

# Two-Component Initiator Systems for the Ring-Opening Polymerization of Oligomeric Cyclic Bisphenol-A Carbonates. Studies with *In Situ* Generated Wittig Salts

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## SYNOPSIS

A two-component initiator system based on the *in situ* generation of Wittig salts (alkyltriarylphosphonium bromides) has been developed for the ring-opening polymerization of cyclic bisphenol-A (BPA) carbonate oligomers for potential use in composite applications so that the prepolymer can suitably wet the composite material before being converted to high molecular weight polymer. The Wittig salt precursors (an alkyl bromide, such as hexadecyl bromide, and a triarylphosphine, such as triphenylphosphine) did not independently initiate significant ring-opening polymerization of the oligomeric cyclic BPA carbonate mixture. However, when the two mixtures of cyclic BPA carbonate oligomers and initiator component were combined, a high molecular weight polymer ( $M_w = \sim 65,000$ ) was produced. The polymerization initiating species is thought to be hexadecyltriphenylphosphonium bromide. Consistent with this hypothesis is the observation that authentic Wittig salts did initiate ring-opening polymerization to provide high molecular weight polycarbonate. The effects of structure and concentration of the initiator components, reaction temperature, time, etc. on polymerization were studied; in general, the degree of polymerization ranged from 65 to 85%. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Considerable research has been carried out over the past few years with the objective of preparing commercially important thermoplastic bisphenol-A (BPA) polycarbonates via the ring-opening polymerization (ROP) of the corresponding low molecular weight cyclic oligomers.<sup>1</sup> A particularly important characteristic associated with the ROP of cyclic oligomeric BPA carbonates is the significantly lower melt viscosity of the cyclic oligomers ( $\sim 10^2$  poise at 250°C) compared to the melt viscosity of the derived polymer ( $\sim 10^5$  poise at 250°C). The relatively low melt viscosity profile of the cyclic oligomeric BPA carbonates offers the potential of utilizing polycarbonates in composite applications. Considering, for example, the pultrusion of composites, the use of thermoplastic polycarbonate as the laminating resin offers the important advantage of part post-

formability, which is not feasible with the highly cross-linked unsaturated polyester resins generally used currently. However, in order to take advantage of the low viscosity of the cyclic oligomeric BPA carbonates in composite applications, it is necessary to control precisely the timing of the initiation of the ROP; i.e., the relatively low viscosity oligomers should penetrate and wet the composite matrix before ROP to relatively high viscosity polymer begins. Thus, the choice of the ROP initiator system is of paramount importance.

It has previously been shown that ROP of cyclic oligomeric BPA carbonates may be initiated in the melt by numerous anionic systems, including phenyllithium, lithium phenoxide, lithium stearate, and tetrabutylammonium tetraphenylborate.<sup>2,3</sup> All of these "one-component" initiators bring about "instantaneous" ROP and thus do not provide for the control (delay) of polymerization required in composite applications. One approach to address this situation is to liberate or generate the initiator after the cyclic oligomers have penetrated the composite

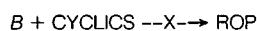
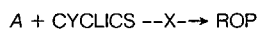
fibers. For example, Valance, Evans, and Kelly reported on the use of an initiator encapsulated in a polymer with a glass transition temperature high enough to prevent its release until the desired point in processing has been attained.<sup>4</sup> Similarly, Stewart discovered that while lithium phenylacetate is not basic enough to initiate ROP at modest temperatures (240°C), heating to slightly higher melt temperatures (280°C) resulted in a decarboxylation reaction to generate the strongly basic benzyl anion which did initiate rapid ROP.<sup>5</sup>

In this report, we present the results of an alternative approach to control the timing for initiation of ROP. We have endeavored to develop a two-component initiator system in which neither of the two components (*A* and *B*) would independently initiate significant ROP of the cyclic BPA carbonate oligomers. However, when combined together, *A* and *B* would react with each other to generate a third species (*C*), which would initiate the ROP of the cyclics (Scheme 1). Such a two-component initiator system should be ideally suited for pultrusion applications. Thus, two independent resin feed lines would deliver separate mixtures of the cyclic oligomeric BPA carbonates and one of the two initiator components to the impregnation/wetting zone of the pultrusion machine.<sup>6,7</sup>

