

Modification of Carbon Black through Grafting Multihydroxyl Hyperbranched Polyether onto Its Surface

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ABSTRACT: The hydroxy methyl groups were introduced onto the pristine carbon black surface through the reaction between unsaturated hydrogen atoms of the polycondensed aromatic rings of carbon black and formaldehyde in alkali condition. Using the resultant hydroxy methyl groups on the carbon black surface as the growth point, multihydroxyl hyperbranched polyether was grafted onto the carbon black surface by cationic ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)-oxetane in the pres-

ence of $\text{BF}_3\cdot\text{OEt}_2$ to improve its dispersion ability in solvents. It was found that the modified carbon black could be dispersed in polar solvents, such as ethanol, chloroform, and DMF. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2086–2092, 2007

Key words: carbon black; hydroxy methyl; multihydroxyl hyperbranched polyether

INTRODUCTION

Carbon materials include carbon nanotubes, carbon sphere, carbon black, and carbon fibers, and have been extensively applied to many fields. To broaden their ranges of applications, the method of grafting polymers onto their surfaces^{1–3} is adopted. Carbon black is used widely as pigment in the coating⁴ and ink⁵ industry, and as reinforcing agent in the rubber industry,⁶ because it has excellent properties, such as chemical, heat resistance, and electroconductivity, etc. Usually, these applications require dispersing the carbon black into polymeric systems or solvents.

To improve its dispersion ability in polymeric systems or solvents, grafting polymer onto the carbon black surface is known to be one of the effective methods. Anionic,^{7,8} cationic,^{9–11} radical,^{12–15} and atom-transfer radical polymerization^{16,17} grafting polymers onto carbon black have been investigated extensively.

However, most of polymers grafted onto the carbon black surface were linear. Present research focuses on grafting hyperbranched polymers onto the surface of carbon black, because hyperbranched polymers have low intrinsic viscosity, controlled molecular weight, and controlled architecture.^{18–20} In this study, we report the results of grafting multihydroxyl hyperbranched polyether on the surface of carbon black.

EXPERIMENTAL

Materials

Primary carbon black particle (VXC 605), with an average size of 30 nm and a specific surface area of 254 m^2/g , was obtained from Cabot Co., and purified by extracting it with toluene to remove resinous substances absorbed on the surface, and dried in vacuum at 50°C. Dichloromethane was dried with 4 Å molecular sieves before use. Other reagents and solvents were used as received.

Introduction of hydroxy methyl groups onto the surface of carbon black

The mixture of 0.1 g carbon black and 0.35 mL 36% formaldehyde at pH 10 were stirred at 50°C for 1 h. After the reaction (as shown in Scheme 1), the resultant carbon black was filtered, washed with deionized water until neutral, and dried in vacuum at 50°C.

Synthesis of 3-ethyl-3-oxetanethanol (EHOX)^{21,22}

Trimethylpropane (26.8 g, 0.2 mol), diethyl carbonate (23.6 g, 0.2 mol), and potassium hydroxide (0.1 g, 1.8 mmol) dissolved in anhydrous ethanol (2 mL) were added into a flask. The mixture was refluxed in oil bath at 110°C for 1 h. Distillation was continued until the oil bath reached 140°C. After the distillation, vacuum was supplied for 1 h to remove the excess solvent. On heating above 200°C, the distilled colorless

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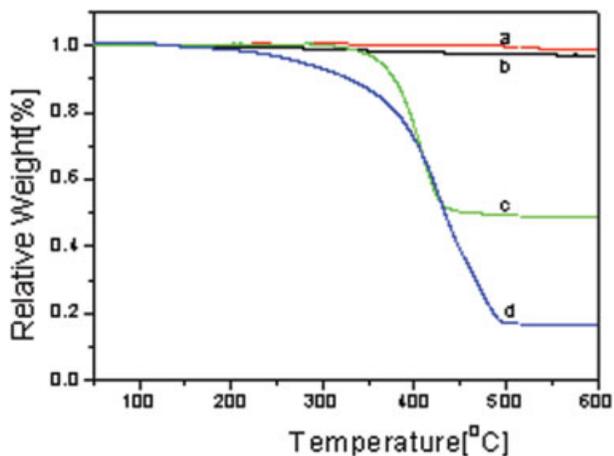


