Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Graft Polymerization of Vinyl Monomers Onto Carbon Black by Use of the Redox System Consisting of Ceric Ions and Carbon Black Carrying Alcoholic Hydroxyl Groups

Norio Tsubokawa[a]; Kazuhiro Fujiki[a]; Yasuo Sone[a]
[a] Faculty of Engineering, Niigata University, Niigata, Japan

To cite this Article Tsubokawa, Norio , Fujiki, Kazuhiro and Sone, Yasuo(1988) 'Graft Polymerization of Vinyl Monomers Onto Carbon Black by Use of the Redox System Consisting of Ceric Ions and Carbon Black Carrying Alcoholic Hydroxyl Groups', Journal of Macromolecular Science, Part A, 25: 9, 1159 — 1171

To link to this Article: DOI: 10.1080/00222338808053413

URL: http://dx.doi.org/10.1080/00222338808053413

J. MACROMOL. SCI.—CHEM., A25(9), pp. 1159-1171 (1988)

GRAFT POLYMERIZATION OF VINYL MONOMERS ONTO CARBON BLACK BY USE OF THE REDOX SYSTEM CONSISTING OF CERIC IONS AND CARBON BLACK CARRYING ALCOHOLIC HYDROXYL GROUPS

NORIO TSUBOKAWA, KAZUHIRO FUJIKI, and YASUO SONE

Faculty of Engineering
Niigata University
8050 Ikarashi 2-nocho, Niigata 950-21, Japan

ABSTRACT

The radical graft polymerization of vinyl monomers onto carbon black initiated by a redox system consisting of ceric ion and carbon black having alcoholic hydroxyl groups was investigated. The introduction of alcoholic hydroxyl groups onto the carbon black surface was achieved by the reaction of carbon black with alcoholic hydroxyl radicals, formed by the reaction of alcohol with benzoyl peroxide. The rate of the polymerization of acrylamide (AAm) initiated by the redox system was found to increase in the following order of hydroxyl groups: 1-hydroxyoctyl < 1-hydroxypropyl < 1-hydroxyethyl < hydroxymethyl < 1-hydroxy-1-methylethyl. In the redox polymerization, poly-AAm was effectively grafted onto carbon black by propagation of the polymer from the radical formed by the reaction of ceric ions with the alcoholic hydroxy groups. The percentage of grafting increased with increasing conversion. By use of this redox system, poly(acrylic acid), polyacrylonitrile, and poly(*N*-vinyl-2-pyrrolidone) could be grafted onto carbon black, but poly(methyl methacrylate) and polystyrene could not be so grafted. The graft polymerization of AAm by use of a redox system consisting of ceric ion and PVA-grafted carbon black was also investigated.

INTRODUCTION

The grafting of various kinds of polymers directly onto carbon black has been widely investigated. For instance, polymer-grafted carbon black can be easily obtained by the polymerization of vinyl monomers in the presence of carbon black by radical [1], cationic [2], and anionic [3] initiators. However, the percentage of grafting of polymer onto carbon black is less than 10% because of the reaction of growing polymer radicals with the carbon black surface.

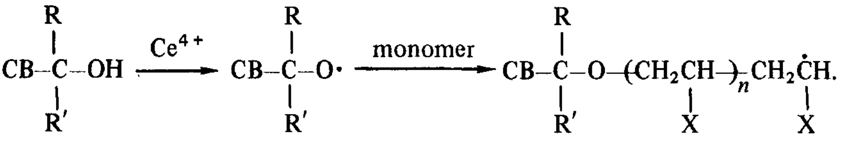
Therefore, to obtain polymer-grafted carbon black with a higher percentage of grafting, the polymerization must be initiated from active sites introduced onto the carbon black surface. We reported anionic grafting from alkali metal carboxylate (COOM) group on carbon black [4] and cationic grafting from acylium perchlorate group on carbon black [5]. However, radical grafting from carbon black has been investigated very little.

It is well known that carbon black has unpaired electrons [6], but because the unpaired electrons do not have the ability to initiate the radical polymerization of vinyl monomers, it is necessary to introduce free radicals onto carbon black. Donnet and coworkers reported the introduction of peroxide groups onto the carbon black surface by reacting it with lauroyl peroxide and the radical grafting of polystyrene by use of carbon black as an initiator [7].

