

Synthesis, Characterization of Polyacrylate-g-Carbon Black and Its Application to Soap-Free Waterborne Coating

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ABSTRACT: Polyacrylate-g-Carbon Black (abbrev. as gCB) was prepared by free radical polymerization of acrylate monomers on the carbon black surface, which was initiated by a redox system consisting of cerium ammonium nitrate and hydroxymethyl carbon black. gCB was ascertained by X-ray Photoelectron Spectrometry (XPS). The optimum conditions of synthesis were studied. The stabilities of gCB dispersing in water were studied by zeta potential measurement and spectrophotometric analysis. The results showed that gCB could disperse in water better than the ungrafted carbon black. gCB could be dispersed in the soap-free hydrosol forming a colored soap-free water-borne coating with satisfactory comprehensive performance. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1100–1106, 2001

Key words: carbon black; graft copolymerization; waterborne coating; dispersion stability

INTRODUCTION

The water-borne coating with water as the main solvent or dispersion medium has the advantage of low pollution, low price, and good quality in comparison with the traditional organic coatings. Its application in the paint industry has been flourishing rapidly in the recent years.¹ But it is difficult for pigment to disperse well in the water-borne coating. This limits its application.²

Carbon black has excellent properties, such as chemical and heat resistance, electroconductivity, which is widely used industrially as a pigment for coatings. But carbon black has a lot of oxygen-containing groups on the surface, it disperses difficultly and forms aggregates easily, affecting the properties of the coating films. To improve the dispersibility of carbon black, surface modifica-

tion of carbon black by grafting of polymers has been widely investigated.^{3–11} Most such grafted carbon black (abbrev. as gCB) were designed for the organic coatings, and when it was applied to the water-borne coating, the dispersibility was remarkably dropped. In this article, we design and prepare the gCB by grafting AA/HEMA polyacrylate onto the carbon black. The polymer chains, which consist of hydrophilic groups, $-\text{COO}^-$ and $-\text{OH}$, can play the roles of electric repulsion and the steric hindrance repulsion in aqueous medium by hydration unfolding. So the dispersibility of the gCB in water can be remarkably improved due to the contribution of the electric repulsion and the steric repulsion. We also try to mix the gCB with the soap-free water-borne coating to form the colored coating. The water-borne coating prepared in our laboratory is composed of polyacrylate hydrosol.¹² It is obvious that the similarity between the grafted polyacrylate on the gCB surface and the polyacrylate in the hydrosol are favorable for the gCB dispersing well in the colored water-borne coating.

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In this article, the preparation of gCB was carried out by two steps: first, introducing the hydroxymethyl groups on the surface of carbon black, and then radical grafting of polyacrylate from carbon black through the hydroxymethyl groups. The conditions of synthesis were studied. The gCB was ascertained by X-ray Photoelectron Spectrometry (XPS). The dispersibility of gCB in water and the properties of the colored water-borne coating film were investigated.

EXPERIMENTAL

Materials

Carbon black (abbrev. as CB) was MONARCH 1300 (Cabot Co., BET-N₂ specific surface area 5600 m² g), purified by extracting it with toluene to remove the resinous substances present on the surface and dried *in vacuo* at 110°C. Hydroxyethyl methacrylate (HEMA) and acrylic acid (AA) were redistilled before use. Other reagents and solvents were used after ordinary purifications.

Introduction of Hydroxymethyl Groups onto the Surface of CB

The introduction of hydroxymethyl groups onto the CB surface was achieved by treatment of CB with formaldehyde in alkali conditions. The mixture of CB and 10% sol. aq. of HCHO at pH ≈ 10 were stirred at 50°C for 1 h. After the reaction, the hydroxymethylated carbon black was filtered, washed with water, and dried *in vacuo*.

Radical Graft Polymerization Procedures

Into a flask, hydroxymethylated carbon black and aqueous solution of AA were charged. After de-aeration of the mixture by bubbling nitrogen, ceric ammonium nitrate in nitric acid was added. The polymerization was conducted at 30°C with stirring under dry nitrogen for 30 min. Then aqueous mixture of AA and HEMA were added, the polymerization was conducted continuously for 3 h. After the reaction, the reaction mixture was filtered, washed with water, and then was extracted with water in a soxhlet extractor to remove the nongrafted polymer, and dried *in vacuo* at 50°C. The grafting percentage (*G*%) was determined by the following equation.

$$G\% = \frac{\text{polymer grafted (g)}}{\text{hydroxymethylated CB used (g)}} \times 100\%$$

XPS Analysis

The XPS analysis was measured by a Kratos Ltd. XSAM-800 XPS instrument; the excitation source was MgK α (1253.6 eV).