Figure 1 TGA curves of (a) carbon black, (b) CB-CH₂OH, (c) CB-HP3, and (d) CB-HP4. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

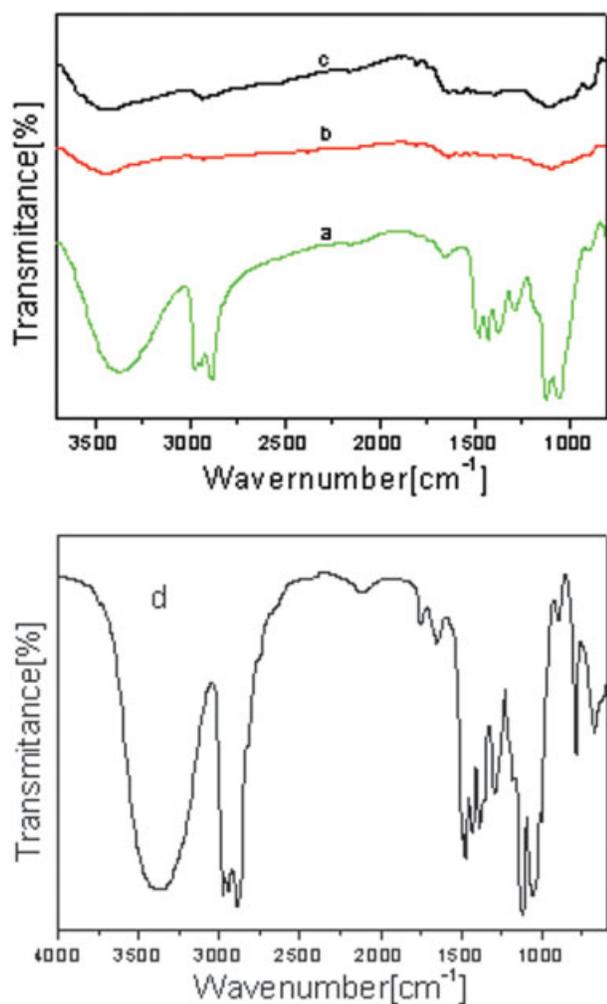


Figure 2 FTIR spectra of (a) CB-HP4, (b) carbon black, (c) CB-CH₂OH and (d) the hyperbranched polyether. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

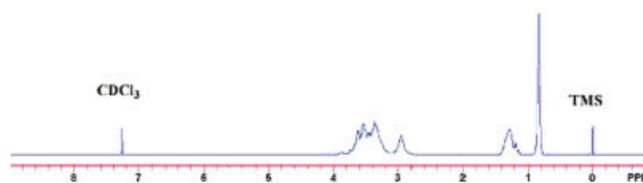


Figure 3 ¹H-NMR spectra of the hyperbranched polyether. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

lary cell, power 70 mW, detector angle 90°, 25°C, dispersant viscosity 1 cP, dispersant refractive index 1.36). The samples were dispersed by ethanol under ultrasonic.

RESULTS AND DISCUSSION

Introduction of hydroxy methyl groups onto the surface of carbon black

In our experiment, the introduction of hydroxy methyl groups onto the carbon black surface was achieved the reaction between unsaturated hydrogen atoms of the polycondensed aromatic rings of carbon black and formaldehyde at pH 10.

The amount of hydroxy methyl groups introduced onto the carbon black surface can be determined by titration. The mixture of CB-CH₂OH (0.1 g), acetic anhydride (1 mL), and ethyl acetate (3 mL) was hydrolyzed. After 20 min, deionized water (20 mL) and pyridine (10 mL) were added and the mixture was hydrolyzed for 10 min. The last hydrolyzed solution was titrated by sodium hydroxide (0.5 mol/L) to pH 7.5. Blank experiment was done by the same method. By calculation, the amount of hydroxy methyl groups was about 30 mmol/g. Compared by TGA, the result of titration was different.