## EXPERIMENTAL SECTION

### Materials

The preparation and purification of the cyclic BPA carbonate oligomers have been described previously.<sup>8</sup> Methyltriphenylphosphonium bromide, butyltriphenylphosphonium bromide, hexadecyltributylphosphonium bromide, hexadecyl bromide, octadecyl bromide, octadecyl chloride, hexadecyl fluoride, triphenylphosphine, *tris*-(4-methoxyphenyl)phosphine, *tris*-(4-chlorophenyl)phosphine, and butyl bromide were obtained from commercial sources and used as received. *Tris*-(4-fluorophenyl)phosphine was prepared and purified according to a literature procedure.<sup>9</sup> Butyl-*tris*-(4-fluorophenyl)phosphonium bromide (**1**) was prepared by heating a solution of *tris*-(4-fluorophenyl)phosphine and butyl bromide at reflux for 48 h; the precipitated **1** was isolated by vacuum filtration, washed with cold butyl bromide, and vacuum-dried to constant mass. The phosphorus-31 NMR spectrum (CDCl<sub>3</sub>) of the product exhibited essentially only one signal (24.48 ppm); there was no signal at 8.30 ppm attributable to the starting *tris*-(4-fluorophenyl)phosphine. Butyl-*tris*-(4-chloro-



**Scheme 1** Two-component initiator approach for ring-opening polymerization of cyclic oligomeric BPA carbonates.

phenyl)phosphonium bromide (**2**) was prepared from *tris*-(4-chlorophenyl)phosphine and butyl bromide and purified by the same procedure utilized for **1**. The phosphorus-31 NMR spectrum (CDCl<sub>3</sub>) of the product **2** displayed virtually only one signal (25.42 ppm); there was no signal at 7.76 ppm attributable to *tris*-(4-chlorophenyl)-phosphine. Concentrates of the cyclic oligomeric BPA carbonates and the various initiator reagents were prepared by dissolving known amounts of each material in methylene chloride, concentrating to dryness with a rotary evaporator, and then drying in a vacuum oven at ~ 70°C for 16 h. Appropriate quantities of these concentrates were then combined with pure cyclics so as to give 2.55 g (0.01 mol) of cyclics with the desired levels of initiator components. The resulting cyclics-initiator mixture was placed in a 100 mL round bottom flask, dissolved in ~ 30 mL of methylene chloride, rotovapped to dryness, and vacuum-dried in an oven (~ 70°C) for 16 h. Prior to conducting the ROP experiment, the mixture was thoroughly pulverized and mixed in the flask.

### Polymer Characterization

GPC analyses were performed with a Perkin Elmer 410 LC pump coupled with 3 Waters  $\mu$ -styrogel GPC columns (500, 1000, and 10,000 Å) and a variable wavelength UV detector set at 254 nm. All molecular weight values reported for the polycarbonate ROP products are relative to polystyrene.

### Polymerizations (General)

The 100 mL reaction flask containing the cyclics and initiator components was first connected to a vacuum line (~ 125 mm Hg); after about a minute, the flask was immersed in a molten salt bath (1 : 1 sodium nitrate and potassium nitrate) maintained at the desired temperature (typically 300°C). After the specified reaction time, the flask was removed from the molten salt bath and allowed to air-cool. After breaking the vacuum, about 30 mL of methylene chloride were added to dissolve the polymeric

material. After the solution was filtered through a cotton plug, a portion of the filtrate was pipetted into a Petri dish and the solvent was allowed to evaporate, leaving behind a cast film; another portion of the filtrate was analyzed by GPC. (Control experiments demonstrated that there was no difference between conducting the ROP under vacuum or at one atmosphere of pressure.)

### Polymerization of Cyclic Oligomeric BPA Carbonates with Butyltriphenylphosphonium Bromide

90 g of cyclic oligomeric BPA carbonates were placed in a Helicone Vertical Mixer (Atlantic Richfield model 4CV), with the oil temperature set at 300°C. After stirring for 16 min, a mixture of 0.79 g of butyltriphenylphosphonium bromide and 10 g of cyclics was added. Samples of the reaction mixture were taken after 15, 17, 25, and 30 min for GPC analyses: 15 min, 0% degree of polymerization (DOP); 17 min, 6% DOP ( $M_w = 76,654$ ;  $M_w/M_n = 1.20$ ); 25 min, 85% DOP ( $M_w = 55,872$ ;  $M_w/M_n = 1.99$ ); 30 min, 85% DOP ( $M_w = 55,322$ ;  $M_w/M_n = 2.01$ ).

