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Polycarbonate networks. 1. Synthesis and characterization of vinylphenylcarbonate terminated oligomers

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Abstract

Vinylphenylcarbonate terminated oligocarbonates were synthesized with number average molecular weights ranging from 1.5 to 10 kg/mol. The oligomers were synthesized by the addition of the hydrolysis products of 4-acetoxystyrene into a bisphenol A and phosgene interfacial polymerization reaction. Good molecular weight control was obtained. The functional oligomers were characterized by differential scanning calorimetry (DSC) and were found to have glass transition temperatures (T_g) that reflected the molecular weight of the oligomers and to undergo an exothermic cure reaction at temperatures that depended on the molecular weight of the oligomers. The cure of the oligomers into insoluble networks was observed after DSC measurements by solubility tests, and the T_g was observed to increase upon a second heat to reflect the high molecular weight polycarbonate obtained after cure. Thermogravimetric analysis (TGA) of the polymers showed an increase in the temperature for 5% weight loss with a decrease in molecular weight of the functional oligomers. © 2002 Published by Elsevier Science Ltd.

Keywords: Polycarbonate; 4-Acetoxystyrene; Network

1. Introduction

The properties of thermoplastic materials can be altered by their incorporation into three dimensional networks through the synthesis and subsequent curing reaction of functional polymers. The formation of such thermosets results in materials with improved solvent resistance and increased dimensional stability, but usually with increased brittleness as well. Since bisphenol A polycarbonate is known to be a very tough homopolymer, its incorporation into a network structure may allow retention of this property. While polycarbonate networks have been investigated numerous times, utilizing many different reactive groups, very little information has been published outside of the patent literature.

Many different reactive groups have been incorporated into aromatic polycarbonates, either along the backbone or more commonly at the chain termini. The types of reactive functionalities of interest are those which yield no byproducts during the crosslinking reaction. The first such reactive polycarbonate was synthesized by the incorporation of 2,2-bis(3-allyl-4-hydroxyphenyl)propane (diallyl bisphenol A) into bisphenol A polycarbonates [1,2]. This method was investigated further by Kolesnikov et al. in the late 1960s [3]. Amounts of up to 20 mol% diallyl bisphenol A were incorporated into the copolymer along with bisphenol A. Films were observed to partially crosslink when heated above 200 °C for 5–10 h in air, becoming 20–50% insoluble in chloroform. Acceleration with azobisisobutyronitrile (AIBN) yielded a completely insoluble network from the 20 mol% copolymer.

The incorporation of allyl groups at the chain ends has also been reported in the patent literature [4–6], where the allyl group was derived from allyl phenol, allyl chloroformate, allyl isocyanate, or allyl alcohol.

Cyanate terminated polycarbonates have recently been reinvestigated [7], after first being reported in a 1975 patent [8]. In both references, cyanogen bromide was reacted with phenol terminated polycarbonate oligomers to produce the desired reactive group. Curing above 200 °C resulted in

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reported triazene ring crosslinked networks with high insoluble fractions.

Other typical reactive end groups have been incorporated such as (meth)acrylate [9–13], benzocyclobutene [14,15], ethynyl [16], nadimide [17,18], maleimide [18,19], and maleimide derivatives such as dimethylmaleimide [20] and dichloromaleimide [21], with varied results when curing these materials into network structures. In fact, the objective of some of the research has been to synthesize oligomers, where only some of the chain ends are terminated with reactive functional groups so that branching occurs without crosslinking [13,15,16].

Phenol terminated oligomers and their reaction with diepoxides has also been investigated. Modified epoxy networks have been synthesized by the reaction of phenol terminated polycarbonate oligomers with diepoxides [22, 23]. Similar materials have also been synthesized by the in situ reaction of epoxides with phenol terminated oligomers produced from the ring opening of cyclic carbonates in the presence of linear polycarbonate [24]. A side reaction between the aromatic carbonate and the epoxide ring was found to occur in these reactions [23]. This side reaction alters the structure of the polycarbonate, yielding a highly crosslinked material containing phenoxy type linkages crosslinked with carbonate units. Due to this reaction, it is difficult to form epoxide terminated aromatic polycarbonate oligomers by the reaction of excess epoxide with phenol terminated polycarbonates, or well defined networks from them.

