Synthesis and Properties of Polycarbonate-Poly(methyl methacrylate) Graft Copolymers by Polycondensation of Macromonomers

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ABSTRACT: Polycarbonates (PCs) having poly(methyl methacrylate)s (PMMAs) as graft chains were prepared by the polycondensation of PC oligomers bearing chloroformate groups as the end groups with dicarboxyl-terminated PMMA macromonomers, which were prepared by the radical polymerization of methyl methacrylate in the presence of thiomalic acid as a chain transfer. The resulting PC-PMMA graft copolymers were transparent in comparison with PC/PMMA blend polymers, and had higher Vickers hardness than blend polymers when both of them had the same PMMA content. According to the results of multiple regression analysis, the improvement of Vickers hardness was conducive to length (46%) and number (37%) of PMMA branches. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2670–2675, 2001

Key words: macromonomer; polycarbonate; poly(methyl methacrylate); graft copolymer; Vickers hardness

INTRODUCTION

Polycarbonates (PCs) are excellent engineering thermoplastics and substitutes for metals and glasses because of their good impact strength, transparency, and electrical properties.[1] However, they are inferior to other transparent resins, such as polystyrene (PS) and poly(methyl methacrylate) (PMMA), in scratch resistance. Vickers hardness[2] of PC, PS, and PMMA is 12.20, 17.50, and 20.59 kg/mm^2, respectively.[3–6] It is desired that PCs have high scratch resistance as well as PMMA when they are used as substitute glasses. Recently, it has been reported that the surface hardness of PCs increases with physical surface treatment,[7–10] but there is no such report on the PC copolymer. This paper describes a method of synthesizing PC-PMMA graft copolymers that may reform surface hardness of PCs.[11]

EXPERIMENTAL

Materials

Commercial MMA and tetrahydrofuran (THF) were distilled under vacuum. α, α′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Thiomalic acid (TMA), bisphenol A (BPA), *p*-tert-butylphenol (PTBP), triethylamine (TEA), sodium hydroxide, succinic acid, phenyl chloroformate, dichloromethane, petroleum ether acetone, ethanol, and sodium dithionite were commercially available and were used without further purification.

Preparation of PC Oligomer

Sodium dithionite (120 g, 0.69 mol) and BPA (60 kg, 263 mol) were dissolved in aqueous 5 wt % sodium hydroxide (400 L). This BPA solution, dichloromethane, and phosgene were introduced at a flow rate of 138 L/h, 69 L/h, and 10.7 kg/h (108
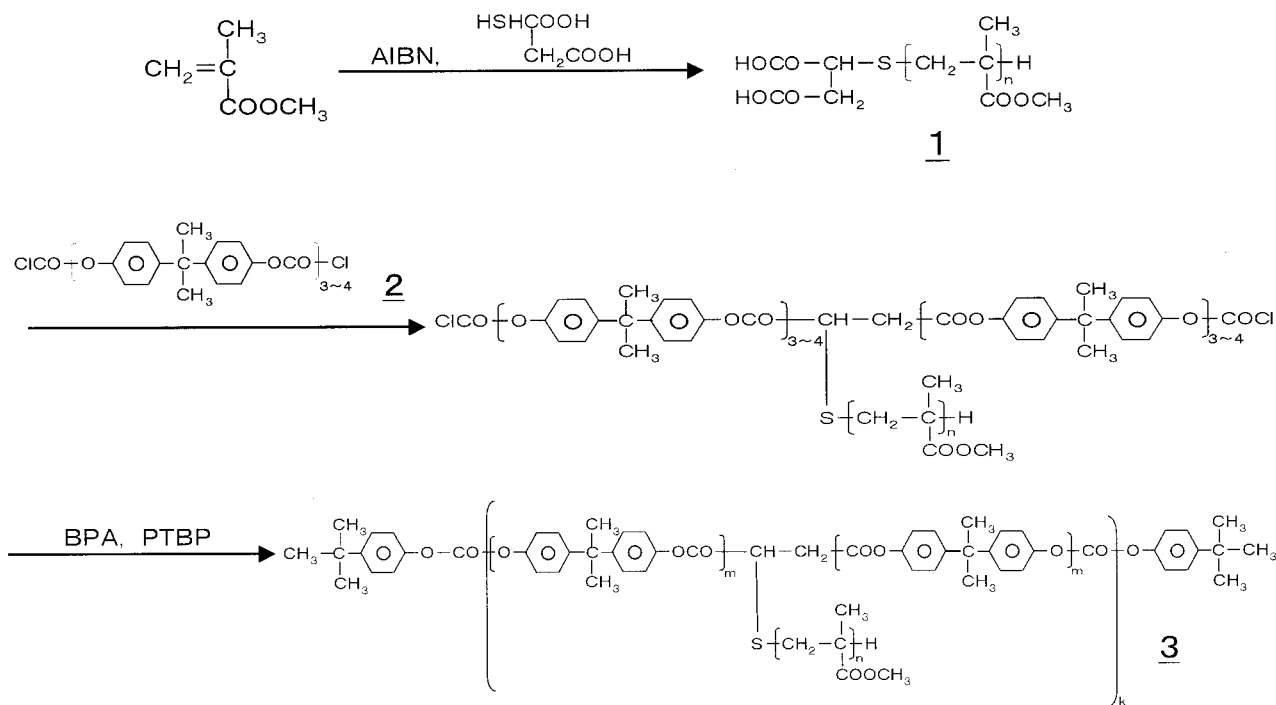
Scheme 1 Synthesis of graft copolymer.