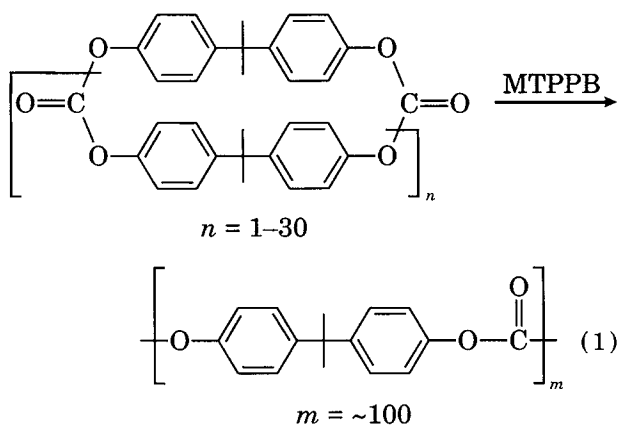
### Polymerization of Cyclic Oligomeric BPA Carbonates with Hexadecyltributylphosphonium Bromide

90 g of cyclic oligomeric BPA carbonates were placed in a Helicone Vertical Mixer (Atlantic Richfield model 4CV), with the oil temperature set at 300°C. After stirring for 10 min, a mixture of 1.0 g of hexadecyltributylphosphonium bromide and 10 g of cyclics was added. Samples of the reaction mixture were taken after 9, 11, 18, and 40 min for GPC analyses: 9 min, 0% DOP; 11 min, 93% DOP ( $M_w = 69,864$ ;  $M_w/M_n = 2.07$ ); 18 min, 94% DOP ( $M_w = 75,742$ ;  $M_w/M_n = 2.12$ ); 40 min, 94% DOP ( $M_w = 66,153$ ;  $M_w/M_n = 2.10$ ). Repetition of this experiment gave virtually identical results: 9 min, 0% DOP; 11 min, 93% DOP ( $M_w = 64,032$ ;  $M_w/M_n = 2.10$ ); 40 min, 93% DOP ( $M_w = 63,432$ ;  $M_w/M_n = 2.13$ ).

## RESULTS AND DISCUSSION

Previous work in our laboratory had suggested that several halides (e.g., sodium fluoride, chloride, and bromide) are capable of initiating the ROP of cyclic BPA-carbonate oligomers. Accordingly, we sought to develop an initiator system in which halide ions would be generated in situ. Investigating the reaction

of a tertiary phosphine (e.g., triphenylphosphine, TPP) and an alkyl halide (e.g., hexadecyl bromide, HDB) to generate the corresponding quaternary phosphonium bromide (i.e., a Wittig salt) in the presence of the cyclic BPA carbonate oligomers seemed like a good place to start.<sup>10</sup>



First, in order to find out if an authentic Wittig salt would initiate the ROP of cyclic BPA carbonate oligomers, the reaction shown in Eq. 1 was carried out. Thus, heating a mixture of cyclic BPA carbonate oligomers and 0.1 mol % methyltriphenylphosphonium bromide (MTPPB) at 300°C for 10 min provided the corresponding polycarbonate ( $M_w = 54,393$ ;  $M_w/M_n = 2.06$ ) in 75% yield. Subsequently, in a relatively large-scale ROP experiment (i.e., with 100 g of cyclics) carried out in a Helicone reactor at 300°C, an 85% conversion to polycarbonate ( $M_w = 55,872$ ;  $M_w/M_n = 1.99$ ) was achieved after 10 min with 0.5 mol % butyltriphenylphosphonium bromide as the initiator. It was also found that 0.5 mol % hexadecyltributylphosphonium bromide initiated the ROP of the oligomeric cyclic BPA carbonates such that a 93% degree of polymerization (DOP) to high molecular weight polycarbonate ( $M_w = 64,032$ ;  $M_w/M_n = 2.10$ ) was realized after just one minute of mixing in a Helicone reactor at 300°C. Clearly, a Wittig salt is capable of effectively initiating the ROP of cyclic BPA carbonate oligomers.

The next order of business was to ascertain if the precursors to a Wittig salt would, when admixed with the cyclic BPA carbonate oligomers, react with each other to form the corresponding Wittig salt which would then initiate ROP. In addition, it was important to establish the degree of stability of the cyclic oligomers to the individual precursors (HDB and TPP). To accomplish these objectives, the matrix of experiments summarized in Table I was carried out; in each case, the reaction mixtures were heated at  $\sim 300^\circ\text{C}$  for 30 min.

