

Studies on a Novel Polymeric Coupling Agent: 3-Glycidoxypropyltrimethoxysilane-Modified Polycarbonate

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SYNOPSIS

A novel polymeric coupling agent was synthesized through the reaction of polycarbonate (PC) and 3-glycidoxypropyltrimethoxysilane (GPS) in the presence of a quaternary ammonium salt. The reaction in the solid state gave a GPS-modified PC, which had a bimodal molecular weight distribution. The solutions of the GPS-modified PC were effective primers for promoting the adhesion of a siliceous abrasion-resistant coating to the PC substrate.

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INTRODUCTION

To improve the abrasion and scratch resistance of polycarbonate (PC) surface, transparent hard coatings have been developed consisting typically of a polysiloxane resin heavily filled with nanosized silica¹ and, optionally, other colloidal hard minerals. The adhesion of the siliceous coatings to the PC substrate is usually weak. Expansion mismatch and the hydrophilic nature of the mineral surfaces are two main deteriorative factors in such organic/inorganic systems, which cause debonding during exposure to moisture. Efforts have been made to improve the adhesion by using primers, as demonstrated in a number of patents.²⁻⁵

On the basis of experience in the area of glass fiber reinforced plastics,⁶ silane coupling agents have been tried as a means for improving the adhesion of the siliceous coatings to the PC substrate. However, direct introduction of a normal silane coupling agent into the interface was not successful, either by using a solution of functional organoalkoxysilane or by using its hydrolysate. There were probably insufficient interactions between the coupling agent and the substrate.

A successful coupling agent should offer mechanisms of strong interaction with both the coating

and the 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. As to the interaction with the polycarbonate substrate, it is preferable to have a PC chain attached to the silane molecule so that the coupling agent can bond to the substrate through interpenetration. In this article we describe the synthesis, properties, and applications of novel polymeric coupling agents of this type.

EXPERIMENTAL

Preparation of GPS-Modified PCs

Bisphenol A PC (10 g, Scientific Polymer Products Inc., weight average molecular weight 53,000 by gel permeation chromatography, GPC), 0.05 g of tetrabutylammoniumiodide (TBAI) and 1–3 g of 3-glycidoxypropyltrimethoxysilane (GPS, from Aldrich Chemical Co.) were dissolved in methylene chloride and mixed well. The solvent was removed. The reaction was carried out in the solid state by heating the residuals in an oven at 60°C for 16–24 h to give GPS-modified PCs, designated as PC-GPS.

Determination of GPS conversion

The conversion of GPS during the reaction with PC was calculated from the change of the epoxy value determined by the pyridinium chloride-pyridine

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method.⁷ A PC-GPS sample of 0.3 g was dissolved in 10 mL of pyridinium chloride-pyridine reagent (0.1 N). The mixture was boiled for 20 min. The flask was cooled and then 6 mL of water and 0.1 mL of phenolphthalein indicator solution were added. The excess acid was titrated with standard 0.05 N alcohol sodium hydroxide solution.

Preparation of Primer Solutions

PC-GPS, 2 g, was dissolved in 100 g of dioxane, and then 20 g of 2-propanol was added. The solutions were used as primers, which were applied onto the surface of the PC substrate prior to a top coating.

Preparation of Top Coating Composition

In a glass flask, 13.6 g of methyltrimethoxysilane and 0.34 g of acetic acid were added, and then 22.3 g of Ludox LS (30% colloidal silica from Du Pont Co.) was introduced. The mixture was stirred at room temperature for 2 h to give a clear solution. Acetic acid, 0.8 g, was added to adjust the pH to 3.94. Finally, 22.8 g of 2-propanol was added. The composition was aged for a week before use.

Coating Procedure

Uncoated PC sheets (from Rohm and Haas Co.) were washed with 2-propanol and dried at 60°C for

10 min. The primer was applied to the PC surface, about 4 mg solution/cm². The primer was air dried. Then the top coating composition was applied, about 10 mg/cm². The sheet was put into an oven, the temperature of which was increased from room temperature to 125°C in 30 min, and kept at 125°C for 2 h to effect the curing.