It is well known that ceric ion/alcohol redox systems are capable of initiating radical polymerization of vinyl monomers [8], as are redox systems consisting of ceric ion and polymers with alcoholic hydroxyl groups, such as poly(vinyl alcohol) (PVA) and cellulose [9].

In a preceding paper, we reported the radical grafting of polyacrylamide from carbon black initiated by ceric ion and carbon black having hydroxymethyl groups [10].

In the present paper we report the radical polymerization of vinyl monomers initiated by a redox system consisting of ceric ion and carbon black with alcoholic hydroxyl groups, resulting in grafting of vinyl polymers onto the carbon black:



$$\mathrm{CB{-}}\underset{\mathrm{R'}}{\overset{\mathrm{R}}{\mathrm{C}}}\mathrm{{-}OH} \xrightarrow{\mathrm{Ce^{4+}}} \mathrm{CB{-}}\underset{\mathrm{R'}}{\overset{\mathrm{R}}{\mathrm{C}}}\mathrm{{-}O\cdot} \xrightarrow{\text{monomer}} \mathrm{CB{-}}\underset{\mathrm{R'}}{\overset{\mathrm{R}}{\mathrm{C}}}\mathrm{{-}O{-}(CH_2}\underset{\mathrm{X}}{\mathrm{CH}}\mathrm{)_{\mathit{n}}{-}CH_2}\underset{\mathrm{X}}{\dot{\mathrm{C}}\mathrm{H}}. \qquad (1)$$

In addition, grafting by poly(vinyl alcohol)-grafted carbon black and ceric ion was investigated.

EXPERIMENTAL

Materials

The carbon black used was furnace black, Philblack O (Phillips Petroleum Co., BET specific surface area, 79.6 m^2/g). The carbon black was extracted with benzene to remove the resinous substances present on the surface and dried *in vacuo* at 110°C before use.

Acrylamide (AAm) was recrystallized from benzene and sublimed under reduced pressure. Acrylic acid and *N*-vinyl-2-pyrrolidone were distilled twice under reduced pressure. Methyl methacrylate was purified by the customary method and distilled twice. Acrylonitrile was purified by distillation.

Guaranteed-grade ceric ammonium nitrate and nitric acid were used without further purification. Benzoyl peroxide (BPO) was purified by reprecipitation (chloroform/ethanol).

Methanol, ethanol, 1-propanol, 2-propanol, and 1-octanol were dried over Molecular Sieves and distilled.

Introduction of Alcoholic Hydroxyl Groups onto Carbon Black

The introduction of alcoholic hydroxyl group onto carbon black was achieved by the reaction of alcohol with carbon black in the presence of BPO according to the method of Ohkita and Tajima [11]. A typical example is as follows: Under dry nitrogen, a mixture of 1.0 g of Philblack O, 1.0 g BPO, and 40.0 mL alcohol were heated at 45°C with stirring. After reaction for 50 h, the resulting carbon black was filtered, extracted with carbon tetrachloride to remove unreacted BPO, and dried *in vacuo* at 110°C.

Grafting of Poly(Vinyl Alcohol) onto Carbon Black

Poly(vinyl alcohol) (PVA)-grafted carbon black was prepared by the saponification of poly(vinyl acetate)-grafted carbon black.

The grafting of poly(vinyl acetate) onto carbon black was carried out as follows: Into a polymerization tube, 2.0 g carbon black, 10.0 mL vinyl acetate, and 2.0 g BPO were charged. The tube was sealed *in vacuo*, and the polymerization was conducted at 45°C for 50 h with stirring. The resulting carbon black was extracted with methanol by use of a Soxhlet apparatus to remove ungrafted polymer and BPO.

The saponification of the poly(vinyl acetate)-grafted carbon black was carried out as follows: A mixture of 2.0 g poly(vinyl acetate)-grafted carbon black, 2.0 mL of 40% potassium hydroxide aqueous solution, and 20.0 mL methanol were stirred at 30°C for 24 h. After the reaction the resulting carbon black was washed with methanol until the filtrate was neutral. The percentage of grafting of PVA onto carbon black was determined to be 8.0%.