**Table I Results from ROP of Cyclic BPA Carbonate Oligomers With HDB/TPP<sup>a</sup>**

Exp	Mol % HDB	Polycarbonate Characteristics	A 0.0 mol % TPP	B 0.1 mol % TPP	C 0.2 mol % TPP	D 0.4 mol % TPP
1	0.0	Film appearance	Grainy	Cracked	Cracked	Cracked
		Film strength	—	—	—	—
		% PC	< 1	20	27	38
		$M_w$	—	14,907	18,202	29,107
		$M_w/M_n$	—	1.45	1.56	1.72
2	0.1	Film appearance	Grainy	Integral	Integral	Integral
		Film strength	—	Brittle	Tough	Tough
		% PC	< 1	56	62	62
		$M_w$	—	54,296	47,316	56,758
		$M_w/M_n$	—	1.93	1.95	1.99
3	0.2	Film appearance	Grainy	Integral	Integral	Integral
		Film strength	—	Tough	Tough	Tough
		% PC	< 1	68	68	66
		$M_w$	—	59,616	50,605	59,742
		$M_w/M_n$	—	2.00	2.00	2.00
4	0.4	Film appearance	Grainy	Integral	Integral	Integral
		Film strength	—	Tough	Tough	Tough
		% PC	~ 3	64	70	83
		$M_w$	—	58,509	49,777	60,313
		$M_w/M_n$	—	2.00	1.97	1.99

<sup>a</sup> For the polycarbonate characteristic film appearance: grainy, a noncontinuous film with numerous grains; cracked, a noncontinuous film with several cracks such that the entire film could not be removed from the Petri dish; integral, a continuous film that could usually be removed in its entirety from the Petri dish. For the polycarbonate characteristic film strength: brittle, the integral film cracked during attempted removal from the Petri dish; tough, the entire film was removed in its entirety from the Petri dish and that the film could be creased and repeatedly flexed back and forth without breaking. % PC, the GPC area percent polycarbonate relative to polycarbonate and oligomeric carbonate. Each of the experiments was carried out at ~ 300°C for 30 min.

Upon inspection of Table I, it is seen that cyclic BPA carbonate oligomers and HDB alone (at the 0.1–0.4 mol % level) did not independently initiate ROP; in each case (experiments 2A, 3A, and 4A), a grainy, nonintegral film was obtained when a methylene chloride solution of the reaction product was allowed to evaporate from a Petri dish. Such poor film-forming character was exactly like that exhibited by the cyclic BPA carbonate oligomers recovered in the control experiment (1A) in which the cyclic BPA carbonate oligomers were heated alone. The corresponding GPC results were in complete accord with these findings, generally showing less than 1% polymer formation. Thus, it was concluded that the cyclic BPA carbonate oligomers are virtually completely stable to up to at least 0.4 mol % HDB while being heated at 300°C for up to at least 30 min.

Similarly, it was found that the reaction products obtained from the mixtures of cyclic BPA carbonate oligomers and TPP alone (experiments 1B, 1C, and 1D) showed poor film-forming ability (i.e., cracked,

nonintegral films). According to the GPC results, however, some (20–38%) ROP to low molecular weight polycarbonate did occur. While not ideal, this situation should be manageable. Moreover, it was subsequently determined that conducting an ROP experiment with 0.2 mol % TPP for 30 min at a lower temperature (250°C) resulted in just 7% polycarbonate formation.

In contrast to the above-described results, each of the various combinations of HDB and TPP with cyclic BPA carbonate oligomers resulted in ROP such that clear, integral polycarbonate films could be cast from solution. Moreover, with but one exception (experiment 2B), each film was tough [i.e., capable of being creased and flexed back and forth numerous times (at least 10–20 times) without breaking], just like films cast from commercially manufactured polycarbonate. GPC analyses of these ROP products revealed that the degree of polymerization was 56–68% when relatively low levels of HDB and TPP were employed (i.e., ≤ 0.2 mol % of each component; experiments 2B, 2C, 3B, and 3C).