Isopropenylphenyl and vinylphenyl groups are recent additions as reactive terminal groups for crosslinking polycarbonates. The incorporation of isopropenylphenyl groups was studied by the addition of 4- or 3-isopropenylphenol, or derivatives, into a typical interfacial polycarbonate reaction [25–27]. This end group does not necessarily lead to highly crosslinked species, as soluble block copolymers were reportedly obtained from the reaction with styrene in the presence of dicumyl peroxide [28]. Vinylphenyl groups on the other hand do lead to highly crosslinked materials as reported by Knauss et al. [29,30] in earlier preliminary publications. This end group has been placed at the chain ends of carbonate oligomers by the introduction of 4-vinylphenolate [29,30], or as described in a patent, by the introduction of 4-vinylbenzoate [31] into typical polymerization reactions.

This series of papers describes in greater detail than previously [29,30], the synthesis and characterization of functionalized oligomers obtained from 4-vinylphenolate and the resulting networks obtained by thermal curing. The research was expected to lead to a convenient method for the synthesis of curable polycarbonate resins. The use of 4-acetoxystyrene as a source of 4-vinylphenolate was anticipated to be advantageous because it is readily available and stable, and the synthesis of the functional oligomers could be done with minimal modification of existing commercial processes. The resulting vinylphenylcarbonate terminal groups were expected to thermally cure under conditions suitable for convenient processing into insoluble networks that should show improved solvent resistance over thermoplastic polycarbonate.

2. Experimental

The following solvents were used as received from Fisher Scientific: methylene chloride (HPLC grade), chloroform, methanol. Reagents were obtained from Aldrich Chemical and used as received unless otherwise noted. Bisphenol A was received as monomer grade Dow Parabis from Dow Chemical and used without further purification. Phosgene was obtained in 1 or 5 lb cylinders from Matheson. The reagent was dispensed from the cylinder as a gas. The amount dispensed was measured by monitoring the gas flow through a calibrated teflon flow meter. Triethylamine was refluxed over pulverized calcium hydride for 24 h and then distilled under argon and stored over molecular sieves. One hundred grams of 4-hydroxybenzaldehyde was recrystallized from 290 ml of toluene and dried at 50 °C for 24 h at 1 mm Hg.

2.1. 4-Acetoxystyrene

4-Acetoxystyrene was synthesized by the following procedure: methyltriphenylphosphonium bromide (198.30 g, 0.56 mol) was added to an oven dried, 3 neck, 2000 ml round bottom flask equipped with a mechanical stirrer and condenser. The flask was flame dried under argon purge. Potassium *t*-butoxide (112.22 g, 1.00 mol) was added and 750 ml THF was transferred via cannula while cooling with an ice bath. A dry addition funnel containing 4-hydroxybenzaldehyde (45.18 g, 0.37 mol) was attached and the solid was dissolved in 150 ml THF. The solution was added dropwise to the yellow ylide solution while the resulting exotherm was controlled by the ice bath. The reaction mixture stirred for 36 h under positive argon pressure. The reaction was stopped by the addition of 100 ml water. Four hundred milliliters of ether was added and the product was extracted with water. The combined water extracts were back extracted with methylene chloride to yield a yellow aqueous layer. The aqueous layer contained the potassium phenolate of 4-hydroxystyrene. This was placed in a 1000 ml Erlenmeyer flask and acetic anhydride (141 ml, 1.50 mol) was added while stirring with a magnetic stir bar. The organic layer quickly separated. After 1 h, the product was extracted with ether and washed with water. The ether was removed by rotary evaporation, and the orange oil was distilled under reduced pressure (67 °C/0.3 mm Hg) leaving behind 10 ml of dark liquid. The colorless product was redistilled from 0.5 g phenothiazene to yield 45.06 g (75% yield) of colorless oil which crystallized upon storage at -10 °C.

2.2. Bis(4-vinylphenyl) carbonate

An aqueous solution of the potassium phenolate of 4-hydroxystyrene was prepared and isolated as described above from 4-hydroxybenzaldehyde (15.00 g, 0.123 mol), methyltriphenylphosphonium bromide (64.50 g, 0.181 mol), and potassium *t*-butoxide (43.0 g, 0.38 mol). The aqueous solution was subjected to interfacial phosgenation in 100 ml of methylene chloride with triethylamine (2.74 ml, 0.02 mol) as catalyst. Phosgene was added until the pH of the mixture dropped to 9.5. The methylene chloride layer was separated, washed twice with 0.5 M HCl, and four times with water. The methylene chloride was then stripped by rotary evaporation and the resulting slightly yellow crystals were recrystallized from 80 ml of 90% ethanol to yield 11.78 g (72% yield) of white crystals, melting point, 87.5–88.5 °C. Elemental analysis calculated for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 75.59; H, 5.35.