mol/h), respectively, through an orifice plate into a tubular reactor with an inner diameter of 10 mm and a length of 10 m at 25°C. This procedure continued for 3 h. (Caution! Phosgene is a toxic, irritating gas and should only be used in an efficient fume hood.) The reaction solution thus obtained was allowed to stand, then the organic phase was separated and evaporated to obtain PC oligomer in flake form.

The number-average molecular weight (M_n) of PC oligomer obtained therein was 890, determined by the VPO method. The chloroformate group (CF) content was 2.154 mmol/g as determined by titrating with aqueous silver nitrate, using uranine as an indicator, after hydrolysis of the CF.

Preparation of PMMA Macromonomers

A solution of MMA (200 g, 1.998 mol), AIBN (2.296 g, 0.0014 mol), and TMA (17.72 g, 0.118 mol) in THF (400 mL) was heated to 60°C for 2.5 h.[12–13] The polymer solution was poured into petroleum ether (4 L), and the polymer precipitated was filtered out and dried. The polymer was dissolved in dichloromethane and washed with water until the aqueous layer became neutral. Then, the solvent was evaporated. The PMMA macromonomer was obtained in a flake form. The carboxyl group (COOH) content was determined by titrating the polymer in methanol with an aqueous potassium hydroxide solution, using phenolphthalein as an indicator.

Table I Preparation of Macromonomers[a]

Run	Name	$[I]_0/[M]_0$ (10^{-3})	$[S]_0/[M]_0$ (10^{-2})	Yield (%)	COOH[b] (mmol/g)	GPC[c]		
						M_n	M_w	M_w/M_n
1	Mac-1	7.00	5.91	41	0.7037	3,000	6,900	2.30
2	Mac-2	7.00	1.95	37	0.2185	8,500	16,500	1.94

[a] Reactions were carried out in THF. [I] = [AIBN], [S] = [TMA], [M] = [MMA].
[b] Calculated by titration with aqueous potassium hydroxide.
[c] Calculated by using calibration curve for polystyrene.

Table II Synthesis and Vickers Hardness of Graft Copolymers

	Feed				Graft Copolymer			
						GPC[c]		
Run	Macromonomer	COOH/CF (Molar Ratio)	PTBP[a] (wt %)	PC/PMMA[b] (wt %)	M_w	M_w/M_n	Vickers Hardness[d] (kg/mm^2)
1	Mac-1	0.10	1.44	89.5/10.5	36,300	2.02	14.5
2	Mac-2	0.10	1.44	78.4/21.6	38,000	1.95	17.0
3	Mac-1	0.25	1.44	78.4/21.6	21,400	1.88	16.2
4	Mac-2	0.25	1.44	62.1/37.9	24,600	2.03	17.3
5	Mac-1	0.10	0.72	89.0/11.0	59,500	2.43	14.8
6	Mac-2	0.10	0.72	80.1/19.9	56,600	2.33	16.8
7	Mac-1	0.25	0.72	76.6/23.4	29,100	2.35	17.2
8	Mac-2	0.25	0.72	65.1/34.9	27,000	2.11	19.3

[a] Ratio of PTBP feedstock to the total amount of BPA, PCO, and PTBP feedstock.
[b] Calculated by using ^{1}H-NMR.
[c] Calculated by using calibration curve for PC.
[d] Measured in conformity to JIS Z 2244.

