Synthesis and Properties of Allyl-Terminated and Silicon-Containing Polycarbonates

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Received February 10, 1999
Revised Manuscript Received July 21, 1999

Introduction

The need of engineering plastics as better and specialized materials is increasing in the world market. In particular, bisphenol A polycarbonates have been used for versatile applications in several industrial fields.[1] To improve the abrasion and scratch resistance of polycarbonate surfaces, the transparency of hard coatings, and nonflammability, compounds have been developed which are typically polysiloxane resins heavily filled with nanosized silica or colloidal hard materials.[2] In general, introducing stable functional groups as substituents is interesting because they can be used to impart a special functionality to polymers as well as to improve processability.[3] Recently, some work on synthesizing polycarbonate oligomers with reactive end groups has appeared in the literature. McGrath et al. reported that vinyl-terminated polycarbonate with *p*-acetoxystyrene and bisphenol A is applicable to adhesives such as styrene/unsaturated polyester sheet molding compounds.[4] Other efforts have been made to improve thermooxidative stability and adhesion by using primers, as demonstrated in a number of papers.[5] Silicone coupling agents have been tried as a means of improving the adhesion of the siliceous coating to the polycarbonate substrate. A functional organoalkoxysilane is readily hydrolyzed, and the formed silanols can condense with the silanol groups in the top coating to form strong siloxane bonds.[6] Davis et al. have reported that phenol−organopolysiloxane chain stoppers can be phosgenated in combination with a bisphenol to make flame retardant organopolysiloxane−polycarbonate block copolymers.[7]

This report focuses on the preparation and characterization of allyl-functionalized polycarbonate precursors based on 2,2′-bis(4-hydroxyphenyl)propane. The main objectives of this work were to produce silicon-containing polycarbonates by hydrosilylation of an allyl polycarbonate precursor and Si−H compounds with a Rh catalyst. It was anticipated that its incorporation into a polycarbonate chain would result in a polymer with enhanced thermal stability. Such a process could be applied to commercial interfacial polymerization.

Experimental Section

Materials. Bisphenol A, TEA (triethylamine), 4-allyl-2-methoxyphenol, 2-allylphenol, 2-allyl-6-methylphenol, triphenylsilane, tripropylsilane, and tetramethyldisiloxane were purchased from Aldrich Chemical Co. and used without further purification. Common reagents such as sodium hydroxide, methylene chloride, and acetone, were used without further purification. TEA was used as a 15 wt % aqueous solution.

Measurements. The ^{1}H NMR spectra were recorded on a Brucker DRX (300 MHz) spectrometer. $CDCl_3$ was used as the solvent and tetramethylsilane (TMS) was used as an internal standard. Molecular weight of polymers were determined relative to polystyrene standards by gel permeation chromatography (GPC) in CH_2Cl_2 as the eluent on a Waters 510 HPLC equipped with a set of four μ-styragel columns (500, 10^4, 10^5, and 100 Å) in series and a UV detector.

Preparation of Allyl-Terminated Polycarbonate (1A). To a 3 L three-necked round-bottom flask, fitted with a nitrogen inlet and ice jacket, were added bisphenol A (114 g, 0.5 mol) and 5.4 wt % aqueous NaOH solution (44.8 g, 1.12 mol). Phosgene (64.35 g, 0.65 mol) dissolved in 950 mL of methylene chloride was slowly added to the solution and stirred for 30 min. The methylene chloride and water layers were separated from the reaction mixture. The molecular weight of the obtained oligomer in methylene chloride was about 1000. In a 1 L three-necked round-bottom flask were placed 200 mL of methylene chloride layer (bisphenol A 0.17 mol) and 300 mL of water layer and added 100 μL of TEA (15 wt %), and 4-allyl-2-methoxyphenol (1.1 g, 6.7 mmol) which was dissolved in 10 mL of NaOH solution (0.32 g, 8 mmol) as a molecular weight controller. The reaction mixture was maintained for 30 min at room temperature. After the reaction was finished, the methylene chloride layer was separated. To the separated methylene chloride solution were added 146 μL of TEA, 80 mL of methylene chloride, and 8.2 g of NaOH in 57 mL of distilled water, and the mixture was reacted for 90 min. The polymer solution was washed with distilled water (3 × 250 mL), neutralized with HCl, and precipitated into a mixture (800 mL) of acetone and distilled water (50:50, v/v) to give a white granular polymer. $T_g = 144$ °C; $T_m = 240$ °C. ^{1}H NMR ($CDCl_3$): δ 1.4−1.7 (s, $C(CH_3)_3$), 3.3 (d, CH_2), 3.8 (s, OCH_3), 4.95−5.05 (m, CH_2 double bond), 5.8−5.95 (m, −CH double bond), 6.6−7.3 (m, bisphenol A aromatic H).

