

# New Macromonomers: Commercially Available Polycarbonate and Polyarylate Grafted with Unsaturated and Alkoxysilyl Group Pendants

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**ABSTRACT:** The insertion reaction of commercially available polycarbonate (PC) and polyarylate (PAR) with unsaturated epoxides produced new macromonomers grafted with many unsaturated group pendants in the middle of the polymer chain in fair to good yields. The insertion reaction readily occurred not only in solvents but also in solid PC. The unsaturated group was hydrosilylated with triethoxysi-

lane to produce triethoxysilyl group pendant PC and PAR, which are expected to be useful for sol-gel precursors for organic-inorganic hybrid materials, in good yields. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2515–2522, 2008

**Key words:** functionalization of polymers; macromonomers; polycarbonates; polyarylate

## INTRODUCTION

In recent years, we reported that sol-gel reactions of a polycarbonate (PC) oligomer with triethoxysilyl groups at both ends of the PC chain (PCS)<sup>1</sup> and of PCS with silicon alkoxides<sup>2</sup> produced PC-silica hybrid materials in which the PC and silica were covalently bound to each other to increase the interfacial interaction between them, and this provided various superior properties. On the other hand, these results led us to the expectation that the use of polymers having many more alkoxysilyl groups would produce higher performing organic-inorganic hybrid materials.

As polymers having many more alkoxysilyl groups, PC and polyarylate (PAR), having many alkoxysilyl group pendants in the middle of the polymer chain, were postulated and prepared through a two-step process. In the first step, the polymer having many unsaturated group pendants in the middle of the polymer chain, which was expected to be useful for macromonomers, was prepared by the insertion reaction of an unsaturated epoxy compound into an aryl ester linkage, which was reported by Funahashi<sup>3</sup> for the first time about 3 decades ago and was later applied and remarkably developed by Nishikubo and coworkers.<sup>4</sup> The insertion reaction of epoxy compounds bearing an unsaturated group into the aryl ester linkage of commercially available PC or

PAR was carried out under solution and solid conditions. Second, the unsaturated group was hydrosilylated with alkoxysilanes to produce the corresponding alkoxysilyl group pendant PC or PAR.

## RESULTS AND DISCUSSION

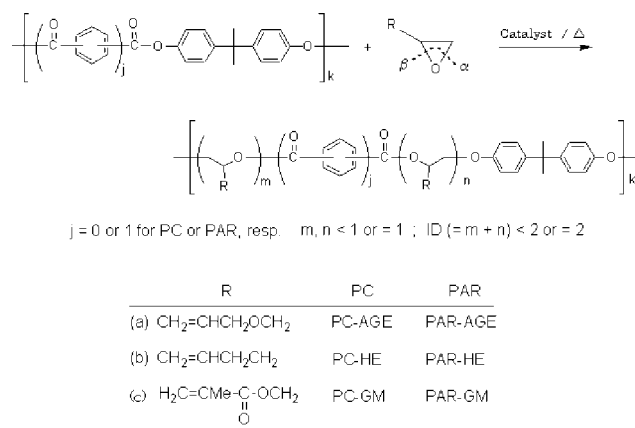
### Unsaturated group pendant polymers

The insertion reactions of commercially available PC and PAR with several unsaturated epoxy compounds were carried out to produce unsaturated group pendant polymers (Scheme 1).

Table I shows the results of the insertion reaction of an allyl glycidyl ether (AGE) into a commercially available PC [weight-average molecular weight ( $M_w$ ) = 37,200] in several solvents. In this reaction, tetrabutylphosphonium bromide (TBPB) was used as the catalyst. Although no insertion product was obtained in pyridine, the PCs inserted with AGE (PC-AGEs), having various insertion degrees (IDs;  $ID = m + n$  in Scheme 1) of AGE in the carbonate group, which were calculated from the intensity ratio of <sup>1</sup>H-NMR peaks, were produced in other solvents. In anisole, although the yield decreased, the ID increased with increasing amounts of AGE and TBPB. When an excess of AGE was used as the solvent, the product was obtained in a relatively high yield. On the other hand, decreases in the molecular weight were observed in all cases.

Funahashi<sup>3</sup> showed that  $\alpha$ -cleavage of the alkyl epoxide ring regioselectively occurred for the insertion reaction into aryl esters. In the insertion reaction of methyloxirane into diphenyl carbonate (Scheme

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Scheme 1

2), the  $\alpha$ -cleavage and  $\beta$ -cleavage products were reported to show signals at  $\delta$  values of 3.98 [d,  $-\text{O}-\text{C}(\text{O})-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{C}_6\text{H}_5$ ] and 5.10 ppm [m,  $-\text{O}-\text{C}(\text{O})-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{C}_6\text{H}_5$ ] and at  $\delta$  values of 4.23 [d,  $-\text{O}-\text{C}(\text{O})-\text{O}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-\text{C}_6\text{H}_5$ ] and 4.58 ppm [m,  $-\text{O}-\text{C}(\text{O})-\text{O}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-\text{C}_6\text{H}_5$ ], respectively.<sup>3(b)</sup> As shown in Figure 1, in this insertion reaction of AGE into PC (Table I, entry 8), the  $^1\text{H-NMR}$  spectrum showed slightly broad signals at  $\delta$  values of 4.2 [d,  $-\text{O}-\text{C}(\text{O})-\text{O}-\text{CH}(\text{CH}_2-\text{O}-)-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-$ ] and 5.1–5.3 ppm [m,  $-\text{O}-\text{C}(\text{O})-\text{O}-\text{CH}(\text{CH}_2-\text{O}-)-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-$ ], which are similar to those of the  $\alpha$ -cleavage product in the reaction of diphenyl carbonate and indicate that the  $\alpha$ -cleavage mainly occurred as shown in Scheme 1. In this case, the ID was calculated to be 0.6 from the intensity ratio of the  $^1\text{H-NMR}$  peaks (1/10): 5.9 ppm for  $\text{CH}_2=\text{CH}-\text{CH}_2-$  and 1.6 ppm for  $(\text{CH}_3)-\text{C}-$  ( $\text{CH}_3$ ). Figure 2 shows the IR spectra of PC and PC-AGE (Table I, entry 8). Absorptions due to an olefin

at  $1647 \text{ cm}^{-1}$  and due to the carbonyl group at  $1766 \text{ cm}^{-1}$  were observed. A weak absorption at  $3290 \text{ cm}^{-1}$  due to phenolic hydroxy group stretching and a weak  $^1\text{H-NMR}$  signal at 4.7 ppm for a phenolic proton (Fig. 1) suggest that the decreases in the molecular weight and yield were caused by hydrolysis with a trace of water in the reaction system. A shift in the absorption due to the carbonyl group stretching from  $1774 \text{ cm}^{-1}$  ( $\text{C}=\text{O}$  in PC) to a lower wave number was observed, corresponding to a partial change of the aryl ester to an alkyl ester linkage: The absorptions due to the carbonyl group stretching for ID = 0.6 (entry 8), ID = 0.96 (entry 10), and ID = 1.32 (entry 11) shifted to 1766, 1760, and  $1756 \text{ cm}^{-1}$ , respectively (Fig. 3).