Preparation of Graft Copolymers

TEA (1.81 mL, 12.98 mmol) was added to a solution of PC oligomer (60 g, CF: 129.8 mmol) and PMMA macromonomer (18.46 g, COOH: 12.98 mmol) in dichloromethane (300 mL). The solution was stirred at room temperature for 1 h, and washed with 0.1M hydrochloric acid solution. The organic phase was separated.

To this organic phase was added a solution of PTBP (1.03 g, 6.86 mmol) in dichloromethane (30 mL). A solution of sodium dithionite (20 mg, 0.11 mmol), BPA (10.67 g, 46.74 mmol), sodium hydroxide (6.54 g, 163.5 mmol), and TEA (0.072 mL, 0.52 mmol) was dissolved in water (110 mL), which was subjected to interfacial polycondensation for 2 h with the solution of the organic solvent at 500 rpm at 23°C. Then, dichloromethane (1 L) was added, and the solution was washed successively with water (1 L), an aqueous 0.01M sodium hydroxide solution (500 mL), an aqueous 0.1M hydrochloric acid (500 mL), and water (500 mL). Thereafter, the solvent was evaporated. Finally, the polymer obtained was extracted with acetone using Soxhlet's extractor to obtain pure graft copolymer.

The resulting copolymer was dried for 12 h at 110°C, press-molded at 290°C, and the resulting molding was used to test Vickers hardness.

Preparation of PC/PMMA Blend Polymers

PC [Toughlon A2500 (M_w = 31,000; M_w/M_n = 2.3) manufactured by Idemitsu Petrochemical Co., Ltd.] (90 g) and PMMA [Acrypet MF (M_w = 89,000; M_w/M_n = 2.0) manufactured by Mitsubishi Rayon Co., Ltd.] (10 g) were dissolved in dichloromethane (300 mL). Then, dichloromethane was evaporated to obtain PC/PMMA blend polymer. It was dried for 12 h at 110°C, press-molded at 290°C, and the resulting molding was used to test Vickers hardness.

Model Reaction

To a solution of succinic acid (2 g, 16.9 mmol) and phenyl chloroformate (5.57 g, 35.6 mmol) in acetone (200 mL), TEA was added (3.6 g, 35.6 mmol). The solution was stirred for 1 h. Then, the TEA · HCl was filtered out, and the solvent was evaporated. The product was dissolved in dichloromethane (200 mL), and washed with water (100 mL). The solvent was evaporated, and the product was recrystallized from ethanol. Its melting point was 120°C. This measured value agreed with that of diphenyl succinate.[14–15]

