

Core-shell particles of poly(methyl methacrylate)-*block*-poly(*n*-butyl acrylate) synthesized via reversible addition-fragmentation chain-transfer emulsion polymerization and the polymer's application in toughening polycarbonate

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ABSTRACT: Poly(methyl methacrylate) (PMMA) block copolymer is interesting because it is compatible with many polymers. A series of poly(methyl methacrylate)-*b*-poly(*n*-butyl acrylate) (PMMA-*b*-PnBA) diblock copolymers with various compositions was synthesized via reversible addition-fragmentation chain-transfer (RAFT) emulsion polymerization with the amphiphilic oligo(methacrylic acid₄₁-*b*-methyl methacrylate₈) RAFT agent as both the polymerization mediator and surfactant. The molecular weights of the block copolymers agreed well with the theoretical prediction, although the polydispersity indices were relatively broad. The resulting core [poly(*n*-butyl acrylate)]-shell (PMMA) particles of PMMA-*b*-PnBA were found to be very effective impact modifiers for polycarbonate (PC). The diblock copolymer was well dispersed in 100–300-nm particles in the PC matrix, and the dispersed particle size was highly dependent on the block copolymer compositions. PMMA₂₅₀-*b*-PnBA₅₅₀ (the subscripted number signifies the designed degree of polymerization), which was dispersed into 100-nm particles, presented the best capability for improving the impacting properties. Compared with the neat PC, the notched impact strength of PC toughened by 5 wt % PMMA₂₅₀-*b*-PnBA₅₅₀ was increased by four times to 62.81 kJ/m² with the same yield strength, a slightly decreased modulus, an increased elongation at break, and an increased tensile strength. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42833.

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INTRODUCTION

The past 2 decades have witnessed an explosive growth of controlled/living radical polymerization (CLRP) research. CLRPs, represented by nitroxide-mediated polymerization,¹ atom transfer radical polymerization,² and reversible addition-fragmentation chain-transfer (RAFT) polymerization,³ have been demonstrated to be powerful tools in the preparation of polymers with precisely designed chain microstructures.

Emulsion polymerization has been considered to be the most promising process to carry out CLRPs.⁴ Among the available CLRP systems, RAFT polymerization shows the same wide tolerance of reaction conditions and monomers as conventional radical polymerization.^{3,5} Recently, well-controlled RAFT emulsion polymerization has been reported.^{6–11} Well-defined homopolymers, block copolymers, and gradient copolymers¹² have been synthesized with this method. RAFT emulsion polymerization with a pre-made^{6,7} or *in situ* formed^{8,11} amphiphilic oligo-

meric RAFT agent as a surfactant has been demonstrated to be a robust approach for synthesizing surfactant-free nano-structured latex of block copolymers.

The block copolymer can be used as a compatibilizer or toughening modifier. Poly(methyl methacrylate) (PMMA)-based block copolymers are of particular interest because PMMA is compatible with a wide range of commercial plastics, including poly(vinyl chloride), polycarbonate (PC), poly(vinylidene fluoride), and epoxy.^{13,14} However, PMMA-based block copolymers synthesized via the RAFT emulsion polymerization technique have rarely been reported.¹⁵ Compared with styrene and butyl acrylate (BA) RAFT emulsion polymerizations, the RAFT emulsion polymerization of methyl methacrylate (MMA) has been less successful in terms of their colloidal instability,^{6,16,17} large deviation in molecular weight from theoretical prediction,^{15,17} and relatively broad molecular weight distribution.^{6,11} Until recently, the successful *ab initio* emulsion polymerization of MMA was achieved with an amphiphilic oligomeric RAFT agent as both

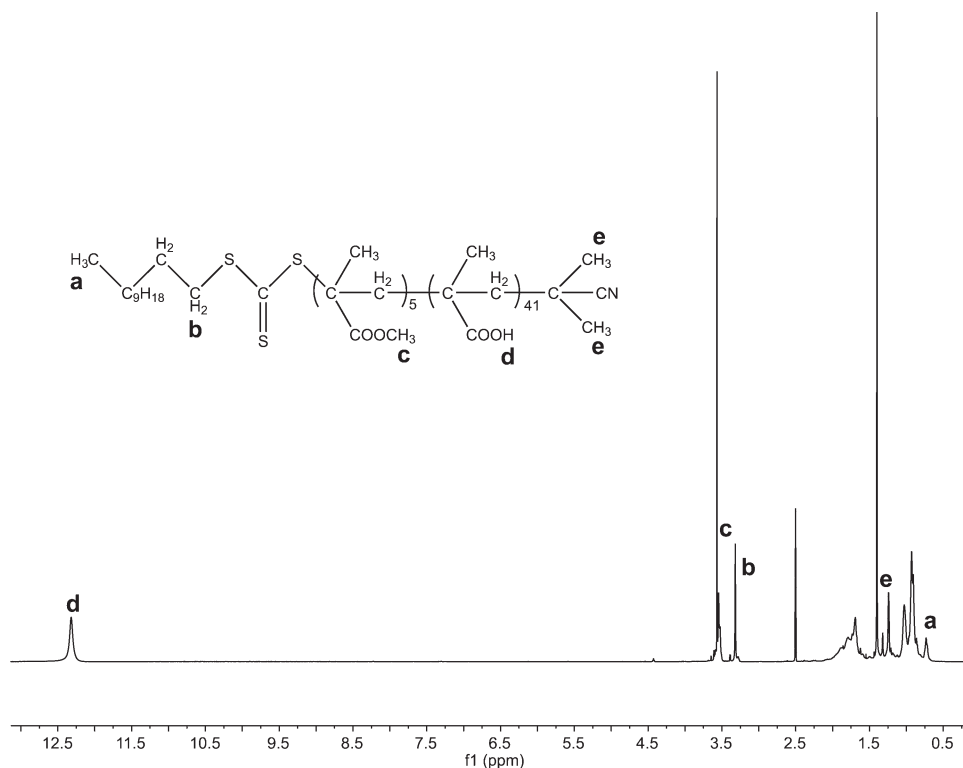


Figure 1. $^1\text{H-NMR}$ spectrum of oligo(MAA₄₁-*b*-MMA₈) RAFT.

the surfactant and polymerization mediator. Charleux *et al.*¹⁸ used a poly[(methacrylic acid)-*co*-poly(ethylene oxide) methyl ether methacrylate] RAFT agent [number-average molecular weight (M_n) = 16,000] as a surfactant in the RAFT emulsion homopolymerization of MMA. They found that the controlled characteristics were much better at pH 3.5 than at pH 5 or 7. More recently, Luo *et al.*¹⁹ carried out the *ab initio* emulsion polymerization of MMA using oligo(methacrylic acid-*b*-methyl methacrylate) RAFT as the surfactant and mediator, and controlled/living MMA polymerization was achieved. The polymerization was completed within 1 h without any coagulum.