2.3. Potassium-4-vinylphenolate

(a) 4-Acetoxystyrene (6.244 g, 38.5 mmol) was added to a vial along with 70 ml of a 1.5 M KOH (0.105 mol KOH) solution and a magnetic stir bar. The mixture was purged with argon and heated to 35–40 °C with vigorous stirring. Within 30 min, the interfacial mixture became homogeneous. Stirring continued at this temperature for a total of 1 h.

(b) Potassium 4-vinylphenolate could also be prepared from bis(4-vinylphenyl) carbonate (5.126 g, 19.3 mmol) by cleavage in an interfacial mixture of 50 ml of methylene chloride and 80 ml of 1.5 M KOH. The interfacial mixture was refluxed for 5 h under positive argon pressure to obtain 100% cleavage to the phenolate.

2.4. Synthesis of vinylphenyl terminated polycarbonate oligomers

Vinylphenylcarbonate terminated polycarbonate oligomers of different molecular weights were synthesized by two different procedures. Each procedure is described below for a $\langle M_n \rangle \approx 5.0$ kg/mol sample. Adjustment of the stoichiometry using Eqs. (1) and (2) was done in order to synthesize other molecular weight samples.

2.5. Conventional route to polycarbonate oligomers (Method A)

Bisphenol A (90.00 g, 0.394 mol) was added to a 5 neck, 2000 ml reaction flask along with 500 ml of water, 79 ml of 10 M NaOH, and 600 ml of methylene chloride. The potassium 4-vinylphenolate solution prepared by hydrolysis of 4-acetoxystyrene was then added to the interfacial mixture followed by triethylamine (8.8 ml, 63 mmol). Phosgene (78 g, 0.78 mol) was introduced to the rapidly stirred mixture through a teflon tube below the liquid surface at the rate of 0.65 g/min for 120 min while maintaining the pH at 10.5–11.0 by the metered addition of 10 M NaOH. The mixture was then purged with argon and the polymer solution was separated from the aqueous layer. The methylene chloride layer was washed twice with 0.5 M HCl and five times with water. The methylene chloride was then flashed off by slowly adding the solution to rapidly stirred boiling water in a Waring commercial blender. The polymer powder was filtered and dried at 60 °C under vacuum to yield 97.11 g (96%).

2.6. Chloroformate route to polycarbonate oligomers (Method B)

Bisphenol A (90.00 g, 0.394 mol) was added to the 5 neck, 2000 ml reaction flask. 600 ml water and 79 ml of 10 M NaOH were added, and the mixture was stirred while purging with argon until the bisphenolate was formed (as indicated by dissolution of the bisphenol A) and the resulting pH was approximately 11.6. Methylene chloride (360 ml) was then added. Phosgene (78 g, 0.79 mol) was introduced into the flask at the rate of 1.0 g/min for 78 min while stirring vigorously. As phosgene was added the pH slowly decreased, but was maintained at 9.5 by the dropwise addition of 10 M NaOH. The reaction mixture was purged with argon for 10 min to displace unreacted phosgene. At this time an aliquot was removed for analysis. The potassium 4-vinylphenolate solution prepared from hydrolysis of 4-acetoxystyrene was then added to the mixture and washed in with 100 ml of water and 240 ml of methylene chloride. The pH was adjusted to 11.0 and triethylamine (8.8 ml, 63 mmol) was added to the rapidly stirred mixture. The pH immediately began to drop and was adjusted to 11.0 by the slow addition of 10 M NaOH. The mixture was stirred for 1 h, after which phosgene was introduced at the rate of 0.55 g/min for 30 min while maintaining the pH at 11.0 to complete the reaction. The reaction mixture was purged with argon for 15 min, and the layers were then separated. The polymer solution was worked up and isolated as above. The isolated white polymer powder was dried for 12 h at 60 °C and a reduced pressure of 1 mm Hg to yield 96.32 g (95% yield).

