

Two-Component Initiator Systems for the Ring-Opening Polymerization of Oligomeric Cyclic Bisphenol-A Carbonates: The *In Situ* Cleavage of Disulfides by Triarylphosphines

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ABSTRACT: A two-component initiator system based on the *in situ* cleavage of phenyl disulfide by a triarylphosphine has been developed for the ring-opening polymerization of cyclic bisphenol-A (BPA) carbonate oligomers. This development has potential use in composite applications such that the prepolymer can suitably wet the composite material *before* being converted to high-molecular-weight polymer. The initiator precursors (phenyl disulfide and triphenylphosphine) do not independently initiate significant ring-opening polymerization of the oligomeric cyclic BPA carbonate mixture. A mixture of cyclic BPA carbonate oligomers and one of the initiator components (phenyl disulfide), combined and heated at 300°C with a mixture of the cyclics and the other initiator component (triphenylphosphine), does produce a high-molecular-weight polymer ($M_w = \sim 70,000$). The polymerization-initiating species is thought to be thiophenyltriphenylphosphonium thiophenoxide. The effects of concentration of the initiator components, reaction temperature, time, and so forth on polymerization were studied; in general, the degree of polymerization ranged from about 65 to 75%. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2251–2255, 1997

Key words: two-component initiator; ring-opening polymerization; cyclic bisphenol-A carbonates; phenyl disulfide; triphenylphosphine

INTRODUCTION

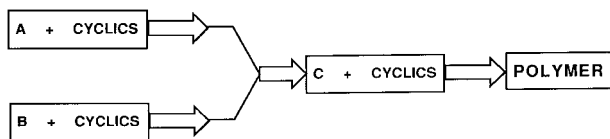
In certain composite applications (such as pultrusion), the use of *thermoplastic* bisphenol-A (BPA) polycarbonate as the laminating resin for the fibrous matrix may offer particular advantages compared with the *thermoset* polyesters currently utilized extensively.¹ For example, the BPA polycarbonates, because of their thermoplastic nature, would permit the postformability of the pultruded parts. Because of the very high melt viscosity ($\sim 10^5$ poise at 250°C) of BPA polycarbonates

(which essentially precludes their facile impregnation of the composite matrix), their direct use in composite applications has not been realized. This problem is potentially resolvable by the use of the cyclic BPA carbonate oligomers, which have relatively low melt viscosity ($\sim 10^2$ poise at 250°C).² It can reasonably be expected that the cyclic BPA carbonate oligomers will first penetrate and wet the composite fibers and then, after suitable initiation, undergo ring-opening polymerization (ROP) to give high-molecular-weight polycarbonate.^{3–5}

Considerable research has been carried out over the past few years with the objective of preparing commercially important thermoplastic BPA polycarbonates via the ROP of the corresponding

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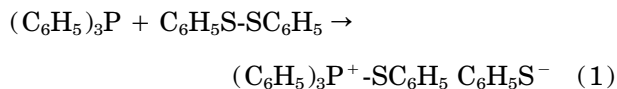
Scheme 1 Two-component initiator approach for ring-opening polymerization of cyclic oligomeric BPA carbonates. Neither A nor B independently initiates ROP, but they react with each other to form C, which does initiate ROP.

low-molecular-weight cyclic oligomers.² In order to take advantage of the low viscosity of the cyclic oligomeric BPA carbonates, particularly in composite applications, it is necessary to control precisely the timing of the initiation of the ROP, that is, 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 tetrphenylborate.^{3–5} 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.

An approach to address this situation is to liberate or generate the initiator after the cyclic oligomers have penetrated the composite fibers. For example, Valence et al. 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.⁶ Similarly, Stewart discovered that while lithium phenylacetate is not basic enough to initiate ROP at modest temperatures ($\sim 240^\circ\text{C}$), heating to slightly higher processing temperatures ($\sim 280^\circ\text{C}$) resulted in a decarboxylation reaction to generate the strongly basic benzyl anion, which did initiate rapid ROP.⁷ Also, in a previous report from this laboratory, a novel two-component initiator system based on the *in situ* generation of alkyltriphenylphosphonium bromides (Wittig salts) via the nucleophilic displacement reaction of an alkyl bromide (such as hexadecyl bromide) and a triarylphosphine (such as triphenylphosphine) for control of the timing for initiation of ROP of cyclic oligomeric BPA carbonates was described (see Scheme 1).^{8,9} Thus, it was found that while neither of the two

individual components (A, for example, an alkyl bromide, and B, for example, a triarylphosphine) would independently initiate significant ROP of the cyclic BPA carbonate oligomers, when combined together, A and B would react with each other to generate a third species (C, that is, an alkyltriphenylphosphonium bromide), which would initiate the ROP of the cyclics. Such a two-component initiator system should be ideally suited for pultrusion applications. For example, 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.^{10,11}

In a subsequent study, we investigated an alternative two-component system based on the cleavage of an aryl disulfide (phenyl disulfide, PDS) by a triarylphosphine (triphenylphosphine, TPP) to generate the corresponding thioaryltriarylphosphonium aryl thiolate [eq. (1)] to initiate the ROP of cyclic BPA carbonate oligomers.¹² The results of that study are presented here.