Compared with the intensive research on CLRPs from both academic and industrial communities, their commercial applications are very limited.²⁰ One of the bottlenecks is the lack of knowledge about the structure–properties relationship of new

Table I. Batch Emulsion Polymerization of nBA for Synthesizing the PnBA Seed Latex (Step I)

Material	Mass (g)
nBA	40.0
EGDMA	0.4
ALMA	0.2
Water	50.8
KPS aqueous solution (2 wt %)	10.0
SDBS aqueous solution (3 wt %)	20.0

The reaction temperature was 75°C. When the temperature reached 75°C, the aqueous KPS solution was added to start the polymerization. The reaction was continued for 2 h so that it could reach complete conversion.

products, such as block copolymers prepared by CLRP. In this study, we took advantage of RAFT emulsion polymerization to design and synthesize novel core–shell particles of poly(methyl methacrylate)-*b*-poly(*n*-butyl acrylate) (PMMA-*b*-PnBA) to seek for more effective impact modifiers for PC.

PC is an important engineering thermoplastic. It is a pseudo-ductile polymer and shows a tendency to undergo brittle fracture under conditions of sharp notch, plane strain, and high rates of deformation because of its low crack-propagation energy,²¹

Table II. Semibatch Seeded Emulsion Polymerization of nBA (Step II)

Material	Mass (g)
Initial materials	
PnBA seed latex	18.0
Water	79.9
KPS aqueous solution (2 wt %)	10.0
SDBS aqueous solution (3 wt %)	8.2
BA emulsion	
nBA	66.0
EGDMA	0.66
ALMA	0.33
Water	16.0
KPS aqueous solution (2 wt %)	6.5
SDBS aqueous solution (3 wt %)	12.6

The reaction temperature was 75°C. The BA emulsion was premade and was then continuously dropped into the reactor, which was charged with the initial materials at a constant rate for 2.5 h. The reaction was continued for another 2 h so that it could reach complete conversion.

Table III. Seeded Emulsion Polymerization of MMA (Step III)

Material	Mass (g)
Initial materials	
PnBA core latex	218.2
KPS aqueous solution (2 wt %)	4.7
SDBS aqueous solution (3 wt %)	4.2
water	53.5
MMA monomer	103.9

The reaction temperature was 80°C. The MMA monomer was added at a constant rate for 2.5 h to the reactor charged with the initial materials. After another 2 h of polymerization, the reaction was completed.

especially at low temperatures.²² Elastomers such as styrene-butadiene-styrene block copolymer (SBS),²³ acrylonitrile-butadiene-styrene copolymers,^{24–26} and core-shell structured particles of poly(methyl methacrylate/styrene) (MBS)^{21,23,27,28} and PnBA/PMMA^{22,29,30} have been used as impact modifiers. In the cases, with SBS and acrylonitrile-butadiene-styrene copolymer elastomers used as modifiers, the impact strength is highly dependent on the processing conditions,²³ which affects the rubber phase size by micrometers. To produce modified PC with a good dispersion of rubber phase and pre-determined rubber phase size under a wide range of process conditions, core-shell particles composed of a PMMA shell and a slightly-crosslinked rubber core, which was synthesized by traditional emulsion polymerization, were applied.^{22,29,30} The PMMA shells provided rigidity and good compatibility to the PC matrix,^{31,32} and the lightly-crosslinked cores retained the integrity of the particle structure in the modified PC. Cheng *et al.*²³ compared three

types of butadiene-based impact modifiers (linear polybutadiene, SBS, and structured particles containing a polybutadiene core and an MBS shell) for PC. We found that the best impact properties were obtained with MBS. More recently, Cho *et al.*²⁹ used home-made PMMA shell/poly(*n*-butyl acrylate) (PnBA) core (PMMA-PnBA) particles to toughen PC and observed that an optimum particle diameter between 80 and 370 nm and a 4–6 wt % rubber phase in the blends resulted in good toughness for the notched PC. It was also reported that in PC modified by core-shell latex particles, the particles with diameters ranging from 115.7 to 231.4 nm had the maximum impact strength with 4 wt % core-shell particles.³⁰

In this study, PMMA-PnBA core-shell particles of PMMA-*b*-PnBA diblock copolymers were designed and synthesized by RAFT emulsion polymerization. The influence of the diblock copolymer compositions and the dosage of the diblock copolymers on the morphology and mechanical properties of the toughened PC are discussed.

EXPERIMENTAL

Materials

MMA [analytical-reagent grade (AR), Sinopharm] and methacrylic acid (AR, Sinopharm) were purified by distillation under reduced pressure before use. *n*-Butyl acrylate (nBA; AR, Sinopharm) was washed with a sodium hydroxide (NaOH) aqueous solution (5 wt %) to remove the inhibitor. 2,2'-Azobisisobutyronitrile (99%, Aladdin) was recrystallized twice from ethanol. Potassium persulfate (KPS; 99%, Aladdin) was recrystallized twice from deionized water. Ethylene glycol dimethacrylate (EGDMA; AR, Aladdin), allyl methacrylate (ALMA; AR, Aladdin), sodium