Preparation of a Silicon-Containing Polycarbonate (1A-1). In a 50 mL three-necked flask fitted with a condenser, a thermometer, and a magnetic stirrer was placed allyl-terminated polycarbonate (1 g) under a nitrogen atmosphere. To the polycarbonate was added methylene chloride, 10 mL, and the mixture was stirred until a clear solution was obtained. Tripropylsilane (0.02 g, 0.13 mol) and $Rh(PPh_3)_3Cl$ (0.06 g, 6.5×10^{-5} mol) were added to the solution. The reaction mixture was heated and stirred at 40 °C for 2 h. During that reaction, the initial reaction mixture became a dark yellow solution. The solution was cooled to room temperature and precipitated in an acetone/water mixture(50:50, v/v) to give a gray powdered polymer. The course of the reaction was followed using ^{1}H NMR spectroscopy by monitoring the bands centered at 5.00 and 5.85 ppm which were assigned to the CH_2 and CH protons of the allyl bond, respectively. When the aforementioned bands had disappeared, the reaction was stopped and allowed to cool to room temperature. $T_g = 142$ °C; $T_m = 240$ °C. ^{1}H NMR ($CDCl_3$): δ −0.09−0.1 (s, Si−CH_2), 0.5 (m, CH_2, Si−CH), 0.8 (t, CH_3), 1.1 (m, CH_2), 1.4−1.7 (s, $C(CH_3)_3$), 2.5 (m, CH_2), 3.75 (s, OCH_3), 6.6−7.3 (m, bisphenol A aromatic H).

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10.1021/ma9901893 CCC: $18.00

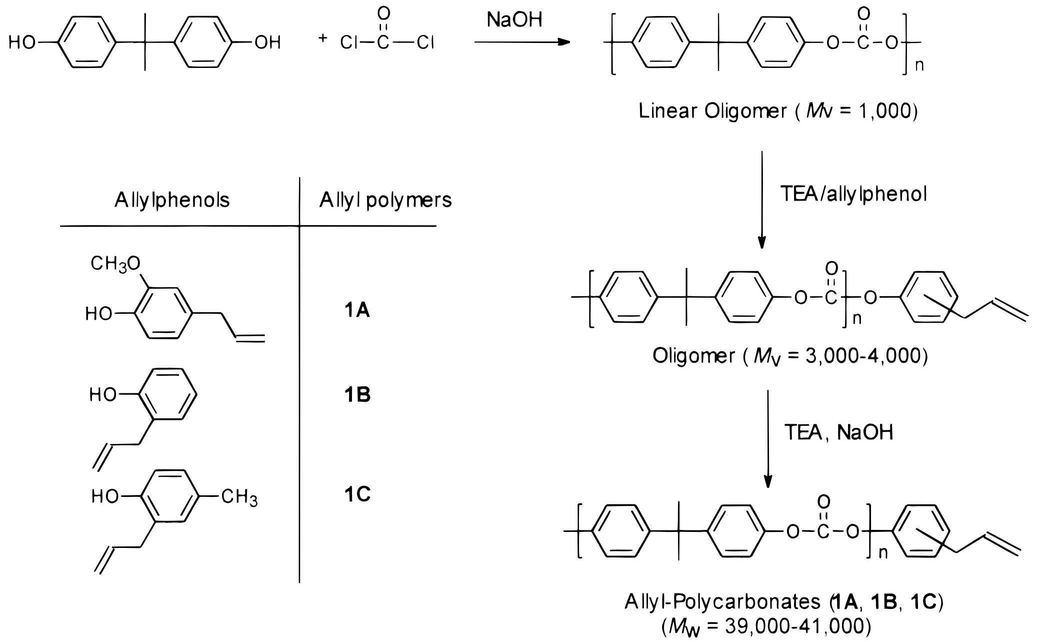

Figure 1. Allyl-terminated polycarbonates obtained by reaction of bisphenol A polycarbonate oligomers with allylphenols

