

# NOTE

## High-Pressure Synthesis of Polystyrene-Bound C<sub>60</sub> Gel

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Received 16 October 1996; accepted 1 January 1997

### INTRODUCTION

Buckminsterfullerene such as C<sub>60</sub> is a soluble new form of carbon<sup>1</sup> and can be obtained by evaporating graphite electrodes in an atmosphere of 100 Torr of helium.<sup>2</sup> This C<sub>60</sub> and its *n*-doped derivatives exhibit outstanding electrical and nonlinear optical properties.<sup>3–5</sup>

The combination of this molecule with a polymer is challenging for improving the processability of C<sub>60</sub>.<sup>6</sup> The polymeric fullerene derivatives were prepared in previous articles.<sup>6–11</sup> A polymeric fullerene based on polystyrene was reported in 1992.<sup>6</sup> The polymeric fullerene was synthesized by addition of a polystyrene carbanion solution into the C<sub>60</sub> solution. Free-radical polymerization of C<sub>60</sub> and *p*-xylylene led to an insoluble C<sub>60</sub>-*p*-xylylene copolymer.<sup>7</sup> Polymer-bound C<sub>60</sub> was prepared by titrating a toluene solution of C<sub>60</sub> with the aminopolymers.<sup>8</sup> Cao and Weber and Bunker et al. recently described a method for direct incorporation of C<sub>60</sub> and C<sub>70</sub> into polystyrene by free-radical copolymerization.<sup>9,10</sup> Soluble polystyrene-bound fullerene was synthesized by reaction-induced high pressure.<sup>11</sup> In this article, we synthesized a polystyrene-bound C<sub>60</sub> gel by high-pressure polymerization of styrene in the presence of C<sub>60</sub>.

### EXPERIMENTAL

#### Materials

C<sub>60</sub> (C<sub>60</sub>: 99.9%) from MER Corp. (U.S.A.) was used without further purification. Styrene was distilled un-

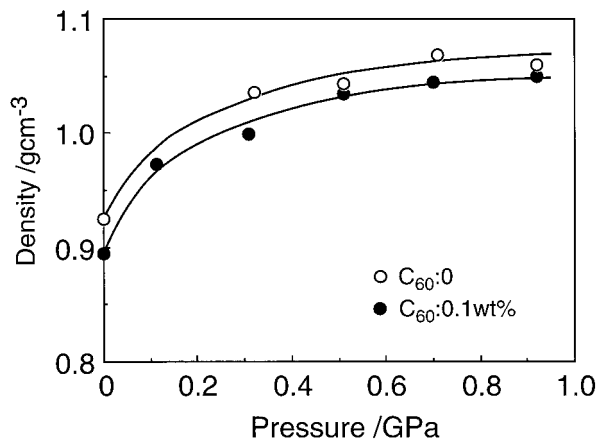
der reduced pressure before use. C<sub>60</sub> was easily soluble in styrene. Reaction of the styrene solution of C<sub>60</sub> under high pressure was carried out using a high hydrostatic pressure reactor, as shown in the previous article.<sup>12</sup> The styrene solution of C<sub>60</sub> with 0.1–0.5 wt % (about 1.3 g) was packed into a polytetrafluoroethylene cell (inside diameter: 8.5 mm; length: 23 mm). After closing the cell, it was introduced into the high-pressure vessel. The specimen solution was compressed at various pressures in the range of 0.1–0.9 GPa by a hand oil pump and substantially reacted at 100°C for a constant time of 5 h with a pressure transmitting medium (silicone oil). After reaction under high pressure, the product was cooled to room temperature, decompressed, and removed from the cell.

#### Characterization

Elementary analysis was made using an instrument of combustion analysis (Perkin–Elmer elemental analyzer 240C) for carbon and hydrogen. The GPC chromatogram, which is absorbance of the product as a function of elution time, was obtained by a chromatograph, a column and, a photodiode array UV-visible light detector (Shimadzu SPD-M6A). Chloroform was used as a mobile phase at a flow rate of 1 mL/min on the column. A Fourier transform infrared spectrophotometer (Japan Spectroscopic Co., FT/IR-5M) was used for infrared studies in the wavenumber from 4000 to 600 cm<sup>-1</sup>. Specimens in powder form were mixed with KBr (0.5 mg of specimen with 200 mg of KBr), and tablets were formed by applying pressure. The density of the specimen was measured with an electric densitometer ED120T from Mirage Trade Co. (Japan). The density of the liquid specimen was calculated from the weight and volume.

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Journal of Applied Polymer Science, Vol. 65, 2781–2783 (1997)  
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**Figure 1** Pressure dependence of density.