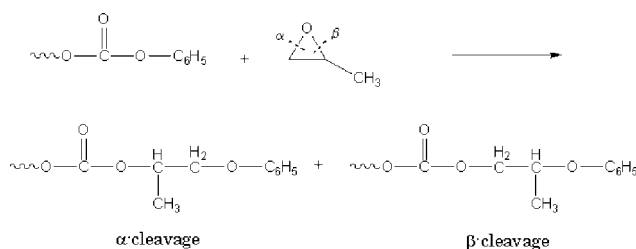
With a large excess of an epoxy compound as the solvent, the insertion reactions of AGE, glycidyl methacrylate (GM), and 1,2-epoxy-5-hexene (EH) into PC and PAR were carried out (Table II). Although decreases in the molecular weight were observed, the unsaturated group pendant PCs (PC-AGE, PC-GM, and PC-EH) and PARs (PAR-AGE, PAR-GM, and PAR-EH) were obtained in fair to good yields. Tetraphenylphosphonium bromide (TPPB) as a catalyst was inferior to TBPB on the basis of the conversion and yield. For the reactions with AGE and EH, the characteristic  $^1\text{H-NMR}$  multiplet signals of  $-\text{CH}_2\text{CH}=\text{CH}_2$  were observed at 5.9 and 5.8 ppm, respectively, both for PC and for PAR (Fig. 4), whereas in PAR-EH (Table II, entry 10), there were many weak signals due to noises and impurities because of its low ID. The IR absorption bands due to an olefin appeared at  $1647$  and  $1643 \text{ cm}^{-1}$ , respectively, for both PC and PAR (Fig. 5). In the case of GM, the singlet signal of the methyl proton of the methacryl group was observed at 1.9 ppm for both PC and PAR (Fig. 6). Figure 7 shows IR spectra of PC-GM (Table II, entry 1) and PAR-GM (Table II,

TABLE I  
Insertion Reaction of AGE into PC in Several Solvents<sup>a</sup>

Entry	Solvent	Carbonate/AGE/ TBPB molar ratio	Reaction time (h)/ temperature ( $^{\circ}\text{C}$ )	ID ( $m + n$ )	Yield (%)	Molecular weight
1	Pyridine	40/10/1	3/97	0	—	2,100
2	DMAC	40/10/1	5/154	0.1	—	2,800
3	NMP	40/10/1	5/152	0.4	—	3,300
4	Sulfolane	40/10/1	5/152	0.3	—	3,200
5	Anisole	40/10/1	5/151	0.48	—	7,100
6	Anisole	40/10/1	5/120–128	0.16	62	10,000
7	Anisole	40/10/5	5/120–128	0.26	49	6,700
8	Anisole	40/50/5	5/120–128	0.6	40	4,800
9	Anisole	40/50/25	5/120–128	0.64	17	4,000
10	— <sup>b</sup>	40/400/0.4	13/77	0.96	62	7,600
11	— <sup>b</sup>	40/400/4	5/95	1.32	77	16,100

<sup>a</sup> Unless otherwise noted, the reactions were carried out with Iupilon H4000 ( $M_w = 37,200$ , 2.00 g, 0.054 mmol) and a solvent (20 mL).

<sup>b</sup> Reactions were carried out with Iupilon E2000F ( $M_w = 65,600$ , 3.0 g, 0.046 mmol) without a solvent.



Scheme 2

entry 9). IR absorption bands due to an olefin appeared at  $1637\text{ cm}^{-1}$  for PC-GM and at  $1635\text{ cm}^{-1}$  for PAR-GM. For PC-GM, the absorption bands due to the carbonyl group stretching appeared at  $1762\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  in the PC main chain) and  $1722\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  in the methacryloyl group). On the other hand, for PAR-GM, two absorption bands due to the carbonyl group stretching in the PAR main chain and in the methacryloyl group joined, appearing only at  $1726\text{ cm}^{-1}$ . The insertion reaction of the epoxy compounds into PC was superior to that into PAR on the basis of the conversion and yield.

Table III summarizes the results of the insertion reaction of AGE into PC under solid conditions. After PC, AGE, and TBPB were dissolved in a solvent, the solvent was removed to obtain the solid PC containing AGE and TBPB. The solid was then heated in an oven to produce the desired product. Although decreases in the molecular weight were observed with the increasing amount of TBPB, similarly to the reaction in solvents, the desired products were obtained in fair to good yields. In view of the yield, ID, and decrease in the molecular weight, the preferred amount of the catalyst appeared to be 1 mol % of the amount of the carbonate group. Although this solventless method gave results only similar to those of the reactions in solvents, it is noteworthy that the insertion reaction readily occurs at a much lower temperature than the glass-transition temperature of PC in the solid PC.

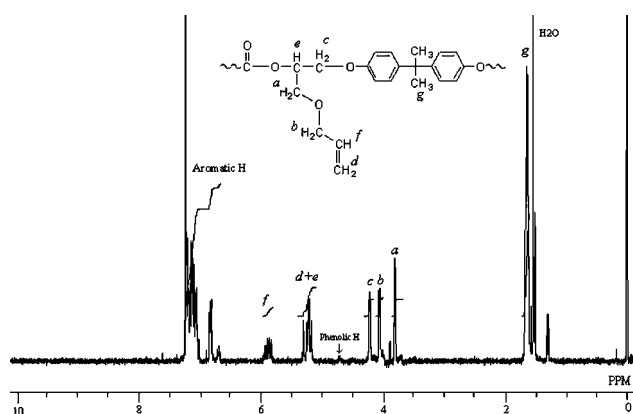
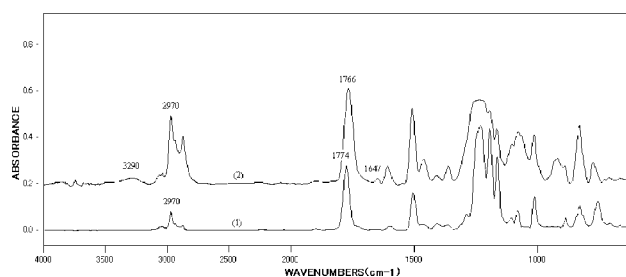
Figure 1  $^1\text{H-NMR}$  spectrum of PC-AGE (Table I, entry 8).