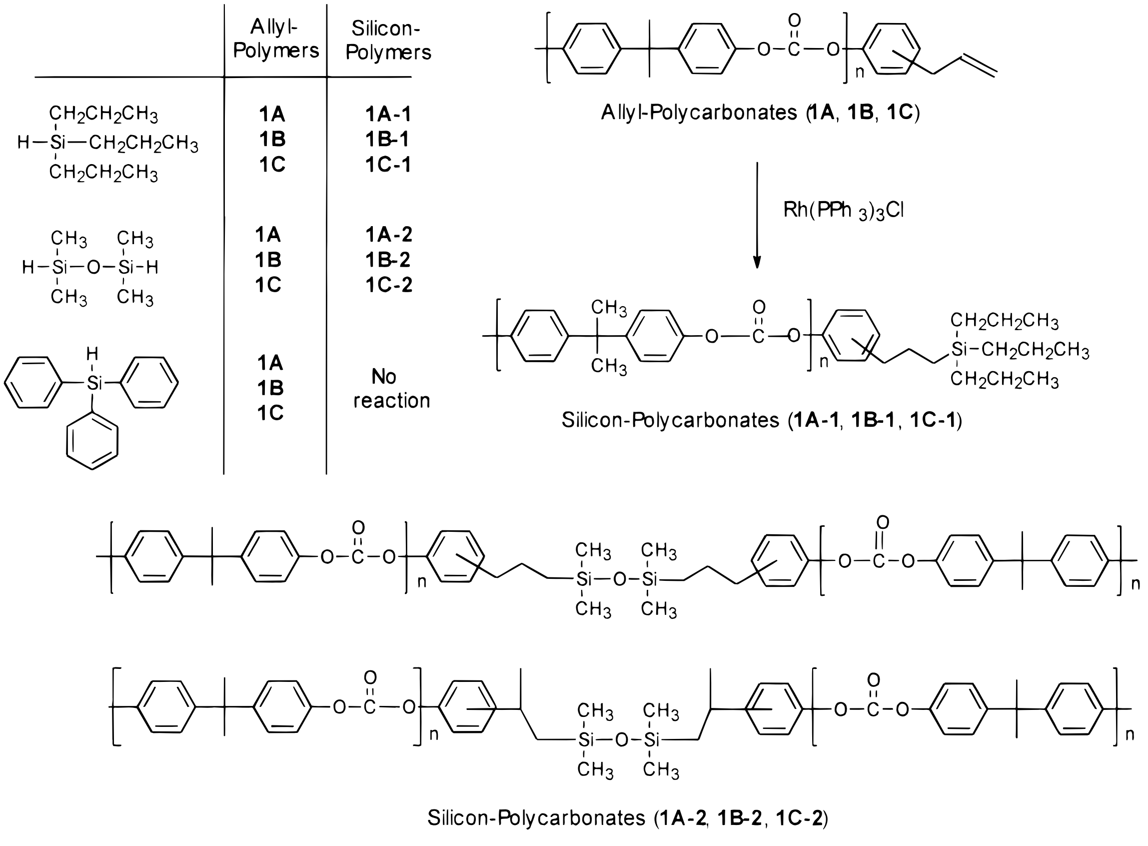

Figure 2. Silicon-containing polycarbonates obtained by a ruthenium-catalyzed hydrosilylation reaction.

Results and Discussion

The introduction of allyl groups into polycarbonate provides a highly reactive precursor for hydrosilylation. Allyphenyl carbonate-terminated polycarbonate precursors were synthesized from bisphenol A, phosgene, and allylphenol as a molecular weight terminator as shown in Figure 1. These compounds are stable materials which can bestored for extended periods of time. The hydrosilylation reaction shown in Figure 2 is an especially attractive route for the preparation of silicon-containing polymers from polycarbonate precursors bearing reactive functional groups for several reasons. First, the silane and siloxane bearing Si−H groups are stable and readily available. Second, the hydrosilylation reaction leads directly to the formation of thermally and hydrolytically stable carbon−silicon bonds. Third, hydrosilylation reactions are catalyzed by transition metal complexes and typically proceed to high conversions without the formation of byproducts.[8] Essentially a