EXPERIMENTAL

Materials

The preparation and purification of the cyclic BPA carbonate oligomers have been described previously.¹³ PDS and TPP were obtained from Aldrich Chemical Company (Milwaukee, WI) and used as received. Concentrates of the cyclic oligomeric BPA carbonates and the particular 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 $\sim 70^\circ\text{C}$ 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 ($\sim 70^\circ\text{C}$) for 16 h. Before the ROP experiment was conducted, 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 three Waters μ -styrogel GPC columns (500, 1,000, and 10,000 Å) and a variable-wavelength ultraviolet detector set at 254 nm. All molecular-weight values reported for the polycarbonate ROP products are relative to polystyrene standards.

Small-Scale Ring-Opening Polymerization of Cyclic Oligomeric BPA Carbonates Initiated by PDS and TPP (Experiments 1–23)

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 the vacuum was broken, about 30 mL of methylene chloride was 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 nitrogen pressure.) The pertinent results are collected in Table I.

Large-Scale Ring-Opening Polymerization of Cyclic Oligomeric BPA Carbonates Initiated by PDS and TPP (Experiment 24)

In a Helicone Vertical Mixer (Atlantic Richfield model 4CV), with the oil temperature set at 300°C, was placed 90 g of cyclic oligomeric BPA carbonates; after stirring for 10 min, a mixture of 1.70 g of PDS, 2.05 g of TPP, and 10 g of cyclics was added. Samples of the reaction mixture were taken after 15, 20, 25, 30, 35, and 40 min for GPC analyses; the relevant results are presented in Table II.

RESULTS AND DISCUSSION

The initial set of experiments carried out with the TPP and PDS initiator components revealed that

neither of the initiator components independently initiated significant ROP (Table I, experiments 1 and 2). Heating a mixture of cyclic oligomeric BPA carbonates (**1**) containing 0.26 mol % PDS at 300°C for 30 min resulted in virtually no ROP. The “film” cast from the methylene chloride solution of the reaction product was uniformly grainy, just like the “film” obtained from the starting cyclics (after having been heated at 300°C for 30 min). Similarly, heating a mixture of **1** and 0.23 mol % TPP resulted in a poor ROP reaction. The cast “film” was highly cracked (although generally clear). GPC analysis of the ROP product indicated that the degree of polymerization was 26%; the weight-average molecular weight of the polymer was 16,700 ($M_w/M_n = 1.56$). In contrast, however (experiment 3), heating **1** containing both TPP (0.31 mol %) and PDS (0.33 mol %) resulted in an 81% conversion to high-molecular-weight polycarbonate ($M_w = 72,700$; $M_w/M_n = 2.27$). Clearly, the PDS/TPP system functions as a potentially viable two-component initiator system. Accordingly, several other experiments were carried out to gain further insight of the utility of this system.

The effect of reaction time was indicated by carrying out the ROP of **1** with 0.2 mol % of both PDS and TPP at 300°C from 5 to 30 min (experiments 4–8). It was observed that the maximum degree of polymerization (72%) was reached after about 10 min, a value similar to that found for the *in situ* generated Wittig salts.⁶

The effect of reaction temperature (experiments 6, 9, and 10) was determined by conducting the ROP of **1** with 0.2 mol % of both PDS and TPP for 10 min at 270, 300, and 320°C. It was found that while 270°C was clearly not sufficient (an oligomer-to-polymer conversion of only 14% being realized), 320°C was essentially as effective as 300°C, the respective cyclics-to-polymer conversion values being 68 and 72%. However, as suggested by considering experiments 11, 12, and 13, at 320°C, a shorter time (7.5 min) could be utilized than at 300°C (10 min), even with a slightly lower initiator level (0.15 mol %).

With regard to the effect of the level of the initiator components (experiments 12 through 20), it was ascertained that while 0.05 mol % of each component was not sufficient to effect satisfactory ROP within 20 min at 300°C, the use of 0.10 mol % of both PDS and TPP did give high-molecular-weight polycarbonate ($M_w = 82,700$) after 20 min of reaction time at 300°C. By utilizing 0.20 mol % of each initiator component, high-

Table I Small-Scale ROP of Cyclic BPA Oligomeric Carbonates Initiated by *In Situ* Cleavage of PDS by TPP