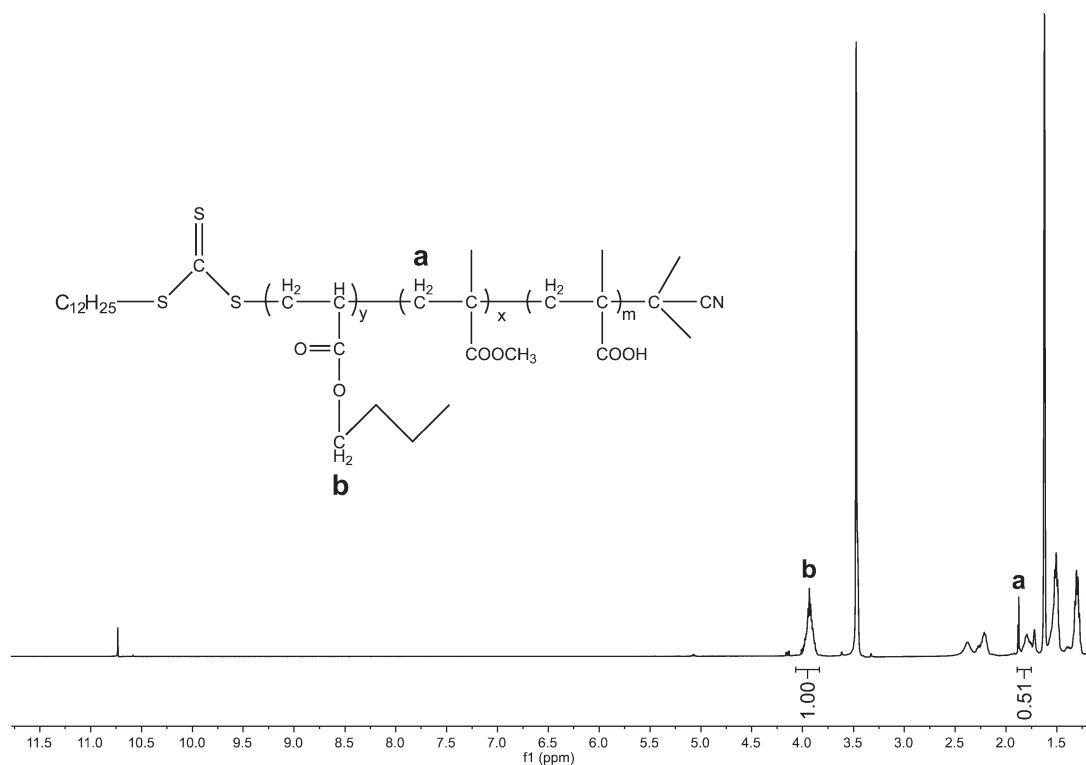


Figure 2. ¹H-NMR spectra of PMMA-*b*-PnBA synthesized via RAFT emulsion polymerization mediated by oligo(MAA₄₁-*b*-MMA₈) RAFT in Exp R2.

Table IV. Synthesis of the PMMA-*b*-PnBA Diblock Copolymers via Emulsion Polymerization Mediated by the Oligo(MAA₄₁-*b*-MMA₈) RAFT Agent

Exp ^a	Designed structures	PMMA					PnBA						
		Time (min)	Conversion (%) ^b	<i>D_v</i> (nm) ^c	<i>M_n</i> (g/mol)	<i>M_n</i> th (g/mol) ^d	<i>D_v</i> (nm) ^c	<i>M_n</i> (g/mol)	<i>M_n</i> th (g/mol) ^d	Conversion (%) ^b	Time (min)	PDI	
R1	PMMA ₂₅₀ - <i>b</i> -PnBA ₃₉₀	60	93	—	33,600	28,100	112	75,400	75,800	98	60	1.56	3.28
R2	PMMA ₂₅₀ - <i>b</i> -PnBA ₅₅₀	60	97	70	38,740	29,300	135	93,700	116,000	100	60	1.51	3.26
R3	PMMA ₂₅₀ - <i>b</i> -PnBA ₇₈₀	60	91	—	31,100	27,900	143	122,900	146,900	97	60	1.58	4.63

^aIn all of the Exp's used KPS as an initiator ([KPS]/[oligoRAFT] = 1:5.5), and the initial aqueous pH values were approximately 3.0. The reaction temperature was 80°C for MMA and was reduced to 70°C for nBA. Postaddition of the NaOH solution was used to increase the colloidal stability.⁷ The final solid content was approximately 30%.

^bThe monomer conversion was measured with gravimetry.

^cThe volume-average diameter was determined via TEM analysis.

^dThe theoretical number-average molecular weight (*M_n*th) values were calculated as follows:

$$M_{n,th} = M_{n,RAFT} + M_{n,monomer} \times [M] / [RAFT]$$

where [M] and [RAFT] are the monomer and oligo(MAA₄₁-*b*-MMA₈) RAFT concentrations, *M_{n,RAFT}* and *M_{n,monomer}* means the molecular weight of small RAFT agent and monomer, respectively, and *x* is the conversion.

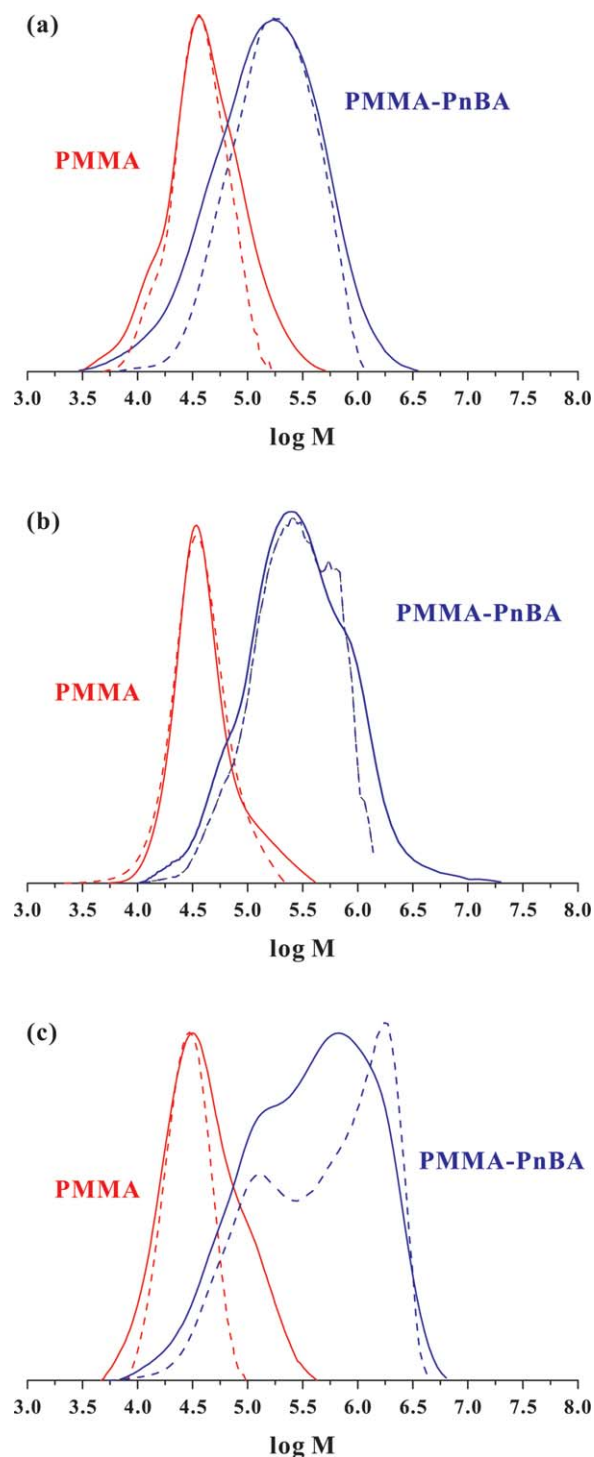


Figure 3. Comparison of the GPC traces of the RI (solid lines) and UV (311 nm; dashed lines) during the synthesis of PMMA-*b*-PnBA: (a) Exp R1, (b) Exp R2, and (c) Exp R3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dodecyl-benzenesulfonate [SDBS, chemically-pure grade (CP), Sinopharm], 1,4-dioxane (AR, Sinopharm), NaOH (AR, Sinopharm), deionized water (conductivity <4 μ S/cm), and hydrazine (85%, Acros Organics) were used as received. The small RAFT agent, 2-cyanopropan-2-yl dodecyl carbonotrithioate, was