Figure 2 IR spectra of (1) PC and (2) PC-AGE (Table I, entry 8).

### Alkoxysilyl group pendant polymers

The hydrosilylations of PC-AGE and PAR-AGE with triethoxysilane (TESH), with chloroplatinic acid as a catalyst, were carried out (Scheme 3). Table IV summarizes the results. In both PC-AGE and PAR-AGE, the hydrosilylation readily occurred and gave the desired products (PC-AGE-Si and PAR-AGE-Si, respectively). Unfortunately, this reaction did not occur under solid conditions at all. The IR absorption due to the olefin decreased as the reaction proceeded and then substantially disappeared at the end of the reaction (Fig. 8). The  $^1\text{H-NMR}$  spectra showed the disappearance of the allyl proton signals (5.1–5.3 ppm,  $\text{CH}_2=\text{CH}-\text{CH}_2-$ , and 5.9 ppm,  $\text{CH}_2=\text{CH}-\text{CH}_2-$ ) and the appearance of characteristic signals due to the  $-\text{SiCH}_2\text{CH}_2\text{CH}_2\text{O}-$  protons [ca. 0.6 ppm (m, 1H) and ca. 0.9 ppm (m, 1H); Fig. 9]. These methylene protons adjacent to silicon shifted out of the range of the other organic functional groups and showed characteristic splitting patterns (peak a in Fig. 9).<sup>5</sup> These spectral data show that all the allyl groups were hydrosilylated. When a large excess of TESH was used, it was difficult to isolate the product without the hydrolysis and condensation of the ethoxysilyl group and an excess of TESH caused by a trace of water. In entries 1–5, in which a large excess of TESH was used, the experi-

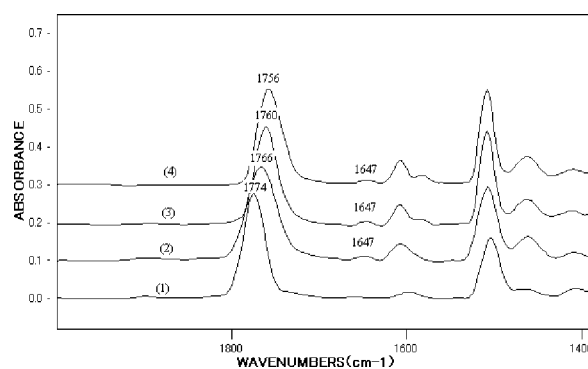
Figure 3 IR spectra of the  $1400\text{--}2000\text{-cm}^{-1}$  region in (1) PC and PC-AGE with (2) ID = 0.6, (3) ID = 0.96, and (4) ID = 1.32.

TABLE II  
Insertion Reaction into PC and PAR in a Large Excess of Epoxide as the Solvent

Entry	Polymer <sup>a</sup>	Carbonate or ester/ epoxide/catalyst <sup>b</sup> (molar ratio)	Reaction time (h)/ temperature (°C)	ID ( <i>m</i> + <i>n</i> )	Yield (%)	<i>M<sub>w</sub></i>
1	PC	1/5 (GM)/0.01	1/100	1.0	87	11,500
2	PC	1/5 (GM)/0.01	2/100	—	Gelation	
3	PC	1/5 (EH)/0.01 (TPPB)	0.8/97–99	0.05	—	10,100
4	PC	1/5 (EH)/0.033 (TPPB)	14/120–4	1.3	24	4,800
5	PC	1/5 (EH)/0.033	14/120–4	2.0	37	5,700
6	PAR	1/5 (AGE)/0.05	14/92–97	1.66	—	9,900
7	PAR	1/5 (AGE)/0.05	5.5/94–96	1.3	71	14,100
8	PAR	1/5 (AGE)/0.1	3/75	0.75	58	6,700
9	PAR	1/5 (GM)/0.01	1/95–99	1.2	69	10,100
10	PAR	1/5 (EH)/0.01(TPPB)	3/97–99	0.02	56	47,600

<sup>a</sup> PC (E2000F, *M<sub>w</sub>* = 65,600, 3.0 g, 0.046 mmol, 11.8 mmol of carbonate group) or PAR (U-100CN, *M<sub>w</sub>* = 62,100, 2.0 g, 0.032 mmol, 11.2 mmol of ester group).

<sup>b</sup> Unless otherwise noted, TBPB was used as the catalyst.

mental Si content data of the products were much higher than the theoretical values, and the yields in entries 2–4 were greater than 100%. In entries 6 and 7, in which a small excess of TESH was used, the experimental Si content values of the products were in fair agreement with the theoretical estimates. The <sup>1</sup>H-NMR spectra, however, showed that the number of ethoxysilyl protons was slightly greater than the theoretical values, leading us to understand that the reactivity of the alkoxyethyl group was so high that even a trace of water should be protected in the isolation.

In summary, the insertion reaction of the unsaturated epoxides into commercially available PC and PAR readily produced polymers having many unsaturated group pendants in the middle of the polymer chain. The reaction also readily occurred in solid PC. The unsaturated group was hydrosilylated with

alkoxysilanes to give the corresponding alkoxyethyl group pendant polymers in good yields.

Although the unsaturated group and alkoxyethyl group pendant PC and PAR are expected to be useful for macromonomers and for sol-gel precursors for organic-inorganic hybrid materials, respectively, the applications of these polymers are the subject of further study.

## EXPERIMENTAL

### Characterization

The Fourier transform infrared (FTIR) and NMR spectra were recorded with a JEOL (JEOL Ltd., Tokyo, Japan) SPX60S and a JEOL AL300, respectively.