Experiment No.	PDS (mol %)	TPP (mol %)	Temperature (°C)	Time (min)	Polycarbonate Film Characteristics	M_w	M_w/M_n	PC (%)
01	0.23	0.00	300	30	Grainy	—	—	—
02	0.00	0.26	300	30	Clear, cracked, brittle	16,700	1.56	26
03	0.33	0.31	300	30	Clear, integral, tough	72,700	1.94	81
04	0.20	0.20	300	5	Grainy	—	—	—
05	0.20	0.20	300	7.5	Clear, integral, brittle	46,100	2.36	46
06	0.20	0.20	300	10	Clear, integral, tough	68,200	1.74	72
07	0.20	0.20	300	15	Clear, integral, tough	62,400	2.37	57
08	0.20	0.20	300	30	Clear, integral, tough	64,200	2.35	66
09	0.20	0.20	270	10	Clear, cracked, brittle	13,600	1.30	14
10	0.20	0.20	320	10	Clear, integral, tough	66,400	2.28	68
11	0.15	0.15	300	10	Clear, integral, tough	58,800	1.90	63
12	0.15	0.15	320	5	Clear, cracked, brittle	—	—	—
13	0.15	0.15	320	7.5	Clear, integral, tough	59,700	1.96	61
14	0.05	0.05	300	10	Clear, cracked, brittle	18,600	1.41	19
15	0.05	0.05	300	20	Clear, integral, brittle	40,000	1.83	34
16	0.10	0.10	300	10	Clear, cracked, brittle	28,100	1.60	26
17	0.10	0.10	300	20	Clear, integral, tough	82,700	2.28	70
18	0.20	0.20	300	10	Clear, integral, tough	75,200	2.25	63
19	0.20	0.20	300	20	Clear, integral, tough	93,100	2.34	74
20	0.40	0.10	300	10	Clear, integral, tough	74,400	2.09	65
21	0.20	0.20	300	10	Clear, integral, tough	65,400	2.09	61
22	0.20	0.20	300	10	Clear, integral, tough	76,500	2.18	62
23	0.20	0.20	300	10	Clear, integral, tough	87,200	2.18	76

For the polycarbonate (PC) film characteristics, *grainy* indicates a noncontinuous film with numerous grains; *cracked* indicates a noncontinuous film with several cracks such that the entire film could not be removed from the Petri dish; *integral* indicates a continuous film that could always be removed in its entirety from the Petri dish; *brittle* indicates that the film cracked during attempted removal from the Petri dish; *tough* indicates that the 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.

molecular-weight polycarbonate (affording a clear, integral, tough film) was produced after just 10 min at 300°C. Finally, it is noted that by using 0.4 mol % of PDS and 0.1 mol % TPP, high-molecular-weight polycarbonate ($M_w = 74,400$) was generated after only 10 min at 300°C.

To evaluate the reproducibility for the ROP of **1**

by the PDS/TPP two-component initiator system, experiment 19 was carried out three additional times (experiments 21–23). The results show that the conversions to polycarbonate ranged from 61 to 76%, and the weight-average molecular weight ranged from 65,000 to 87,000. Thus, there was substantial batch-to-batch variability in the

Table II Large-Scale ROP at 300°C of Cyclic BPA Oligomeric Carbonates Initiated by *In Situ* Cleavage of PDS by TPP (Experiment 24)

Time (min) ^a	Polycarbonate (%)	M_w	M_w/M_n
15	61	59,600	1.97
20	84	61,800	2.36
25	79	68,200	2.02
30	73	72,100	2.04
35	77	64,400	2.19
40	85	67,000	2.07

^a Time includes the 10 min of heating before the addition of the mixture of **1** and the initiator components PDS and TPP.

ROP initiated by the PDS/TPP system. Nonetheless, in each case, a clear, integral, tough film was obtained from the methylene chloride solutions of the reaction products.

Finally, a relatively large-scale ROP reaction (experiment 24) was carried out in which 0.2 mol % of both PDS and TPP were utilized; Table II gives the results. The ROP was essentially complete within 10–15 min after the initiator components (admixed with a portion of the cyclic carbonate oligomers) were added to the bulk of **1**. The cyclics-to-polymer conversion remained at ~ 80% during the latter 25 min of the 30-min run. Significantly, on the basis of the molecular-weight measurements, the polycarbonate produced was stable to 300°C for at least 30 min.

The fact that the conversion of cyclic oligomers to polycarbonate generally did not proceed beyond 70–75% with the PDS/TPP two-component initiator system is an item of some concern. It is noted that a similar situation was obtained with the two-component *in situ* Wittig initiator system.⁸ Efforts to increase the cyclics' oligomer-to-polymer conversion in that system by using a second addition of the initiator components were not successful. At this time, we do not have a satisfactory explanation to rationalize why the reaction does not proceed beyond 70–75%.

CONCLUSION

We have demonstrated that the *in situ* cleavage of PDS by TPP [to presumably generate thiophenyltriphenylphosphonium thiophenoxide, eq. (1)] is a viable alternative to the *in situ* generation of Wittig salts for a two-component initiator system for the ROP of cyclic oligomeric BPA carbonates.^{14,15} The PDS/TPP system initiates the ROP such that a good conversion (up to ~ 80%) of the cyclic oligomer to high-molecular-weight polycarbonate (~ 65,000 M_w) is accomplished with a

short reaction time (~ 10 min) at a process temperature of about 300°C. Furthermore, integral, tough films were obtained with the polycarbonate produced via the PDS/TPP two-component initiator system (in spite of the incomplete conversion), which suggests the suitability of the polycarbonate for composite applications.

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