Effect of Polycarbonate–Poly(methyl methacrylate) Graft Copolymer as a Modifier Improving the Surface Hardness of Polycarbonate

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ABSTRACT: With the use of macromonomers that have a dicarboxyl group, polycarbonate–poly(methyl methacrylate) (PC–PMMA) graft copolymers were prepared, and the relationship between the length of PMMA branches and Vickers hardness of the graft copolymer was investigated. With the use of the PC–PMMA graft copolymer as a modifier to improve the surface hardness of PC, Vickers hardness of PC/PC–PMMA blend polymers was examined. PC/PC–PMMA blend polymers are more transparent than PC/PMMA blend polymers. PC/PC–PMMA blend polymers are superior in Vickers hardness to PC/PMMA blend polymers, although the content of PMMA in PC/PC–PMMA blend polymers is smaller than that of PC/PMMA blend polymers. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2774–2779, 2002; DOI 10.1002/app.10252

INTRODUCTION

Polycarbonates (PCs) are excellent engineering thermoplastics because of their good impact strength, thermal resistance, and transparency.[1–2] Their scratch resistance, however, is inferior to other transparent resins, such as polystyrene (PS) and poly(methyl methacrylate) (PMMA). Vickers hardness for PC, PS, and PMMA are 12.20, 17.50, 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 was reported that the surface hardness of PCs increases with physical surface treatment,[7–10] and high-molecular-weight PCs have excellent abrasion resistance properties,[11] but there is no report using PC copolymer as the modifier.

In a previous report,[12] the author reported that PCs with PMMA graft chains were prepared by the polycondensation of PC oligomer, which bears chloroformate end groups, with dicarboxyl-terminated PMMA macromonomers. The resulting PC–PMMA graft copolymers were transparent in contrast to PC/PMMA blend polymers and had higher Vickers hardness than blend polymers even though both of them had the same PMMA content. From the result of multiple regression analysis, the improvement of Vickers hardness was shown to come from the length (46%) and the number (37%) of PMMA branches.

This article describes the relationship between the length of PMMA branches and the Vickers hardness of the graft copolymers and the effect of polycarbonate–poly(methyl methacrylate) (PC–PMMA) graft copolymer as a modifier from an investigation of PC/PC–PMMA blend polymers.

EXPERIMENTAL

Materials

Commercial MMA and tetrahydrofuran (THF) were distilled under vacuum. α,α'-Azobisisobutyronitrile (AIBN) was recrystallized from metha-

nol. Thiomalic acid (TMA), bisphenol-A (BPA), *p-tert*-butyl phenol (PTBP), triethylamine (TEA), sodium hydroxide, succinic acid, phenyl chloroformate, dichloromethane, petroleum ether acetone, ethanol, and sodium dithionite were commercially available and used without further purification. The PC used was Toughlon A2500 (M_w = 31,000; M_w/M_n = 2.3) manufactured by Idemitsu Petrochemical Co., Ltd. (Sumida, Tokyo, Japan), and the PMMA used was Acrypet MF (M_w = 89,000; M_w/M_n = 2.0) manufactured by Mitsubishi Rayon Co., Ltd. (Minato, Tokyo, Japan).

Preparation of the PC Oligomer

Sodium dithionite (120 g, 0.69 mol) and BPA (60 kg, 263 mol) were dissolved in 5 wt % aqueous sodium hydroxide (400 L). Dichloromethane and phosgene were introduced to this solution through an orifice plate at 25°C with a flow rate of 138 L/h, 69 L/h, and 10.7 kg/h (108 mol/h), respectively, into a tubular reactor with an inner diameter of 10 mm and a length of 10 m. This procedure was continued for 3 h. Because phosgene is a toxic, irritating gas, it was dealt with only in an efficient fume hood. After allowing the reaction solution to stand for a certain time, the organic phase was separated and evaporated to obtain a PC oligomer in flake form.

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

Preparation of the PMMA Macromonomer[13–14]

A solution prepared by dissolving MMA (200 g, 1.998 mol), AIBN (2.296 g, 0.0014 mol), and TMA (25.32 g, 0.1686 mol) in THF (400 mL) was heated at 60°C for 3 h. The resulting solution was poured into petroleum ether (4 L), and the precipitate obtained was filtered out and dried. The precipitate was then dissolved in dichloromethane and washed with water until the aqueous layer became neutral. By evaporating the solvent, a PMMA macromonomer was obtained in a flake form. Its carboxyl group (COOH) content was determined by titrating the polymer in methanol with aqueous potassium hydroxide by using phenolphthalein as an indicator.