Grafting hyperbranched polyether onto the surface of carbon black

The low ratio of catalyst to monomer results in a mainly linear or slightly branched polyether, and the

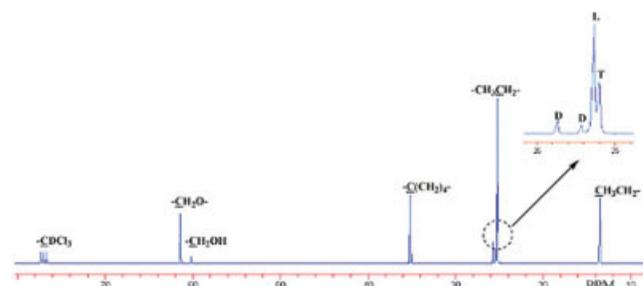


Figure 4 ¹³C-NMR spectra of the hyperbranched polyethers of CB-HP4. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

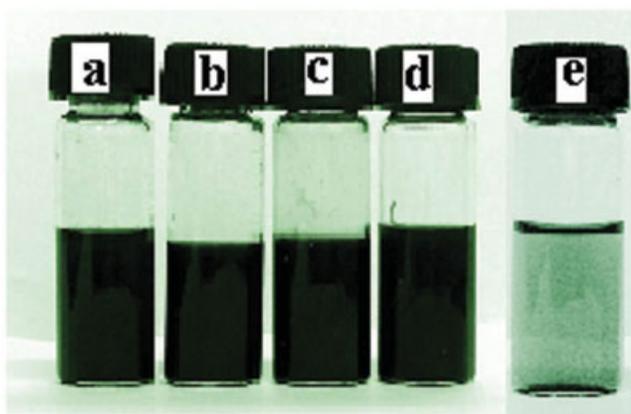


Figure 5 Photo of the samples placed in solvents (a) CB-HP1, (b) CB-HP2, (c) CB-HP3, (d) CB-HP4 in DMF, and (e) CB-CH₂OH in DMF solution containing HP. The content of the sample is around 10 mg of sample per 1 mL of solvent. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

high catalyst to monomer ratio leads to a hyperbranched polyether.²³ In our experiments, the amount of BF₃·OEt₂ was 1 mL that can ensure grafting the

hyperbranched polyether other than the linear polyether onto the carbon black surface. The detailed reaction conditions were listed in Table I.

Scheme II(C) illustrates a possible reaction process for grafting the hyperbranched polyethers onto the surface of carbon black. However, the 3-ethyl-3-oxetanethanol can also be self-initiated to become the hyperbranched polyether at the same time [as shown in Scheme II(B)]. To remove the hyperbranched polymer adsorbed onto the surface of carbon black, the grafted carbon black was successively filtrated, redispersed in ethanol, and separated centrifugally. Such procedures were repeated until there was no white sediment detected in the supernatant solution by the addition of water.

The grafted polyether content of the CB-HP can be estimated from TGA by the weight loss between 200 and 600°C. Figure 1 shows TGA of the carbon black, CB-CH₂OH, and grafted carbon black. There was not obvious decrease in weight for the sample of carbon black (the weight loss was only about 1%). For the sample of CB-CH₂OH, it decomposed slowly with the increasing of temperature and the weight loss was 3.58%. On the contrast, the weight losses were about