The mean molecular weights were measured with a Shimadzu (Shimadzu Co., Kyoto, Japan) CTO-6A

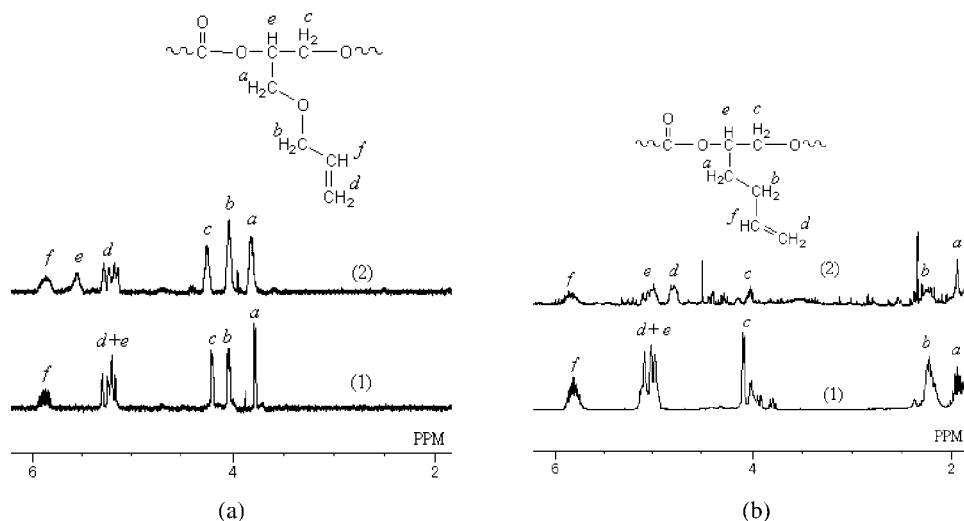
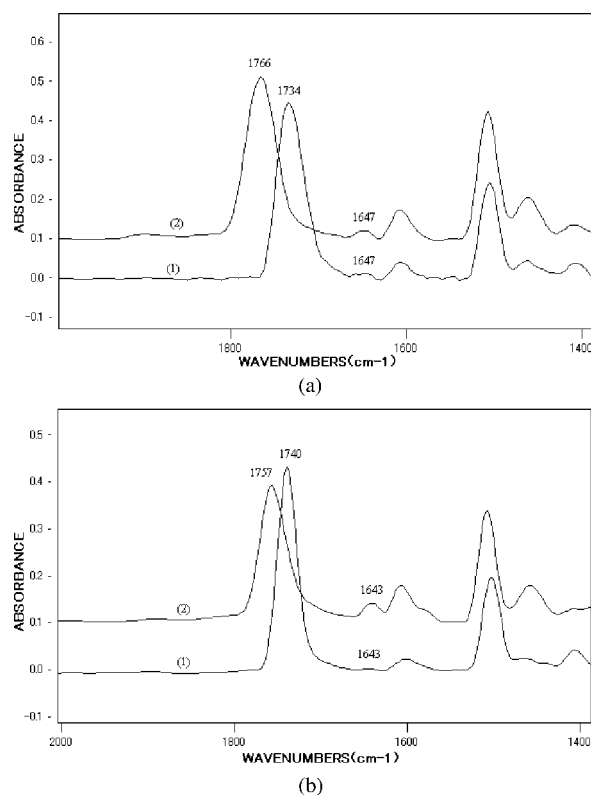


Figure 4 <sup>1</sup>H-NMR spectra of the corresponding regions of the inserted group in (a-1) PC-AGE (Table I, entry 8), (a-2) PAR-AGE (Table II, entry 8), (b-1) PC-EH (Table II, entry 5), and (b-2) PAR-EH (Table II, entry 10).



**Figure 5** IR spectra of the 1400–2000-cm<sup>-1</sup> region in (a-1) PAR-AGE (Table II, entry 8), (a-2) PC-AGE (Table I, entry 8), (b-1) PAR-EH (Table II, entry 10), and (b-2) PC-EH (Table II, entry 5).

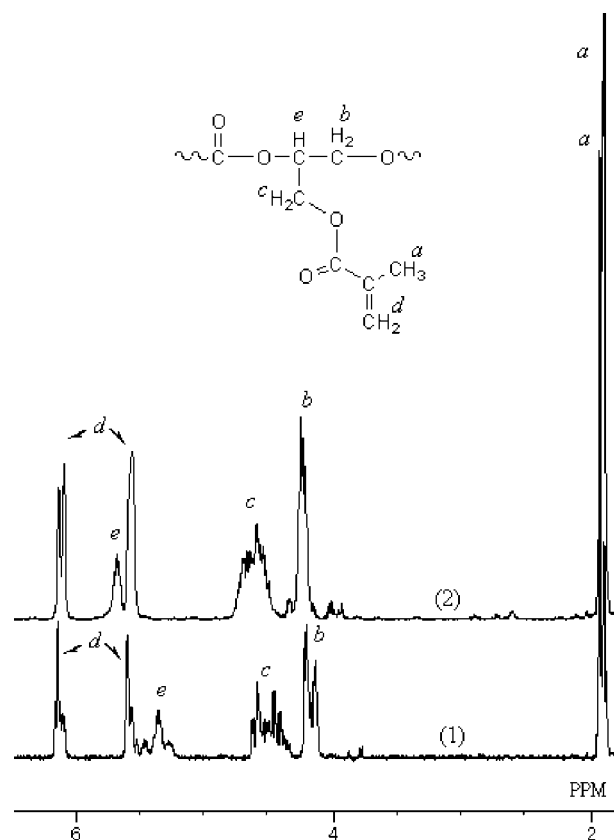
system equipped with a UV detector and a Shodex gel permeation chromatography column set [KF-804L and KF-802.5 (Showa Denko K.K., Tokyo, Japan); carrier: 0.8 mL of tetrahydrofuran (THF)/min, temperature: 40°C]. The system was calibrated with polystyrene standards ( $M_w = 1300, 7000, 22,000, \text{ or } 66,000$ ).

### Materials

Commercially available PC [bisphenol A type; Iupilon S2000 ( $M_w = 53,700$ ), H4000 ( $M_w = 37,200$ ), and E2000F ( $M_w = 65,600$ ), Mitsubishi Engineering-Plastics Co., Tokyo, Japan] and PAR [bisphenol A/terephthalic and isophthalic acid (50 and 50) type; U-100CN ( $M_w = 58,000$ ), Unitika, Tokyo, Japan] were used after drying at 80°C for 15–18 h. AGE, GM, EH, TBPB, TPPB, chloroplatinic acid hydrate, and TESH were purchased from commercial sources and used without further purification. Chloroform, methanol, THF, pyridine, anisole, dimethyl acetamide (DMAC), sulfolane, and *N*-methylpyrrolidone (NMP) were dried over 3-Å molecular sieves before use.