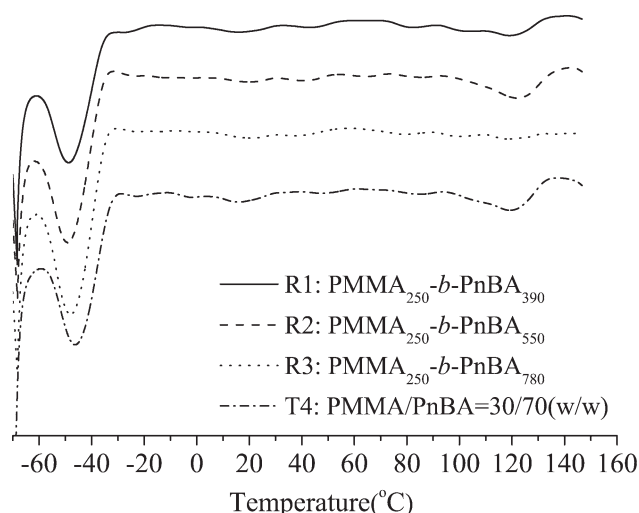
Table V. Particle Size and PSD of the Core–Shell Particles Synthesized by Traditional Emulsion Polymerization (Exp T4)

Batch nBA			Semibatch nBA			Semibatch MMA			
Conversion (%) ^a	D_v (nm) ^b	PSD ^b	Conversion (%) ^a	D_v (nm) ^b	PSD ^b	Conversion (%) ^a	D_v (nm) ^b	PSD ^b	D_v (nm) ^c
100	86	1.09	100	187	1.04	100	217	1.16	114

^aThe monomer conversion was measured with gravimetry.

^bDetermined with Malvern dynamic light scattering. PSD = D_v/D_n , where D_n is the number-average diameter.

^cDetermined with TEM analysis.

**Figure 4.** DSC derivative curves of the core-shell particles.

synthesized and purified as described in the literature,^{5,33–36} and the RAFT agent was of high purity (>98%), as indicated by ¹H-NMR. PC (Panlite L-1250Y, by Teijin, Japan) was used as the matrix with a melt flow rate of 8 m³/10 min (300°C, load 1.2 kg). The phenolic and phosphate antioxidants were homemade.

Synthesis of the Oligo(methacrylic acid-*b*-methyl methacrylate) Trithiocarbonate RAFT Agent

The oligo(MAA₄₁-*b*-MMA₈) RAFT (the subscripted number signifies the designed degree of polymerization) was synthesized by a two-step RAFT solution polymerization mediated by the small

RAFT agent 2-cyanopropan-2-yl dodecyl carbonotrithioate, as described elsewhere.¹⁹ The structure of the amphiphilic oligomeric RAFT agent was analyzed by ¹H-NMR, as shown in Figure 1. ¹H-NMR signals of oligo(MAA₄₁-*b*-MMA₈) RAFT were assigned as follows.

¹H-NMR (ppm): 0.73 (3H, —CH₃ of —C₁₂H₂₅ chain moiety), 1.32 [6H, —C₂H₆ of —C(CH₃)₂CN chain moiety], 3.28 (2H, —CH₂ of —C₁₂H₂₅ chain moiety), 3.55 (—COOCH₃ of PMMA chain), 12.32 (—COOH of PMMA chain), and 3.57 (H of impurities in dioxane).¹⁹

Synthesis of the PMMA-*b*-PnBA Diblock Copolymer via Emulsion Polymerization Mediated by Oligo(MAA₄₁-*b*-MMA₈) RAFT

RAFT emulsion polymerization was run in a 250-mL, four-necked, round-bottomed flask equipped with a condenser, a thermometer, a nitrogen inlet, and a mechanical agitator. In a typical experiment (Exp; e.g., Exp R2): 3.00 g of oligo(MAA₄₁-*b*-MMA₈) RAFT was dissolved in 95.00 g of deionized water at 45°C for 2 h without neutralization (the initial aqueous pH value was about 3.0). The aqueous solution and 14.60 g of MMA were transferred to the flask reactor. During 30 min of deoxygenation by nitrogen purging, the reactor temperature was increased to 80°C. The KPS initiator (0.028 g in 5.00 g of deionized water) was injected to start the emulsion polymerization. After 15 min, 0.45 g of NaOH (1.1 × 10⁻² mol in 9.00 g of deionized water) was injected to improve the colloidal stability.⁷ After 60 min, the reaction temperature was decreased to 70°C, and 38.00 g of nBA was added at a rate of 4.27 mL/min. The polymerization of nBA proceeded for another 60 min and reached complete conversion. The regular withdrawal of samples

Table VI. Mechanical Properties of PC Toughened by 5 wt % Core–Shell Particles

Sample ^a	Elastic modulus (MPa) ^b	Yield strength (MPa) ^b	Elongation at break (%) ^b	Izod impact strength (kJ/m ²) ^c
Neat PC	2320 ± 30	60.6 ± 0.2	92.8 ± 4.6	12.75 ± 0.50
PC + R1	2050 ± 30	56.3 ± 0.3	94.3 ± 4.6	40.37 ± 2.66
PC + R2	2210 ± 30	60.9 ± 2.9	118.4 ± 6.3	62.81 ± 3.02
PC + R3	2100 ± 10	56.0 ± 0.1	93.5 ± 1.3	42.90 ± 2.40
PC + T4	2270 ± 90	56.8 ± 0.8	90.7 ± 6.5	51.21 ± 1.56

^aAll of the specimens prepared by injection molding were 4 mm thick and were placed at ambient temperature for at least 2 days before testing. For each sample, at least five specimens were tested.

^bDetermined by the method in GB1040. The tensile speed was 50 mm/min. The elastic modulus was calculated from the engineering stress-strain data at a low elongation (<1%).

^cDetermined by the method in GB1843-2008.