Preparation of the PC–PMMA Graft Copolymer[12]

TEA (3.61 mL, 25.85 mmol) was added to a solution prepared by dissolving the PC oligomer (60 g,

CF: 129.2 mmol) and the PMMA macromonomer (38.32 g, COOH: 25.85 mmol) in dichloromethane (300 mL). The solution was stirred at room temperature for 1 h and washed with 0.1M aqueous hydrochloric acid, and the organic phase was then separated.

A solution prepared by dissolving PTBP (0.74 g, 4.9 mmol) in dichloromethane (30 mL) was added to this organic phase for use as an organic solvent in the following reaction. Separately, a solution was prepared by dissolving sodium dithionite (20 mg, 0.11 mmol), BPA (9.44 g, 41.3 mmol), sodium hydroxide (5.79 g, 145 mmol), and TEA (0.086 mL, 0.62 mmol) in water (110 mL). This solution, mixed with the above organic solvent, was subjected to interfacial polycondensation at 500 rpm at 23°C for 2 h. Dichloromethane (1 L) was then added to the resulting solution, which was washed successively with water (1 L), 0.01M aqueous sodium hydroxide (500 mL), 0.1M aqueous hydrochloric acid (500 mL), and water (500 mL). After washing, the solvent was evaporated to obtain a coarse graft polymer. A part of the coarse graft copolymer was washed with acetone at room temperature to obtain a refined graft copolymer.

Both the coarse graft copolymer and the refined one were dried for 12 h at 110°C and the refined graft copolymer was press-molded at 290°C; the resulting molding was used for Vickers hardness.

Preparation of PC/PC–PMMA Blend Polymers

The PC (Toughlon A2500, 90 g) and the coarse PC–PMMA graft copolymer (10 g) were dissolved in dichloromethane (300 mL). Then, dichloromethane was evaporated to obtain a PC/PC–PMMA blend polymer. It was dried for 12 h at 110°C and press-molded at 290°C, and the resulting molding was used for Vickers hardness.

Measurement

The molecular weight and molecular weight distribution for the macromonomer and the PC–PMMA graft copolymer were determined by gel permeation chromatography (GPC, Waters 410) with polystyrene gel columns (Tosoh TSK-GEL GMH6) at 40°C by using THF. The molecular weights of the macromonomer and the PC–PMMA graft copolymer were calculated according to a standard procedure based on the universal calibration curves for PS and PC, respectively.

Ten specimens were prepared to measure Vickers hardness in conformity to JIS Z 2244. The
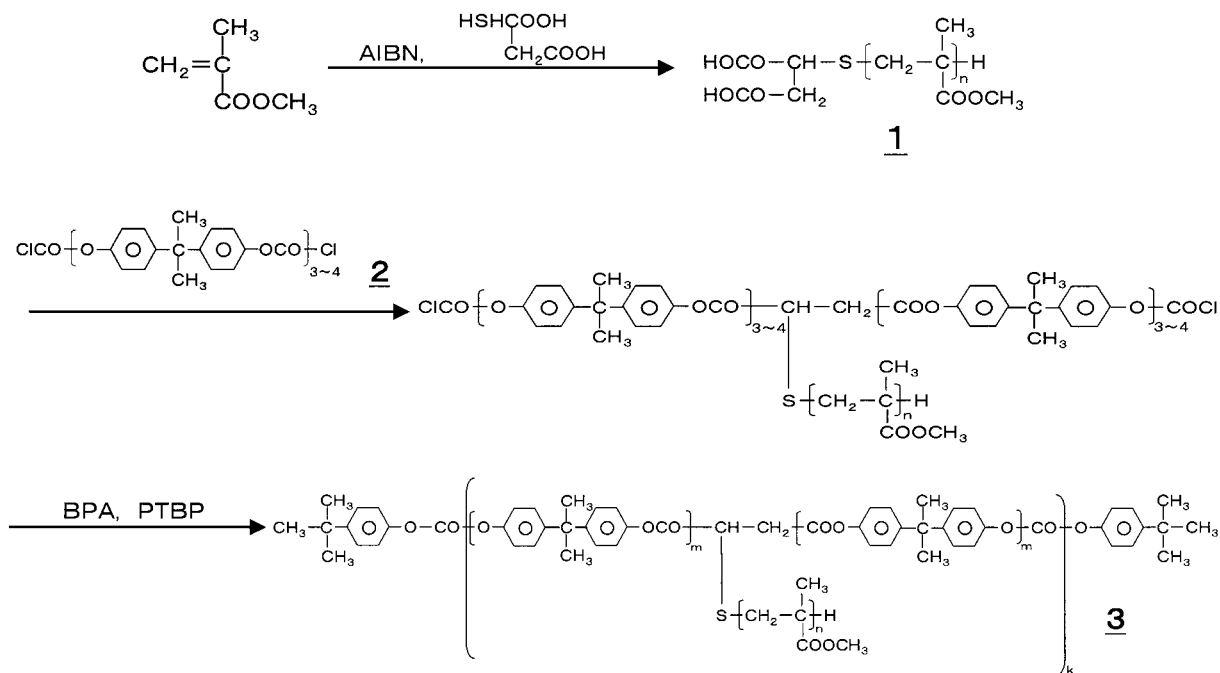
Scheme 1