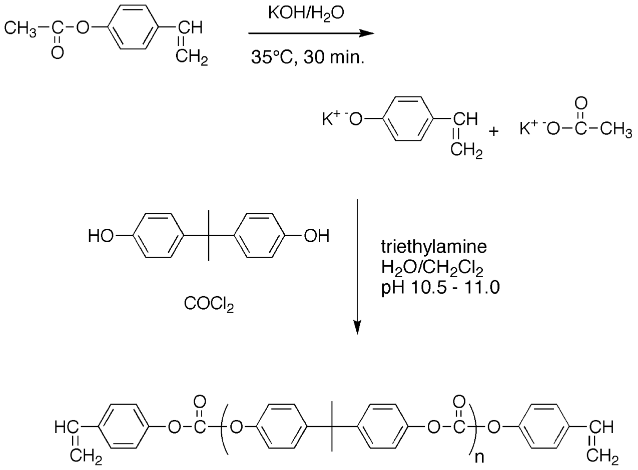
2.7. Characterization

Intrinsic viscosities $[\eta]$ were measured in chloroform at 25 °C with a size 50 Cannon-Ubbelohde viscometer. Oligomers were characterized by GPC using a Waters 150 GPC instrument equipped with a differential refractive index detector and chloroform as elution solvent. Molecular weights were determined relative to polystyrene standards. Samples were measured at a flow rate of 1.0 ml/min and a temperature of 30 °C. Solution ^1H NMR spectra were measured on a Varian 400 MHz instrument in $CDCl_3$. The average number of bisphenol A repeat units between end groups was obtained from the ^1H NMR spectra by measuring the ratio of the normalized vinyl proton resonances to that of the normalized isopropylidene proton resonances. Normalization was accomplished by dividing by the number of respective protons for that resonance. The integrated values for the vinyl protons at 5.22 ppm divided by 2 were compared to the integration values for the isopropylidine methyl protons at 1.68 ppm divided by 6. Multiplying by 254.29 g/mol, the molecular weight of the polycarbonate repeat unit, gave the $\langle M_n \rangle$ between end groups. The total $\langle M_n \rangle$ was determined by adding 266.30 g/mol. Similarly the $\langle M_n \rangle$ for *t*-butylphenyl terminated polycarbonates could be found by replacing the value of the integrated vinyl protons with those of the normalized (18 *t*-butyl protons) *t*-butyl protons at 1.32 ppm. Glass transition temperatures (T_g) and cure temperatures were determined with a Perkin Elmer Series 7 DSC. Samples were either powder or films contained in sealed aluminum pans. Measurements were made from 30 to 250–400 °C at a scanning rate of 10 °C/min under nitrogen. Second and third scans were performed on some samples by heating to the desired temperature in the previous scan and quench cooling to room temperature before reanalysis. Thermal stabilities and char yields were determined by thermogravimetric analysis (TGA) on a Perkin Elmer Series 7 instrument. A heating rate of 10 °C/ min in an air atmosphere was used to analyze samples. Samples were measured to a temperature greater than 750 °C to determine the residual char at elevated temperatures. The temperature at which 5% of the initial weight had been lost was compared for different samples to determine relative thermal stabilities.

3. Results and discussion

The objective of this research was to synthesize low molecular weight polycarbonate oligomers with styrene-like end groups. This could be accomplished by the addition of vinylphenol to conventional interfacial polycarbonate reactions to form vinylphenylcarbonate terminal groups. The vinylphenylcarbonate capped oligomers were expected to react in a similar fashion to styrene at elevated temperature, resulting in highly crosslinked network structures with improved solvent resistance properties compared to linear polycarbonate.

Unfortunately, 4-vinylphenol is an unstable compound that is known to undergo spontaneous polymerization [32–34]. The compound is so unstable that uncontrolled polymerization is found to occur in the solid state in the presence of free radical inhibitors [34]. An alternative source of this simple compound was required for this to be an attractive method of vinyl-functional polycarbonate synthesis. Stable precursors to 4-vinylphenol were obtained that could be conveniently hydrolyzed under basic conditions to the phenolate of 4-vinylphenol prior to polymerization.



Scheme 1. Synthesis of vinylphenylcarbonate terminated polycarbonates.

3.1. Synthesis of oligomers

4-Vinylphenyl carbonate terminated polycarbonate oligomers were synthesized from bisphenol A, phosgene, and 4-vinylphenol as generally demonstrated in Scheme 1.

The 4-vinylphenol, or more correctly the potassium phenolate of 4-vinylphenol, could be obtained by the facile hydrolytic cleavage of 4-acetoxystyrene [35] or bis(4-vinylphenyl) carbonate prior to polymerization. The benefit of these compounds is that they are both stable materials which can be purified and stored for extended periods of time, circumventing the problems associated with the instability of 4-vinylphenol. Commercially available 4-acetoxystyrene could only be obtained in 96% purity, with the remainder being 4-acetoxyethylbenzene. This was not suitable for the synthesis of quantitatively reactive functionalized polycarbonates. 4-Acetoxystyrene was synthesized in high purity and high yields by a modified literature procedure [36]. Potassium 4-vinylphenolate was synthesized by the literature method and was extracted from the reaction as the aqueous solution. Reaction with acetic anhydride produced the desired compound, which was then purified by fractional distillation. Synthesis of bis(4-vinylphenyl) carbonate was also accomplished by reacting the similarly obtained aqueous potassium 4-vinylphenolate with phosgene under interfacial phase transfer catalyzed reaction conditions.

