed in steel die at 250°C.

^b Sonication time.

^c Glass preregs prepared by mixing slurried cyclics (in CH₂Cl₂) with E-glass fibers, then dried at 150°C for 24 h.

^d Added as powder to molten cyclics.

^e Initiator was solution dispersed.

The time needed to complete polymerization was reduced by at least a factor of seven in the case of lithium salicylate. Lithium chloride initiates polymerization only at temperatures above 300°C (the temperature at which BPA polycarbonates start to degrade) in the absence of ultrasound. However, a combination of LiCl and ultrasound allowed the polymerization to take place at significantly lower temperatures and much shorter time.

The mechanism by which ultrasound induces ring-opening polymerization is not known. Given the nature of the functional groups involved, the results seem inconsistent with a radical process. The ^1H NMR spectrum of the polymer prepared with ultrasound shows no significant crosslinking of the BPA methyl groups or substitution of the rings that might be expected from a radical process. The IR spectrum shows free phenol groups are present. The polymer was also readily soluble in chloroform, which suggests no crosslinking has occurred. Polymers are known to be degraded by shear forces created in solution by ultrasound. "Larger molecules are more resistant to flow, have larger shear forces, and rupture more easily than shorter macromolecules. Below a certain molecular weight, shear forces are smaller than bond strengths, and polymers cannot degrade."¹⁰ High molecular weight ($M_w = 200,000$) BPA-polycarbonate is degraded in chloroform solution to half the original molecular weight when exposed to high-power ultrasound in a little over 2 h.¹¹ However, commercial grades of LexanTM ($M_w \sim 55,000$) are not degraded by ultrasound under any conditions, nor was polymerization seen when a solution of BPA cyclics in *o*-dichlorobenzene was sonicated.¹¹ The higher viscosity of neat molten cyclics compared to *o*-dichlorobenzene may allow the generation of shear forces capable of rupturing the cyclics, and thus initiate polymerization. This seems unlikely since, as previously stated, polycarbonates of much higher molecular weight than the cyclic oligomers are not affected by ultrasound, and inconsistent with the high molecular weights obtained with ultrasound initiation. Cyclic carbonates are claimed to undergo polymerization at very high temperatures in the absence of added nucleophilic initiators. The localized extreme heating effects associated with ultrasound and cavitation may initiate the polymerization. The need to promote efficient cavitation explains the need for pressure to make polymerization of neat BPA cyclics occur. Another plausible hypothesis is that trace impurities, such as NaOH, Na_2CO_3 , or even NaCl left behind from the cyclization reaction, combine with ultrasound to initiate an anionic polymerization (as seen in entry 6 of Table I with LiCl and ultrasound). The

large entropy driving force of polymerization allows very low concentrations of chemical initiators to cause virtually complete conversion of the cyclic polycarbonates to linear polymer.^{8c} Ultrasound may be activating the normally torpid trace residues to react faster and at lower temperatures and to serve as initiators.

Other ring systems were examined to see if the ring-opening polymerization was a general reaction, but experimental difficulties precluded a fair evaluation. Cyclic oligomeric terephthalic esters do not polymerize, but the polymer fraction within the cyclics was degraded from 200,000 to 100,000 molecular weight. Caprolactam did not polymerize (pressure could not be applied to the reaction). Caprolactone did not polymerize (no pressure) nor did THF when ultrasound was applied to the neat liquid, but the addition of an acid catalyst caused ready polymerization. Hexamethylcyclotrisiloxane sublimed when sonicated.

In summary, a new ring-opening polymerization has been discovered. This method allows precise control of the polymerization because the initiation is independent of the processing conditions and can be applied upon demand. The polymerization proceeds rapidly with high conversion to give polymers of high molecular weight and without destabilizing residues remaining in the resin as with chemical initiators.

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