## RESULTS AND DISCUSSION

High-pressure polymerization of the styrene in the presence of  $C_{60}$  was carried out at  $100^\circ\text{C}$ . Styrene is transparent and has no absorption in the visible region. A styrene solution of  $C_{60}$  is violet, but the product made by reacting the  $C_{60}$  solution under high pressure was colored orange. The change of the color indicates the reaction of  $C_{60}$  with styrene. Figure 1 shows the density of the product as a function of pressure. The density increases with pressure, approaching a constant value. The mainly solid-state product (styrene content  $< 4$  wt %) was obtained by reacting the styrene solution of  $C_{60}$  ( $C_{60}$  content: 0.1 wt %) under high pressure above 0.3 GPa at  $100^\circ\text{C}$  for 5 h. The infrared spectra of the mainly solid-state products were similar to that of polystyrene but the spectrum was absent of the absorption band of the substituted  $C_{60}$  ( $520\text{--}530\text{ cm}^{-1}$ )<sup>11,13</sup> due to the dilute concentration of  $C_{60}$ . As the density of the styrene and polystyrene are  $0.907$  and  $1.04\text{--}1.07\text{ g cm}^{-3}$ , respectively,<sup>14,15</sup> it is indicated that the  $C_{60}$ -containing polystyrene content in the product increases with pressure. The dependence of the rate constant of polymerization  $K_{\text{pol}}$  in pressure  $P$  is given by<sup>16</sup>

$$\left(\frac{\partial \ln K_{\text{pol}}}{\partial P}\right)_T = \frac{-\Delta V_{\text{pol}}^\ddagger}{RT} \quad (1)$$

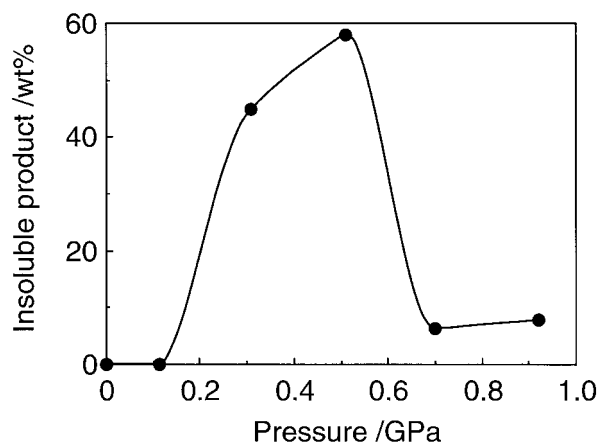
where  $R$  is the gas constant;  $T$ , the absolute temperature; and  $\Delta V_{\text{pol}}^\ddagger$ , the activation volume of the polymerization reaction and is expressed by the following relation:

$$\Delta V_{\text{pol}}^\ddagger = \Delta V_p^\ddagger + \Delta V_d^\ddagger/2 - \Delta V_t^\ddagger/2 \quad (2)$$

where  $\Delta V_p^\ddagger$ ,  $\Delta V_d^\ddagger$ , and  $\Delta V_t^\ddagger$  are the activation volumes of propagation, decomposition, and termination, respec-

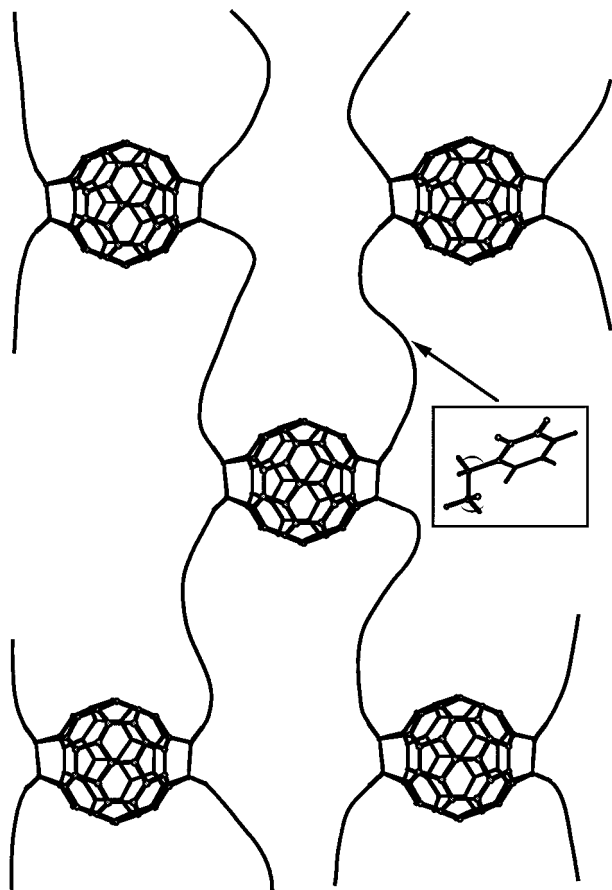
tively. The activation volume is the volume change in going from the ground state to the transition state.  $\Delta V_{\text{pol}}^\ddagger$  of the polymerization reaction of styrene is obtained as  $-18\text{ cm}^3/\text{mol}$  (ref. 16) and the polymerization is accelerated by pressure. Figure 1 also includes the density of the product by reaction of styrene under high pressure. The density of the product with  $C_{60}$  is small compared with that of the product by reaction of styrene.  $C_{60}$  plays an important role in hindering the polymerization of styrene.