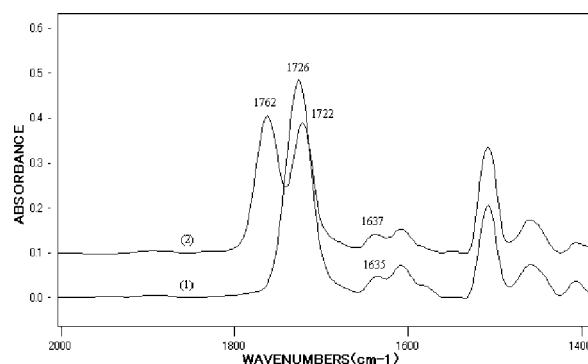
### General procedure for the reaction of PC with AGE in a solvent

For PC-AGE (Table I, entry 8), a mixture of PC (Iupilon H4000;  $M_w = 37,200$ , 2.0 g, 0.054 mmol, 7.6



**Figure 6** <sup>1</sup>H-NMR spectra of the corresponding regions of the inserted group in (1) PC-GM (Table II, entry 1) and (2) PAR-GM (Table II, entry 9).

mmol of carbonate group), AGE (1.1 g, 9.5 mmol), and TBPB (0.3 g, 0.95 mmol) in anisole (20 mL) was heated at 120–128°C for 5 h with stirring under an N<sub>2</sub> atmosphere. After being cooled to room temperature, the reaction mixture was poured into a large quantity of methanol, and the resulting precipitate was collected. The precipitate was dissolved in chloroform and then poured into a large quantity of methanol. The precipitated solid was dried to give 1.2 g (40% yield) of PC-AGE ( $M_w = 4800$ ). The calculated ID was 0.6 from the intensity ratio of the <sup>1</sup>H-



**Figure 7** IR spectra of the 1400–2000-cm<sup>-1</sup> region in (1) PAR-GM (Table II, entry 9) and (2) PC-GM (Table II, entry 1).

TABLE III  
Insertion Reaction of AGE into PC Under Solid Conditions

Entry	Carbonate/AGE/ TBPB (molar ratio)	ID ( $m + n$ )	$\nu_{\text{C=O}}$ ( $\text{cm}^{-1}$ )	Yield (%)	$M_w$
1	100/10/1	0.06	1774	92	13,800
2	100/25/1	0.15	1772	89	11,600
3	100/50/1	0.25	1770	82	14,200
4	100/100/0.1	0.004	—	—	18,400
5	100/100/0.5	0.05	1774	64	18,400
6	100/100/1	0.32	1770	64	13,700
7	100/100/5	0.39	1768	32	5,900
8	100/100/10	0.54	1764	33	5,100

All reactions were carried out with PC (Iupilon S2000,  $M_w = 53,700$ , 10.0 g, 0.2 mmol, 39 mmol of carbonate group) at 70°C for 9 h.

NMR peaks (1/10): 5.9 ppm for  $\text{CH}_2=\text{CH}-\text{CH}_2-$  and 1.6 ppm for  $(\text{CH}_3)-\text{C}-(\text{CH}_3)$ .

FTIR (neat,  $\text{cm}^{-1}$ ): 3290 (Ar-OH), 1766 (C=O), 1647 ( $\text{CH}_2=\text{CH}-$ ).  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 1.6 [s, 10H,  $(\text{CH}_3)-\text{C}-(\text{CH}_3)$ ], 3.8 (d, 2H,  $-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_2-$ ), 4.0 (d, 2H,  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-$ ), 4.2 (d, 2H,  $-\text{CH}_2-\text{CH}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-$ ), 5.1–5.3 (m, 3H,  $\text{CH}_2=\text{CH}-\text{CH}_2-$  +  $-\text{CH}_2-\text{CH}-\text{CH}_2-$ ), 5.9 (m, 1H,  $\text{CH}_2=\text{CH}-\text{CH}_2-$ ), 6.7–7.3 (m, 14H, Ar-H). ANAL. Calcd for  $(\text{C}_{19.6}\text{H}_{20}\text{O}_{4.2})_k$  (ID = 0.6): C, 72.95%; H, 6.20%. Found: C, 72.8%; H, 6.4%.

#### General procedure for the reaction of PC or PAR in an excess of epoxide

PAR-GM (Table II, entry 9)

A mixture of PAR (U-100CN;  $M_w = 62,100$ , 2.0 g, 0.032 mmol, 11.2 mmol of ester group), GM (7.9 g, 56 mmol), and TBPB (0.04 g, 0.111 mmol) was heated at 95–99°C for 1 h with stirring in air. After being cooled to room temperature, the reaction mixture was dissolved in chloroform. The chloroform solution was poured into a large quantity of methanol to collect the precipitated solid. The solid was purified by reprecipitation from methanol and then dried to give 2.5 g (69% yield) of PAR-GM ( $M_w = 10,100$ ). The calculated ID was 1.2 from the intensity ratio of the  $^1\text{H-NMR}$  peaks (3/5): 1.9 ppm for  $\text{CH}_2=\text{C}(\text{CH}_3)-$  and 1.6–1.7 ppm for  $(\text{CH}_3)-\text{C}-(\text{CH}_3)$ .

FTIR (neat,  $\text{cm}^{-1}$ ): 1726 (C=O), 1635 [ $\text{CH}_2=\text{C}(\text{CH}_3)-$ ].  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 1.6–1.7 [s, s, 5H,  $(\text{CH}_3)-\text{C}-(\text{CH}_3)$ ], 1.9 [s, 3H,  $\text{CH}_2=\text{C}(\text{CH}_3)-$ ], 4.1–4.7 (m, 4H,  $-\text{CH}_2-\text{CH}-\text{CH}_2-$ ), 5.5–6.1 [m, 3H,  $\text{CH}_2=\text{C}(\text{CH}_3)-$  +  $-\text{CH}_2-\text{CH}-\text{CH}_2-$ ], 6.7–7.3 (m, 5H, Ar-H), 7.5–9.0 (m, 3H, Ar-H). ANAL. Calcd for  $(\text{C}_{31.4}\text{H}_{30}\text{O}_{7.6})_k$  (ID = 1.2): C, 71.31%; H, 5.68%. Found: C, 70.21%; H, 5.74%.