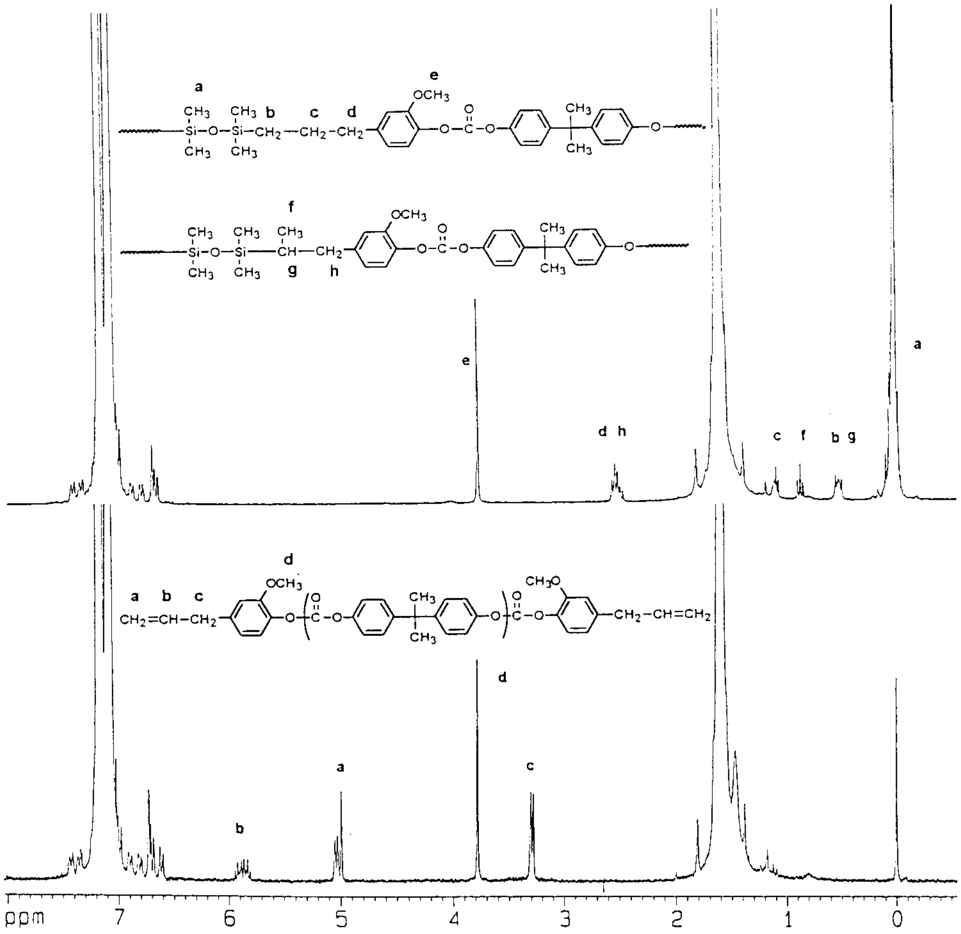

Figure 3. ^{1}H NMR spectra of **1A** and **1A-2** in $CDCl_3$.

quantitative yield of the silicon-containing polycarbonate can be obtained using Wilkinson's catalyst $Rh(PPh_3)_3Cl$ for the hydrosilylation reaction.[9] Using this synthetic approach, a series of silicon-containing polycarbonates have been prepared by hydrosilylation with tripropylsilane, triphenylsilane, and tetramethyldisiloxane Si−H containing compounds. Triphenylsilane failed to react with the allyl group probably because of steric hindrance. Figure 3 depicts the ^{1}H NMR spectrum of **1A** and **1A-2**. The hydrosilylation reaction may be conveniently monitored by following the decrease of the bands at δ 5.00 and 5.85 ppm due to the attachment at the carbon of double bond of the allyl group or the appearance and increase of the band at δ 1.1 ppm due to the CH_2 groups which are newly formed. The ^{1}H NMR spectrum is complicated by the peaks in the area of aliphatic groups as expected. The ^{1}H NMR spectrum of **1A-2** shows peaks at δ 0.5 ppm corresponding to the proton of Si−CH_2 and CH−Si groups. The peaks at δ 0.8 ppm appear as a triplet for the CH_3 protons, presumably, because the compound would have a chiral center which gives *R* and *S* configurations. The average molecular weights of the polycarbonate copolymers were controlled for the range of 38 000−52 000 which is useful for commercial applications. The allyl-terminated polycarbonates had 39 000−43 000 average molecular weights and the silicon-terminated polycarbonates, prepared from allyl terminated polycarbonate precursors and silanes, had 38 000−39 000 average molecular weights. Average molecular weights of silicon−polycarbonates obtained from siloxane increased by 10 000 units due to hydrosilylation at both end groups.