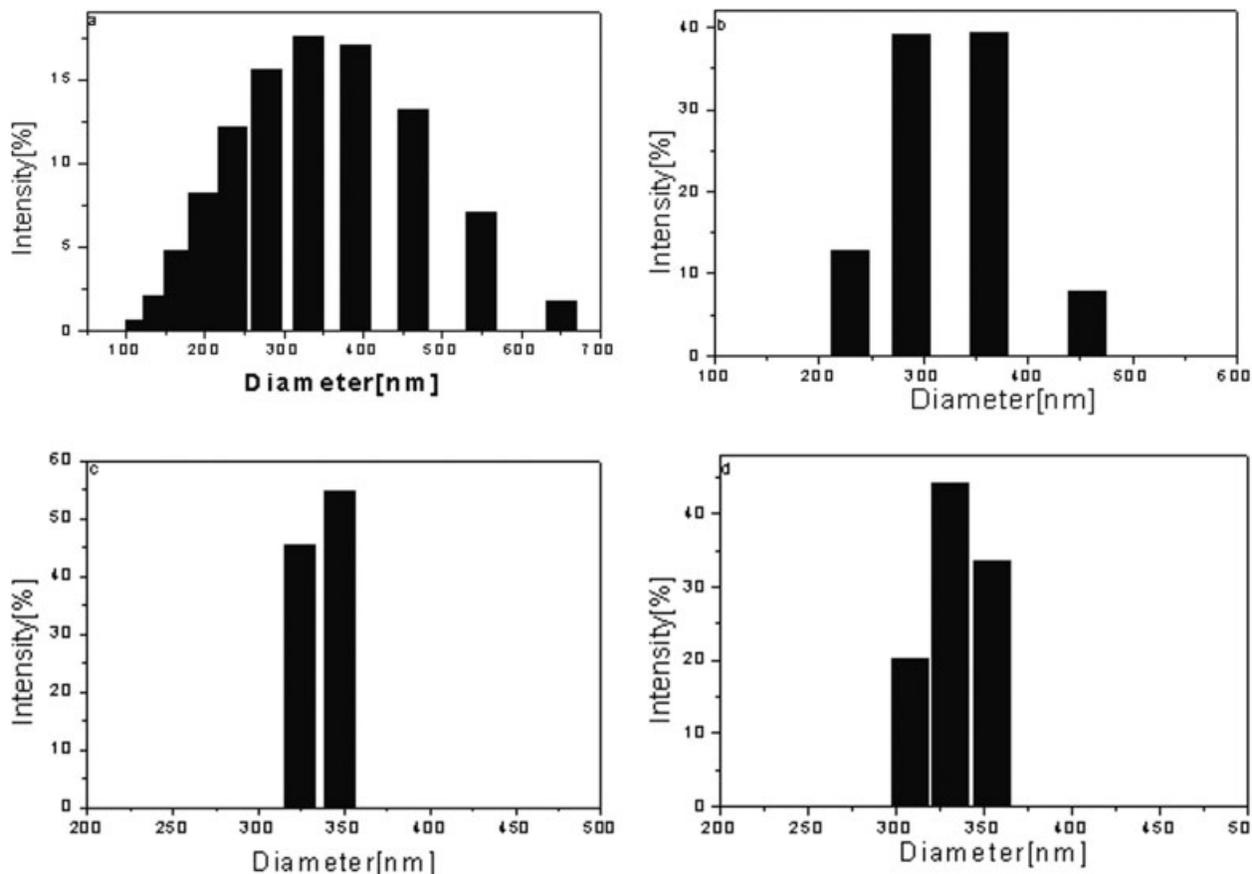


Figure 6 Distribution histogram according to dynamic light scattering of the diameter of (a) carbon black, (b) CB-CH₂OH, (c) CB-HP1, and (d) CB-HP3.

51 and 83%, respectively, for the samples of CB-HP3 and CB-HP4. From the increasing tendency, it can be found that higher the ratio of EHOX (mL) and carbon black (g), the higher the grafted polyether amount.

Figure 2 shows the FTIR spectra of the carbon black, CB-CH₂OH, and grafted carbon black. The obvious features are the much stronger bands at around 3442 cm⁻¹ ($\nu_{\text{O-H}}$), 2937 cm⁻¹ ($\nu_{\text{C-H}}$), and 1082 cm⁻¹ ($\nu_{\text{CH}_2\text{O-H}}$) for the CB-HP samples. Figure 2(d) shows the FTIR spectra of the hyperbranched polyether (HP).

Figure 3 shows the ¹H-NMR spectra of the hyperbranched polyether (HP). ¹H-NMR (δ , ppm): 0.82–0.85 (—CH₃), 1.16–1.29 (—CH₂CH₃), 2.85–3.10 (—OCH₂—), 3.35–3.68 (—CH₂OH). To characterize the CB-HP, we have got ¹³C-NMR spectra of the CB-HP4. Owing to its complicated chemical structure and component, the part of carbon black cannot be explicated completely. But, the part of hyperbranched polyether of CB-HP4 can be assigned. Figure 4 shows the ¹³C-NMR of the hyperbranched polyether of CB-HP4. ¹³C-NMR (δ , ppm): 13.5 (—CH₃CH₂—), 25.2–25.7(CH₃CH₂—), 35.2(—C(CH₂)₄—), 60.2(—CH₂OH), 61.4(—CH₂OCH₂—). A hyperbranched polymer generally contains dendritic units (*D*), linear units (*L*), terminal units (*T*). By Fréchet's equation ($\text{DB} = (D+T)/(D+T+L)$),²⁵ the degree of branching (DB) may be calculated. Four adjacent peaks are found at 25.2 (*T*), 25.3 (*L*), 25.4 and 25.7 (*D*). The relative integration value of the four peaks was 1% (*D*), 0.76% (*D*), 8.35% (*L*), and 4.58% (*T*). By calculation, the degree of branching (DB) was 0.43.