Each of these compounds could be hydrolyzed under aqueous base conditions to quantitatively yield an aqueous solution of the 4-vinylphenolate. The acetate of 4-acetoxystyrene was found to be much more easily cleaved than the aromatic carbonate of the bis(4-vinylphenyl) carbonate. The benefit to using the carbonate is that no reactive byproduct is formed, contrary to the formation of potassium acetate from the cleavage of 4-acetoxystyrene. However, the potassium acetate produced from the hydrolysis was found not to interfere in the subsequent polymerization reaction, since it could not form a stable chain end under the basic reaction conditions. The greater ease of cleavage of the 4-acetoxystyrene led to its predominate use as the precursor to vinylphenylcarbonate terminated polycarbonate oligomers.

The aqueous solution of potassium 4-vinylphenolate was found to be stable for up to two months at 25 °C. After two months of storage with no added inhibitor, approximately 1% of polymerization products was observed by ^{1}H NMR. This demonstrates the ability of the potassium salt of 4-vinylphenolate to be stored for extended periods of time prior to use.

3.2. Molecular weight control in the synthesis of polycarbonates

The molecular weight of the oligomers was controlled through a simple offset of stoichiometry. Due to the interfacial nature of the reaction, and since the reaction involves the hydrolyzable chloroformate group, an excess of phosgene does not limit the molecular weight. The molecular weight can therefore, be controlled by the addition of a monofunctional reagent such that the bisphenol is incorporated completely within the monofunctional end groups. The desired molecular weight between end groups can be achieved by use of the following formulae

$$\mathrm{DP} = \langle M_\mathrm{n}\rangle / \langle M_0\rangle \tag{1}$$

$$X = (2)\,(\text{moles of monomer})/\mathrm{DP} \tag{2}$$

where DP is the number average degree of polymerization or number of repeating groups, $\langle M_\mathrm{n}\rangle$ the number average molecular weight desired, $\langle M_0\rangle$ the molecular weight of repeat unit (254.29 g/mol), and X is the number of moles of monofunctional reagent.

The functional oligomers were synthesized by two different interfacial methods. Both methods involve the phosgenation of an interfacial mixture of bisphenol A disodium salt, the hydrolysis products from the 4-acetoxystyrene, and phosgene, with a catalytic amount of triethylamine. The two methods differ in the addition of reactants, resulting in a change in mechanism for the overall reaction. A series of molecular weights were produced by the two methods and the oligomers were characterized by GPC, intrinsic viscosity (IV), and ^{1}H NMR (Table 1). As a control, polycarbonate oligomers with non-reactive functional end groups were synthesized to similar molecular weights by Method A. 4-*t*-Butylphenol was substituted for the hydrolysis products of 4-acetoxystyrene to synthesize 4-*t*-butylphenyl carbonate terminated oligomers. These oligomers were designated *t*-Bu-A($\langle M_\mathrm{n}\rangle$) and characterized along with the reactive oligomers for comparison.

In the first method, (Method A) an excess of phosgene was introduced into the mixture with all reactants and catalyst present while maintaining the pH between 10 and 11. The samples synthesized by this method were labeled A ($\langle M_\mathrm{n}\rangle$), where A designates the polymerization method and ($\langle M_\mathrm{n}\rangle$) designates the projected molecular weight between end groups. This method resulted in close to the expected number average molecular weights ($\langle M_\mathrm{n}\rangle$), but with broader molecular weight distributions, and intrinsic viscosities higher than expected. Quantitative termination was determined by both ^{1}H NMR and UV–vis spectroscopy, each of which detected no phenolic protons to be present. A ^{1}H NMR spectrum for a projected 2.5 kg/mol vinylphenyl terminated oligomer is depicted in Fig. 1. Analysis of the ^{1}H NMR spectra for each of the samples yielded $\langle M_\mathrm{n}\rangle$ values that were in agreement with the GPC results and with that which was predicted from stoichiometry. The broad molecular weight distribution was therefore, attributed to the formation of terminated oligomers with molecular weights lower than expected, early in the polymerization.