Spectrophotometric Analysis

gCB or CB was dispersed in water, and diethylaminoethyl alcohol (DEAE) was added to adjust pH 9. Aqueous solution of potassium chloride (KCl) was added, and the mixture was kept at room temperature for 24 h. The light transmittance (*T*%) of the upper layer fluid was determined by a 721 spectrophotometer.

Zeta Potential Analysis

gCB or CB was dispersed in water and DEAE was added to adjust to pH 9. The zeta potential was measured by a Model 501 Lazer Zee Metertm instrument.

Storage Stability of Coating

gCB or CB was dispersed in the soap-free hydrosol, and hexamethoxy methyl cyanuramide (HMMM) was added, forming colored soap-free water-borne coating. The coating was put into a seal flask and storage for some time. The change of the coating was observed, and the rotating viscosity of the coating was determined by a Rheotest2-50Hz-Tyrrv2 rotating viscometer.

Measurement of the Properties of Coating Films

The coating film was prepared by drying the film on the surface of the iron plate at room temperature, and then the dry coating film was cured at 160°C for 30 min. Five physical properties of the coating film were determined by the national standard test methods.

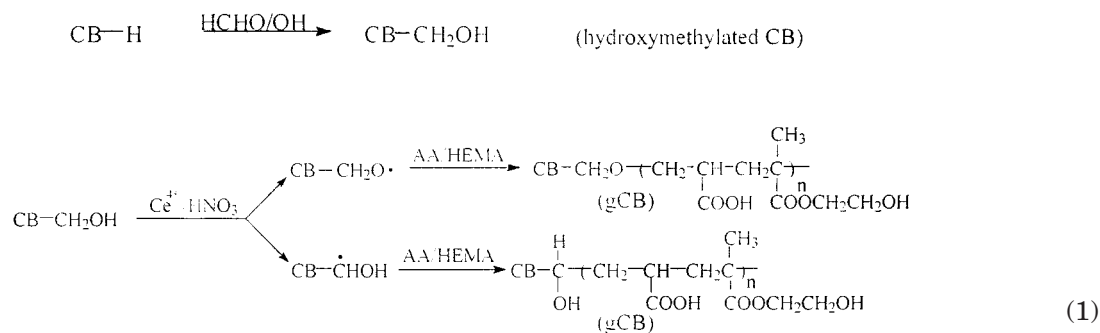
RESULT AND DISCUSSION

Synthesis of gCB

CB is well known to contain free radicals, but the radicals have no ability to initiate the radical polymerization of vinyl monomers. It is necessary to introduce active radicals onto the surface. Referring to the ref. 4, the grafting of carbon black with AA/HEMA polyacrylate could be carried out by two steps, as shown by eq. (1):

Table I XPS Data for Different Carbon Black Systems

Sample	C_{1s} Displacement of Different Oxidation State						Ratio of O/C Atomic Concentration
	C—OH		COOH		C—C		
	Displacement/eV	Area (%)	Displacement/eV	Area (%)	Displacement/eV	Area (%)	
CB	1.9	13.9	4.3	5.4	285.0	81.5	0.108
CB—CH ₂ OH	1.8	15.6	4.3	10.2	285.0	74.7	0.110
gCB	1.8	18.1	4.3	12.1	285.0	70.1	0.277



To identify the grafting product gCB, XPS was used for determining the surface groups of the gCB.¹³ The results are shown in Table I.

It can be seen that the O/C ratio of gCB is much larger than that of CB. This is due to the increasing content of —COOH and —OH on the gCB surface, showing that the AA/HEMA polyacrylate has been effectively grafted onto the CB.

Effect of Reaction Conditions on the Grafting Percentage

Figure 1 shows that the grafting percentage increased to 30.7% with increasing the feeding HEMA/AA ratio, but decreased as the HEMA/AA ratio was larger than 20/80. This may be due to the fact that in the presence of more HEMA, the acrylates were initiated by —CH₂O• in the HEMA/Ce⁴⁺ system to form a nongrafted polymer, instead of by —CH₂O• in the CB—CH₂OH/Ce⁴⁺ system to form gCB.