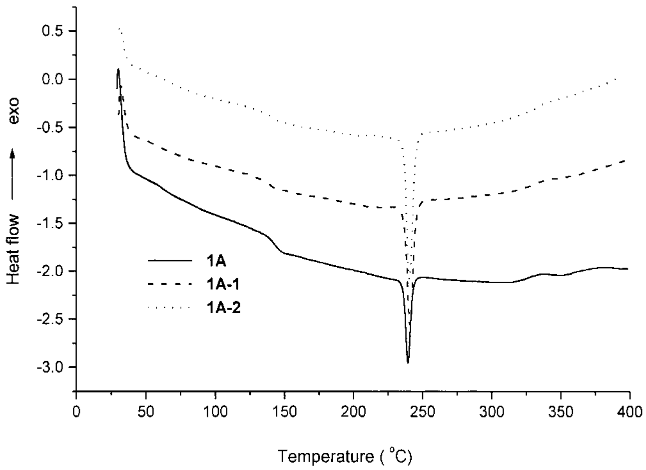

Figure 4. DSC curves of polymers **1A**, **1A-1**, and **1A-2**.

The thermal behavior of the polycarbonate copolymers was investigated by differential scanning calorimetry (DSC). The copolymers are semicrystalline and show both glass transition temperatures (T_g) and melting temperature (T_m) as shown in Figure 4. Commercial polycarbonate did not show a melting temperature by DSC but they have 10−20% crystallinity.[10] Presumably, the new copolymers have crystallized well when the polymers were powered in a solution of acetone and water. The T_g values of allyl-terminated polymers (**1A**, **1B**, **1C**) decreased compared with bisphenol A polycarbonate, as expected. The silicon−polycarbonates (**1A-2**, **1B-2**, **1C-2**) obtained from siloxane have lower glass

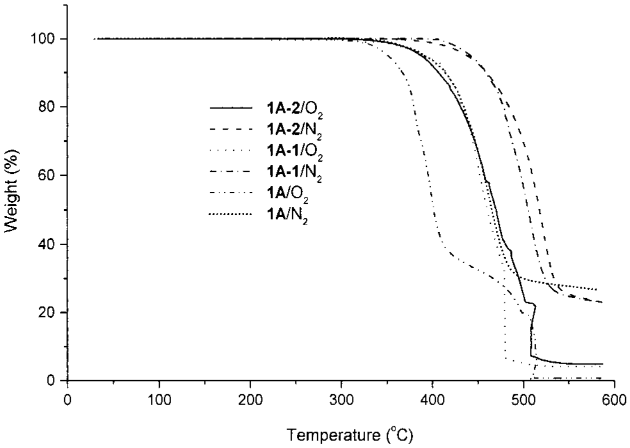

Figure 5. TGA of polymers **1A**, **1A-1**, and **1A-2** under air and nitrogen atmospheres.

Table 1. Physical and Thermal Properties of Polymers

polymers	T_g/T_m (°C)	M_w	M_w/M_n	TGA(O_2/N_2) (°C)
1A	144/240	41 000	1.60	353/395
1B	145/240	39 000	1.87	371/417
1C	142/238	43 000	2.08	364/415
1A-1	142/240	38 000	1.55	396/453
1B-1	140/247	38 000	1.71	398/451
1C-1	142/240	39 000	1.68	404/452
1A-2	140/237	47 000	1.47	391/440
1B-2	125/238	47 000	1.64	381/425
1C-2	137/239	52 000	1.68	396/457
bisphenol A PC	151/249	41 000	1.83	383/415

transition temperatures than those of silicon-terminated polycarbonates (**1A-1**, **1B-1**, **1C-1**) because the Si−O bond of siloxane provides additional flexibility. Thermooxidative stability of the polymers was studied using thermogravimetric analysis (TGA) and results are shown in Figure 5. The properties of the allyl- and silicon-containing polycarbonates prepared are summarized in Table 1. Most of the polymers show excellent thermal stability at high temperature in both air and nitrogen atmospheres. The allyl−polycarbonates (**1A**, **1B**, **1C**) have lower thermooxidative stability with 5% weight loss at 353−371 °C compared to the bisphenol A polycarbonate which has 5% weight loss at 383 °C, perhaps because of the benzyl protons. The silicon-containing polycarbonates (**1A-2**, **1B-2**, **1C-2**) showed relatively higher thermooxidative stability than that of linear and allyl-terminated polycarbonates, which can be attributed to the incorporation of silicon.[10]

In summary, polycarbonates containing reactive functional groups were synthesized with allylphenols as a molecular weight controller. The allyl-terminated polycarbonates and Si−H compounds were converted to new silicon-containing polycarbonates by hydrosilylation reaction with Rh catalyst. The silicon-containing polymers had lower glass transition temperatures than those of linear and allyl-terminated polycarbonates and had higher thermally oxidative stability.

Acknowledgment. This work was supported by the Korea Science and Engineering Foundation through the Advanced Material Research Center for Better Environment at Taejeon National University of Technology and partly by Sam Yang Group Research Center.

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MA9901893