Adhesion Test

A cross-cut test method⁸ was used for the evaluation of the adhesion. In the test, six parallel cuts of 1-mm interval were made in each of two directions at right angles, and a peeling test was performed by using standard pressure sensitive adhesive tape. The adhesion was rated according to the number of squares in which the top coating layer remained. To evaluate the durability of the adhesion the specimens were immersed in a water bath at 80°C for 1 h before the cross-cut test.

Instrumentation

¹H-NMR spectra were recorded on a 60 MHz Hitachi R-1200 NMR instrument, by using CDCl₃ as solvent. Infrared (IR) spectra were taken by using a Nicolet Fourier transform (FT)/IR with a PC data station. For the differential scanning calorimetry (DSC) studies a Perkin-Elmer DSC 7 system was used. GPC chromatograms were obtained by using

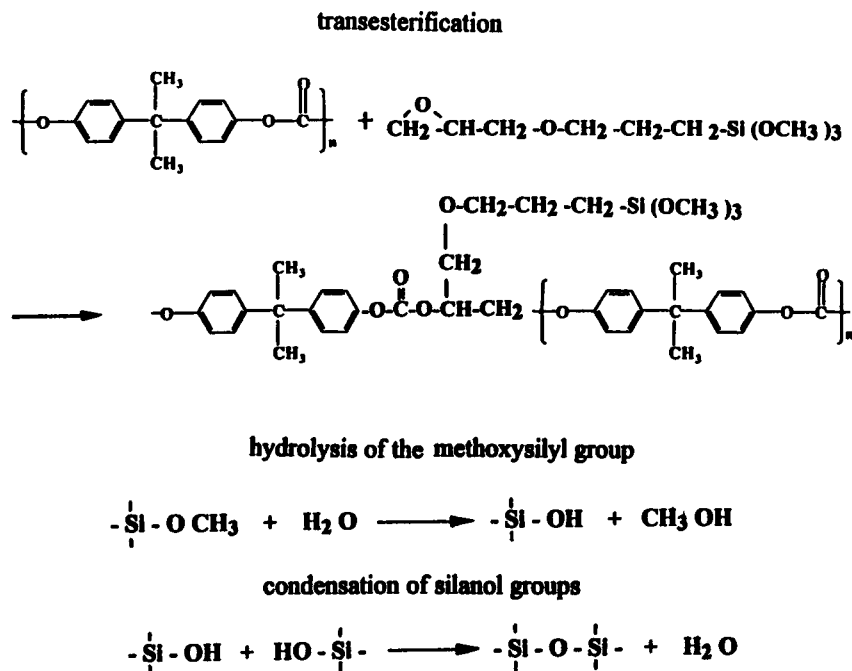


Figure 1 Chemical reactions in a PC-GPS-TBAI system.

a Waters 1-80-252-HPLC (high-performance liquid chromatography) system with Ultrastyrigel columns and a refractive index (ri) detector. Chloroform was used as eluent.

RESULTS AND DISCUSSION

Synthesis of PC-GPS

There are two kinds of functional groups in a GPS molecule: the epoxy group and the methoxysilyl group. According to the previous works^{9,10} the transesterification between carbonate groups and epoxy groups gives GPS-grafted PC (Fig. 1).

The reaction was studied by using ¹H-NMR spectroscopy. Figure 2(a) shows the spectrum of the mixture of 100 parts PC and 20 parts GPS in the presence of 0.5 part TBAI. Figure 2(b) shows the spectrum of the above mixture after being heated at 60°C for 12 h. As the reaction continued a new peak around δ 3.90 ppm appeared; this is where the signal of the methylene protons adjacent to the phenoxy group and the methine proton adjacent to the carbonate group should be found. New peaks at δ 6.65 ppm and 6.81 ppm were due to the *ortho*-phenylene protons of the phenyl ether formed by the transesterification. The signal at δ 3.58 ppm, which was contributed by the methoxysilyl protons, decreased during the reaction. The methylene protons adjacent to the alkoxy group cause the resonance signals at δ 3.49 ppm and 3.44 ppm.

The possibility of transesterification between the methoxysilyl group and the carbonate group was ruled out by a control experiment, in which methyltrimethoxysilane was used instead of GPS. Except for the original signals from the PC and the methyltrimethoxysilane, no new signal in the NMR spectrum appeared after the mixture of PC, methyltrimethoxysilane, and TBAI was heated at 60°C for 12 h (Fig. 3).