Graft Polymerization by the Redox System

Into a 100 mL flask, 0.30 g carbon black having alcoholic hydroxyl groups and 9.0 mL of a 4.7 mol/L aqueous solution of AAm were charged. After the deaeration of the mixture by bubbling nitrogen, 1.0 mL of 0.2 mol/L solution of ceric ammonium nitrate in 1 *N* nitric acid was added. The polymerization was conducted at 30°C with stirring by a magnetic stirrer under dry nitrogen.

After the reaction the mixture was poured into an excess of acetone to precipitate the polymer containing carbon black. The precipitant for polyacrylonitrile, poly(methyl methacrylate), and polystyrene was methanol. When *N*-vinyl-2-pyrrolidone and acrylic acid were used as monomer, unreacted monomer was removed under reduced pressure at 50°C after the addition of *N*-phenyl-β-naphthylamine. The conversion was determined by

$$\text{conversion } (\%) = \frac{\text{precipitate (g)} - \text{carbon black (g)}}{\text{monomer (g)}} \times 100.$$

Determination of Percentage of Grafting and Grafting Efficiency

In order to isolate polymer-grafted carbon black, the product was dispersed in a solvent (dispersion medium) for the grafted polymer and the dispersion was centrifuged at 1.2×10^4 rpm until the carbon black had precipitated completely. Subsequently, the precipitated carbon black was extracted with a good solvent for the grafted polymer with a Soxhlet extractor. The solvents used for the dispersion and extraction of poly-AAm, polyacrylonitrile, and poly(acrylic acid) and poly(*N*-vinyl-2-pyrrolidone) were water, *N,N*-dimethylformamide, and methanol, respectively. The percentage of grafting and grafting efficiency were determined by the following equations:

$$\text{percentage of grafting (\%)} = \frac{\text{polymer grafted (g)}}{\text{carbon black used (g)}} \times 100,$$

$$\text{grafting efficiency (\%)} = \frac{\text{polymer grafted (g)}}{\text{total polymer obtained (g)}} \times 100.$$

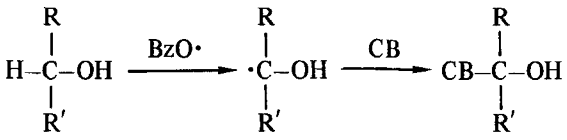
RESULTS AND DISCUSSION

Proof of Initiation by the Redox System of Ceric Ion/Alcoholic Hydroxyl Group on Carbon Black

It has been reported that vinyl polymerizations are initiated by ceric ion in combination with reducing agents such as alcohols [8, 12], aldehydes [13], and acids [14]. Particularly, ceric ion/alcohol systems have been used for the grafting of vinyl monomers onto polymers having alcoholic hydroxyl groups [9].

On the other hand, Ohkita and Tajima reported that, during the reaction of BPO with methanol in the presence of carbon black, hydroxymethyl radicals produced were trapped by the carbon black surface in preference to the benzoyloxy radical (BzO•) [11].

In a preceding paper we reported that the polymerization of AAm is initiated by the redox system ceric ion/carbon black having hydroxymethyl groups and that poly-AAm is effectively grafted onto the carbon black surface [10]. Therefore, the graft polymerization of AAm is expected to be initiated by the present system of ceric ion/alcoholic hydroxyl groups on carbon black. The introduction of alcoholic hydroxyl groups onto carbon black was achieved by the reaction of the corresponding alcohol with BPO in the presence of carbon black:



$$\text{H}-\overset{\displaystyle\text{R}}{\underset{\displaystyle\text{R}'}{\text{C}}}-\text{OH} \xrightarrow{\text{BzO}\cdot} \cdot\overset{\displaystyle\text{R}}{\underset{\displaystyle\text{R}'}{\text{C}}}-\text{OH} \xrightarrow{\text{CB}} \text{CB}-\overset{\displaystyle\text{R}}{\underset{\displaystyle\text{R}'}{\text{C}}}-\text{OH} \qquad (2)$$

The polymerization of AAm by the use of ceric ion with various kinds of treated carbon black is compared in Table 1.