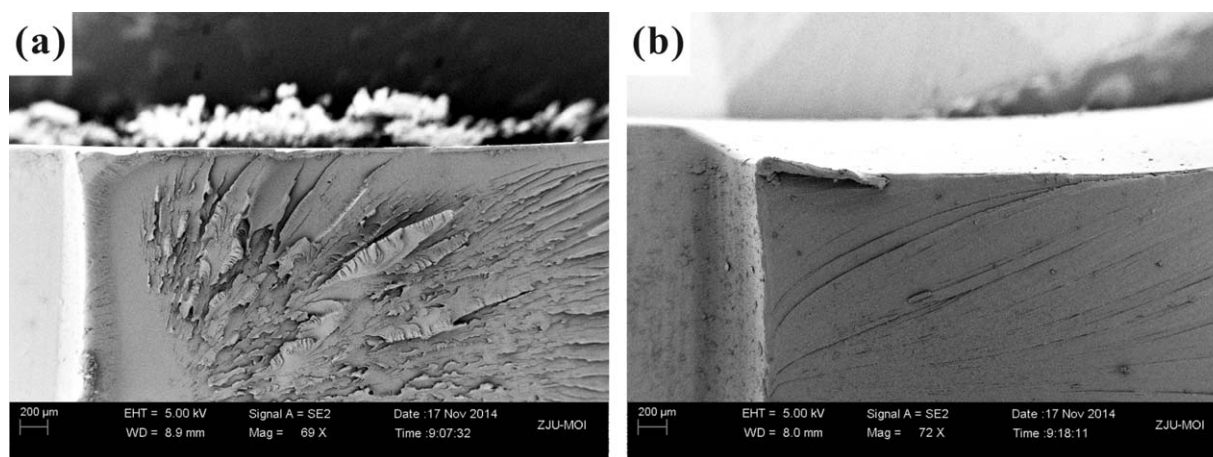


Figure 5. Fracture surfaces of the impacted blends at 20°C: (a) neat PC and (b) PC + 5 wt % R2.

allowed us to follow the polymerization by gravimetric analysis, gel permeation chromatography (GPC), and Malvern dynamic light-scattering analysis.

Synthesis of Acrylic Core–Shell Particles via Traditional Emulsion Polymerization

Acrylic core–shell particles were synthesized by traditional emulsion polymerization through three steps under a nitrogen atmosphere in a four-necked glass reactor equipped with a mechanical stirrer, a reflux condenser, and a thermometer. The resulted core–shell particles had a core–shell ratio of 70 : 30 w/w. The recipe and polymerization conditions for each step are summarized in Tables I–III.

Blending and Injection Molding

PC was dried at 140°C in a vacuum oven for 24 h. The latex was de-emulsified, and the collected polymer was dried at 120°C in a vacuum oven for 24 h. The dried PC together with the polymeric modifiers and antioxidant were pre-mixed by manual stirring. The toughened PC was fabricated by a Brabender single-screw extruder (Brabender Measurement & Control System) at 290°C and 70 rpm. Each sample was extruded twice to ensure good mixing.

Tensile and impact specimens with a thickness of 4 mm were injection-molded into a PNX40III-2A machine (NESSI Plastic Industrial Co., Ltd.).

Mechanical Testing

The tensile properties were measured by a Zwick/Roell Z020 universal material tester at 20°C according to GB1040. The tensile specimens were extended at a rate of 50 mm/min. For each sample, at least five specimens were tested.

The Izod impact strength was tested on a CEAST impactor at 20°C. The 4 mm thick rectangle specimens were obtained by compression-molding and then sharply notched to have an A-type notch with a radius of 0.25 ± 0.05 mm according to GB1843-2008.

Characterization

¹H-NMR. The structure of oligo(MAA-*b*-MMA) RAFT and PMMA-*b*-PnBA diblock copolymers were characterized by 500-MHz ¹H-NMR with dimethyl sulfoxide and tetrahydrofuran-*d*₈

as solvents with tetramethylsilane as a reference on a Bruker Avance DMX 500 spectrometer.

GPC Analysis. M_n , weight-average molecular weight (M_w), and polydispersity index (PDI; M_w/M_n) were measured by GPC [with a refractive index (RI)/UV dual detector]. UV (311-nm) signals were detected by a Waters 2489 dual- λ absorbance detector. The samples were dried in a vacuum oven at 120°C for 24 h and then dissolved in tetrahydrofuran. The eluent was tetrahydrofuran with a flow rate of 1.0 mL/min, and the measured temperature was 35°C. Waters Styragel columns HR 5, 4, and 3 (measurement range = 4,000,000–500 g/mol) were used. The molecular weights and PDIs were derived from a calibration curve based on narrow PMMA standards.

Particle Size Analysis. The volume-average particle size or diameter (D_v) of the block copolymer particles was obtained by transmission electron microscopy (TEM; JEM-1230) image analysis. The samples were diluted and dipped onto carbon-coated copper grids. TEM was done at 80 kV. About 300 particles were randomly selected to calculate D_v . D_v of the PnBA particles was measured by the dynamic light-scattering method in a Malvern Zetasizer 3000HSA instrument at 25°C. The samples were diluted and placed in a vacuum oven at 35°C for 2 h to remove residual monomer before the measurement.

Differential Scanning Calorimetry (DSC). The glass-transition temperatures of the polymeric modifiers were determined by a DSC Q200 instrument. The samples were scanned from –90 to 150°C at a rate of 10°C/min. Before the measurement, we erased the thermal history of the samples heating them to 150°C and holding them there for 3 min.

Scanning Electron Microscopy (SEM). The fracture surfaces of the impacted specimens were examined in a Zeiss ULTRA 55 scanning electron microscope. The specimens were coated with a thin layer of Au/Pd before SEM examination.

TEM Morphology Observation. Sections for TEM (JEM-1230) were prepared with an ultramicrotome (Leica EM UC7) at room temperature. Those 50 nm thick sections were reacted with 85% hydrazine in a closed vessel at 45°C for 2 h to selectively convert the ester groups of the acrylic modifiers to

hydrazide.³⁷ Then, the sections were placed in a vacuum oven at 50°C for 12 h to remove moisture and then exposed to OsO₄ vapor to stain the hydrazide groups for 10 min.

RESULTS AND DISCUSSION

Synthesis of the PMMA-*b*-PnBA Diblock Copolymers via RAFT Emulsion Polymerization

The latex of PMMA-*b*-PnBA was synthesized via RAFT emulsion polymerization with oligo(MAA₄₁-*b*-MMA₈) RAFT as both the polymerization mediator and the surfactant. Because the oligomeric RAFT agent was used as the surfactant, the polymer chains grew inward during the polymerization in a living manner. This was a simple and robust method for tailor making the core-shell particles of the block copolymer.³⁸ A series of PMMA-*b*-PnBA diblock copolymers was synthesized by the sequential addition of monomers. The MMA, added first, formed the shell, and the BA, added second, produced the core. Such a core-shell morphology is difficult to achieve via RAFT emulsion polymerization mediated by a small-molecular RAFT agent with sodium dodecyl sulfate (SDS) as surfactant, such as that discussed in a previous report.^{16,17,39} The molecular weight of the PMMA block was fixed at 30 kg/mol, whereas the PnBA block was changed from 50 to 100 kg/mol to fine-tune the copolymer compositions. The polymerization conditions and results are listed in Table IV. The polymerization proceeded quite rapidly, and the diblock copolymers were obtained in one pot within 2 h. At each stage, the monomer conversion was higher than 90%, as shown in Table IV. All of the latexes showed good colloidal stability with a negligible amount of coagulum. The copolymer compositions were verified by ¹H-NMR. A typical ¹H-NMR spectrum of PMMA-*b*-PnBA synthesized by RAFT emulsion polymerization is presented in Figure 2. ¹H-NMR signals of PMMA-*b*-PnBA diblock copolymer were assigned as follows.