The decrease of the NMR signal at δ 3.58 ppm during the reaction of GPS with PC was accounted for by the hydrolysis of the methoxysilyl group, which gave silanol groups. It is known that methoxysilanes can be easily hydrolyzed by moisture, which is present in the PC and in the solvent, and also can be picked up from the atmosphere. In the NMR spectrum of the reaction product the signal of the silanol protons overlapped that of the oxirane protons [δ 2.5–2.8 ppm, Fig. 4(b)] when CDCl₃ was used as solvent. The silanol protons were exchanged with D₂O as shown in Figure 4(c), in which the signal from the silanol protons disappeared and only the signals from the oxirane protons remained.

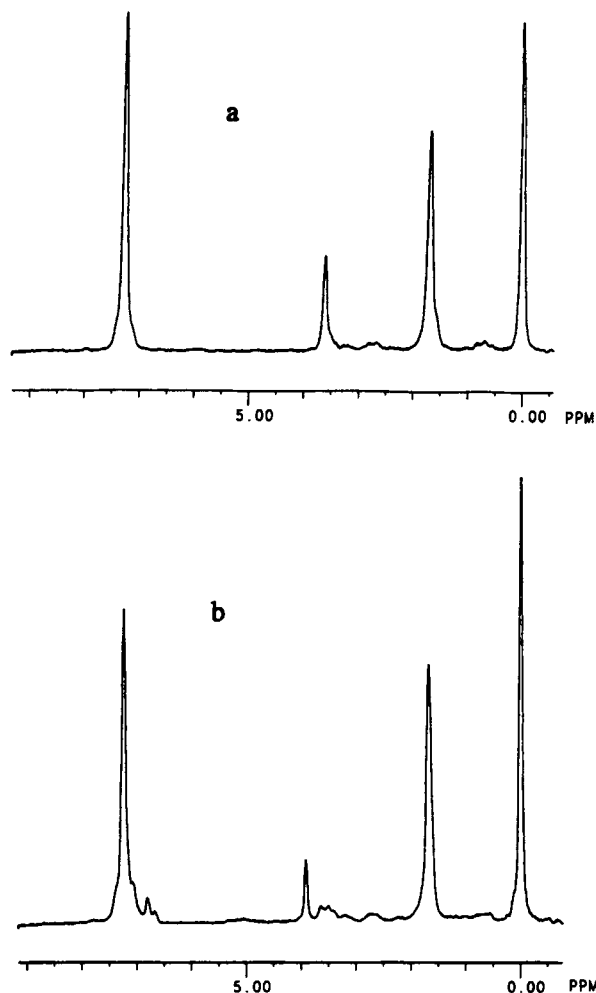


Figure 2 NMR spectra of a PC-GPS-TBAI mixture (a) before reaction and (b) after heating at 60°C for 12 h.

The change of functional groups was also studied by IR spectroscopy. The decrease of the epoxy band at 910.0 cm⁻¹ is shown in Figure 5. The characteristic peak of the methoxysilyl group at 2840.6 cm⁻¹ disappeared after the reaction mixture was heated at 60°C for 16 h. The bands at 3500, 935.3, and 946.9 cm⁻¹, which might be attributed to the silanol groups, increased remarkably.

The conversion of the epoxy group was determined by a pyridinium chloride-pyridine method. The results are in agreement with the decrease of the integrated resonance intensity at δ 2.5–2.8 ppm with the integration at δ 1.67 ppm as reference. Some results are given in Table I.

In the solid state the reaction proceeded smoothly at 60°C, and even at room temperature. Desired products were obtained from the reaction for 16–24 h at 60°C.

