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Grafting of Polymers Having Pendant Peroxycarbonate Groups Onto Carbon Black and Postpolymerization of Vinyl Monomers

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GRAFTING OF POLYMERS HAVING PENDANT PEROXYCARBONATE GROUPS ONTO CARBON BLACK AND POSTPOLYMERIZATION OF VINYL MONOMERS

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Key Words: Carbon Black, Surface Grafting, Postgrafting, t-Butylperoxy-2-methacryloyloxyethyl-carbonate, Branched Polymer, Dispersibility

ABSTRACT

Postpolymerization of vinyl monomers initiated by pendant peroxycarbonate groups of grafted polymer chains on carbon black (CB) was investigated. The grafting of polymers having pendant peroxycarbonate groups onto CB was achieved by the trapping of polymer radicals formed by the thermal decomposition of copolymers of t-butylperoxy-2-methacryloyloxyethyl-carbonate (HEPO) with vinyl monomers such as vinyl acetate (VAc), styrene (St) and methyl methacrylate (MMA). The copolymers having pendant peroxycarbonate groups were prepared by copolymerization of HEPO with vinyl monomers using azo initiator under irradiation of UV light at room temperature. The amount of remaining pendant peroxycarbonate groups of the poly(VAc-co-HEPO)-grafted CB obtained from the reaction at 90°C was maximum and decreased above the temperature. Furthermore, the postpolymerization of vinyl monomers, such as St, MMA, and VAc was initiated in the presence of poly(VAc-co-HEPO)-grafted and poly(St-co-HEPO)-grafted CB and the corresponding polymers were postgrafted onto CB to give branched polymer-grafted CB. The percentage of poly(St)-postgrafting (proportion of postgrafted poly(St) to poly(MMA-co-HEPO)-grafted CB used) increased with increasing polymerization time, but became constant at 20% after 4 hours.

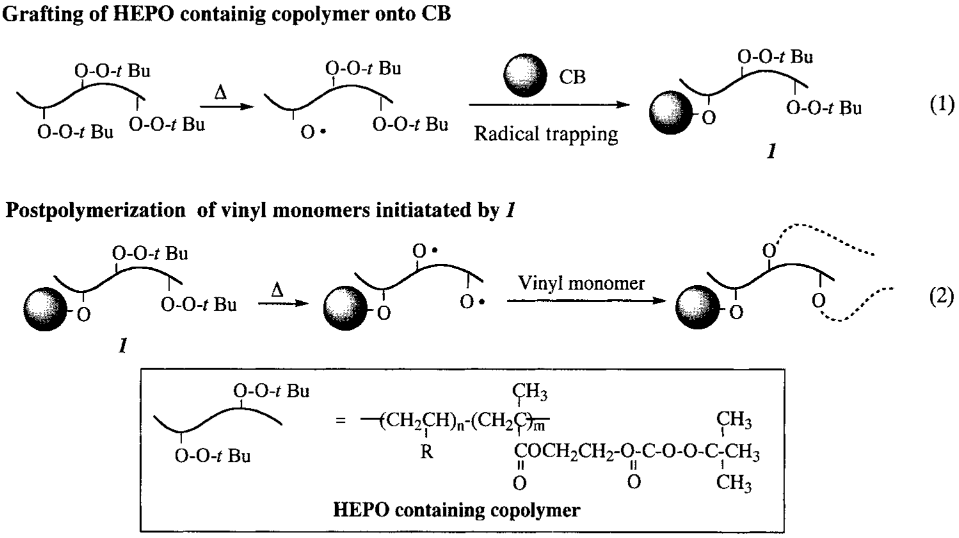
INTRODUCTION

The surface functional groups on CB, such as carboxyl and phenolic hydroxyl groups, are used as sites for the introduction of initiating groups for graft polymerization. For example, radical, cationic, and anionic graft polymerizations of various monomers initiated by azo [1] and peroxyester, [2] acylium perchlorate,[3] and potassium carboxylate groups [4, 5], respectively, introduced onto CB surface were reported. The introduction of initiating groups onto CB having much functional groups, such as channel black, is readily achieved and graft polymerization of various vinyl monomers was initiated [1-5]. But the grafting of polymers onto CB having few functional groups, such as furnace and acetylene black, was hardly achieved because these CBs scarcely have surface functional groups for the grafting sites [5].