The grafting percentage increased to more than 35% with increasing ceric ion concentration (Fig. 2). But the grafting percentage decreased when ceric ion concentration was larger than 2.7×10^{-3} mol/L. This may be attributed to the steric repulsion that resulted from too many grafting chains, so that it is difficult for the monomers in

contact with the free radicals on the chain to increase the grafting percentage.

The introduction of hydroxymethyl group onto CB is beneficial to the graft reaction. It can be seen from Figure 3 that the grafting percentage

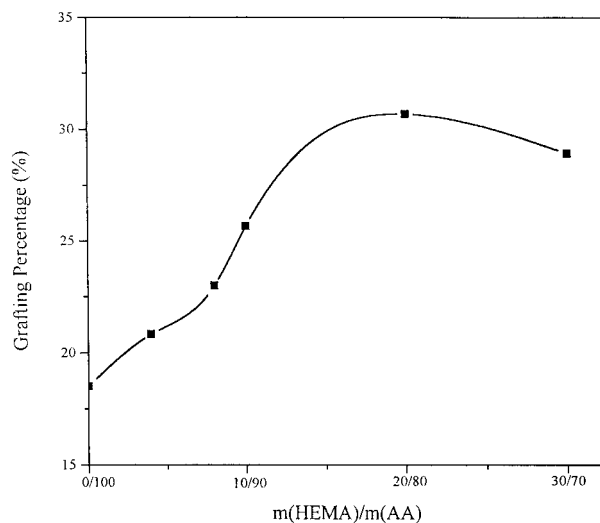


Figure 1 Effect of HEMA/AA ratio on grafting percentage [$c(\text{Ce}^{4+}) = 1.1 \times 10^{-2}$ mol/L, $V(\text{HCHO})/m(\text{CB}) = 7/1$ (mL/g), $c(\text{HNO}_3) = 1.6$ mol/L, reaction time = 3 h, $V(\text{monomer})/m(\text{CB}) = 12/1$ (mL/g)].

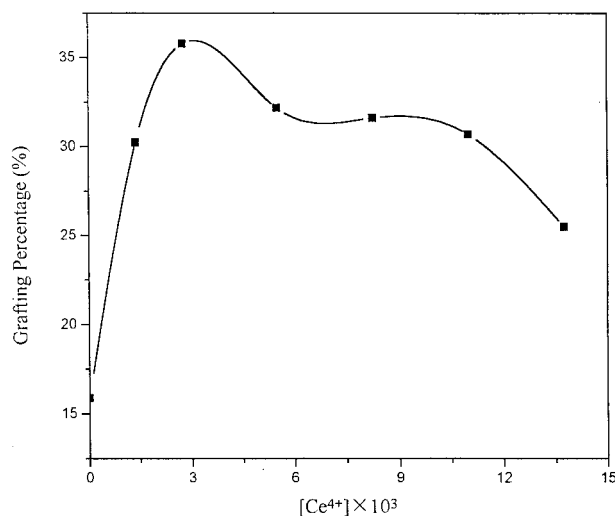


Figure 2 Effect of $c(\text{Ce}^{4+})$ on grafting percentage [m(HEMA)/m(AA) = 20/80, other conditions were same as in Fig. 1].

increased with increasing formaldehyde concentration. When $V(\text{HCHO})/m(\text{CB})$ was more than 3.5/1 (mL/g), the O/C ratio decreased (Table II), indicating that the hydroxymethyl group on the CB was reduced, so the grafting percentage decreased.

Figure 4 shows the relationship between nitric acid concentration and the grafting percentage. As the nitric acid concentration increased, the grafting percentage increased. When the nitric

