

Novel Comb-Structured-Polymer-Grafted Carbon Black by Surface-Initiated Atom Transfer Radical Polymerization and Ring-Opening Polymerization

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ABSTRACT: Novel comb-structured-polymer-grafted carbon black (CB) was synthesized with a combination of surface-initiated atom transfer radical polymerization and ring-opening polymerization. First, poly(2-hydroxyethyl methacrylate) (PHEMA) was grafted onto the CB surface by surface-initiated atom transfer radical polymerization. The prepared CB-g-PHEMA contained 35.6–71.8% PHEMA, with the percentage depending on the molar ratio of the reagents and the reaction temperature. Then, with PHEMA in CB-g-PHEMA as the macroinitiator, poly(ϵ -caprolactone) (PCL) was grown from the CB-g-PHEMA surface by ring-opening polymerization in the presence of stannous

octoate. CB-g-PHEMA and CB-g-(PHEMA-g-PCL) were characterized with Fourier transform infrared, ¹H-NMR, thermogravimetric analysis, dynamic light scattering, and transmission electron microscopy. The resultant grafted CB had a shell of PHEMA-g-PCL. On the whole, the CB nanoparticles were oriented in dendritic lamellae formed by these shells. This hopefully will result in applications in gas sensor materials and nanoparticle patterns. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 824–827, 2010

Key words: atom transfer radical polymerization (ATRP); core-shell polymers; nanocomposites

INTRODUCTION

Carbon black (CB) has attracted much attention because of its potential applications in sensors, positive temperature coefficient materials, fuel cells, inks, and so forth. Many applications require CB to be dispersed in a certain solvent or polymer matrix. Grafting a polymer onto the surface of CB has proved to be a good choice for improving the dispersion of CB. Surface-initiated ring-opening polymerization (SI-ROP; anionic and cationic) and radical polymerization (the trapping of polymer radicals) have been used to prepare polymer-grafted CB.^{1,2} CB surface properties, such as hydrophobic and hydrophilic properties, crystallization properties, and temperature responsiveness, are determined by the properties and structures of the grafted polymers.^{3,4} The stabilization of CB in solvents is mostly decided by the structure of the grafted polymer. In general, a polymer with a comb structure can supply much stronger steric stabilization than a linear polymer for CB. In our previous work,³ linear poly(ϵ -caprolactone) (PCL) was grafted onto the surface of

CB. Although having an obvious shell of PCL, the grafted CB could not disperse stably in solvents for a long time. A possible solution is to graft a polymer with a comb structure onto the surface of CB, and this can supply much stronger steric stabilization. Surface-initiated atom transfer radical polymerization (SI-ATRP) has been used recently to graft polymers onto CB surfaces.^{5–8} A combination of SI-ATRP and SI-ROP has proved to a promising tool for preparing comb-structured polymers.⁹

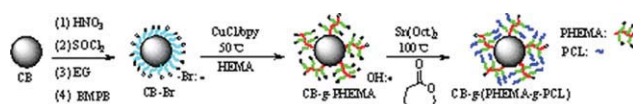
In this study, poly(2-hydroxyethyl methacrylate) (PHEMA) chains were grown from the surface of CB by SI-ATRP. Then, PCL was grafted from CB-g-PHEMA by SI-ROP in the presence of stannous octoate [Sn(Oct)₂]. Both CB-g-PHEMA and CB-g-(PHEMA-g-PCL) were characterized with Fourier transform infrared (FTIR), ¹H-NMR, thermogravimetric analysis (TGA), dynamic light scattering, and transmission electron microscopy (TEM).