On the other hand, it is well known that polycondensed aromatic rings of CB act as a strong radical trapping agent [6, 7]. We pointed out that polymer radicals formed by the thermal decomposition of polymers having azo and peroxide group in the main chain was efficiently trapped on CB surface [8, 9]. The grafting method is very useful in the grafting of polymers onto CB surface having few functional groups.

More recently, we have reported that the polymer having pendant peroxycarbonate groups was successfully grafted onto CB surface through the trapping of polymer radicals formed by the thermal decomposition of copolymers prepared by the copolymerization of HEPO with vinyl monomers [10].

In the present paper, the grafting of the copolymers having pendant peroxycarbonate groups onto CB by radical trapping [Scheme 1 (1)] and the postpolymerization of vinyl monomers initiated by the remaining pendant peroxycarbonate groups of the grafted copolymers on CB [(Scheme 1 (2)] were investigated.


Grafting of HEPO containig copolymer onto CB

Postpolymerization of vinyl monomers initiatated by 1

HEPO containing copolymer

Scheme 1

EXPERIMENTAL

Materials

CBs used were furnace blacks Philblack O and Philblack I (Phillips Petroleum Co.), channel black Neospectra II (Columbian Carbon Corp.), and acetylene black Denkablack (Denki Kagaku Kogyo Co. Ltd.). Furnace blacks were extracted with chloroform to remove resinous substances. Neospectra II and Denkablack were used without further purification. These CBs were dried *in vacuo* at 120°C before use. The properties of these CBs are shown in Table 1.

Styrene (St) was washed with 10% aqueous solution of sodium hydroxide and water, dried over calcium chloride, and distilled under reduced pressure. Methyl methacrylate (MMA) was washed with dilute aqueous solution of sodium hydrogen sulfite, dried over sodium sulfate, and distilled under reduced pressure. Vinyl acetate (VAc) was distilled before use. t-Butylperoxy-2-methacryloyloxyethylcarbonate (HEPO) obtained from Nippon Oil and Fats Co., Ltd., was used without further purification. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Toluene was washed with concentrated sulfuric acid, aqueous solution of sodium hydroxide, and water, dried over calcium chloride, refluxed over sodium for 8 hours, and distilled. All other reagents and solvents were used after ordinary purification.

TABLE 1. Properties of CBs

CB	Surface area (m^2/g)	Particle size (nm)	Functional group (mmol/g)		
			Phenolic hydroxyl	Quinonic oxygen	Carboxyl
Philblack O [a)]	79.6	29.4	0.02	0.18	0
Philblack I [a)]	116.8	28	0.05	0.23	0
Neospectra II [b)]	906	13	0.24	0.92	0.40
Denkablack [c)]	65.0	40	0.02	0.01	0

a) Furnace black b) Channel black c) Acetylene black

Polymers having pendant peroxycarbonate groups, such as poly(VAc-co-HEPO), poly(St-co-HEPO) and poly(MMA-co-HEPO), were prepared by copolymerization of vinyl monomers with HEPO. The detailed procedures were described in the previous paper [10]. The properties of peroxide polymers are shown in Table 2.

Grafting of Polymer having Pendant Peroxycarbonate Groups onto CB Surface

The grafting of polymer having pendant peroxycarbonate groups onto CB surface was achieved by the reaction of CB surface with polymer radicals formed by the thermal decomposition of poly(VAc-co-HEPO), poly(St-co-HEPO) and poly(MMA-co-HEPO). The detailed procedures were described in the previous paper [10].

Determination of Pendant Peroxycarbonate Group of Polymer-Grafted CB

The amount of peroxycarbonate groups of grafted polymer on CB surface was determined by iodometry [11]. A typical example is as follows. Into a 100 mL flask, 0.10 g of HEPO containing copolymer-grafted CB, 0.20 g of potassium iodide, 10.0 mL of degassed water and 1.0 mL of 0.5 mol/L H_2SO_4 were charged. The mixture was stirred with a magnetic stirrer for 20 minutes and isolated iodide was titrated with 0.1 mol/L sodium hyposulfite using starch as an indicator.