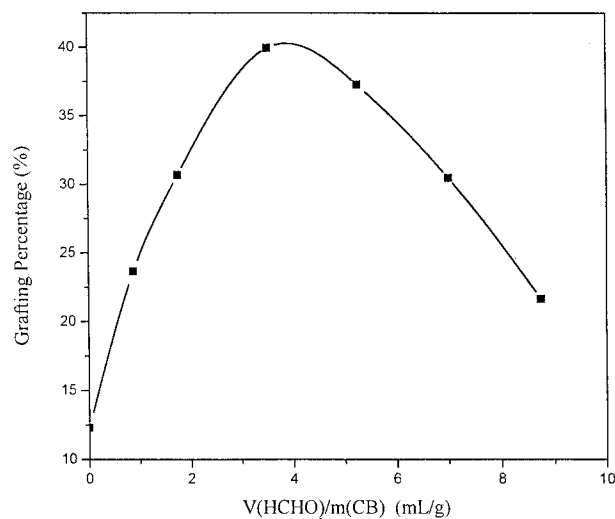
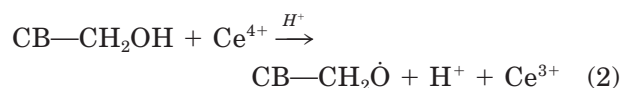
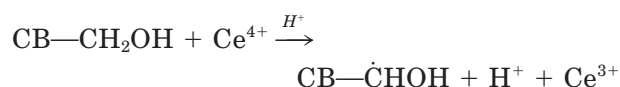


Figure 3 Effect of the HCHO concentration in hydroxymethyl of CB on grafting percentage [m(HEMA)/m(AA) = 20/80, $c(\text{Ce}^{4+}) = 2.7 \times 10^{-3}$ mol/L, other conditions were same as in Fig. 1].

Table II Ratio of O/C Atomic Concentration for Different Hydroxymethylated CB Systems

	Hydroxymethylated CB: $V(\text{HCHO})/m(\text{CB})$ (mL/g)			
	CB	1.75/1	3.50/1	7.0/1
Ratio of O/C atomic concentration	0.108	0.111	0.139	0.110

acid was too much, it was disadvantageous to the initiating reaction [eq. (2)] shifting to left to form free radicals, so the grafting percentage decreased.



The grafting percentage increased to 39.5% with progress of polymerization, but changed no more after 3 h (Fig. 5). This may be related to the fact that the residual ceric ion concentration became too low and could not promote the grafting reaction to a larger extent.

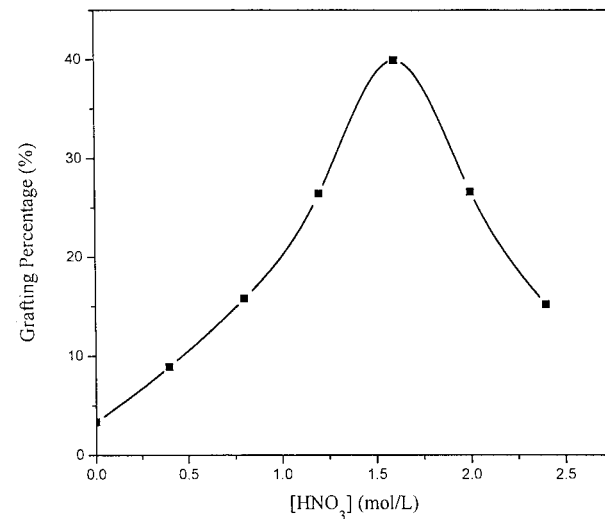


Figure 4 Effect of $c(\text{HNO}_3)$ on grafting percentage [m(HEMA)/m(AA) = 20/80, $c(\text{Ce}^{4+}) = 2.7 \times 10^{-3}$ mol/L, $V(\text{HCHO})/m(\text{CB}) = 3.5/1$ (mL/g), other conditions were same as in Fig. 1].

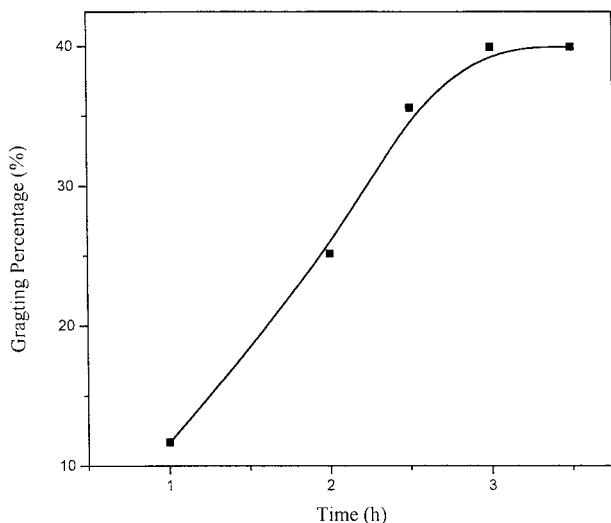


Figure 5 Effect of reaction time on grafting percentage (conditions were same as in Fig. 4).