As shown in Table 1, the polymerization of AAm was scarcely initiated by ceric ion alone and not at all by untreated carbon black, but in the presence

TABLE 1. Redox Polymerization of AAm under Several Conditions[a]

CB[b]	Ce^{4+} solution,[c] mL	Conversion, %
None	1.0	1.8
Untreated CB	–	0
Untreated CB	1.0	4.0
2-Propanol-adsorbed CB	1.0	4.5
CB–$C(CH_3)_2OH$	–	0
CB–$C(CH_3)_2OH$	1.0	55.5

[a] CB, 0.30 g; AAm aqueous solution (4.7 mol/L), 9.0 mL; 30.0°C; time, 3 h.
[b] Philblack O.
[c] 0.2 mol/L solution of ceric ammonium nitrate in 1 *N* nitric acid.

of both untreated carbon black and ceric ion, initiation was somewhat greater but still very low. The result suggests the possibility of radical formation by the redox reaction of ceric ion with a functional group, probably a phenolic hydroxyl group, on the carbon black. Still, the initiating ability of the ceric ion/Philblack O system was negligibly small. In contrast, the polymerization of AAm was initiated by ceric ion with Philblack O having 1-hydroxy-1-methylethyl ($C(CH_3)_2OH$) groups.

The initiating ability of the untreated Philblack O/ceric ion system was not increased by adsorption of 2-propanol. This suggests that it is not necessary to take into account the effect of adsorbed alcohol on the initiation. Furthermore, Philblack O with a $C(CH_3)_2OH$ group alone has no ability to initiate polymerization. Accordingly, BPO used for the introduction of the $C(CH_3)_2OH$ group onto carbon black was considered to have been removed completely from the surface by the extraction with carbon tetrachloride.

In conclusion, it became apparent that the free radical produced by the redox reaction of the $C(CH_3)_2OH$ group on carbon black with ceric ion initiates the polymerization of AAm. Therefore, it is expected that the grafting of poly-AAm, depending on the propagation of the polymer, proceeds by redox polymerization.

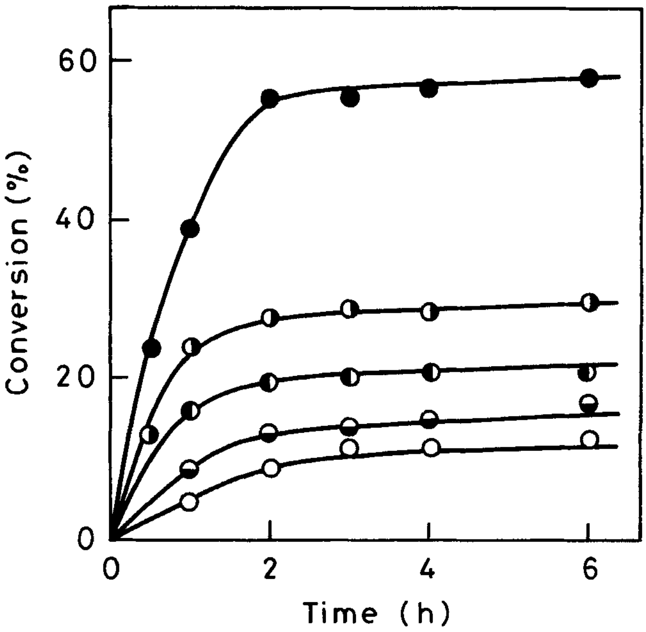
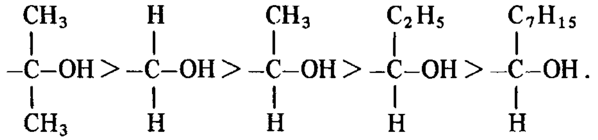


FIG. 1. Polymerization of AAm initiated by the redox system ceric ion/alcoholic hydroxyl group on carbon black: carbon black, 0.30 g; AAm aqueous solution (4.7 mol/L), 9.0 mL; Ce^{4+} (0.2 mol/L 1 *N* HNO_3 solution), 1.0 mL; temperature, 30.0°C. (●) 1-Hydroxy-1-methylethyl group; (◑) hydroxymethyl group; (◒), 1-hydroxyethyl group; (○) 1-hydroxy-propyl group; (○) 1-hydroxyoctyl group.