standard deviation (σ_{n-1}) for the 10 points was 0.9 kg/mm^2.

RESULTS AND DISCUSSION

Preparation of the PMMA Macromonomer

The preparation of the PMMA macromonomer and the 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 transfer agent. The results are summarized in Table I. To restrain the formation of inactive PMMA that do not have a dicarboxyl group, the conversion of the monomer was controlled at about 40%. When the TMA feedstock increased, the difference between M_n determined by GPC and M_n determined by titration decreased, so the formation of inactive PMMA was considered to be restrained. M_n that was less than 8000 (determined by GPC) was inversely proportional to the concentration of the TMA chain transfer agent (Fig. 1). M_n that was more than 8000 was not inversely proportional to the concentration of TMA, and the difference between

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)	M_n (Tit^c)	GPC^d		
							M_n	M_w	M_w/M_n
1-1	Mac-1	7.00	8.44	42	0.6746	2,700	2,100	4,100	1.95
1-2	Mac-2	7.00	4.22	43	0.3731	5,400	3,600	7,800	2.17
1-3	Mac-3	7.00	2.11	40	0.2012	9,900	7,700	14,900	1.93
1-4	Mac-4	7.00	1.06	39	0.1001	20,000	12,800	25,100	1.96
1-5	Mac-5	7.00	0.60	37	0.0613	32,600	19,200	35,900	1.87

^{a} Reactions were carried out in THF. $[I]$ = [AIBN], $[S]$ = [TMA], $[M]$ = [MMA].
^{b} Calculated by titration with aqueous pottassium hydroxide.
^{c} Determind by end-group titaration assuming two hydroxyl groups per molecule.
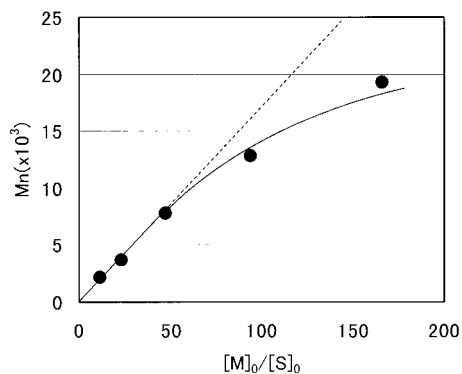^{d} Calculated by using calibration curve for polystyrene.

Figure 1 Relationship between $[M]_0/[S]_0$ and M_n (GPC). $[M] = $ [MMA], $[S] = $ [TMA].

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

M_n determined by GPC and M_n by titration increased. It is presumed that the disproportion and the recombination reaction augment when the concentration of TMA is thin.