With the increasing of the monomer content, the grafting percentage increased (Fig. 6). But when the monomer content was too large, the grafting percentage decreased due to the formation of the nongrafted polymer.

From the above results, the optimum conditions of synthesis were: $V(\text{HCHO})/m(\text{CB})$ was 3.5/1 (mL/g), $V(\text{monomer})/m(\text{CB}-\text{CH}_2\text{OH})$ was 6/1 (mL/g), the ratio of HEMA/AA was 20/80 (g/g), the ceric ion concentration was 2.7×10^{-3} mol/L, the nitric acid concentration was 1.6 mol/L, reaction time was 3 h, reaction temperature was 30°C .

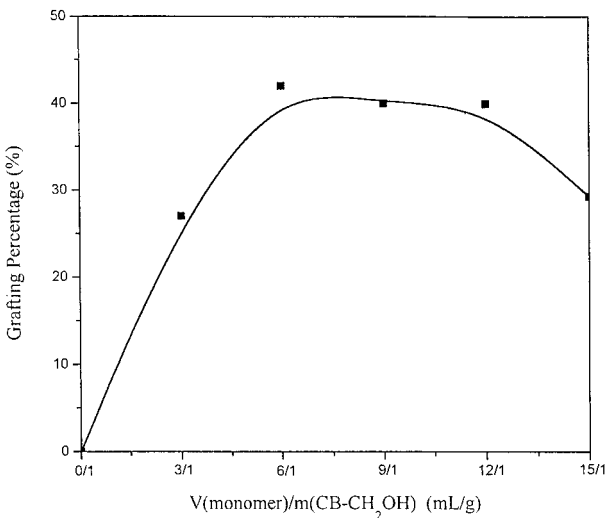


Figure 6 Effect of the monomer content on grafting percentage [conditions were same as in Fig. 4].

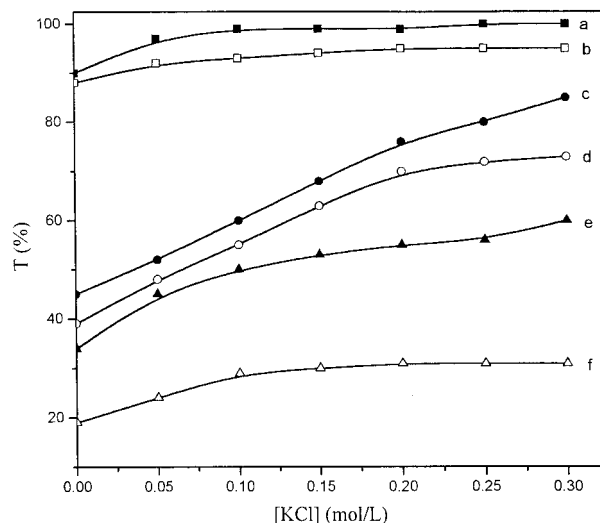


Figure 7 Effect of grafting percentage of gCB on the transmittance [a. CB/H₂O; b. CB-CH₂OH/H₂O; c. gCB(G% = 18.5%)/H₂O; d. gCB(25.2%)/H₂O; e. gCB(32.2%)/H₂O; f. gCB(42.0%)/H₂O].

Dispersion Stability of gCB in Water

In case KCl is added to the gCB/water dispersion system, the polyacrylate chain with $-\text{COO}^-$ would curl up, owing to the shielding effect of K^+ to $-\text{COO}^-$, then the electric repulsion and steric repulsion would be destroyed, leading to the aggregation and precipitation of gCB. Thus, the upper layer fluid of the dispersion system would become clearer or the transmittance ($T\%$) larger.