Initiation by Various Alcoholic Hydroxyl Group on the Carbon Black/Ceric Ion Redox System

Figure 1 shows the time-conversion curves of the polymerization of AAm initiated by ceric ion/alcoholic hydroxyl group redox systems at 30°C. The alcoholic hydroxyl groups introduced onto carbon black were hydroxymethyl (CH_2OH), 1-hydroxyethyl ($CH(CH_3)OH$), 1-hydroxy-1-methylethyl ($C(CH_3)_2OH$), 1-hydroxypropyl ($CH(C_2H_5)OH$), and 1-hydroxyoctyl ($CH(C_7H_{15})OH$).

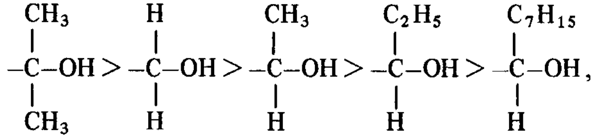
Figure 1 clearly shows that the polymerizations of AAm are initiated by these redox systems. The initiating activity of the redox system decreased, depending on the alcoholic hydroxyl group introduced onto carbon black, in the following order:



$$-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{OH} > -\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{OH} > -\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{OH} > -\overset{\mathrm{C_2H_5}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{OH} > -\overset{\mathrm{C_7H_{15}}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{OH}.$$

It is believed that the initiating activity of these redox systems is affected by the amount of an alcoholic hydroxyl group introduced onto carbon black. The hydroxy methyl group content introduced onto Philblack O by the reaction of methanol with carbon black in the presence of BPO was reported to be 0.06 meq/g (by the use of ^{14}C-methanol as tracer) by Ohkita and Tajima [11].

It was reported that the bond dissociation energy of the α-hydrogen atom from 2-propanol, methanol, and ethanol is about 381, 385, and 393 kJ/mol, respectively [15]. Increasing the bond dissociation energy of the alcohol will cause a decrease in the rate of the formation of the alcoholic hydroxyl radical, which leads to a decrease in the amount of alcoholic hydroxyl groups introduced onto carbon black. Therefore, the amount of alcoholic hydroxyl group on the carbon black was expected to decrease in the following order:



$$-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{OH} > -\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{OH} > -\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{OH} > -\overset{\mathrm{C_2H_5}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{OH} > -\overset{\mathrm{C_7H_{15}}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{OH},$$

which is the same as that of decreasing activity of initiation by the redox system.

Based on the results, it is concluded that the 1-hydroxy-1-methylethyl group is introduced onto carbon black to a greater extent than the other alcoholic hydroxyl groups, and that 2-propanol-treated carbon black has a higher initiation activity in combination with ceric ion.

Proof of Grafting onto Carbon Black

It can be seen from Fig. 2 that the percentage of grafting increases with an increase in conversion. However, the percentage of grafting is not influ-

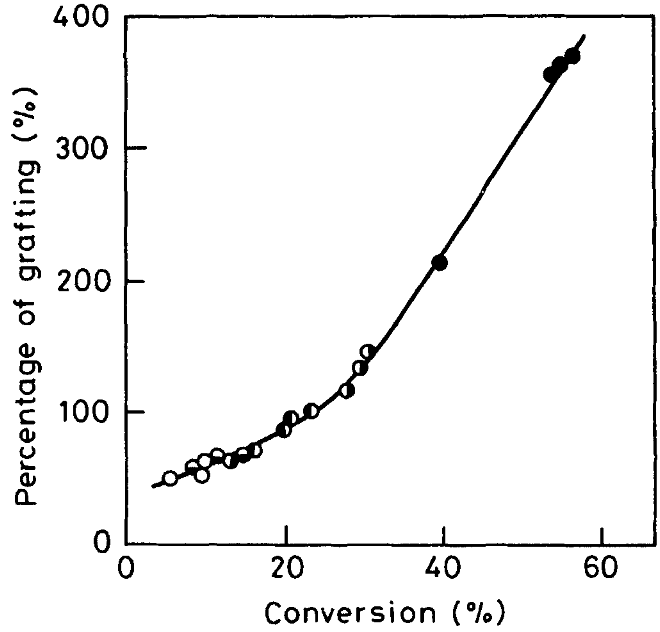


FIG. 2. Relationship between conversion and percentage of grafting of poly-AAm onto carbon black. Polymerization conditions are given in Fig. 1. (●) 1-Hydroxy-1-methylethyl group; (◑) hydroxymethyl group; (◐) 1-hydroxy-ethyl group; (◒) 1-hydroxy-propyl group; (○) 1-hydroxyoctyl group.