¹H-NMR (ppm): 1.7 (—CH₂— in MMA units), 3.9 (—CH₂— in the pendant butyl ester from nBA units).

PMMA-*b*-PnBA was synthesized via RAFT emulsion polymerization mediated by a small-molecular RAFT agent with SDS as the surfactant.¹⁵ No colloidal stability information was available.¹⁵ However, it seemed that the molecular weight was out of control, just as has been often reported.^{16,17} In Table IV, it is clear that the measured molecular weights were in good agreement with the theoretical values. The relatively high PDI of PMMA (~1.5) compared to that of styrene^{7,11} or nBA¹² homopolymerization in RAFT emulsion was attributed to the nonuniform distribution of the RAFT agent molecules; this was due to the homogeneous particle nucleation in MMA emulsion polymerization¹⁹ and the diffusion-controlled RAFT reactions in the late stage of polymerization.^{19,40} The higher final PDIs of the block copolymers might have been caused by the chain branching of the PnBA block.^{41,42} The development of the GPC traces during the synthesis of the PMMA-*b*-PnBA diblock copolymers is shown in Figure 3. After chain extension, the GPC curves shifted as a whole in all three Exp's; this indicated that the block copolymer was formed. When the designed *M_n* of PnBA was over 50 kg/mol, a shoulder of high molecular weight of the diblock copolymers appeared in the GPC curves because of

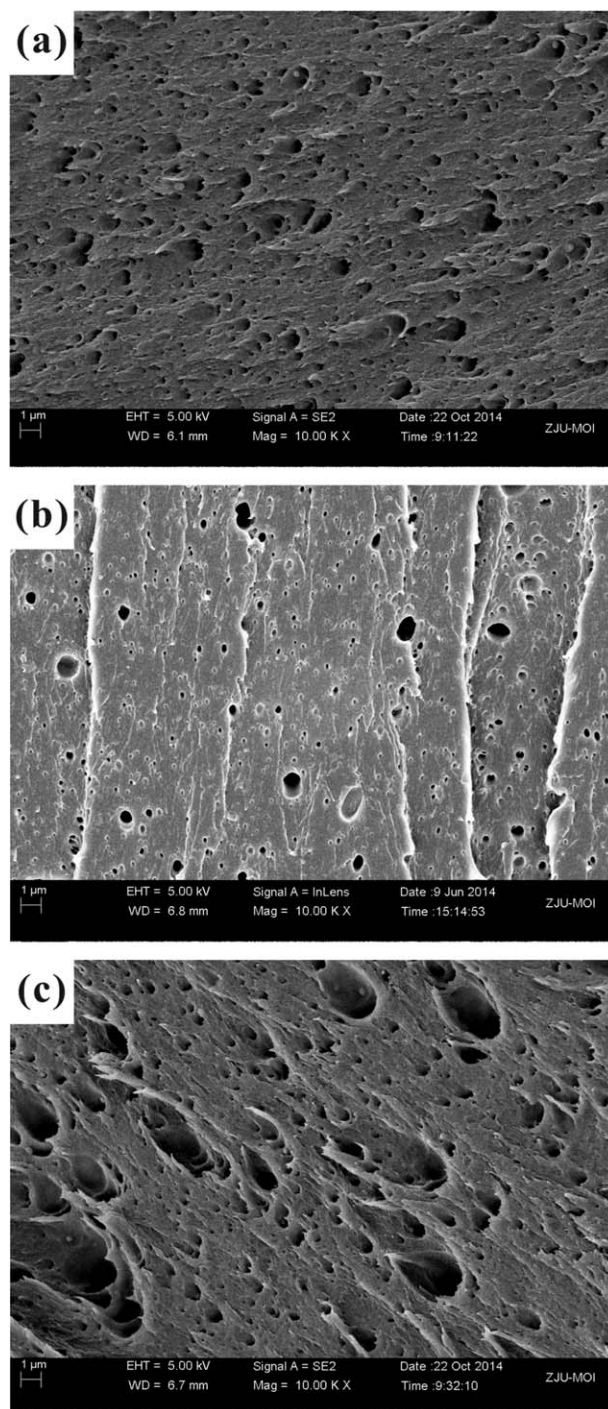


Figure 6. Fracture surfaces of the impacted PC modified with 5 wt % core-shell particles at 20°C: (a) R1: PMMA₂₅₀-*b*-PnBA₃₉₀, (b) R2: PMMA₂₅₀-*b*-PnBA₅₅₀, and (c) R3: PMMA₂₅₀-*b*-PnBA₇₈₀.

chain branching during nBA polymerization.^{41,42} The distribution of the trithiocarbonate RAFT groups was also monitored by a GPC UV detector with an incident light wavelength of 311 nm,¹⁰ as shown in Figure 3. For those PMMA samples, a shoulder peak of high molecular weight appeared in the RI curves but did not appear in the UV curves; this suggested that some poorly controlled polymer chains were formed in the late