**Table II** Effect of Time on ROP of Cyclic BPA Carbonate Oligomers Initiated By HDB (0.2 mol %) and TPP (0.1 mol %) at 300°C

Exp	Time (min)	Polycarbonate Film Characteristics	$M_w$	$M_w/M_n$	PC (%)
5	05	Integral, tough	60,691	1.94	62
6	10	Integral, tough	67,751	1.99	68
7	15	Integral, tough	64,142	1.96	67
8	20	Integral, tough	66,745	1.99	70
9	30	Integral, tough	66,848	1.99	68

Significantly, the weight-average molecular weights of the polycarbonates were quite respectable, approximately 47,000–60,000. Similarly, combinations involving 0.4 mol % of either HDB or TPP (experiments 2D, 3D, 4B, and 4C) produced degrees of polymerization of 62–70% (with molecular weights of 51,000–60,000). And, when 0.4 mol % of both HDB and TPP were employed (experiment 4D), an 83% conversion to polycarbonate ( $M_w = 60,313$ ) was achieved. Clearly, the viability of the in situ generated Wittig salt as a two-component initiator system for the ROP of cyclic oligomeric BPA carbonates (Scheme 1) was demonstrated.

Having evaluated the effect of the levels of the Wittig salt precursors on the conversion of the cyclic oligomers to polycarbonate, it was deemed appropriate to examine the effects of several other parameters on the ring-opening polymerization. With regard to the effect of reaction time, it was found that the ROP of cyclic BPA carbonate oligomers with 0.2 mol % HDB and 0.1 mol % TPP at 300°C is a reasonably fast process, as illustrated in Table II. The maximum degree of polymerization (~ 68%) was accomplished between 5 and 10 min. Furthermore, there was no degradation of the molecular weight when the process time was extended up to at least 30 min.

With respect to the effect of reaction temperature, it was found that similar results were obtained when the ROP reactions (utilizing 0.2 mol % HDB and 0.1 mol % TPP) were conducted at 250, 300, and 330°C for 20 min, as shown in Table III. Thus, each

experiment afforded an integral, tough polycarbonate film; the  $M_w$  values ranged from 59,000 to 63,000. The DOP ranged from 64 to 68%.

The effect of structure of each of the two components of the initiator system was also examined. Thus, with respect to the structure of the alkyl halide, it was found that while hexadecyl bromide (HDB) worked reasonably well at the 0.1 mol % level (in combination with 0.1 mol % TPP), neither the analogous octadecyl chloride (ODC) nor hexadecyl fluoride (HDF) were effective. As indicated in Table IV, neither ODC nor HDF initiated satisfactory ROP of the cyclic BPA carbonate oligomers. That ODC and HDF were not as effective as HDB is consistent with previous results on the nucleophilic displacement of halides from alkyl halides by triphenylphosphine.<sup>10</sup>

With regard to the structure of the triarylphosphine, it was felt that its basicity should be very important from the perspective of maximizing the degree of ROP in the presence of HDB and minimizing ROP in the absence of HDB. Accordingly, we examined the use of *tris*-(4-methoxyphenyl)phosphine (TMPP), which has a  $pK_a$  of 4.6, and *tris*-(4-chlorophenyl)phosphine (TCPP), which has a  $pK_a$  of 1.0, in conjunction with HDB for the initiation of the ROP cyclic BPA carbonate oligomers. TPP, which has a  $pK_a$  of 2.7, was also used as a control. In each ROP experiment, 0.2 mol % of each initiator component was employed; the reactions were carried out for 5 or 10 min at 270°C. As shown in Table V, the pair of TMPP and HDB was a very effective

**Table III** Effect of Temperature on ROP of Cyclic BPA Carbonate Oligomers Initiated by HDB (0.2 mol %) and TPP (0.1 mol %) for 20 Min Reactions

Exp	Temp (°C)	Polycarbonate Film Characteristics	$M_w$	$M_w/M_n$	PC (%)
10	250	Integral, tough	61,336	1.94	64
11	300	Integral, tough	59,427	1.96	67
12	330	Integral, tough	63,211	1.97	68

**Table IV** Effect of Alkyl Halide Structure on ROP of Cyclic BPA Carbonate Oligomers Initiated by HDB, ODC, or HDF (0.1 mol %) and TPP (0.1 mol %) at 300°C for 10 or 20 Min Reaction Times