Table 1
Molecular weight characterization of oligomers

Sample (projected $\langle M_\mathrm{n}\rangle$)	$\langle M_\mathrm{n}\rangle$ (^{1}H NMR) (kg/mol)	IV (25 °C; $CHCl_3$) (dl/g)	$\langle M_\mathrm{n}\rangle$ (GPC) (kg/mol)	$\langle M_\mathrm{w}\rangle/\langle M_\mathrm{n}\rangle$ (GPC)
Vinyl terminated (Method A)				
A(2.5K)	3.0	0.20	2.8	5.2
A(5K)	5.4	0.30	4.7	6.0
A(7.5K)	7.6	0.43	7.2	6.1
A(10K)	10.5	0.70	10.2	6.0
Vinyl terminated (Method B)				
B(1.5K)	1.8	0.10	1.3	1.8
B(2.5K)	3.0	0.21	3.6	3.7
B(5K)	5.3	0.32	6.5	3.2
B(7.5K)	7.0	0.37	8.8	4.5
t-Butyl terminated (Method A)				
t-Bu-A(2.5K)	3.2	0.24	2.8	4.0
t-Bu-A(5K)	5.8	0.31	4.7	4.4
t-Bu-A(7.5K)	7.9	0.43	7.2	4.9
t-Bu-A(10K)	9.5	0.60	10.2	5.5

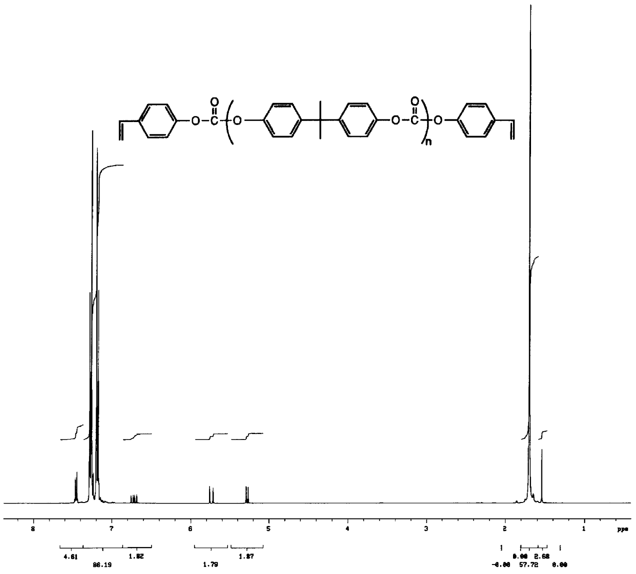


Fig. 1. ^{1}H NMR spectrum of 2.5 kg/mol vinylphenylcarbonate terminated polycarbonate oligomer.

The terminated lower molecular weight species are presumably formed preferentially because of a difference in the solubilities of the phenolates in methylene chloride. Since 4-vinylphenol is soluble in methylene chloride while bisphenol A is not, it can be assumed that the phenolate of 4-vinylphenol is more soluble in the methylene chloride layer than is the phenolate of bisphenol A. This difference in phase distribution results in a ratio of phenolate reactants in the methylene chloride layer different from that in the bulk reaction mixture. As the phosgene (which is soluble in the methylene chloride layer) is introduced, reaction with the monofunctional material can preferentially occur leading to low molecular weight terminated oligomers. With a smaller amount of the unreacted monofunctional reactant remaining, higher molecular weight terminated oligomers are subsequently formed leading to the broad molecular weight distribution.

In order to obtain a more narrow molecular weight distribution, polymerization was accomplished in a two step procedure (Method B), whereby low molecular weight chloroformate terminated oligomers were first synthesized in the absence of catalyst and subsequently hydrolyzed and condensed following addition of triethylamine. It is noted in the literature that such a process yields polymers with lower polydispersities [37]. Phosgene was introduced in the absence of both the triethylamine catalyst and the potassium 4-vinylphenolate, producing low molecular weight chloroformate terminated oligomers. Subsequent addition of the potassium 4-vinylphenolate and triethylamine catalyst resulted in the hydrolysis and condensation reactions. Additional phosgene was introduced in order to insure complete reaction. Oligomers synthesized by this method were labeled B($\langle M_n \rangle$). Oligomers of the desired number average molecular weight were obtained, as measured by GPC and ^{1}H NMR. The oligomers were found to have lower polydispersities than for samples obtained by Method A and this is reflected in the intrinsic viscosity measurements.

The participation of the potassium acetate (produced during the hydrolysis of the 4-acetoxystyrene) was considered in the synthesis of these oligomers. In either of the methods, it is possible for the acetate to be incorporated as an end group into the polycarbonate as a mixed carboxylic–carbonic anhydride or as an ester. Under anhydrous conditions, it is known for mixed anhydrides to form [38]. The mixed anhydrides formed under anhydrous conditions are thermally unstable and decompose to the esters at room temperature. Under interfacial polycarbonate reaction conditions with a quaternary ammonium phase transfer catalyst, aliphatic aromatic esters can be formed while no mixed anhydrides could be detected in the final product [39].