EXPERIMENTAL

Materials

Primary CB particles (VXC 605) with an average size of 30 nm and a specific surface area of 254 m²/g were obtained from Cabot. 2-Bromo-2-methylpropionyl bromide (BMPB) and 2-hydroxyethyl methacrylate (HEMA) were purchased from Acros. 2,2-

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Scheme 1 Synthesis of CB-Br and CB-g-(PHEMA-g-PCL). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Bipyridyl (bpy) was obtained from Shanghai No. 1 Chemical Reagent Factory (Shanghai, China). Ethylene glycol and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Copper(I) chloride (CuCl) was purified by stirring in acetic acid and was washed with methanol. Dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) were dried with 4-Å molecular sieves before being used. CB-OH ($-\text{OH}$, 1.55 mmol/g) was prepared according to our previously reported method.⁵

Characterization

TGA curves were determined with a PerkinElmer TGA-7 (at a heating rate of $20^\circ\text{C}/\text{min}$ from 25 to 800°C in a flow of nitrogen). $^1\text{H-NMR}$ spectra were recorded with an Avance 400-MHz NMR spectrometer. FTIR spectra were recorded on a Jasco IR-700 infrared spectrophotometer. The hydrodynamic diameter was measured by dynamic light scattering (Zetasizer 3000, Malvern Instruments; wavelength = 633 nm, detector angle = 90°). A TEM image was obtained with a JEOL 1200EX instrument operated at an accelerating voltage at 160 keV.

Preparation of CB-Br⁵

CB-OH (1.0 g, 1.55 mmol/g), 25 mL of CH_2Cl_2 , 11.5 mL of triethylamine (81 mmol), 0.7545 g of DMAP (6 mmol), and 10 mL of 2-bromo-2-methylpropionyl bromide (81 mmol) were added to a 50-mL, two-necked flask, and the mixture was sonicated for 30 min. The mixture was stirred at 0°C for 3 h and was reacted then at room temperature for 24 h. The resultant solid was separated centrifugally and was washed with CH_2Cl_2 , deionized water, and THF to

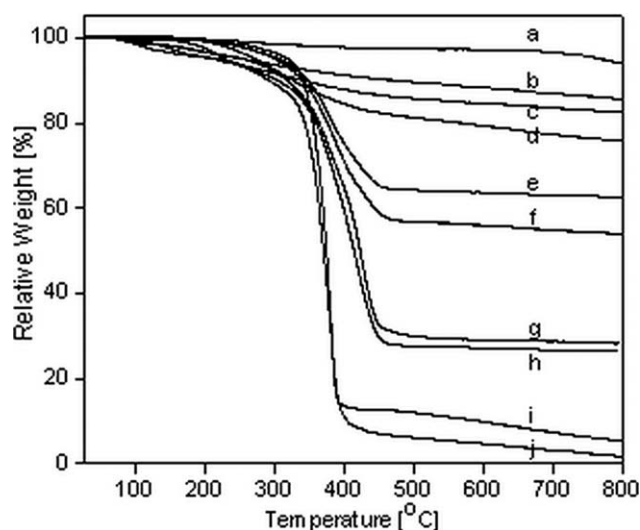


Figure 1 TGA curves of (a) CB, (b) CB-COOH, (c) CB-OH, (d) CB-Br, (e) CB-g-PHEMA-1, (f) CB-g-PHEMA-4, (g) CB-g-PHEMA-2, (h) CB-g-PHEMA-3, (i) CB-g-(PHEMA-g-PCL)-1, and (j) CB-g-(PHEMA-g-PCL)-2.

remove any absorbed 2-bromo-2-methylpropionyl bromide. The resultant CB-Br ($-\text{Br}$, 0.28 mmol/g) was dried *in vacuo* at 50°C .

Synthesis of CB-g-PHEMA¹⁰

Typically, 50 mg of CB-Br (14.0 μmol of $-\text{Br}$, 0.28 mmol/g), 5.2 mg of CuCl (0.05 mmol), 15.3 mg of bpy (0.10 mmol), 0.9 mL of methanol, and 0.6 mL of HEMA (24.12 mmol) were placed in a dried 25-mL, two-necked flask. After being evacuated and back-filled with argon three times, the flask was immersed at 50°C for 12 h. At the end of the reaction, the product was separated centrifugally, was washed with THF repeatedly, and was dried *in vacuo* at 50°C .