PC-EH (Table II, entry 5)

$M_w = 5700$  (ID = 2.0, 37% yield). FTIR (neat,  $\text{cm}^{-1}$ ): 1757 (C=O), 1643 ( $\text{CH}_2=\text{CH}-$ ).  $^1\text{H-NMR}$  (300

MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 1.6 [s, 3H,  $(\text{CH}_3)-\text{C}-(\text{CH}_3)$ ], 1.8–2.0 (m, 2H,  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}$ ), 2.2–2.3 (m, 2H,  $\text{CH}_2=\text{CH}-\text{CH}_2-$ ), 4.2 (d, 2H,  $-\text{CH}_2-\text{CH}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-$ ), 4.9–5.1 (m, 3H,  $\text{CH}_2=\text{CH}-\text{CH}_2-$  +  $-\text{CH}_2-\text{CH}-\text{CH}_2-$ ), 5.7–5.9 (m, 1H,  $\text{CH}_2=\text{CH}-\text{CH}_2-$ ), 6.7–7.3 (m, 5H, Ar-H).

The calculated ID was 2.0 from the intensity ratio of the  $^1\text{H-NMR}$  peaks (1/3): 5.7–5.9 ppm for  $\text{CH}_2=\text{CH}-\text{CH}_2-$  and 1.6 ppm for  $(\text{CH}_3)-\text{C}-(\text{CH}_3)$ .

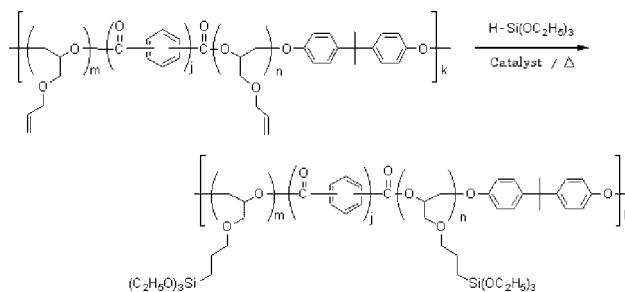
ANAL. Calcd for  $(\text{C}_{28}\text{H}_{34}\text{O}_5)_k$  (ID = 2.0): C, 74.64%; H, 7.61%. Found: C, 74.8%; H, 7.5%.

PC-GM (Table II, entry 1)

$M_w = 11,500$  (ID = 1.0, 87% yield). FTIR (neat,  $\text{cm}^{-1}$ ): 1762 (C=O in the PC main chain), 1722 (C=O in the methacryloyl group), 1637 [ $\text{CH}_2=\text{C}(\text{CH}_3)-$ ].  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 1.6 [s, 6H,  $(\text{CH}_3)-\text{C}-(\text{CH}_3)$ ], 1.9 [s, 3H,  $\text{CH}_2=\text{C}(\text{CH}_3)-$ ], 4.1–4.6 (m, 4H,  $-\text{CH}_2-\text{CH}-\text{CH}_2-$ ), 5.2–5.5 (m, 1H,  $-\text{CH}_2-\text{CH}-\text{CH}_2-$ ), 5.6–6.1 [m, 2H,  $\text{CH}_2=\text{C}(\text{CH}_3)-$ ], 6.8–7.3 (m, 8H, Ar-H).

The calculated ID was 1.0 from the intensity ratio of the  $^1\text{H-NMR}$  peaks (1/2): 1.9 ppm for  $\text{CH}_2=\text{C}(\text{CH}_3)-$  and 1.6 ppm for  $(\text{CH}_3)-\text{C}-(\text{CH}_3)$ .

ANAL. Calcd for  $(\text{C}_{23}\text{H}_{24}\text{O}_6)_k$  (ID = 1.0): C, 69.68%; H, 6.10%. Found: C, 68.98%; H, 6.10%.



$j = 0$  for PC-AGE-Si;  $j = 1$  for PAR-AGE-Si;  $m, n = 1$  or  $< 1$ ;  $m + n = 2$  or  $< 2$

Scheme 3

TABLE IV  
Hydrosilylation of PC-AGE and PAR-AGE

Entry	PC or PAR-AGE (ID, $M_w$ )	Allyl group/HSi(OEt) <sub>3</sub> /catalyst (molar ratio)	Time (h)	Yield (%)
1	PC-AGE (0.60, 4800)	1/3/0.002	5	89
2	PC-AGE (0.10, 4200)	1/9/0.01	21	108
3	PC-AGE (0.05, 6700)	1/6/0.008	16	109
4	PAR-AGE (1.3, 14,100)	1/2/0.01	5	127
5	PAR-AGE (0.66, 6700)	1/2/0.01	5	85
6	PAR-AGE (1.3, 14,100)	0.75/1/0.002	10	77
7	PAR-AGE (0.66, 6700)	1/1.05/0.002	6	97

All reactions were carried out with 5–8 g of PC-AGE or PAR-AGE in chloroform (150 mL).

PAR-AGE (Table II, entry 8)

$M_w = 6700$  (ID = 0.75, 58% yield). FTIR (neat,  $\text{cm}^{-1}$ ): 1734 (C=O), 1647 (CH<sub>2</sub>=CH–). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.6–1.7 (s, s, 8H, [CH<sub>3</sub>–C–(CH<sub>3</sub>)], 3.8 (d, 2H, –O–CH<sub>2</sub>–CH–CH<sub>2</sub>–), 4.0 (d, 2H, CH<sub>2</sub>=CH–CH<sub>2</sub>–O–), 4.3 (d, 2H, –CH<sub>2</sub>–CH–CH<sub>2</sub>–O–C<sub>6</sub>H<sub>4</sub>–), 5.1–5.3 (m, 2H, CH<sub>2</sub>=CH–CH<sub>2</sub>–), 5.56 (m, 1H, –CH<sub>2</sub>–CH–CH<sub>2</sub>–), 5.9 (m, 1H, CH<sub>2</sub>=CH–CH<sub>2</sub>–), 6.7–7.3 (m, 11H, Ar–H), 7.6–9.0 (m, 7H, Ar–H).

The calculated ID was 0.75 from the intensity ratio of the <sup>1</sup>H-NMR peaks (1/8): 5.9 ppm for CH<sub>2</sub>=CH–CH<sub>2</sub>– and 1.6–1.7 ppm for (CH<sub>3</sub>)–C–(CH<sub>3</sub>).

ANAL. Calcd for (C<sub>27.5</sub>H<sub>25.5</sub>O<sub>5.5</sub>)<sub>k</sub> (ID = 0.75): C, 74.41%; H, 5.75%. Found: C, 74.4%; H, 5.6%.