The formation of oligomers, which by GPC correspond well to the theoretical number average molecular weights, is one indication that no acetate end groups are formed. The intrinsic viscosities and the GPC number average molecular weights for the *t*-butylphenyl terminated oligomers, where no possibility for acetate end group formation is possible, are also similar. Furthermore, no resonances attributable to the acetate could be detected in the ^{1}H NMR spectra. From these indications, it can be concluded that no methyl ester is formed under the reaction conditions. If mixed anhydride is formed during the reaction, it is unstable and displaced by phenolate or hydroxide before completion.

3.3. Thermal properties

The thermal properties of the reactive vinylphenyl terminated and non-reactive *t*-butylphenyl terminated oligomers were characterized by DSC. This technique was used to characterize the cure temperature, the heat of reaction, and the glass transition temperatures (T_g). Multiple scans were required with a quench to room temperature in between scans in order to obtain the T_gs before and after cure. The results are compiled in Table 2 with respect to $\langle M_n \rangle$ of the oligomers, while typical DSC scans obtained from the first and second heat of a $\langle M_n \rangle \approx 2.5$ kg/mol reactive oligomer (A(2.5K)) are depicted in Fig. 2a and b.

The T_gs obtained on the first heat reflect the low molecular weight of the samples. The T_gs are observed to increase with molecular weight, approaching 150 °C, the value for high molecular weight polycarbonate. The exothermic cure reaction of the vinylphenyl end groups

Table 2
Characterization of oligomers by DSC

Vinylphenylcarbonate terminated			*t*-Butylphenylcarbonate terminated		
Sample	T_g (°C)		Sample	T_g (°C)	
	First heat DSC[a]	Second heat DSC[b]		First heat DSC[a]	Second heat DSC[b]
B(1.5K)	85	177			
A(2.5K)	105	155	*t*-B(2.5K)	111	111
A(5K)	126	152	*t*-B(5K)	132	132
A(7.5K)	137	152	*t*-B(7.5K)	139	138
A(10K)	140	150	*t*-B(10K)	142	143

[a] First heat to 350 °C at 10 °C/min.

[b] Second heat to 350 °C at 10 °C/min.

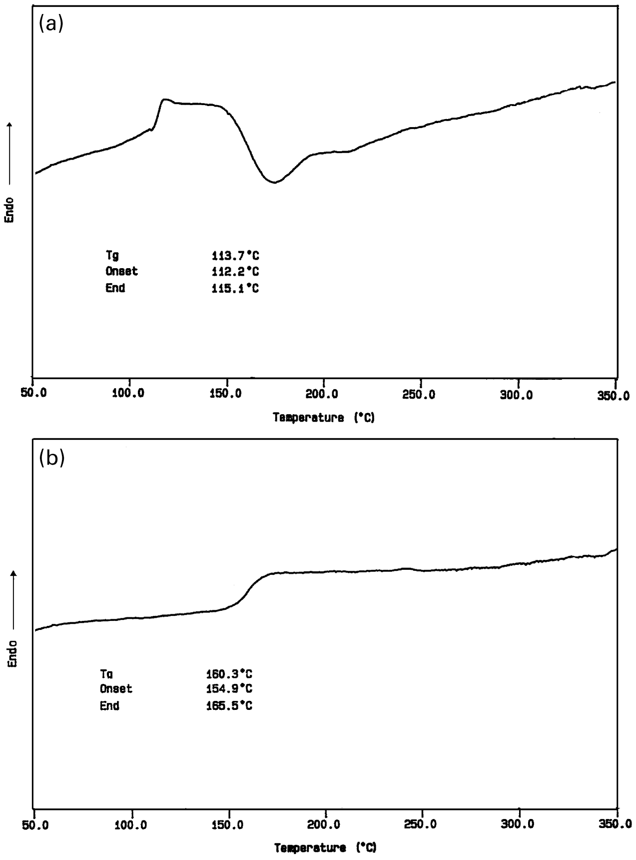


Fig. 2. DSC trace of 2.5K vinylphenylcarbonate terminated polycarbonate oligomer. (a) First heat to 350 °C at 10 °C/min. (b) Second heat at 10 °C/min.

can be detected on the first heat above the T_g of the oligomers. The start of the exotherm as well as the range was found to vary with the molecular weight of the oligomers (Table 3), as the exotherm began at higher temperatures for higher molecular weight samples. The heat of the exotherm could also be measured and was found to increase with the molar amount of reactive end group (i.e. with a decrease in molecular weight) as expected.