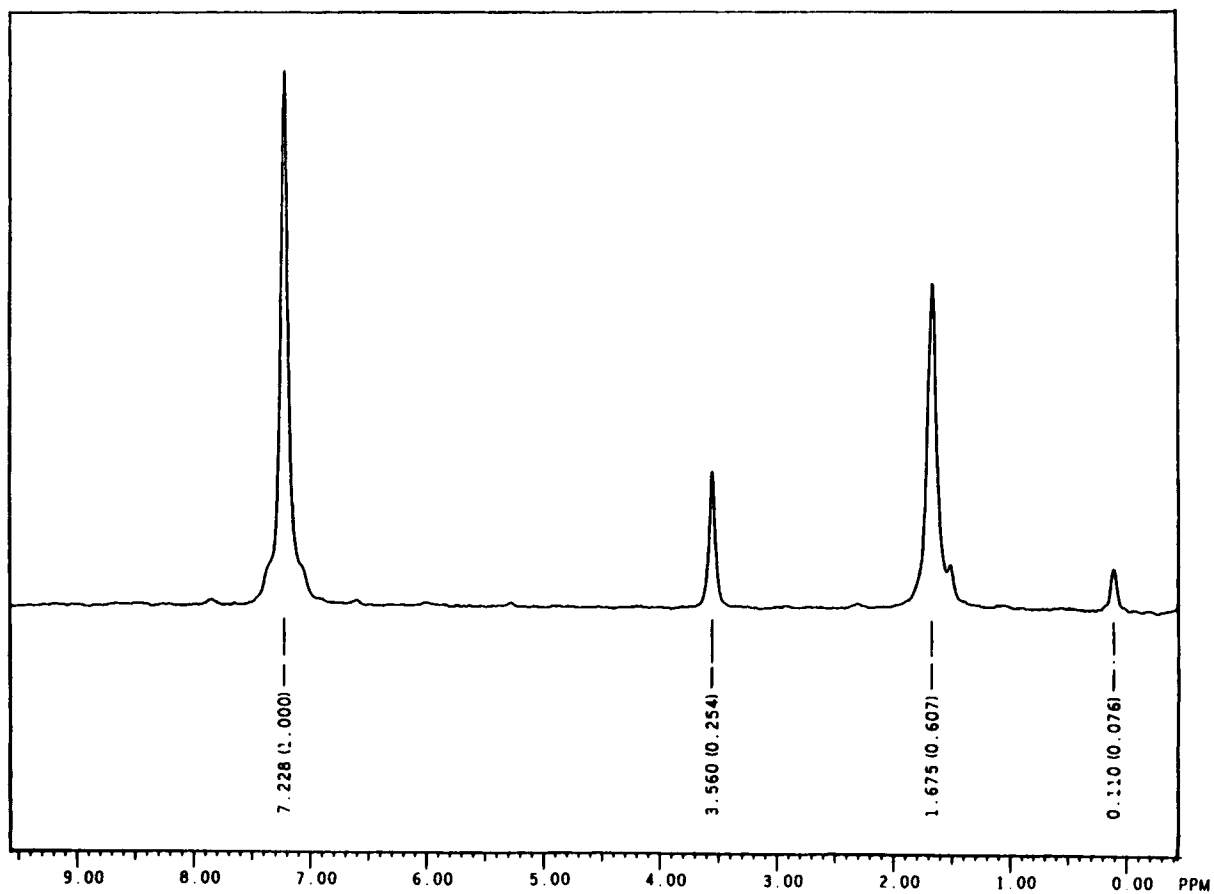


Figure 3 NMR spectrum of the mixture of methyltrimethoxysilane and PC after heating at 60°C for 12 h, in the presence of TBAI.