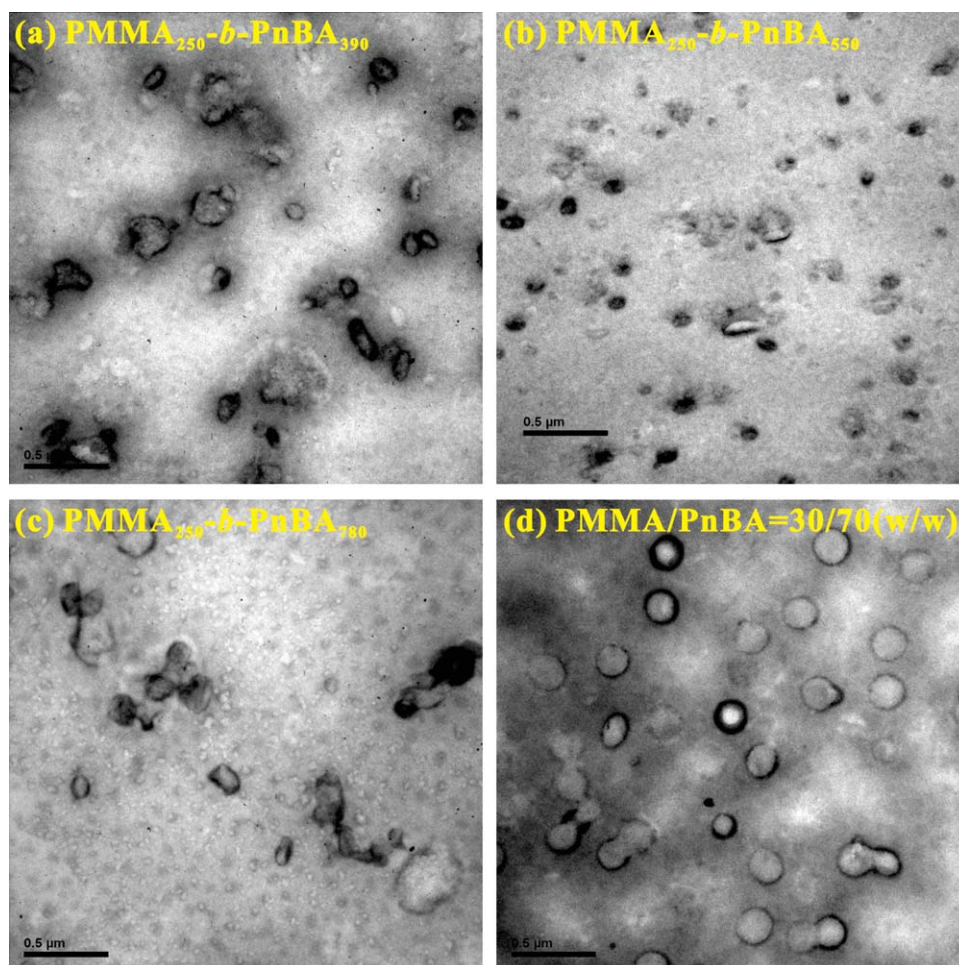


Figure 7. TEM micrographs of the undeformed PC blending with 5 wt % acrylic core-shell particles: (a) PC/R1, (b) PC/R2, (c) PC/R3, and (d) PC/T4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stage of polymerization. The reason might have been that RAFT reactions became diffusion-controlled at high monomer conversions.¹⁹ The RI and UV signals of the final diblock copolymer in Exp R1 almost overlapped; this revealed that most of the polymer chains should have been end-capped with RAFT moieties. As the preset M_n of PnBA increased, the shoulder peak of high molecular weight became pronounced as a result of the branching reactions of PnBA.^{41,42} The final particle size distributions (PSDs) were all unimodal, as observed through TEM, with diameters between 100 and 150 nm (Table IV).

As a comparison, PMMA-PnBA core-shell particles were also prepared by traditional emulsion polymerization (T4 in Table V). The core-shell mass ratio was designed as 70 : 30, the same as used in Exp R2 (Table IV). Full conversion was reached. The final PSD was unimodal, with an average particle diameter of 114 nm, as given in Table V. The measured diameter from dynamic light scattering was much larger than that from TEM; this was likely because some limited coagulation occurred during the polymerization.

The DSC derivative curves of the core-shell particles are presented in Figure 4. Two glass-transition temperatures corresponding to PMMA and PnBA, respectively, were clearly

observed with the exception of PMMA₂₅₀-*b*-PnBA₇₈₀; this suggested that good phase separation occurred. Similar microphase separation was observed by DSC in the PMMA-*b*-PnBA diblock copolymers synthesized via RAFT solution polymerization within a wide range of compositions.⁴¹

Toughening Properties

Effect of the Core-Shell Particle Types. In toughening PC, the optimum amount of elastomeric modifiers was about 4–10 wt %.^{29,43} The tensile properties and the notched impact strength of PC toughened by 5 wt % core-shell particles are summarized in Table VI. As shown in Table VI, it was clear that all four modifiers dramatically increased the impact strength of PC. PC toughened by PMMA₂₅₀-*b*-PnBA₅₅₀ showed the highest impact strength. The impact strength was increased by four times to 62.81 kJ/m² compared with the neat PC. In most cases, the toughened PCs showed lower modulus, lower yield strength, and similar elongation at break values compared with the neat PC. Most interestingly, PC toughened by PMMA₂₅₀-*b*-PnBA₅₅₀, which showed the highest impact strength, presented a much longer elongation at break, the same yield strength, and only a slightly decreased modulus than the neat PC. This performance has been rarely observed in the toughened polymer. Compared with the

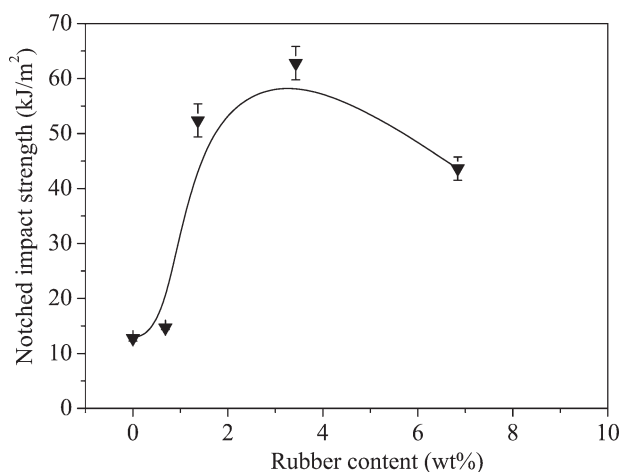


Figure 8. Influence of the rubber-phase levels on the impact strength of PCs.

modifier from the conventional emulsion polymerization, PMMA₂₅₀-*b*-PnBA₅₅₀ presented as a better modifier in terms of the impact strength, elongation at break, and yield strength.