Scanning a second time after quench cooling from a temperature above the end of the cure exotherm produced a DSC scan which showed an increased T_g from that of the low molecular weight oligomers. For the higher molecular weight oligomers, the T_g increased to 150 °C upon cure. The increase in T_g was even more pronounced for the low molecular weight reactive oligomers, exceeding the value obtained for linear polycarbonate. This reflects the more highly crosslinked network derived from the lower molecular weight oligomers. In comparison, the non-reactive *t*-butylphenyl terminated oligomers showed no change in T_g during the second scan as demonstrated in Table 2.

Table 3
Heat of cure reaction

Sample ($\langle M_n \rangle$)	$-\Delta H$ (J/g)	Range of exotherm (°C)
Bis(4-vinylphenyl) carbonate	107.8	90–200
B(1.5K)	30.8	114–208
A(2.5K)	24.2	129–226
A(5K)	8.7	151–233
A(7.5K)	3.6	161–208
A(10K)	1.9	161–234

The contents of the DSC pans for both the reactive and non-reactive oligomers were analyzed after the second heats. Each of the samples was placed in 1 ml of methylene chloride. None of the products from the vinyl terminated samples dissolved in the methylene chloride, while all of the products from the *t*-butylphenyl terminated samples dissolved readily.

Dynamic thermogravimetric analysis (TGA) was performed on the reactive oligomers. The material was scanned from 30 to 800 °C at 10 °C/min under an air atmosphere in order to determine the thermooxidative stabilities (Fig. 3). The samples undoubtedly undergo a cure reaction during the course of the analysis, as indicated by the DSC measurements, resulting in networks with styrene-like aliphatic linkages at the crosslink points. These linkages do not decrease the thermal stabilities of the polycarbonates. In fact, the lower molecular weight oligomers (which result in a higher concentration of these linkages) yield networks which begin to lose volatiles at a higher temperature than for the higher molecular weight oligomers. This apparent greater thermooxidative stability is a reflection of the more highly crosslinked samples and the possibly slowed oxygen diffusion within the networks.

The residual material remaining at elevated temperatures (char yield) is also observed to be greater for the crosslinked samples than for linear polycarbonates. This is one possible indication that these materials may be more fire resistant than commercial linear polycarbonates. Qualitatively, it is observed that these crosslinked samples do have a reduced tendency to continue burning. Samples were placed in a Bunsen burner flame until ignited, and upon removal from the flame, self-extinguished in less than 1 s. Furthermore,

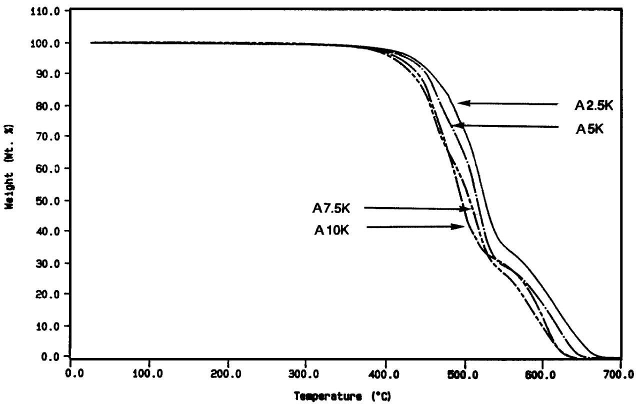


Fig. 3. Thermogravimetric analysis of reactively terminated carbonate oligomers: A(2.5K, 5K, 7.5K, 10K) (air atmosphere, 10 °C/min).

the samples did not have a tendency to drip when continuing to burn within the Bunsen burner flame.

4. Conclusions

The synthesis of vinylphenylcarbonate terminated oligocarbonates was accomplished by the introduction of the hydrolysis products of 4-acetoxystyrene into a bisphenol A/phosgene interfacial polymerization reaction. The number average molecular weight of the oligomers was controlled by the ratio of reactive monofunctional material to bisphenol A introduced to the reaction. Good molecular weight control was obtained for all reactions, and the potassium acetate from the hydrolysis of 4-acetoxystyrene was determined not to participate in the reaction. The isolated oligomers were observed to undergo a thermally induced cure reaction to form insoluble networks with increased glass transition temperatures that were more thermooxidatively stable than typical polycarbonates. A more detailed study of the cure reaction and the resulting material properties are reported in the following paper [40].

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