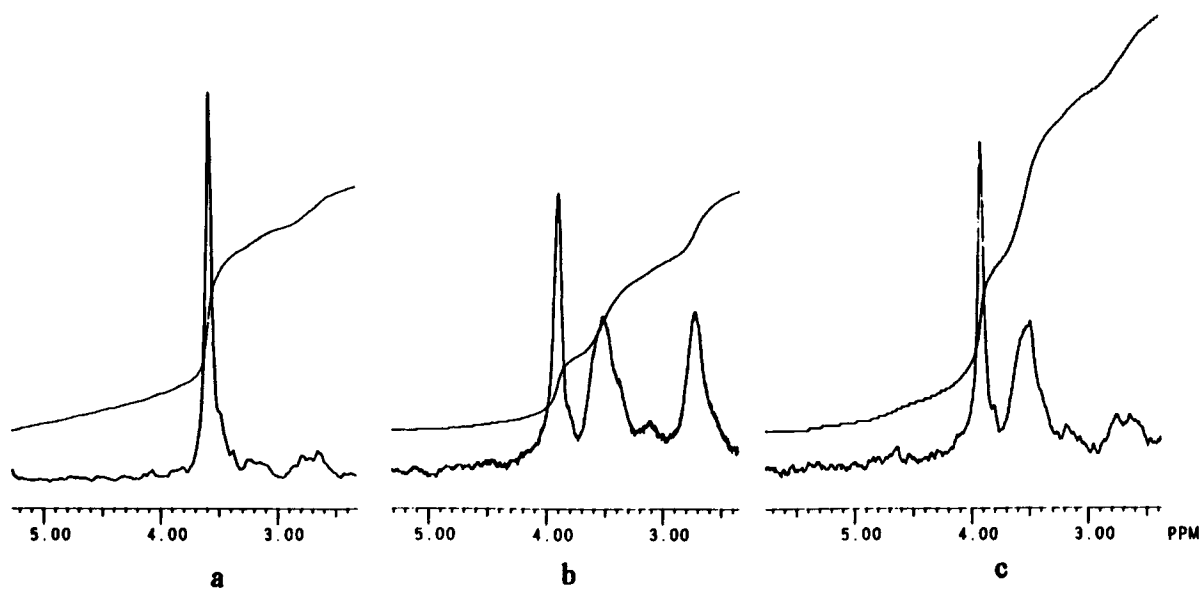


Figure 4 NMR spectra of the PC-20-GPS product: (a) before reaction, solvent CDCl_3 ; (b) after 16 h at 60°C, solvent CDCl_3 ; (c) after 16 h at 60°C, solvent CDCl_3 ; the silanol protons were exchanged with D_2O .

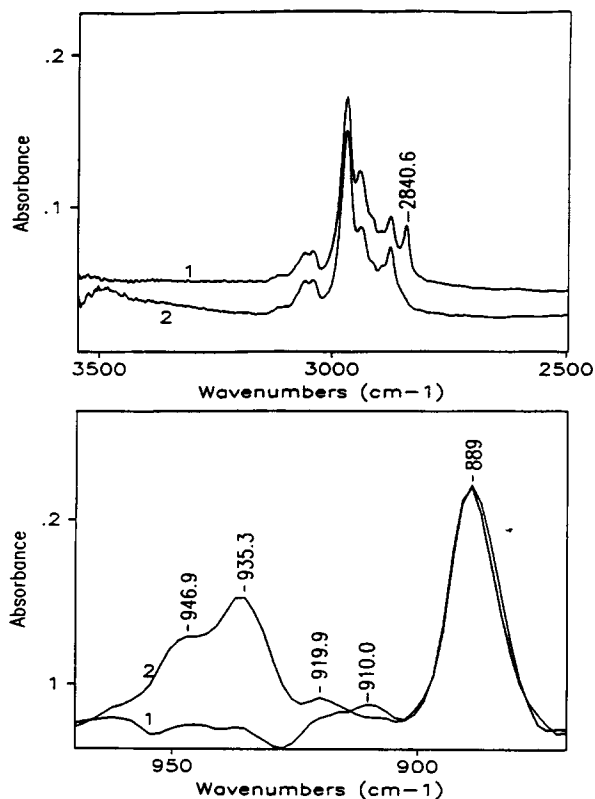


Figure 5 IR spectra of the PC-20-GPS product, (1) before reaction and (2) after 16 h at 60°C.

The reaction between GPS and PC in solution was much slower than in the solid state. Therefore a higher reaction temperature was needed. For example, 10 g PC, 2 g GPS, and 0.1 g TBAI was dissolved in 50 g dioxane. The solution was refluxed (101°C) for 8 h to give a product. The conversion of epoxy groups was 33%.

Condensation of the silanol groups took place concurrently during the reaction, which led to the formation of crosslinks. Microgel particles were present in the PC-GPS products when the reaction time exceeded 16 h at 60°C in the solid state. Macroscopic gelation was observed when the solid products were stored at room temperature for 2 weeks. However, the solution of the PC-GPS was stable when stored at room temperature for several months.

The presence of a catalyst was necessary for the transesterification of the epoxide and the carbonate. In the absence of catalyst the reaction was so slow that no NMR resonance signal at δ 3.9 ppm could be identified even after the mixture of GPS and PC was heated at 180°C for 2 h.

According to the NMR studies and the IR studies it can be concluded that in the PC-GPS products

the GPS molecules were grafted onto the PC chains through transesterification. Meanwhile the methoxysilyl groups were hydrolyzed, and the formed silanol groups condensed during the synthesis. The reaction should be stopped before gelation.