Figure 7 shows the relationship between the

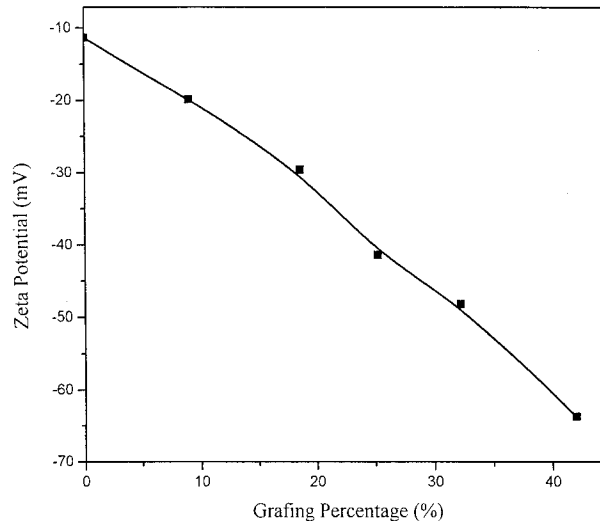


Figure 8 Effect of grafting percentage of the zeta potential of gCB dispersed in water.

Table III Storage Stability of Different Coating Systems

Storage Time (month)	0	1	3	6	12
$\eta_{\text{waterborne coating}}$ (Pa · S)	0.184	0.185	0.186	0.186	0.187
$\eta_{\text{CB/waterborne coating}}$ (Pa · S)	0.159	0.172	—	—	—
$\eta_{\text{gCB/waterborne coating}}$ (Pa · S)	0.223	0.224	0.225	0.225	0.227

concentration of KCl and $T\%$ of CB, CB—CH₂OH, and gCB systems. Within 1 day, CB precipitated completely and $T\%$ of the system was 100%, $T\%$ of the CB—CH₂OH system was about 90%, $T\%$ of the gCB system was smaller than 80%. This showed that the stable dispersion of gCB in water was not due to the hydroxymethyl groups. With increasing of grafting percentage, the carboxyl anion of the polymer chains was more, the electric repulsion and the steric repulsion were larger, the dispersion stability of gCB in water was much better, and the resistance to electrolyte was stronger.¹⁴

Figure 8 shows that the zeta potential of the gCB/water system becomes more negative distinctly with increasing the grafting percentage. In other words, more negative zeta potential corresponds to a more stable dispersion system. This result further demonstrates that the number of negative charge of the grafting chain (or number of —COO[−]) plays the most important role for the dispersion stability of the gCB/water system.

The Properties of Coating

CB is difficult to disperse well in water and destroy the stability of coating, especially to the soap-free water-borne coating that has no emulsifying agent. So the coloration of soap-free water-borne coating is a problem. From the above results we can conclude that the dispersion stability of gCB in water is much better than CB. When gCB was applied in soap-free water-borne coat-

ing, the storage stability and the properties of coating films were the two most important properties.

Table III showed that gCB coating had good storage stability and did not have coacervation and demixion, and its viscosity did not change with time for 1 year. But CB coating had a demixion after a month. These suggested that the dispersibility of carbon black in coating was remarkably improved by grafting of polyacrylate onto the surface.

The properties of different coating films are shown in Table IV. It can be seen that the properties including adhesion, impact strength, hardness, and flexibility were excellent; lustre and hardness of the gCB coating film were even better than the carbon black coating film. This was due to the fact that the polymer chain of gCB had the electric repulsion and the steric repulsion, and the composition of the grafted polymer chain was similar to hydrosol. These improved the compatibility of gCB and hydrosol, so gCB could disperse well in coating and its coating film had good hardness and lustre.

CONCLUSION

Polyacrylate-g-carbon black was prepared by free radical polymerization of acrylate monomers (AA/HEMA) on the carbon black surface, and characterized by XPS. The optimum conditions of syn-

Table IV The Coating Film Properties of Different Systems

	Thickness (μm)	Lustre (%)	Adhesion (Grade)	Pencil Hardness (H)	Impact Strength (J)	Flexibility (mm Axis)
Coating	15	114	1	2	4.9	1
CB/coating	15	84	1	2	4.9	1
gCB/coating	15	91	1	3	4.9	1

thesis were studied. The results of zeta potential measurement and spectrophotographic analysis indicated that stabilization of gCB was due to the contribution of the electric repulsion and the steric repulsion. With the increasing of grafting percentage, the electric repulsion was larger, zeta potential was more negative, the dispersion stability of gCB in water was much better and the resistance to electrolyte was stronger. gCB could be dispersed well in the soap-free hydrosol forming a colored coating, and its rotating viscosity did not change with time for 1 year. Five properties of the colored coating films had been determined by the national standard test methods. The results showed that the properties including adhesion, impact strength, hardness, and flexibility were excellent; lustre and hardness of the gCB coating film were even better than those of the CB coating film.

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