Preparation and Properties of the PC–PMMA Graft Copolymers

The PC oligomer with chloroformate groups at the ends of the chain (2) was prepared by the condensation of BPA and excess phosgene (phosgene/BPA: 1.4/1) in aqueous sodium hydroxide. Because the number-average molecular weight was 890, the degree of polymerization of the PC oligomer was estimated at 3 to 4. The synthesis of the 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 a prepolymer with chloroformate groups at the ends of the chain. Then, the interfacial polycondensation of BPA and the prepolymer, in the presence of TEA as a phase-trans-
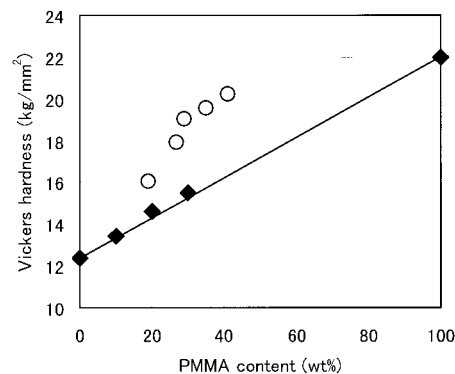
fer catalyst, led to producing (3), which was washed with acetone to remove un-reacted PMMA and low-molecular-weight copolymers.

To set the number of branches and the trunk length of the graft copolymer, the feed ratio of the carboxyl group (COOH) of (1) to the chloroformate group (CF) of (2) and the amount of PTBP as a chain stopper agent were made constant, that is, COOH/OH: 0.2, PTBP: 1%, which is the ratio of the PTBP feedstock to the total feedstock of BPA, PC oligomer, and PTBP.

The reaction of the carboxyl group and the chloroformate group produces acylcarbonate, which undergoes decarboxylation to give an ester.[15] This decarboxylation was confirmed by the model reaction of succinic acid and phenyl chloroformate.[12]

The structure of (3) was characterized by IR and ^{1}H-NMR spectroscopies.[12] The PMMA content of (3) was calculated from the integral ratio of

Table II Characterization and Vickers Hardness of Graft Copolymers

		Coarse Copolymer			Refined Copolymer			
			GPC[b]			GPC[b]		
Run	Macromonomer	PC/PMMA[a] (wt %)	M_w	M_w/M_n	PC/PMMA[a] (wt %)	M_w	M_w/M_n	Vickers Hardness[c] (kg/mm²)
2-1	Mac-1	66.3/33.7	41,500	2.40	80.9/19.1	44,900	1.76	16.0
2-2	Mac-2	53.1/46.9	44,200	2.62	73.1/26.9	53,800	1.80	17.9
2-3	Mac-3	38.7/61.3	42,100	2.48	71.1/28.9	56,700	1.80	19.0
2-4	Mac-4	26.6/73.4	38,500	2.05	64.8/35.2	52,600	1.82	19.5
2-5	Mac-5	16.3/83.7	41,700	2.00	58.8/41.2	49,500	1.94	20.2

[a] Calculated by using ^{1}H-NMR.
[b] Calculated by using calibration curve for PC.
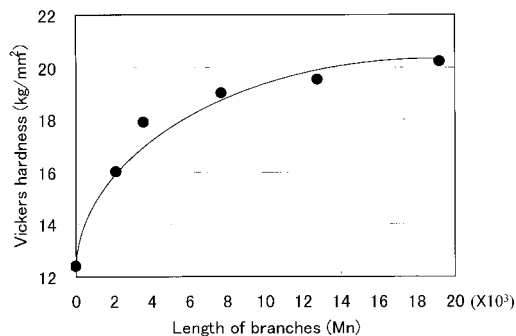[c] Measured in conformity to JIS Z 2244.

Figure 3 Relationship between length of branches (GPC) and Vickers hardness of the copolymers in Table II.

Figure 4 Relationship between amount of modifier and Vickers hardness. Modifier: (●) coarse graft copolymer; (○) refined graft copolymer; (♦) PMMA.

the phenyl proton (7.2 ppm) of the PC unit to the methoxy proton of the PMMA unit (3.8 ppm).

The characterization and Vickers hardness of the graft copolymers are summarized in Table II. Figure 2 shows the relationship between PMMA content and Vickers hardness. Vickers hardness of the refined graft copolymers increases with the increasing PMMA content. Furthermore, Vickers hardness of the refined graft copolymers was better than that of PC/PMMA blend polymers when both of them had the same PMMA content. The refined graft copolymers were more transparent than PC/PMMA blend polymers. On the other hand, the coarse copolymers could not be press-molded and it is thought that they contained a lot of low-molecular-weight copolymers.