Characterization of PC-GPS

DSC Studies of PC-GPS

In the reaction mixtures of PC, GPS, and TBAI the polymer was in a semicrystalline state. The reaction products were also semicrystalline. A DSC thermogram of the reaction product of 100 parts PC and 20 parts GPS (designated as PC-20-GPS) is shown in Figure 6. There was an exothermal process above 150°C, which was overlapped by a broad endothermal melting process with a peak at 217°C. A second run of the same sample gave a glass-transition temperature, T_g , at 86°C, which was 60° lower than that of the starting PC.

The lowering of the T_g may be attributed to the change of the polymer chain composition and to the presence of low molecular fractions. Insertion of aliphatic units into the PC made the polymer chain more flexible, and the low molecular weight fractions formed by the chain redistribution, or by the degradation during the transesterification, plasticized the polymer.

GPC Studies of PC-GPS

The GPC chromatograms of the starting PC and GPS are given in Figure 7. The refractive index of GPS is lower than that of the eluent, therefore the peak is negative in the chromatogram.

The GPC chromatograms of the PC-20-GPS products obtained from the solid-state reaction at different reaction times are given in Figure 8. Before the injection the sample solutions were filtered using a 0.45- μ m filter. The presence of microgel particles

Table I Conversion of the Epoxy Group

| Code | Reaction Conditions | Conversion (%) by | |
|-------|-------------------------------|-------------------|-----|
| | | Titration | NMR |
| HY713 | 60°C, 16 h, and RT 60 days | 32.2 | 34 |
| HY810 | RT 33 days | 29.0 | 25 |
| HY831 | 60°C, 24 h, and RT 10 days | 27.5 | 27 |

Weight ratio of TBAI : GPS : PC = 0.5 : 20 : 100.

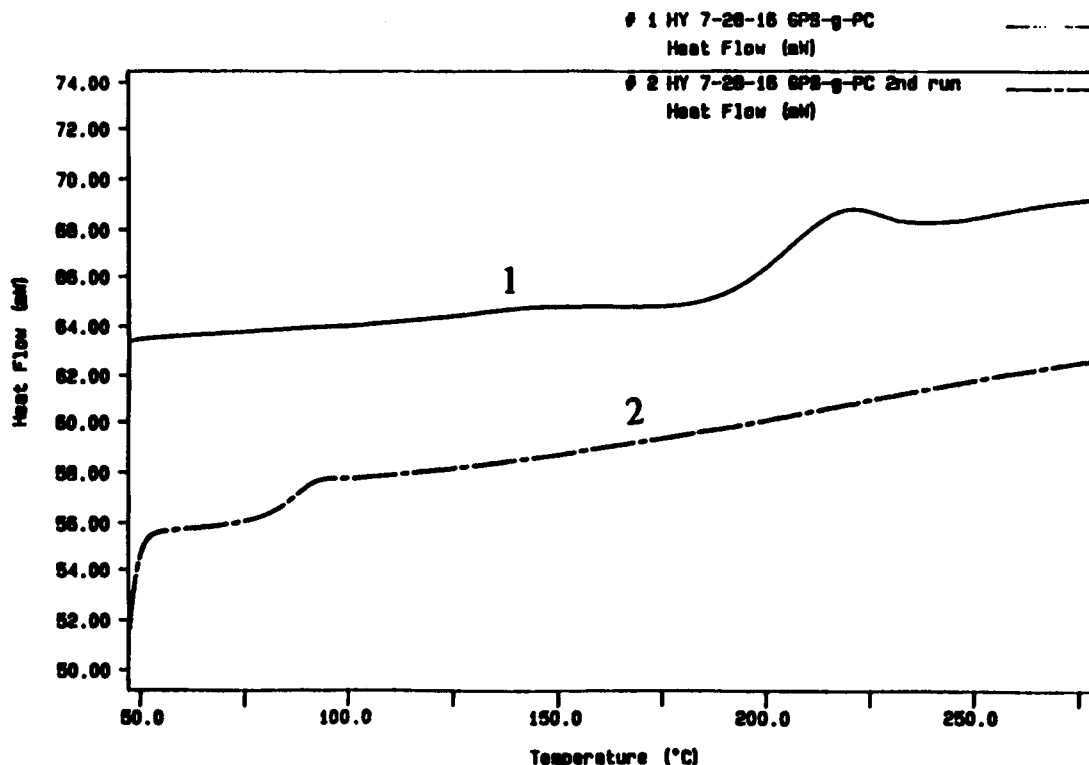


Figure 6 DSC thermogram of the PC-20-GPS product: (1) first run and (2) second run.

made the filtration difficult. The chromatograms show that the reaction products have a bimodal molecular weight distribution. The distribution would be much broader than that in the chromatograms because the very high molecular weight fractions had been removed by the filtration. Meanwhile a few very low molecular weight fractions can be seen in the chromatograms.