Postpolymerization of Vinyl Monomers Initiated by Pendant Peroxycarbonate Groups of Grafted Polymer on CB

Into a glass tube, 0.10 g of HEPO containing copolymer-grafted CB and 10.0 mL of vinyl monomer were charged. The tube was frozen-thawed three times and sealed under vacuum. The sealed tube was heated with shaking. After the polymerization, the content of the tube was poured into a large excess of precipitant for the polymer. The precipitate was filtered and dried *in vacuo* at 60°C. The conversion was calculated by the following equation.

$$\text{Conversion (\%)} = \frac{\text{Product (g) - CB used (g)}}{\text{Monomer used (g)}} \times 100$$

Determination of Percentage of Grafting and Postgrafting

The product was dispersed in THF and the dispersion was centrifuged at 1.2 x10^4 rpm until CB was precipitated completely. The CB precipitated was dispersed again in THF and the dispersion was centrifuged. The procedures were repeated until no more polymer was detected in the supernatant solution. After the

TABLE 2. Properties of HEPO Containing Copolymer

HEPO containing copolymer	HEPO in feed (wt%)	HEPO content in copolymer (mol%)	$\overline{\mathrm{Mn}}$ ($\times 10^3$)	$\overline{\mathrm{Mw}}/\overline{\mathrm{Mn}}$
Poly(MMA-co-HEPO)	4.0	8.0	7.0	2.32
Poly(St-co-HEPO)	10.0	10.0	9.6	2.03
Poly(VAc-co-HEPO)	10.0	8.0	29.8	1.62

above procedures, the resulting CB was dried *in vacuo* at 60°C. The percentage of postgrafting and overall grafting were calculated by the following equations.

$$\text{Grafting (\%)} = \frac{\text{Polymer grafted (g)}}{\text{CB used (g)}} \times 100$$

$$\text{Postgrafting (\%)} = \frac{\text{Polymer postgrafted (g)}}{\text{Polymer-grafted CB used (g)}} \times 100$$

Stability of Polymer-Grafted CB Dispersion

The stability of polymer-grafted CB in THF was estimated from the CB content in the dispersion after standing at room temperature. The detailed procedures were described in the previous paper [12].

RESULTS AND DISCUSSION

Grafting of Polymers Having Peroxycarbonate Groups onto CB Surface

The grafting of polymer having pendant peroxycarbonate groups onto CB surface by the trapping of polymer radicals formed by the thermal decomposition of poly(MMA-co-HEPO) was examined. The results are shown in Figure 1. It was found that the percentage of grafting increased with increasing reaction temperature, but no longer increased above 100°C. These results indicate that the decomposition of poly(MMA-co-HEPO) was accelerated at a high temperature and polymer radicals formed were effectively trapped by CB surface.

On the other hand, the remaining pendant peroxycarbonate group content of the poly(MMA-co-HEPO)-grafted CB increased with increasing reaction temperature, but decreased above 90°C. These results indicate that the decomposition of pendant peroxycarbonate groups of grafted polymer chains on CB are accelerated above 90°C: the temperature is closed to 10 hours half-life of HEPO[13].

Postpolymerization of Vinyl Monomer Initiated by Poly(MMA-co-HEPO)-Grafted CB

As mentioned above, the pendant peroxycarbonate groups of poly(MMA-co-HEPO)-grafted CB still remain after grafting reaction. Therefore, the postpolymerization of St initiated by pendant peroxycarbonate groups of the poly(MMA-co-HEPO)-grafted CB obtained from the reaction at 90°C was investigated. The results are shown in Table 3.