PAR-EH (Table II, entry 10)

$M_w = 47,600$  (ID = 0.02, 56% yield). FTIR (neat,  $\text{cm}^{-1}$ ): 1740 (C=O), 1643 (very weak, CH<sub>2</sub>=CH–). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.6–1.7 [s, s, 6H, (CH<sub>3</sub>)–C–(CH<sub>3</sub>)], 1.8–2.0 (m, 0.05H, CH<sub>2</sub>=CH–CH<sub>2</sub>–CH<sub>2</sub>–CH), 2.2–2.3 (m, 0.05H, CH<sub>2</sub>=CH–CH<sub>2</sub>–), 4.2 (d, 0.05H, –CH<sub>2</sub>–CH–CH<sub>2</sub>–O–C<sub>6</sub>H<sub>4</sub>–), 4.9–5.1 (m, 0.07H, CH<sub>2</sub>=CH–CH<sub>2</sub>– + –CH<sub>2</sub>–CH–CH<sub>2</sub>–), 5.7–5.9 (m, 0.02H, CH<sub>2</sub>=CH–CH<sub>2</sub>–), 6.7–7.3 (m, 8H, Ar–H), 7.6–9.0 (m, 4H, Ar–H).

The calculated ID was 0.02 from the intensity ratio of the <sup>1</sup>H-NMR peaks (1/50): 5.7–5.9 ppm for CH<sub>2</sub>=CH–CH<sub>2</sub>– and 1.6 ppm for (CH<sub>3</sub>)–C–(CH<sub>3</sub>).

ANAL. Calcd for (C<sub>23.12</sub>H<sub>18.2</sub>O<sub>4.02</sub>)<sub>k</sub> (ID = 0.02): C, 77.07%; H, 5.06%. Found: C, 76.66%; H, 5.06%.

#### General procedure for the reaction of PC with AGE under solid conditions

For PC-AGE (Table III, entry 6), after the PC (Iupilon S2000;  $M_w = 53,700$ , 10.0 g, 0.2 mmol, 39 mmol of carbonate group), AGE (4.5 g, 39 mmol), and TBPB (0.14 g, 0.4 mmol) were dissolved in chloroform (200 mL), the chloroform solution was cast onto a glass Petri dish, and then the chloroform was volatil-

ized to give a solid PC containing AGE and TBPB. The solid PC was heated at 70°C for 9 h in an oven. The resulting solid was dissolved in chloroform and then poured into a large quantity of methanol to precipitate the product. After collection and drying, PC-AGE was obtained [64% yield,  $M_w = 13,700$ , ID = 0.32, FTIR (neat,  $\text{cm}^{-1}$ ): 1770 (C=O), 1647 (CH<sub>2</sub>=CH–)].

#### General procedure for the hydrosilylation

Table IV, entry 1

A mixture of PC-AGE ( $M_w = 4800$ , ID = 0.6, 8.0 g, 1.7 mmol, 12 mmol of allyl group), TESH (5.9 g, 36

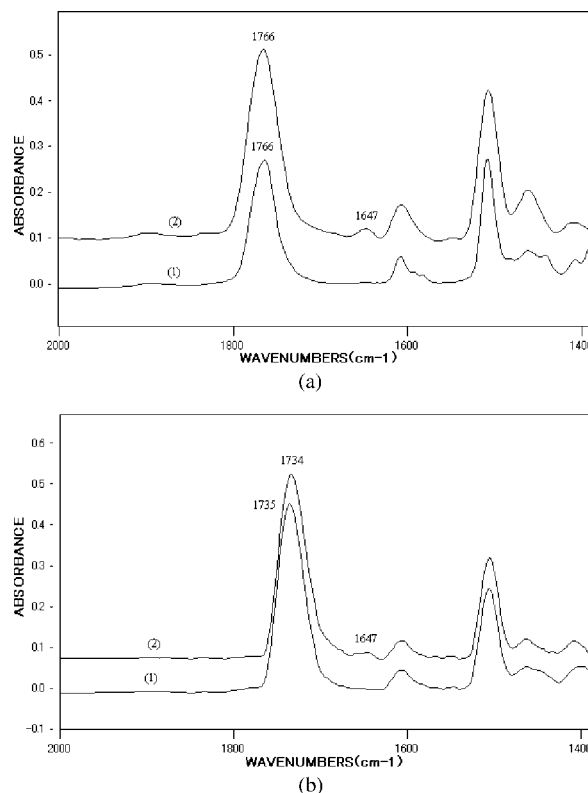


Figure 8 IR spectra of the 1400–2000- $\text{cm}^{-1}$  region in (a-1) PC-AGE (Table I, entry 8), (a-2) PC-AGE-Si (Table IV, entry 1), (b-1) PAR-AGE (Table II, entry 8), and (b-2) PAR-AGE-Si (Table IV, entry 7).

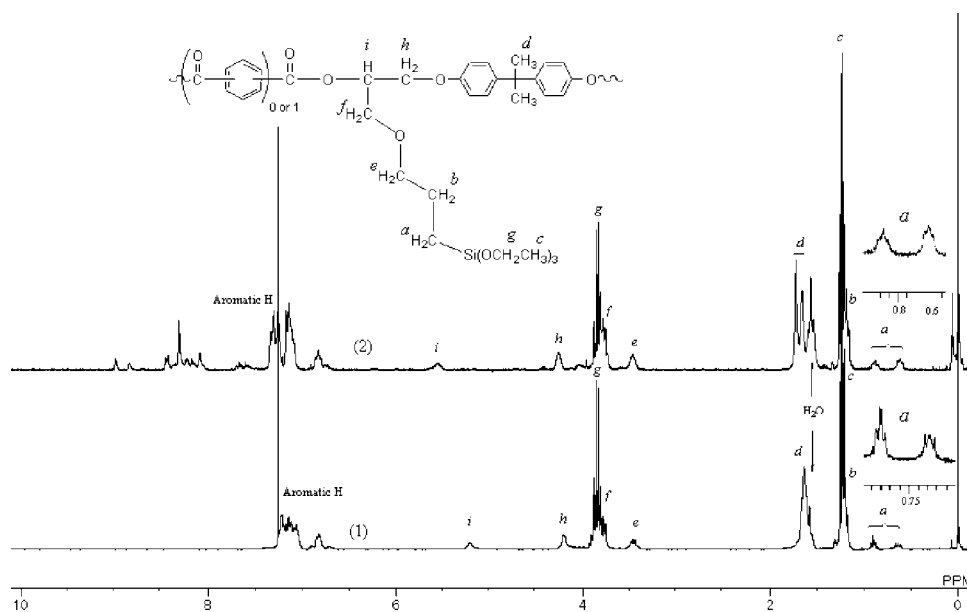


Figure 9  $^1\text{H-NMR}$  spectra of (1) PC-AGE-Si (Table IV, entry 1) and (2) PAR-AGE-Si (Table IV, entry 7).

mmol), a THF solution of  $\text{H}_2\text{PtCl}_6$  (0.25 mol/L, 100  $\mu\text{L}$ , 25  $\mu\text{mol}$ ), and chloroform (150 mL) was heated at  $62^\circ\text{C}$  for 5 h with stirring under a nitrogen atmosphere. The resulting reaction mixture was cooled to room temperature and filtered. After the filtrate was poured into a large volume of ethanol, the precipitated solid was filtered and dried to give the hydrosilylated PC-AGE (PC-AGE-Si; 8.9 g, 89% yield,  $M_w = 5200$ ).