The broad molecular weight distribution indicates the redistribution of the polymer chain in the course of the transesterification. A tentative mechanism of

the chain redistribution is given in Figure 9 that would finally lead to a statistical distribution of the molecular weight.

The bimodal distribution may be related to the difference between the reaction in the amorphous region and that in the crystalline region of the PC. It is understandable that the crystalline region was not accessible to the reagents so that unreacted PC

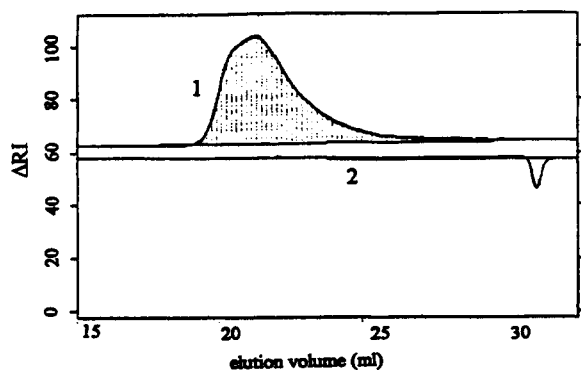


Figure 7 GPC chromatograms of (1) PC and (2) GPS.

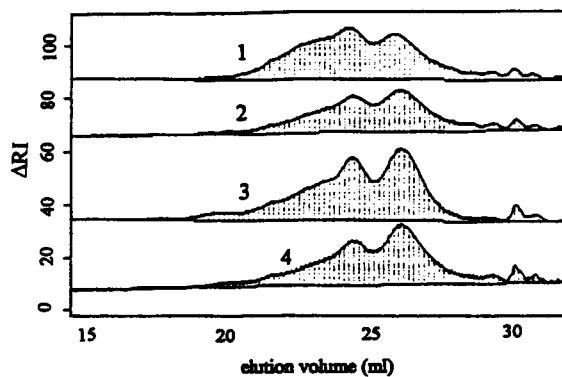


Figure 8 GPC chromatograms of the PC-20-GPS products obtained by different reaction conditions, 1-7 days at room temperature, 2-8 h at 60°C, 3-12 h at 60°C, and 4-24 h at 60°C.

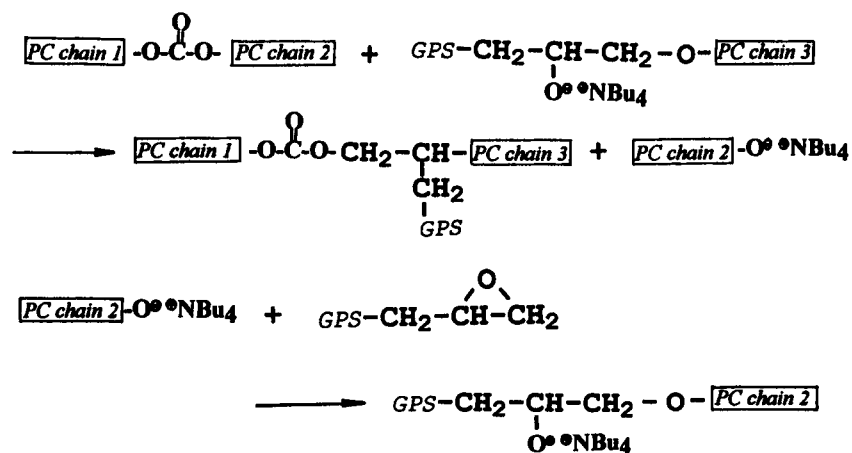


Figure 9 Redistribution of the polymer chain in the course of transesterification.

blocks remained in the reaction products, which may be responsible for the excellent adhesion to the PC substrate when the PC-GPS is used as primer.

The unreacted GPS did not appear in the chromatograms, and must have combined with the grafted copolymer through siloxane bonds.