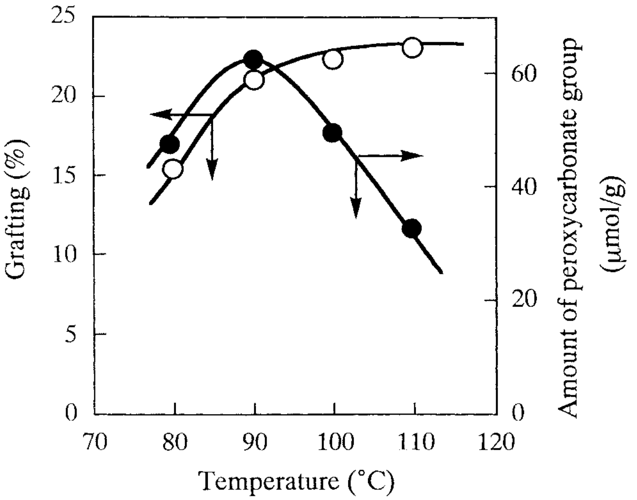


Figure 1. Grafting reaction of poly(MMA-co-HEPO) with CB. Philblack O, 0.30 g; poly(MMA-co-HEPO), 1.0 g; toluene, 20.0 mL; 10 hours.

Although the thermal polymerization of St was initiated even in the absence of CB, the rate of the polymerization was very small. The conversion of St in the presence of untreated CB was almost equal to that in the absence of CB and no grafting of poly(St) onto the surface was observed. On the contrary, in the presence of poly(MMA-co-HEPO)-grafted CB, polymerization was found to be initiated and poly(St) was postgrafted onto the surface.

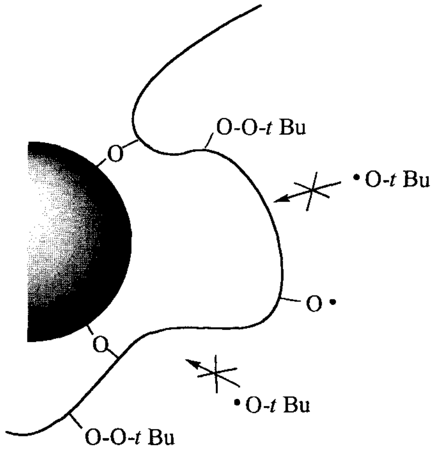
By the way, it has been reported that the polymerization of vinyl monomers with negative e-value was hardly initiated in the presence of CB using peroxides, such as benzoyl peroxide, as an initiator [14-16]. The same tendency has been also observed in the polymerization of vinyl monomers with negative e-value initiated by peroxide groups introduced onto CB surface [17]. This may be due to the fact that the radicals formed by the decomposition of peroxides have abilities to abstract hydrogen atoms from CB to give surface active radicals. The surface active radicals on CB readily capture the growing polymer radicals with negative e-value, but not with positive e-value [14-16]. Therefore, the polymerization of vinyl monomers with negative e-value in the presence of CB using peroxides as initiator is markedly retarded, whereas that with positive e-value is scarcely retarded.

In addition, we have also reported that the retardation of polymerization of St in the presence of CB using benzoyl peroxide as an initiator is considerably

TABLE 3. Postpolymerization of St in the Presence of poly(MMA-co-HEPO)-Grafted CB

Carbon black	Conversion (%)	Postgrafting (%)
None	0.8	—
Untreated	0.7	0
Poly(MMA-co-HEPO) grafted	1.4	7.9

Poly(MMA-co-HEPO)-grafted Philblack O (Grafting=21.0%), 0.10g ; St, 10.0 mL; 100°C; 1 h.



Scheme 2

reduced by the surface grafting of polymers, because CB surface was blocked by grafted polymer chains [18].

Therefore, it is considered that in the postpolymerization initiated by poly(MMA-co-HEPO)-grafted CB, the retardation of polymerization of St by CB surface is overcame by grafted polymer chains and by the reduction of radical trapping site (Scheme 2).