FTIR (film,  $\text{cm}^{-1}$ ): 3490 (Si—OH), 1766 (C=O), 1103 (Si—O—C).  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.67 and 0.91 [(m, 1H) and (m, 1H), Si— $\text{CH}_2$ —], 1.2–1.3 (m, 14H, O— $\text{CH}_2$ — $\text{CH}_2$ — $\text{CH}_2$ —Si + SiO $\text{CH}_2\text{CH}_3$ ), 1.6 [s-br, 10H, ( $\text{CH}_3$ )—C—( $\text{CH}_3$ )], 3.47 (t-br, 2H, O— $\text{CH}_2$ — $\text{CH}_2\text{CH}_2\text{Si}$ ), 3.7–3.9 (m, 11H, — $\text{CH}_2$ —O— $\text{CH}_2\text{CHCH}_2$ — + SiO— $\text{CH}_2$ — $\text{CH}_3$ ), 4.21 (br, 2H, — $\text{CH}_2$ —CH— $\text{CH}_2$ —O—Ar), 5.21 (br, 1H, — $\text{CH}_2$ —CH— $\text{CH}_2$ —O—), 6.7–7.3 (m-br, 13H, Ar—H).

The calculated ID was 0.6 from the intensity ratio of the  $^1\text{H-NMR}$  peaks (1/10): 5.21 ppm for — $\text{CH}_2$ —CH— $\text{CH}_2$ —O— and 1.6 ppm for ( $\text{CH}_3$ )—C—( $\text{CH}_3$ ).

ANAL. Calcd for  $(\text{C}_{23.2}\text{H}_{29.6}\text{O}_6\text{Si}_{0.6})_k$  (ID = 0.6): C, 66.16%; H, 7.03%; Si, 3.99%. Found: C, 62.4%; H, 7.2%; Si, 5.4%.

#### Table IV, entry 7

A mixture of PAR-AGE ( $M_w = 6700$ , ID = 0.75, 5.0 g, 0.75 mmol, 7.5 mmol of allyl group), TESH (1.3 g, 7.9 mmol), a THF solution of  $\text{H}_2\text{PtCl}_6$  (0.25 mol/L, 60  $\mu\text{L}$ , 15  $\mu\text{mol}$ ), and chloroform (150 mL) was heated at  $62^\circ\text{C}$  for 5 h with stirring under a nitrogen atmosphere. The hydrosilylated PAR-AGE (PAR-AGE-Si; 6.1 g, 97% yield,  $M_w = 7800$ ) was obtained by the same posttreatment shown in Table IV, entry 1.

FTIR (film,  $\text{cm}^{-1}$ ): 3460 (Si—OH), 1735 (C=O), 1103 (Si—O—C).  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.62 and 0.88 [(m, 1H) and (m, 1H), Si— $\text{CH}_2$ —], 1.2–1.3 (m, 12H, O— $\text{CH}_2$ — $\text{CH}_2$ — $\text{CH}_2$ —Si + SiO $\text{CH}_2\text{CH}_3$ ), 1.6–1.7 [s, s, 8H, ( $\text{CH}_3$ )—C—( $\text{CH}_3$ )], 3.48 (t-br, 2H, O— $\text{CH}_2$ — $\text{CH}_2\text{CH}_2\text{Si}$ ), 3.7–3.9 (m, 10H, — $\text{CH}_2$ —O— $\text{CH}_2\text{CHCH}_2$ — + SiO— $\text{CH}_2$ — $\text{CH}_3$ ), 4.26 (br, 2H, — $\text{CH}_2$ —CH— $\text{CH}_2$ —O—Ar), 5.56 (br, 1H, — $\text{CH}_2$ —CH— $\text{CH}_2$ —O—), 6.7–7.3 (m-br, 11H, Ar—H), 7.6–9.0 (m, 6H, Ar—H).

The calculated ID was 0.6 from the intensity ratio of the  $^1\text{H-NMR}$  peaks (1/8): 5.56 ppm for — $\text{CH}_2$ —CH— $\text{CH}_2$ —O— and 1.6–1.7 ppm for ( $\text{CH}_3$ )—C—( $\text{CH}_3$ ).

ANAL. Calcd for  $(\text{C}_{32}\text{H}_{37.5}\text{O}_{7.75}\text{Si}_{0.75})_k$  (ID = 0.75): C, 67.78%; H, 6.62%; Si, 3.71%. Found: C, 67.9%; H, 6.4%; Si, 3.3%.

#### References

1. Arakawa, M.; Shimada, M.; Agari, Y.; Sukata, K. *Kobunshi Ronbunshu* 2000, 57, 180.
2. Arakawa, M.; Sukata, K.; Shimada, M.; Agari, Y. *J Appl Polym Sci* 2006, 100, 423.
3. (a) Funahashi, K. *Chem Lett* 1978, 1043; (b) Funahashi, K. *Bull Chem Soc Jpn* 1979, 52, 1488; (c) Funahashi, K. *Makromol Chem* 1979, 180, 501.
4. (a) Nishikubo, T.; Iizawa, T.; Saito, Y. *J Polym Sci Polym Chem Ed* 1983, 21, 2291; (b) Nishikubo, T.; Iizawa, T.; Takahashi, E.; Nono, F. *Macromolecules* 1985, 18, 2131; (c) Nishikubo, T.; Shimokawa, T. *Makromol Chem Rapid Commun* 1986, 7, 179; (d) Nishikubo, T.; Shimokawa, T.; Hirano, T.; Shiina, A. *J Polym Sci Polym Chem Ed* 1989, 27, 2519; (e) Nishikubo, T.; Kameyama, A. *Prog Polym Sci* 1993, 18, 963 (review article).
5. Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1989; Vol. 1, Chapter 8, p 513.