Measurements

The molecular weight and molecular weight distribution of the macromonomers and the graft copolymers were determined by gel permeation chromatography (GPC; Waters 410) with polystyrene gel columns (Tosoh TSK-GEL GMH6) at 40°C using THF. The molecular weight was calculated by standard procedure based on the universal calibration curve of PS and PC.
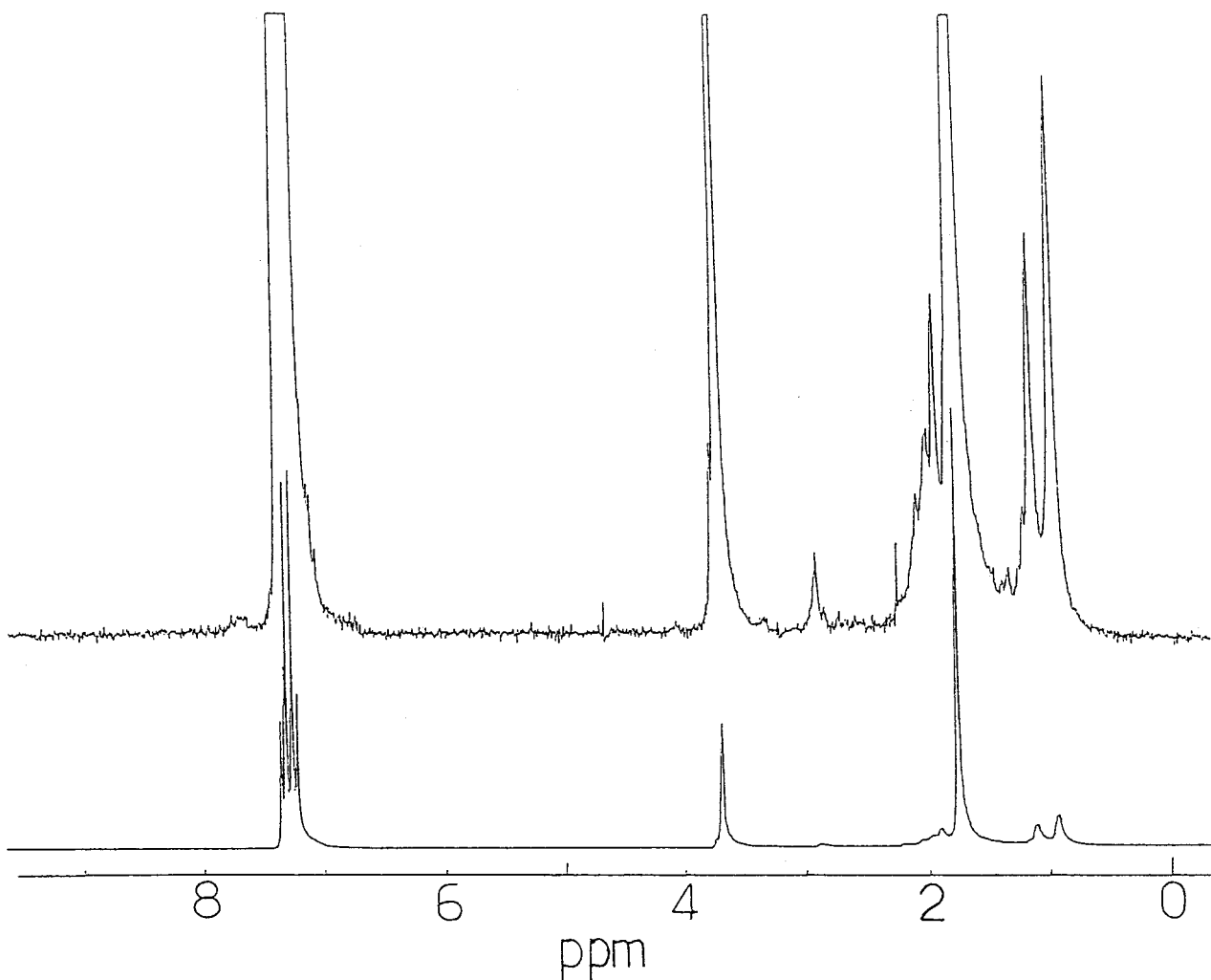
Figure 1 ^{1}H-NMR spectrum of graft copolymer (Run 3) in CDCl$_3$.

^{1}H-NMR spectrum was recorded with a JEOL EX-400 NMR spectrometer operating at 400.15 MHz. The copolymer solution prepared had a concentration of 70 mg/mL in CDCl$_3$.

Vickers hardness was measured in conformity to JIS Z 2244. Ten specimens were tested for each point and standard deviation (σ_{n-1}) was 0.9 kg/mm^{2}.

RESULTS AND DISCUSSION

Preparation of PC-PMMA Graft Copolymer

The preparation of PC-PMMA graft copolymer was carried out according to Scheme 1. The dicarboxyl-terminated macromonomer **(1)** was prepared by radical polymerization of MMA initiated by AIBN in the presence of TMA as a chain trans-fer agent. The results are summarized in Table I. PC oligomer with CF groups at the ends **(2)** was prepared by condensation of BPA and excess phosgene (phosgene/BPA: 1.4/1) in the presence of aqueous NaOH. The number-average molecular weight was 890, so the degree of polymerization of PC oligomer was three to four. The synthesis of graft copolymer **(3)** was carried out as follows. The first step was the condensation of **1** and **2** in dichloromethane in the presence of TEA as an acid acceptor, giving the prepolymer with CF groups at the ends of the chains. Then, the interfacial polycondensation of BPA and the prepolymer, in the presence of TEA as a phase transfer catalyst, produced graft copolymers **(3)**, which were washed with acetone to remove unreacted PMMA. The syntheses of **3** are summarized in Table II. The properties of graft copolymers **3**

were determined using the length of branches, the number of branches, and the length of trunk. The properties were controlled by the molecular weight (M_n) of the macromonomer, the feed ratio of carboxyl group (COOH) of **1** to chloroformate group (CF) of **2**, and the amount of PTBP as a chain stopper agent, respectively. There were three parameters and two standards. Thus, eight (2^3) graft copolymers were synthesized with multiple regression analysis.