It is well-known that carbon black is strongly hydrophobic and cannot be well-dispersed in organic solvent. After grafting the multihydroxyl hyperbranched polyether on the surface of carbon black, CB-HP could be partially soluble in ethanol and chloroform. Figure 5 shows that the CB-HP samples have good solubility in DMF, because the multihydroxyl hyperbranched polyether has good solubility in DMF. Figure 5(e) shows that CB-CH₂OH cannot be dispersed in DMF solution containing the multihydroxyl hyperbranched polyether, which proves further that the hyperbranched polyether has been grafted onto the carbon black surface.

Figure 6 shows the typical size distribution of the carbon black and grafted carbon black nanoparticles determined by dynamic light scattering. After introduction of hydroxy methyl groups onto the surface of carbon black, the number of relatively larger agglomerates decreased obviously, and the diameter of the carbon black was mostly between 250 and 400 nm. After grafting the polyether onto the surface of carbon black, the distribution of particles was relatively uniform, and the average diameter was between 300 and 375 nm.

The dispersion effect was shown in the TEM images of Figure 7. As we know, the pristine carbon black particles easily trend to large agglomerates. Figure

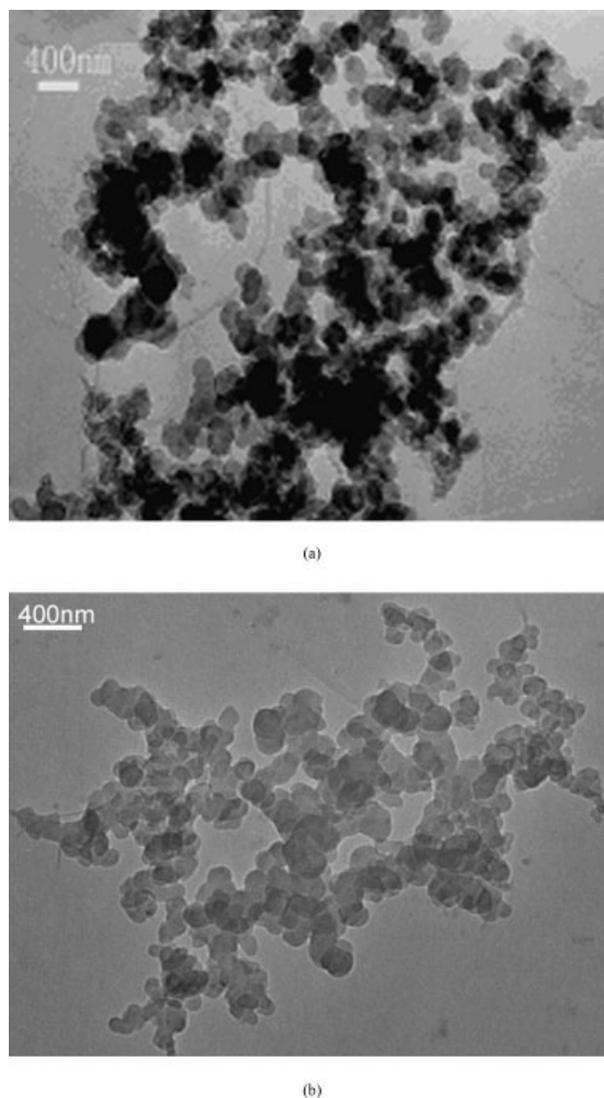


Figure 7 TEM images of (a) CB-CH₂OH and (b) CB-HP1.

7(a) shows that, after the introduction of hydroxy methyl groups onto the surface of carbon black, there are also a large number of large agglomerates. Figure 7(b) shows that the number of larger agglomerates decreased obviously after the polyether grafted onto carbon black.

The morphological changes of the grafted carbon black were shown in the SEM images of Figure 8. By comparison, the modified carbon black particles are less spherical, with the presence of “dimples.”