The fracture surfaces of the neat PC and toughened PC specimens are compared in Figure 5. The fracture surface of the neat PC at ambient temperature [Figure 5(a)] showed a typical craze breakdown pattern,^{28,44} whereas the fracture surface of the toughened PC [Figure 5(b)] showed characteristic stress-whitening of the surface and sucking-in of the edges, and these were indicative of plane-stress shear fracture.^{23,27,28}

The SEM micrographs of the fracture surfaces of the impacted PCs toughened by 5 wt % block copolymers are shown in Figure 6. In all cases, the cavitation effect was pronounced. The PC toughened by PMMA₂₅₀-*b*-PnBA₅₅₀ [Figure 6(b)] presented a relatively smooth fracture surface, and the voids were uniformly dispersed. In comparison, PC modified by 5% PMMA₂₅₀-*b*-PnBA₃₉₀ or PMMA₂₅₀-*b*-PnBA₇₈₀ showed a typical surface texture created by a pulled-out matrix.²⁷ Similar surface textures were observed in a PC toughened by an interpenetrating polymer network²⁷ and SBS,²⁴ where the modifying elastomers had poor compatibility with PC. It was proposed that this type of surface texture could be caused by poor interfacial adhesion between the matrix and modifier particles.²⁷

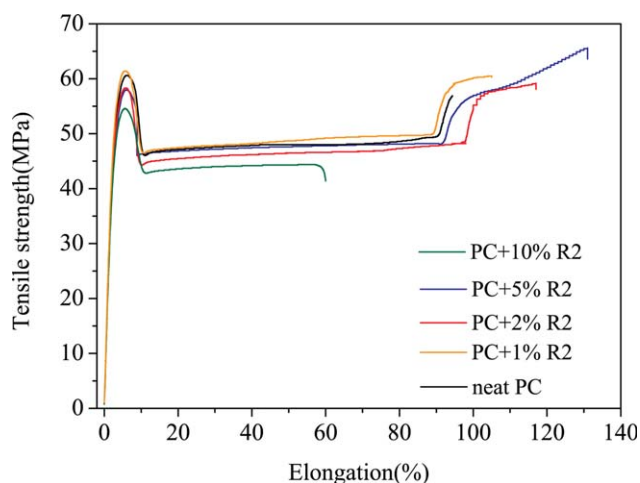
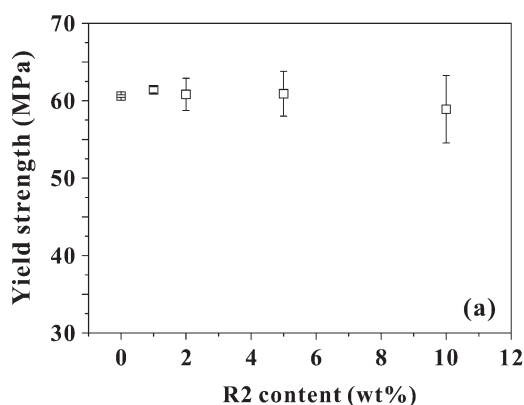


Figure 10. Influence of the modifier levels on the engineering stress–strain curves for the PC/R2 blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7 shows that the crosslinked core–shell particles synthesized by conventional emulsion polymerization were well dispersed in the PC matrix. In those samples modified by the core–shell particles of the block copolymers, the size of the dispersed phase was much smaller than that of SBS-toughened PC²³ because of the better compatibility of PMMA with PC. However, the dispersed phase size was highly dependent on the compositions of the block copolymer. For PMMA₂₅₀-*b*-PnBA₅₅₀, the rubber phase was well dispersed into about 100-nm particles, which were close to the size of the original core–shell particles. For PMMA₂₅₀-*b*-PnBA₃₉₀ and PMMA₂₅₀-*b*-PnBA₇₈₀, the rubber phase was composed of much larger particles with irregular shape. We assumed that those larger particles might have had poorer mechanical properties. As a result, the toughened PC could be cavitated at a lower stress and generated a pulled-out fracture surface. This also explained why PC toughened by PMMA₂₅₀-*b*-PnBA₅₅₀ showed the best tensile properties.

Effect of the Modifier Dosages. Figure 8 presents the effect of the dosage of PMMA₂₅₀-*b*-PnBA₅₅₀ on the impact properties of the toughened PC. It was clear that PMMA₂₅₀-*b*-PnBA₅₅₀ was a highly efficient impact modifier. The addition of 2 wt % block

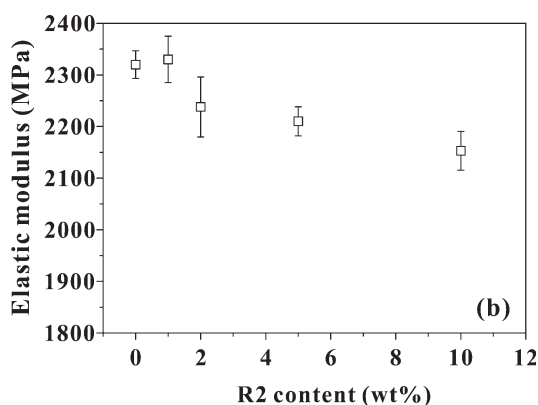


Figure 9. Tensile properties of the toughened PCs at various R2 dosages: (a) yield strength and (b) elastic modulus.

copolymer increased the impact strength of PC from 12.75 to 52.73 kJ/m². The optimum dosage of the block copolymer was about 5 wt %. The existence of an optimum dosage has been well reported in other rubber-toughened PC systems.^{21,28} With a low dosage of rubber modifier, the fracture mode should have been a brittle one, so the impact strength would increase with increasing modifier levels. With a high dosage of rubber modifier, the fracture would have been in a ductile mode, and the increased modifier levels would harm the impact strength by decreasing the yield strength.

The tensile properties at various dosages of the block copolymer are presented in Figure 9. At large strains of the tensile curves, an apparent stress-hardening platform was observed in most cases, as shown in Figure 10. The sudden increase in stress occurred because the neck of the testing specimens reached the grip areas. Similar observations have been reported.⁴⁵ So, the exact tensile strength could not be calculated. As shown in Figure 9, the dosage of PMMA₂₅₀-*b*-PnBA₅₅₀ exerted little influence on the yield strength, whereas the modulus slightly decreased with increasing dosage. The elongation at break increased with increasing dosage and then decreased at 10 wt %.

CONCLUSIONS

A series of PMMA-*b*-PnBA diblock copolymers with changing compositions was synthesized by design via RAFT emulsion polymerization with an amphiphilic oligo(MAA₄₁-*b*-MMA₈) RAFT agent as both a mediator and surfactant. Compared with the conventional emulsion polymerization, the RAFT emulsion polymerization was a simpler and robust route for synthesizing well-defined core-shell structured particles of block copolymers with predesigned structures. The molecular weights of the block copolymer agreed well with the theoretical prediction, but the PDIs were broad. The resulting core-shell particles of the diblock copolymers were found to be very efficient impact modifiers. The diblock copolymer were well dispersed into 100–300-nm particles in the PC matrix, and the dispersed phase size was highly dependent on the block copolymer compositions. PMMA₂₅₀-*b*-PnBA₅₅₀, which was dispersed into the finest particles of about 100 nm in diameter, presented the best ability to improve the impact properties of PC. Compared with the neat PC, the notched impact strength of the PC toughened by 5 wt % PMMA₂₅₀-*b*-PnBA₅₅₀ was increased by four times up to 62.81 kJ/m² with the same yield strength, a slightly decreased modulus, an increased elongation at break, and an increased tensile strength.

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