The reaction of the C004 group and the CF will produce an acylcarbonate, which undergoes a decarboxylation to give an ester.[16] This decarboxylation was confirmed by the model reaction of succinic acid and phenyl chloroformate. The melting point of the reaction product, 120°C, was accorded with that of diphenyl succinate.[14–15]

Polymer Characterization

The structure of **3** was characterized by IR and ^{1}H-NMR spectroscopy. The IR spectrum of **3** showed characteristic carbonate and ester carbonyl stretchings at 1780 and 1720 cm^{-1}, respectively. The ^{1}H-NMR spectrum of the graft copolymer (Run 3 in Table II) is shown in Figure 1. Aromatic protons of PC units appeared at 7.2 ppm (d) and 7.3 ppm (d), and methyl protons appeared at 1.8 ppm. The signals observed at 3.8, 2.0–2.1, and 0.8–2.1 ppm, are assigned to methoxy, methylene, and methyl protons of PMMA units, respectively. A characteristic peak due to the methyne proton between the thio ether and the carbonyl group is also observed at 2.9 ppm. The PMMA content of **3** was calculated from the integral ratio of the phenyl protons (7.2 ppm) of PC units to the methoxy protons of PMMA units (3.8 ppm).
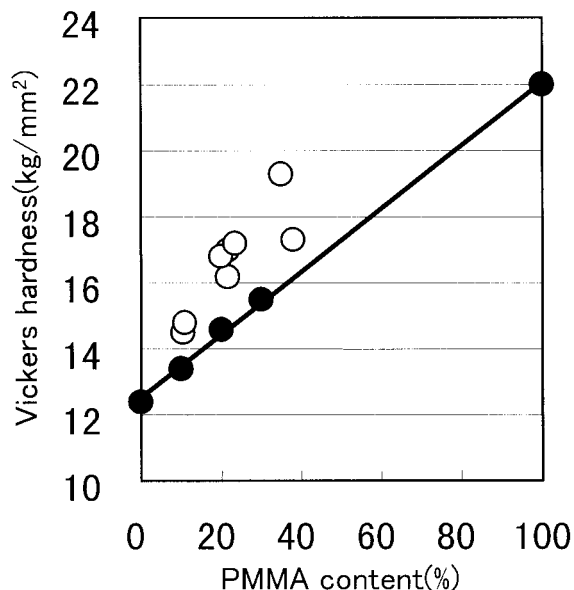
Vickers Hardness of 3

The Vickers hardness of the graft copolymers and the PC/PMMA blend polymers is summarized in

Table III   Vickers Hardness of Blend Polymer

Run	PC/PMMA[a] (wt %)	Vickers Hardness (kg/mm^2)
1	90/10	13.4
2	80/20	14.6
3	70/30	15.5
4	100/0	12.4
5	0/100	22.0

[a] PC: Toughlon A2500 manufactured by Idemitsu Petrochemical Co., Ltd. PMMA: Acrypet MF manufactured by Mitsubishi Rayon Co., Ltd.

Figure 2   Relationship between PMMA content and Vickers hardness. ○: Graft copolymer. ●: PC/PMMA blend.

Table II and III, respectively. Figure 2 shows the relationship between PMMA content and Vickers hardness. The Vickers hardness of **3** increases with increasing PMMA content. Furthermore, their Vickers hardness was better than that of PC/PMMA blend polymers when both of them had the same PMMA content. It is considered that the increase of surface hardness is due to the formation of PMMA surface on the moulds.[11] The graft copolymers **3** were more transparent compared with PC/PMMA blend polymers. Therefore, PMMA domain size of the graft copolymers is smaller than that of PC/PMMA blend polymers,[17] and smaller than the wavelength of visible light. The results of the multiple regression analysis show that there was positive correlation between Vickers hardness and the three parameters of the graft copolymers. The contributions of the length of branches, the number of branches, and the length of trunks were 46, 37, and 7%, respectively. Error was 10%, and the correlation coefficient was 0.9024. It is concluded that using higher molecular weight macromonomer in the synthesis of graft copolymer is effective for improving the surface hardness of PCs.

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