Based on the above results, it is concluded that the remaining pendant perooxycarbonate groups of poly(MMA-co-HEPO)-grafted CB have an ability to

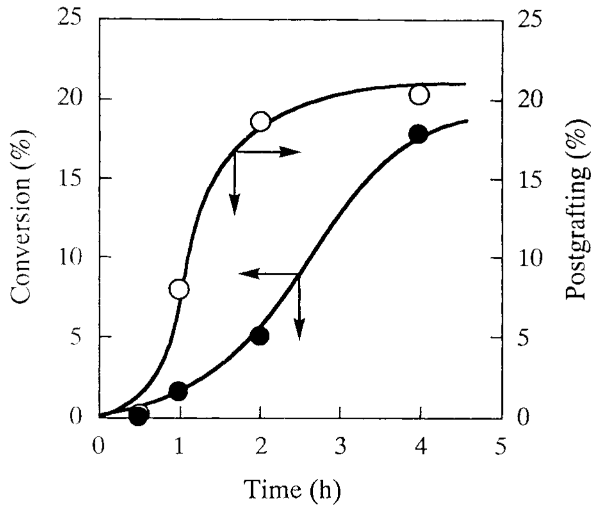


Figure 2. Postpolymerization of St initiated by peroxycarbonate groups of the poly(MMA-co-HEPO)-grafted CB. Poly(MMA-co-HEPO)-grafted Philblack O (Grafting=21.0%), 0.10 g; St, 10.0 mL; 100°C.

initiate the polymerization of St and poly(St) is postgrafted to poly(MMA-co-HEPO)-grafted CB.

Figure 2 shows time *versus* conversion curve and time *versus* percentage of poly(St)-postgrafting curve in the polymerization of St initiated by poly(MMA-co-HEPO)-grafted CB. It was found that the conversion and the percentage of postgrafting increase with progress of the polymerization, but the percentage of postgrafting is constant about 21% after 4 hours.

This may be due to the fact that the propagation of poly(St) from pendant peroxycarbonate groups of polymer-grafted CB is readily hindered by neighboring grafted chains and/or the chain transfer from the grafted chain occurs frequently at the last stage of the polymerization.

Effect of Temperature on the Postpolymerization of St in the Presence of Poly(MMA-co-HEPO)-Grafted CB

The effect of temperature on the postpolymerization of St initiated by poly(MMA-co-HEPO)-grafted CB was investigated. The results are shown in Figure 3. The rate of polymerization of St increased with increasing polymerization temperature and the percentage of postgrafting reached to 25.3% at 120°C. These

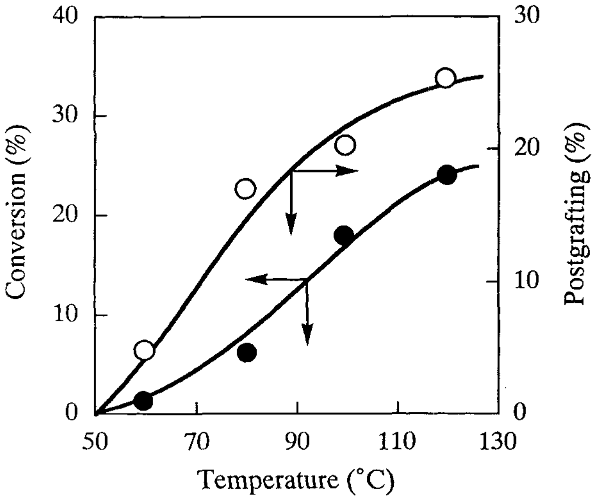


Figure 3. Effect of temperature on the postpolymerization of St in the presence of poly(MMA-co-HEPO)-grafted CB. Poly(MMA-co-HEPO)-grafted Philblack O (Grafting=21.0%), 0.10 g; St, 10.0 mL; 4 hours.

results indicate that pendant peroxycarbonate groups are efficiently decomposed with increasing polymerization temperature.

Postpolymerization of St Initiated by Poly(MMA-co-HEPO)-Grafted Various CB

Postpolymerization of St initiated by poly(MMA-co-HEPO)-grafted various CBs was investigated. The results are shown in Table 4. It was found that the polymerization of St is also initiated in the presence of poly(MMA-co-HEPO)-grafted Neospectra II, Philblack I, and Denkablack to give the corresponding poly(St)-postgrafted CB.

These results suggest that the pendant peroxycarbonate groups of poly(MMA-co-HEPO) grafted onto various CBs also have an ability to initiate the postpolymerization of St.