Products of Solution Reaction

In the solution reaction products there were more methoxysilyl groups remaining unhydrolyzed. The products were easy to dissolve, and the solutions were very easily passed through a 0.45- μm filter. The GPC chromatogram (Fig. 10) showed that the product of the solution reaction had a monomodal molecular weight distribution and many more low molecular weight fractions. The reason for the degradation is not yet known. The glass-transition

temperature of the PC-20-GPS product obtained from the solution reaction was only 75°C.

Application of PC-GPS as Primer

It was found that the PC-GPS products from the solution reaction were not very effective in promoting the adhesion of the siliceous coating to the PC substrate. Therefore, in the following only the solid-state reaction products are discussed.

As evaluated by a crosshatched pressure sensitive adhesive tape pull-off test,⁸ the adhesion of the siliceous coating to the PC substrate in the absence of primer was very poor. When a dilute solution of PC-GPS products was applied on the PC surface prior to the top coating, the adhesion was improved greatly.

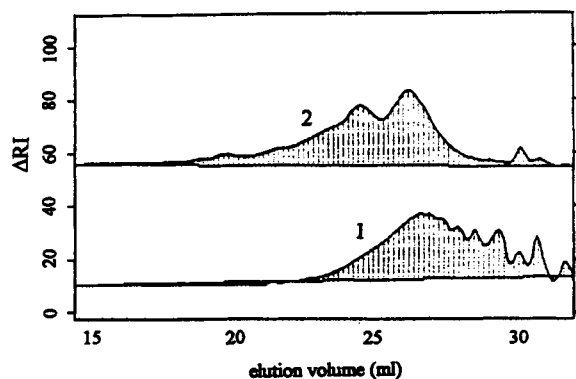


Figure 10 GPC chromatograms of the PC-20-GPS product obtained (1) by the reaction in dioxane solution at 100°C for 8 h and (2) by the reaction in solid state at 60°C for 16 h.

Table II Effect of GPS Proportion on Adhesion of Top Coating to Substrate

| Code | Ratio of GPS to Polycarbonate (wt) | Adhesion | |
|----------------|------------------------------------|----------|------------------------------------|
| | | Initial | After Water Immersion ^a |
| Without primer | | 0/100 | 0/100 |
| PC-10-GPS | 10 : 100 | 90/100 | 0/100 |
| PC-15-GPS | 15 : 100 | 100/100 | 30/100 |
| PC-20-GPS | 20 : 100 | 100/100 | 100/100 |
| PC-25-GPS | 25 : 100 | 100/100 | 75/100 |
| PC-30-GPS | 30 : 100 | 100/100 | 0/100 |

^a 1 h at 80°C.

Table III Effect of Drying Conditions of Primer on Adhesion of Top Coating

| °C | Drying Conditions | | Adhesion | |
|-----|-------------------|---------|------------------------------------|--|
| | Min | Initial | After Water Immersion ^a | |
| RT | 15 | 100/100 | 100/100 | |
| | 30 | 100/100 | 100/100 | |
| | 60 | 100/100 | 100/100 | |
| | 120 | 100/100 | 100/100 | |
| 50 | 15 | 100/100 | 100/100 | |
| 75 | 15 | 100/100 | 100/100 | |
| 100 | 15 | 100/100 | 60/100 | |

^a 1 h at 80°C.

The effect of the GPS proportion in the PC-GPS primer on the adhesion of the top coating to the PC substrate is shown in Table II. It can be seen that the PC-20-GPS product makes the best coupling agent for strong adhesion of the siliceous top coating to the PC substrate.

The application of the primer solution is easy. It can be applied by spraying, dipping, or spreading. A primer layer of 0.5 μm is effective for good adhesion. Table III indicates that the drying temperature has a significant effect on the adhesion results; drying at temperatures above 80°C should be avoided.

The hardness of the transparent coating depends upon the proportion of the silica colloid in the composition. Nevertheless the polymeric coupling agent was equally effective in enhancing adhesion for

coatings in which the ratio of silica to siloxane resin changed from 1 : 2 to 1 : 1.

The adhesion of the coating to the PC substrate with the aid of the PC-20-GPS coupling agent was durable even in the presence of water. No change in the adhesion was found even after water immersion for 1 month at room temperature, or 1 h at 80°C.

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