enced by the kind of alcoholic hydroxyl group on the carbon black surface. The apparent percentage of grafting increased up to 350% because of the formation of a gel that contained carbon black above 30% conversion. The carbon blacks obtained below 30% conversion gave stable colloidal dispersions in water.

It is concluded, therefore, that poly-AAm is effectively grafted onto the carbon black surface by the propagation of the polymer from radicals on carbon black produced by the redox reaction of alcoholic hydroxyl groups with ceric ion (Eq. 1).

On the other hand, the relationship between the grafting efficiency and conversion is shown in Fig. 3. The grafting efficiency in such a redox grafting system was found to be about 43% before the formation of a gel. The results indicates that, in the course of the polymerization, ungrafted polymer is formed by chain transfer from the growing polymer chain to the monomer.

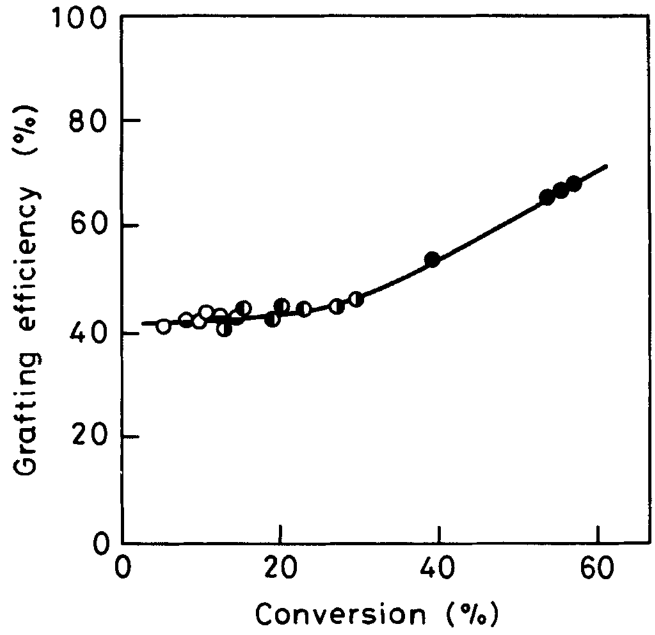


FIG. 3. Relationship between conversion and grafting efficiency of poly-AAm onto carbon black. Polymerization conditions are given in Fig. 1. (●) 1-Hydroxy-1-methylethyl group; (◑) hydroxymethyl group; (◐) 1-hydroxyethyl group; (◒) 1-hydroxy-propyl group; (○), 1-hydroxyoctyl group.

As previously reported, the grafting efficiency in anionic [4] and cationic [5] grafting from carbon black rapidly decreased to less than 10% with increasing conversion. In contrast to this, the grafting efficiency of the radical grafting system was considerably higher, even at high conversion, suggesting that chain transfer of the growing polymer radical does not appreciably occur in radical grafting compared to ionic grafting.

Graft Polymerization of Several Vinyl Monomers

The $C(CH_3)_2OH$-based redox system was used for the graft polymerization of acrylic acid, acrylonitrile, *N*-vinyl-2-pyrrolidone, methyl methacrylate, and styrene, and is compared with that of AAm in Table 2.

Table 2 shows that this redox system has the ability to initiate the radical

TABLE 2. Graft Polymerization of Vinyl Monomers by the Redox System Ceric Ion/Carbon Black Having 1-Hydroxy-1-methylethyl Groups[a]

Monomers	Time, h	Conversion, %	Percentage of grafting
Acrylamide	2	55.5	368.0[b]
Acrylic acid	2	83.6	367.6[b]
Acrylonitrile	20	37.1	71.3
N-Vinyl-2-pyrrolidone	20	20.2	86.5
Methyl methacrylate	20	Trace	–
Styrene	20	Trace	–

[a] Philblack O-$C(CH_3)_2OH$, 0.30 g; monomer, 42 mmol; Ce^{4+} (0.2 mol/L in 1 *N* HNO_3 solution), 1.0 mL; total volume (H_2O), 10.0 mL; 30.0°C.