Figure 3 shows the relationship between the length of PMMA branches and Vickers hardness of the refined graft copolymers. Their Vickers hardness increases with an extension of the
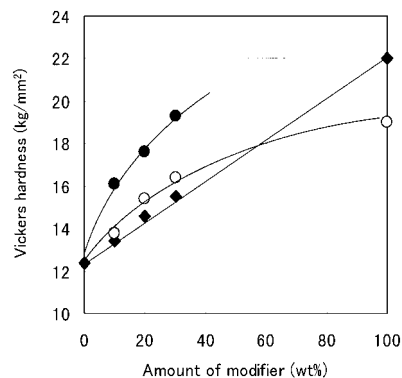
length of PMMA branches, but the increasing rate gradually becomes smaller.

Effect of Graft Copolymer as a Modifier

The values of Vickers hardness of blend polymers using, as modifiers, refined graft copolymers, coarse graft copolymers (Run 2-3 in Table II), and PMMA are summarized in Table III. PC/PC–PMMA blend polymers are more transparent than PC/PMMA blend polymers. Figure 4 shows the relationship between the amount of modifier and Vickers hardness of the blend polymers. Figure 5 shows the relationship between the PMMA content and Vickers hardness. With up to 30% of the modifier, PC/PC–PMMA blend polymers are superior in Vickers hardness to PC/PMMA blend polymers even though the PMMA content of PC/PC–PMMA blend polymers is smaller than that of

Table III   Vickers Hardness of Blend Polymer

Run	Modifier	PC[a]/Modifier (wt %)	PMMA Content (wt %)	Vickers Hardness (kg/mm^2)
3-1	Run 2-3 (refined)	90/10	2.9	13.8
3-2	Run 2-3 (refined)	80/20	5.8	15.4
3-3	Run 2-3 (refined)	70/30	8.7	16.4
3-4	Run 2-3 (coarse)	90/10	6.1	16.1
3-5	Run 2-3 (coarse)	80/20	12.2	17.6
3-6	Run 2-3 (coarse)	70/30	18.3	19.3
3-7	PMMA[b]	90/10	10.0	13.4
3-8	PMMA	80/20	20.0	14.6
3-9	PMMA	70/30	30.0	15.5
3-10	PMMA	0/100	100	22.0
3-11	—	100/0	0	12.4

[a] Toughlon A2500 manufactured by Idenitsu Petrochemical Co., Ltd.
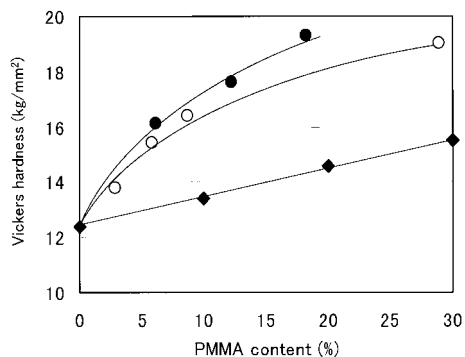[b] Acrypet MF manufactured by Mitsubishi Rayon Co., Ltd.

Figure 5 Relationship between PMMA content and Vickers hardness. Modifier: (●) coarse graft copolymer; (○) refined graft copolymer; (♦) PMMA.

PC/PMMA blend polymers. It is considered that the increase of surface hardness is due to the formation of a PMMA surface on the molds.[16] The coarse copolymers could not be press-molded independently, but they acted as a useful modifier which improved the surface hardness of PC compared to the refined graft copolymers. This is supposed to be because coarse copolymers contain a short-trunk graft copolymer with a high PMMA content.

CONCLUSION

With the use of macromonomers that have a dicarboxyl group, polycarbonate–poly(methyl methacrylate) (PC–PMMA) graft copolymers were prepared. PC/PC–PMMA blend polymers are more transparent than PC/PMMA blend polymers and PC/PC–PMMA blend polymers are superior in

Vickers hardness to PC/PMMA blend polymers even though the PMMA content of PC/PC–PMMA blend polymers is smaller than that of PC/PMMA blend polymers. So, it is considered that PC–PMMA graft copolymer acts as a useful modifier, improving the surface hardness of PC.

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