Exp	Alkyl Halide	Time (min)	Polycarbonate Film Characteristics	$M_w$	$M_w/M_n$	PC (%)
13	HDB	10	Integral, tough	61,467	2.00	63
14	HDB	20	Integral, tough	58,931	2.04	65
15	ODC	10	Cracked, brittle	—	—	—
16	ODC	20	Cracked, brittle	—	—	—
17	HDF	10	Grainy	—	—	—
18	HDF	20	Grainy	—	—	—

initiator system, producing 99% yields of high molecular weight polycarbonate (experiments 21 and 22). However, it was subsequently shown that TMPP was a very efficient ROP initiator even in the absence of HDB, with 90–94% yields of high molecular weight polycarbonate ( $M_w = 50,000$ – $61,000$ ) being obtained from reactions carried out for 30 min at temperatures of 240–300°C. In contrast, the pair of TCPP and HDB was not an effective initiator system (experiments 23 and 24). It is also mentioned that, not surprisingly, TCPP alone (even at the 1.0 mol % level) did not efficiently initiate the ROP [no polycarbonate being produced after 30 min at either 240 or 270°C and only 23% polycarbonate ( $M_w = 25,035$ ) being formed at 300°C]. Finally, it is pointed out that the TPP/HDB pair (experiments 19 and 20) performed as expected, based on previous results.

The Table V results pointed toward the use of a triarylphosphine having a  $pK_a$  between 1.0 and 2.7. Accordingly, *tris*-(4-fluorophenyl)phosphine (TFPP), which has a  $pK_a$  of 2.0, was prepared and examined. When TFPP (1.0 mol %) was admixed with cyclic BPA carbonate oligomers and heated at 275°C, no polycarbonate was produced after 10 min (and only a 20% conversion resulted after 30 min). Thus, as an-

anticipated, TFPP alone and cyclic BPA carbonate oligomers displayed greater stability toward ROP than the cyclics mixture and TPP alone. However, when the cyclic BPA carbonate oligomers were heated (at 275°C for 10–20 minutes) in the presence of 0.5 mol% of the two-component initiator pair of TFPP and octadecyl bromide (ODB), only 55–57% polycarbonate formation ( $M_w = 71,000$ – $74,000$ ) resulted.

That the relatively low conversion of cyclics to polymer was due to a sluggish reaction between TFPP and ODB (to generate the Wittig salt) rather than to a sluggish ring-opening reaction was determined by employing the analogous butyl-*tris*-(4-fluorophenyl)phosphonium bromide salt (**1**) as a one-component initiator. Thus, heating the cyclic BPA carbonate oligomers with 0.25 mol % **1** at 300°C for 30 min resulted in a 99% yield of high molecular weight polycarbonate ( $M_w = 84,840$ ). Similarly, heating the cyclic BPA carbonate oligomers with 0.25 mol % butyl-*tris*-(4-chlorophenyl)phosphonium bromide at 300°C for 10 min resulted in a 96% yield of high molecular weight polycarbonate ( $M_w = 62,084$ ). These results clearly demonstrated (again) that the corresponding Wittig salts are efficient initiators for the ROP of cyclic oligomeric BPA carbonates.

**Table V** Effect of Triarylphosphine Structure on ROP of Cyclic BPA Carbonate Oligomers Initiated by HDB (0.2 mol %) and TPP, TMPP, or TCPP (0.2 mol %) at 270°C for 5 or 10 Min Reaction Times

Exp	Triaryl-phosphine	Time (min)	Polycarbonate Film Characteristics	$M_w$	$M_w/M_n$	PC (%)
19	TPP	5	Integral, tough	68,957	1.99	65
20	TPP	10	Integral, tough	74,272	2.00	73
21	TMPP	5	Integral, tough	78,572	2.50	99
22	TMPP	10	Integral, tough	73,954	2.57	99
23	TCPP	5	Grainy	—	—	—
24	TCPP	10	Cracked	17,335	1.47	14

## CONCLUSIONS

We have succeeded in demonstrating that a novel, two-component initiator system based on the *in situ* generation of Wittig salts is viable for initiating the ring-opening polymerization of cyclic oligomeric BPA carbonates to afford high molecular weight polycarbonates. Accordingly, this two-component initiator system may have potential utility in composite applications, such as pultrusion [where separate feed lines would deliver independently each initiator component (admixed with the cyclic oligomeric BPA carbonate) to the impregnation zone of the pultruder] so as to allow good wetting of the composite fibers before ROP commences.<sup>11</sup> The best two-component system identified (thus far) is triphenylphosphine and either hexadecyl or octadecyl bromide. This system initiates ROP such that a good conversion ( $\sim 75\%$ ) to high molecular weight polycarbonate ( $\sim 60,000 M_w$ ) is achieved within 5–10 min at process temperatures of about 300°C. Moreover, the fact that integral, tough films were obtained with the polycarbonate produced via the two-component *in situ* generated Wittig salts suggests the suitability of the polycarbonate for composite applications.<sup>12</sup>

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