[b] Gel containing carbon black was formed.

polymerization of acrylic acid, acrylonitrile, and *N*-vinyl-2-pyrrolidone, and the polymers formed are effectively grafted onto the carbon black surface. However, the system was unable to initiate the polymerization of methyl methacrylate and styrene, perhaps because these monomers are scarcely soluble in water. Graft polymerization of these monomers initiated by the redox system in a mixed solvent are now under investigation.

Initiation by the Redox System Ceric Ion/PVA-Grafted Carbon Black

It has been reported that, during the polymerization of vinyl acetate initiated by BPO in the presence of carbon black, a part of the poly(vinyl acetate) formed was grafted onto carbon black, depending on the capture of the growing polymer radical by the carbon black surface [1]. As mentioned above, however, the percentage of grafting of poly(vinyl acetate) was less than 10%, but PVA-grafted carbon black can be obtained by the saponification of poly(vinyl acetate)-grafted carbon black.

Figure 4 shows the result of the polymerization of AAm initiated by ceric ion/PVA-grafted carbon black. The percentage of grafting of PVA onto carbon black was estimated to be about 8.0%.

As shown in Fig. 4, the rate of the polymerization initiated by this system is higher than that by systems based on alcoholic hydroxyl groups, but the

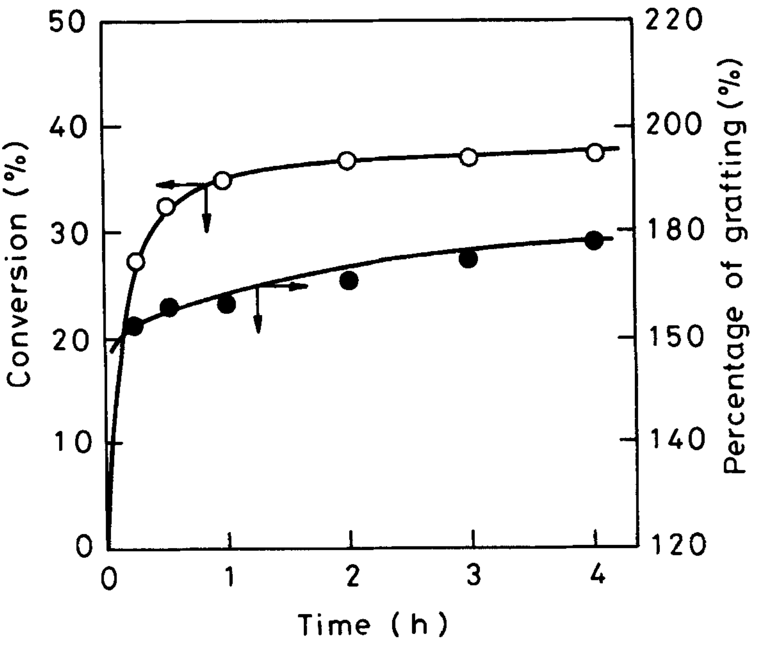
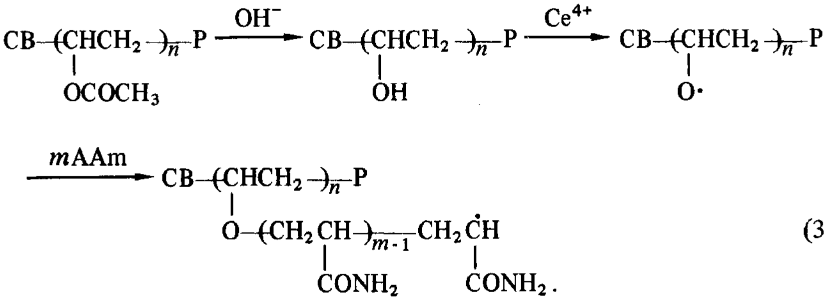