The  $C_{60}$ -containing polystyrene synthesized by reaction of the  $C_{60}$  solution above 0.3 GPa was classified to the soluble and insoluble products in chloroform. Figure 2 shows the pressure dependence of the fraction of the insoluble product in chloroform. The fraction has the maximum value at a pressure of 0.5 GPa. The insoluble product synthesized under 0.3–0.5 GPa was swollen in chloroform. The degree of swelling with chloroform (the weight of sample at the swollen state/the weight of sample at the dry state) is 28–34. The polystyrene synthesized under high pressure was absent of the insoluble product. The infrared spectrum of the insoluble product (pressure: 0.3–0.5 GPa,  $100^\circ\text{C}$ , 5 h) was similar to that of polystyrene and absent of the band of the substituted  $C_{60}$  ( $520\text{--}530\text{ cm}^{-1}$ ).<sup>13</sup> Furthermore, the H/C value of the insoluble product was 1.00–1.01 and agreed well with that of polystyrene. These results are due to the dilute concentration of  $C_{60}$  in the product. We found that polystyrene-bound  $C_{60}$  gel was synthesized under high pressure. The fraction of the insoluble product increased with the concentration of  $C_{60}$  (insoluble product [ $C_{60}$ : 0.1 wt %]: 6.2 wt %, insoluble product [ $C_{60}$ : 0.5 wt %]: 7.6 wt %). Figure 3 shows the structure model of the polystyrene-bound  $C_{60}$  gel.  $C_{60}$  is composed of 12 five-membered rings and 20 six-membered rings. The coupling to the polystyrene chain proceeded according to the styrene addition to the  $C_{60}$  double bond between two six-membered rings.<sup>13</sup>

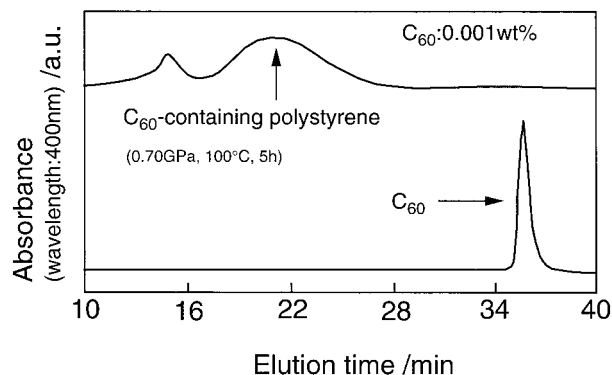


**Figure 2** Influence of pressure on fraction of insoluble product.

GPC chromatograms at the wavelength of 400 nm were obtained by the three-dimensional GPC chromatograms of the soluble  $C_{60}$ -containing polystyrene. Figure 4 shows the GPC chromatograms of the  $C_{60}$ -containing polystyrene and  $C_{60}$  at the wavelength of 400 nm. In Figure 4, the  $C_{60}$  concentration in the polystyrene is similar to that of the chloroform solution of  $C_{60}$ . The chromatogram of the  $C_{60}$ -containing polystyrene showed absorbance below the elution time of 28 min and has the peaks at 17 and 20 min. The chromatogram of the  $C_{60}$  was obtained at 36.5 min of the elution time. The polystyrene did not have a GPC chromatogram at the wavelength. Thus, for the  $C_{60}$ -containing polystyrene, the chromatogram at the elution time below 28 min indicates the presence of polystyrene-bound  $C_{60}$ .<sup>11</sup> The molecular weight of the polystyrene-bound  $C_{60}$  is between 4000 and  $10^8$ . In conclusion, polystyrene-bound  $C_{60}$  gel was prepared under pressures of 0.3–0.5 GPa at 100°C. The degree of swelling of the gel was 28–34 in chloroform.



**Figure 3** Structure model of polystyrene-bound  $C_{60}$  gel.



**Figure 4** GPC chromatograms of soluble  $C_{60}$ -containing polystyrene and  $C_{60}$ .

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