Postpolymerization of MMA Initiated by HEPO Containing Copolymer-Grafted CB

The postpolymerization of MMA initiated by poly(St-co-HEPO)-grafted and poly(VAc-co-HEPO)-gafted CB was also investigated. The results are shown in Table 5. As well as poly(MMA-co-HEPO)-grafted CB, postpolymerization of MMA was successfully initiated in the presence of poly(St-co-HEPO)-grafted and

TABLE 4. Postpolymerization of St in the Presence of poly(MMA-co-HEPO)-Grafted Various CBs

Poly(MMA-co-HEPO)-grafted CB	Poly(MMA-co-HEPO) grafting (%)	Conversion (%)	Postgrafting (%)
Neospectra II	30.2	0.7	19.5
Philblack I	21.8	5.0	18.2
Denkablack	20.9	3.5	19.9

CB, 0.10 g; St, 10.0 mL; 100°C; 4 h.

TABLE 5. Postpolymerization of MMA in the Presence of Various HEPO Containing Copolymer-Grated CBs

CB	Grafted polymer	HEPO containing copolymer grafting (%)	Time (h)	Postgrafting (%)
Neospectra II	Poly(St-co-HEPO)	51.6	2	16.2
Philblack O	Poly(St-co-HEPO)	29.8	2	22.4
Philblack I	Poly(St-co-HEPO)	26.0	2	34.5
Denkablack	Poly(St-co-HEPO)	21.5	2	54.3
Neospectra II	Poly(VAc-co-HEPO)	88.2	1.5	4.0
Philblack O	Poly(VAc-co-HEPO)	49.7	1.5	5.1
Philblack I	Poly(VAc-co-HEPO)	48.7	1.5	10.0
Denkablack	Poly(VAc-co-HEPO)	40.4	1.5	22.8

HEPO containing copolymer-grafted CB , 0.10 g ; MMA, 10.0 mL; 100 °C.

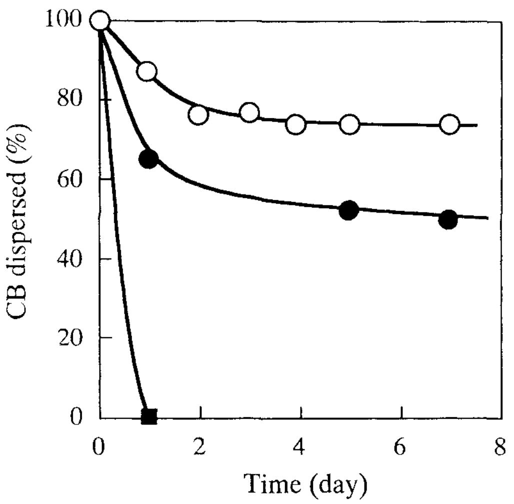


Figure 4. Stability of polymer-grafted Philblack O dispersion in THF at room temperature. (■ , ungrafted; (O), poly(MMA-co-HEPO)-grafted (Grafting=27.9%); (●), poly(St)-postgrafted (Postgrafting=20.2%).

poly(VAc-co-HEPO)-grafted CB to give the corresponding branched polymer-grafted CB.

Stability of Polymer-Grafted CB Dispersion

The stability of branched polymer-grafted CB (after the postpolymerization) and HEPO containing polymer-grafted CB (before the postpolymerization) dispersion in THF were compared with that of untreated CB. The results are shown in Figure 4. It was found that the dispersibility of CB was remarkably improved by the grafting of polymers onto the surface. Especially, branched polymer-grafted CB (after the postpolymerization) gave a very stable colloidal dispersion in THF. This suggests that branched polymer chains on CB surface effectively interfere with the aggregation of CB particles.

CONCLUSION

By the heating of CB with poly(MMA-co-HEPO), poly(St-co-HEPO) and poly(VAc-co-HEPO) at 100°C, polymer radicals formed by thermal decomposition of pendant peroxycarbonate groups of these copolymers were effectively trapped by CB surface to give the corresponding HEPO containing copolymer-grafted CBs.

The postpolymerization of vinyl monomers was initiated by the undecomposed pendant peroxycarbonate groups of the above copolymer-grafted CBs to give branched polymer-grafted CB.

The vinyl polymer-postgrafted CB thus obtained gave a very stable colloidal dispersion in a good solvent of the polymer.

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