FIG. 4. Graft polymerization of AAm initiated by the redox system ceric ion/PVA-grafted carbon black: PVA-grafted carbon black, 0.30 g; AAm aqueous solution (4.7 mol/L), 9.0 mL; Ce^{4+} (0.2 mol/L 1 *N* HNO_3 solution), 1.0 mL; temperature, 30.0°C.

polymerization does not proceed to more than 37% conversion, perhaps because of the higher content of hydroxyl groups on the PVA-grafted carbon black. These experiments established that copoly(vinyl alcohol-*g*-AAm) can be effectively grafted onto carbon black by the redox system



$$\mathrm{CB}\text{-}(\underset{\substack{|\\ \mathrm{OCOCH_3}}}{\mathrm{C}}\mathrm{HCH_2})_n\text{-}\mathrm{P} \xrightarrow{\mathrm{OH^-}} \mathrm{CB}\text{-}(\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{C}}\mathrm{HCH_2})_n\text{-}\mathrm{P} \xrightarrow{\mathrm{Ce^{4+}}} \mathrm{CB}\text{-}(\underset{\substack{|\\ \mathrm{O}\cdot}}{\mathrm{C}}\mathrm{HCH_2})_n\text{-}\mathrm{P}$$

$$\xrightarrow{m\mathrm{AAm}} \mathrm{CB}\text{-}(\underset{\substack{|\\ \mathrm{O}\text{-}(\mathrm{CH_2}\underset{\substack{|\\ \mathrm{CONH_2}}}{\mathrm{C}}\mathrm{H})_{m-1}\text{-}\mathrm{CH_2}\underset{\substack{|\\ \mathrm{CONH_2}}}{\dot{\mathrm{C}}}\mathrm{H}}}{\mathrm{C}}\mathrm{HCH_2})_n\text{-}\mathrm{P}. \qquad (3)$$

CONCLUSIONS

The radical polymerization of vinyl monomers can be initiated by redox system consisting of ceric ion and alcoholic hydroxyl groups on carbon black to give polymer-grafted carbon black. The percentage of grafting increased with increasing conversion because the polymer was propagated from the radicals formed by the redox reaction of the alcoholic hydroxyl groups with ceric ion. Furthermore, copoly(vinyl alcohol-*g*-AAm)-grafted carbon black can be obtained by the redox polymerization of AAm by the ceric ion/PVA-grafted carbon black redox system.

REFERENCES

[1] K. Ohkita, N. Tsubokawa, E. Saitoh, M. Noda, and N. Takashina, *Carbon, 13,* 443 (1975).
[2] K. Ohkita, M. Shimomura, and T. Tsujita, *Ibid., 16,* 155 (1978).
[3] K. Ohkita, N. Nakayama, and M. Shimomura, *Ibid., 18,* 277 (1980).
[4] N. Tsubokawa, A. Funaki, Y. Hada, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed., 20,* 3297 (1982).
[5] N. Tsubokawa, *Ibid., 22,* 1515 (1984).
[6] G. Kraus and R. L. Collins, *Rubber World, 139,* 219 (1958).
[7] J. B. Donnet, G. Henrich, and G. Riess, *Rev. Gen. Caoutch. Plast., 38,* 1083 (1959).
[8] G. Mino, S. Kaizerman, and E. Rasmussen, *J. Polym. Sci., 38,* 393 (1959).
[9] G. Mino and S. Kaizerman, *Ibid., 31,* 242 (1958).
[10] N. Tsubokawa, K. Fujiki, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed., 24,* 191 (1986).
[11] K. Ohkita and T. Tajima, *Nippon Gomu Kyokaishi, 43,* 379 (1970).
[12] M. D. Fernandez, T. Fernandez, M. J. Fernandez, and G. M. Guzman, *J. Polym. Sci., Polym. Chem. Ed., 22,* 2729 (1984).
[13] S. V. Subramanian and M. Santappa, *Makromol. Chem., 112,* 1 (1968).
[14] S. V. Subramanian and M. Santappa, *J. Polym. Sci., Part A-1, 6,* 493 (1968).
[15] F. Gray, A. A. Herod, and A. Jones, *Chem. Rev., 71,* 247 (1971).

Received December 26, 1987