$^1\text{H-NMR}$ [400 MHz, dimethyl sulfoxide (DMSO)]: 4.87–4.75 (1H, in $-\text{CH}_2\text{OH}$), 4.00–3.82 (2H, in $-\text{OCOCH}_2\text{CH}_2\text{O}-$), 3.69–3.52 (2H, in $-\text{OCOCH}_2\text{CH}_2\text{O}-$), 2.03–1.67 (2H, in $-\text{CH}_2\text{CCH}_3-$), 1.07–0.69 (3H, in $-\text{CH}_2\text{CCH}_3-$).

TABLE I
Reaction Conditions and Results for the Preparation of CB-g-PHEMA

Sample	HEMA (mL)	$-\text{Br}$ (μmol)	HMEA/CuCl/bpy (mol/mol/mol)	Time (h)	F_{wt} (%)
CB-g-PHEMA-1 ^a	0.6	14.0	154.6/1/2	8	35.6
CB-g-PHEMA-2 ^a	0.6	14.0	154.6/1/2	10	70.4
CB-g-PHEMA-3 ^a	0.6	14.0	154.6/1/2	12	71.8
CB-g-PHEMA-4 ^b	3.0	112	773.0/1/2	12	42.5

^a CB-Br (50 mg, 14.0 μmol of $-\text{Br}$, 0.28 mmol/g), 5.2 mg of CuCl (0.05 mmol), 15.3 mg of bpy (0.10 mmol), 0.6 mL of HEMA (24.12 mmol), and 0.9 mL of CH_3OH at 50°C .

^b CB-Br (0.4 g, 112 μmol of $-\text{Br}$, 0.28 mmol/g), 31.2 mg of CuCl (0.3 mmol), 92.5 mg of bpy (0.6 mmol), 3 mL of HEMA (144.7 mmol), and 4.5 mL of CH_3OH at 50°C for 12 h. F_{wt} represents the polymer content, calculated from TGA under N_2 .

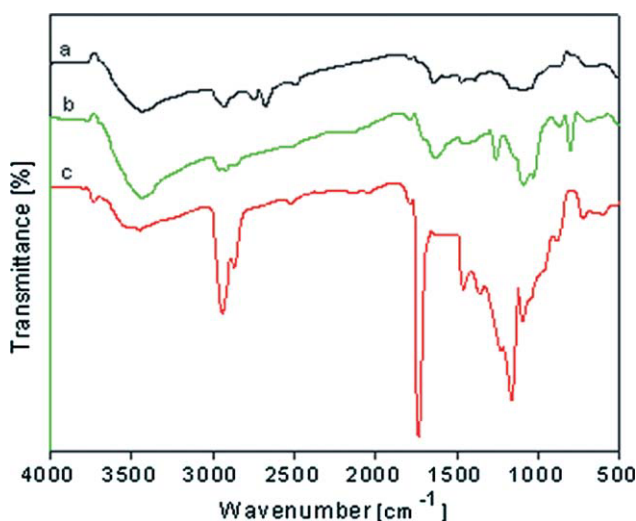


Figure 2 FTIR spectra of (a) CB-Br, (b) CB-g-PHEMA, and (c) CB-g-(PHEMA-g-PCL). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Synthesis of CB-g-(PHEMA-g-PCL)⁹

Typically, 0.2002 g of CB-g-PHEMA, 4.05 mg of Sn(Oct)₂ (0.01 mmol), 5 mL of ϵ -caprolactone (CL; 46.88 mmol), and 3 mL of dimethylformamide (DMF) were placed in a dried 25-mL, two-necked flask. After being evacuated and back-filled with argon three times, the flask was immersed at 90°C for 12 h. At the end of the reaction, the product was separated centrifugally, was washed with THF repeatedly, and was dried *in vacuo* at 50°C.

¹H-NMR (400 MHz, CDCl₃): 4.35–4.30 (2H, in $-\text{OCOCH}_2\text{CH}_2\text{O}-$), 4.15–3.93 (2H, in $-\text{[COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}]_m-$), 3.65–3.57 (2H, in $-\text{OCOCH}_2\text{CH}_2\text{O}-$), 2.37–2.16 (2H, in $-\text{[COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}]_m-$), 1.94–1.88 (2H, in $-\text{[CH}_2\text{CCH}_3]_n-$), 1.72–1.49 (4H, in $-\text{[COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}]_m-$), 1.43–1.13 (2H, in $-\text{[COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}]_m-$), 0.94–0.80 (3H, in $-\text{[CH}_2\text{CCH}_3]_n-$).