CONCLUSIONS

The introduction of hydroxy methyl groups onto the surface of carbon black could be achieved by treatment of carbon black with formaldehyde in alkali conditions. The multihydroxyl hyperbranched polyethers were successfully grafted onto the surface of

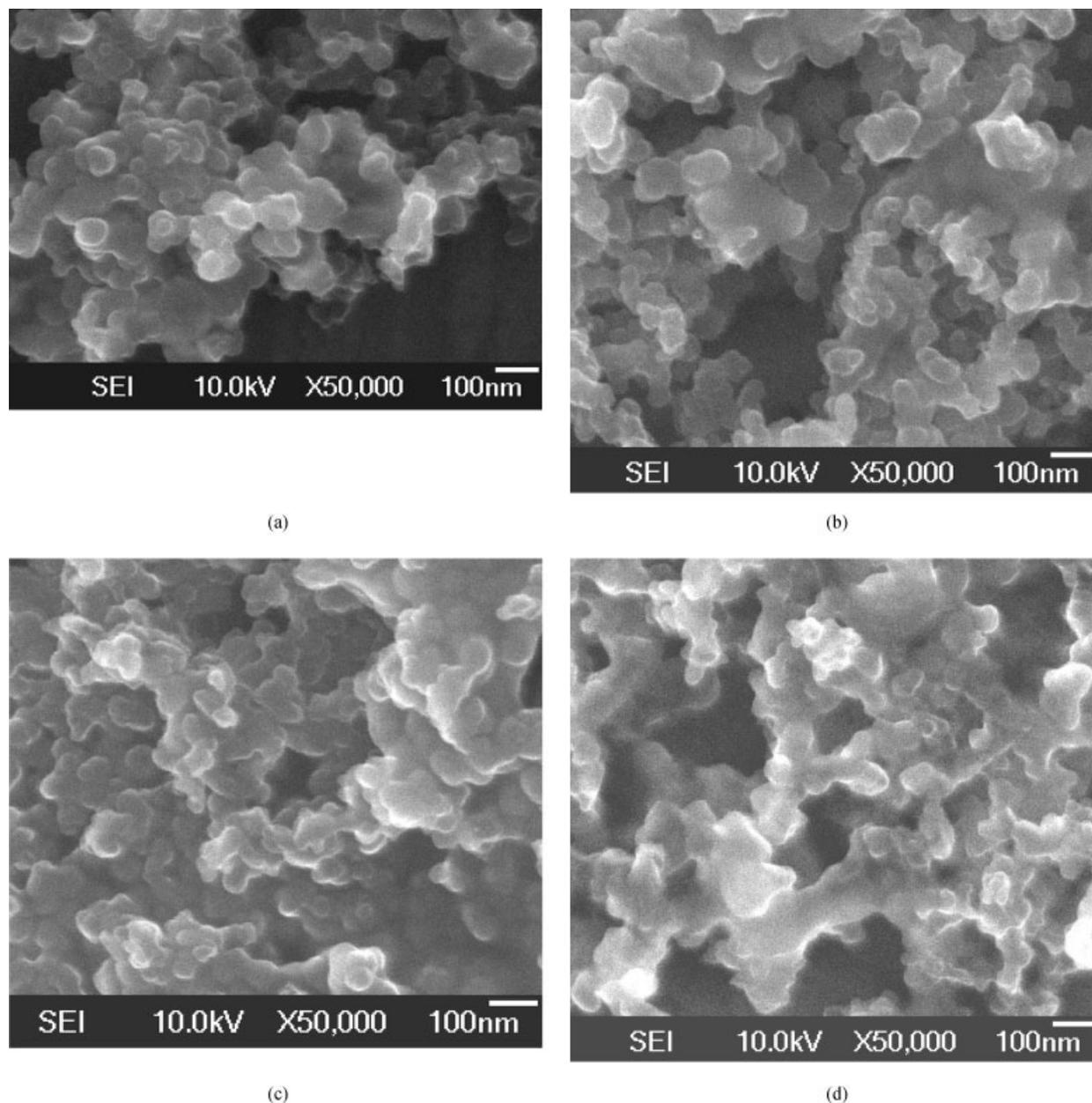


Figure 8 SEM images of (a) carbon black, (b) CB-CH₂OH, (c) CB-HP1, and (d) CB-HP3.

carbon black by cationic ring-opening polymerization of 3-ethyl-3-(hydroxy methyl) oxetane (EHOX). The amount of polyether grafted increase with increasing of the ratio of the EHOX to carbon black in our experiments. These samples of the grafted carbon black can be dispersed in polar solvents, such ethanol, chloroform, and DMF, especially showing good solubility in DMF.

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