RESULTS AND DISCUSSION

Synthesis of CB-g-PHEMA

In our experiment, we employed the method adopted by Yan et al.¹¹ to attach the ATRP initiators

TABLE II
Reaction Conditions and Results for CB-g-(PHEMA-g-PCL)

Sample	CL (mL)	DMF (mL)	Time (h)	F_{wt} (%)
CB-g-(PHEMA-g-PCL)-1	5	4	22	86.3
CB-g-(PHEMA-g-PCL)-2	6	3	22	92.7

F_{wt} represents the polymer content, calculated from TGA under N₂.

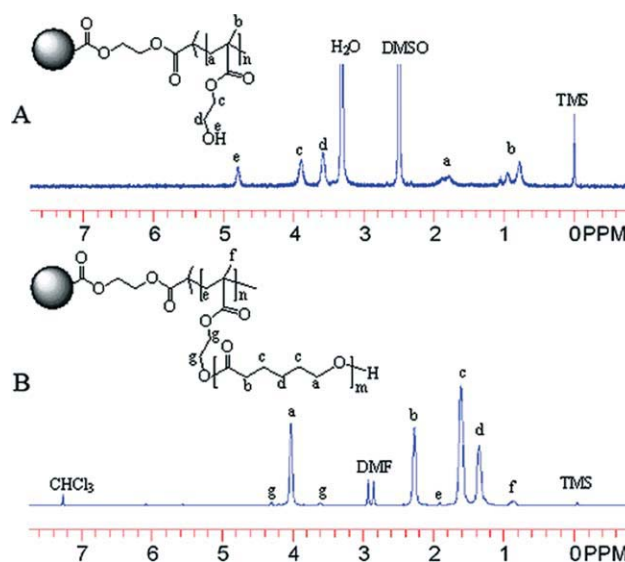


Figure 3 ¹H-NMR spectra of (A) CB-g-PHEMA and (B) CB-g-(PHEMA-g-PCL). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

onto the CB surface, as shown in Scheme 1. The density of the ATRP initiator was approximately 0.28 mmol/g, as calculated by TGA (see Fig. 1).

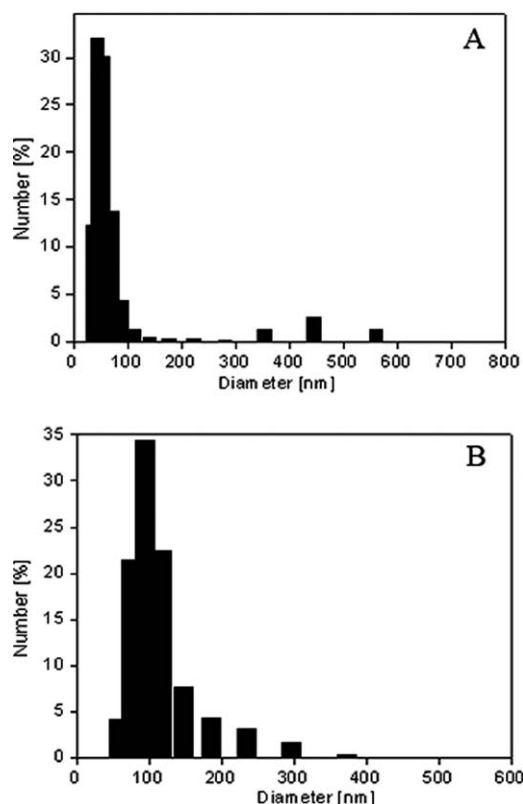


Figure 4 Size distributions of (A) CB-g-PHEMA and (B) CB-g-(PHEMA-g-PCL) in THF.

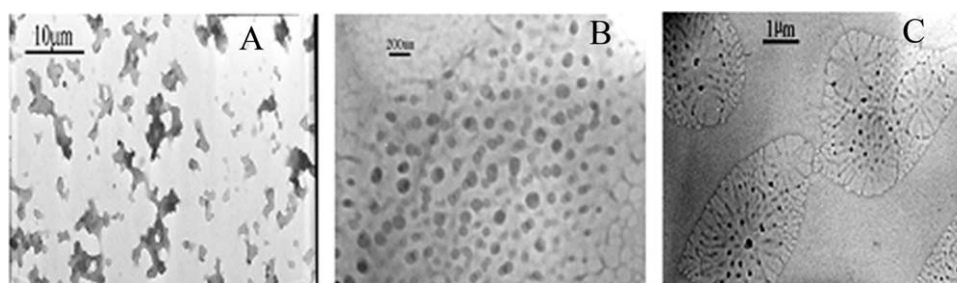


Figure 5 TEM images of (A) CB-g-PHEMA and (B,C) CB-g-(PHEMA-g-PCL) in THF.

Matyjaszewski et al.⁹ studied ATRP of HEMA. PHEMA was grafted onto the CB surface by SI-ATRP, as shown in Scheme 1. The prepared CB-g-PHEMA contained 35.6–71.8% PHEMA, with the percentage depending on the molar ratio of the reagents and the reaction temperature (Table I).

CB-g-PHEMA was characterized with FTIR and ¹H-NMR. As shown in Figure 2, the CB-Br sample displayed three strong peaks⁵ at 2677–2972 cm⁻¹ corresponding to the C–H stretching and a strong peak at 1740 cm⁻¹; after it was grafted with PHEMA, a strong peak at 1711 cm⁻¹ was assigned to the stretching vibration of the carbonyl group (C=O). The spectrum of CB-g-PHEMA is shown in Figure 2(b). The chemical composition of CB-g-PHEMA was further proved by ¹H-NMR.

Synthesis of CB-g-(PHEMA-g-PCL)

Then, PHEMA was used as a macroinitiator for the ring-opening polymerization of CL. The ring-opening polymerization of CL, initiated by hydroxyl groups in PHEMA, was carried out in dry DMF at 100°C with Sn (Oct)₂ as the catalyst,⁹ as shown in Scheme 1 and Table II.

The produced CB-g-(PHEMA-g-PCL) was characterized with FTIR and ¹H-NMR. With respect to CB-g-PHEMA, after the grafting with PCL, the characteristic peak of the carbonyl shifted from 1711 to 1726 cm⁻¹, as shown in Figure 2(c). The chemical composition of CB-g-(PHEMA-g-PCL) was further proved by ¹H-NMR, as shown in Figure 3(B).

CB is well known to be strongly hydrophobic and to aggregate easily in THF. After PHEMA was grafted onto the CB surface, CB-g-PHEMA formed 50-nm agglomerates, as shown in Figure 4(A). The grafted CB existed with the crosslinking structure in THF because of hydroxyl bonds between the PHEMA molecules, as shown in Figure 5(A). When PCL was introduced onto the grafted CB surface, CB-g-(PHEMA-g-PCL) formed core-shell structures, as shown in Figure 5(B), in which the shell of

PHEMA-g-PCL could supply strong steric stabilization in THF.

Interestingly, PHEMA-g-PCL in CB-g-(PHEMA-g-PCL) formed lamellae with a dendritic pattern¹² in which the CB nanoparticles were oriented, as shown in Figure 5(C). A similar phenomenon has been observed in CB-g-PCL.³

CONCLUSIONS

PHEMA was grafted onto the surface of CB by SI-ATRP. Then, PHEMA in CB-g-PHEMA was used as the macroinitiator, and PCL was grafted from the CB-g-PHEMA surface by SI-ROP. The resultant grafted CB had a dissymmetric shell of PHEMA-g-PCL. On the whole, the CB nanoparticles were oriented in dendritic lamellae formed by these shells. Hopefully, this will result in applications in gas sensor materials and nanoparticle patterns.

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