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GRAFTING ONTO CARBON BLACK: REACTION OF FUNCTIONAL GROUPS ON CARBON BLACK WITH ACYL CHLORIDE-CAPPED POLYMERS

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ABSTRACT

The grafting of acyl chloride-capped polymers onto carbon black by the reaction of the acyl chloride group with the phenolic hydroxyl group on the surface was investigated. Acyl chloride-capped polymers were prepared by the reaction of functional polymers having terminal hydroxyl groups, such as poly(propylene glycol) (PPG), poly(ethylene glycol) (PEG), and silicone diol (SDO), with adipoyl dichloride or isophthaloyl dichloride. When acyl chloride-capped PPG (PPG-COCl) ($\bar{M}_n = 2.4 \times 10^3$) was reacted with carbon black, PPG was grafted onto the surface: the percentage of grafting reached to 27.7%. On the contrary, the reaction of PPG-COCl with carbon black treated with diazomethane was scarcely observed. The PPG grafted onto carbon black was largely removed by hydrolysis with a dilute methanol solution of KOH. Based on these results, it was concluded that PPG grafted onto the surface with ester bonds. The percentage of grafting increased with an increase in the molecular weight of PPG-COCl. In addition, it was found that carbon black containing amino and imidazoline groups has high reactivity with PPG-COCl and gives PPG-grafted carbon black with a high percentage of grafting. PPG-grafted carbon black produced a stable colloidal dispersion in organic solvents.

INTRODUCTION

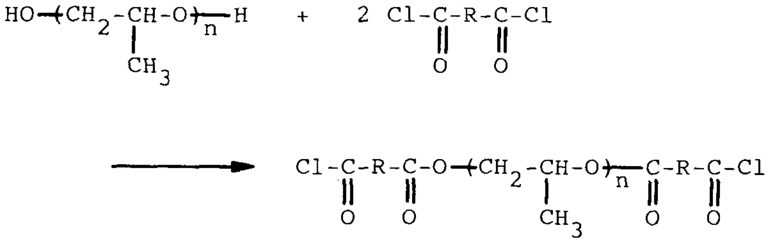
The grafting of polymers onto carbon black is achieved by the polymerization of various monomers by initiating group introduced onto the surface [1, 2].

Although polymer-grafted carbon blacks with a high percentage of grafting can be obtained in these graft polymerizations, it is impossible to control the molecular weight and the number of grafted polymer chains.

Polymer-grafted carbon black can also be obtained by the reaction of functional groups on the surface with various polymers having reactive groups [1, 2]. This grafting method enabled us to control the molecular weight and the number of grafted polymer.

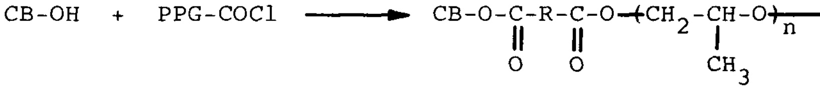
In previous papers we reported that isocyanate-capped poly(propylene glycol) is grafted onto carbon black by the reaction of the isocyanate group with phenolic hydroxyl and carboxyl groups on the surface [3, 4]. Furthermore, it has been demonstrated that reactive carbon blacks having acyl azide [5], acyl chloride [6], isocyanate [7], chlorotriazinyl [8], and expoxide [9] groups react with hydroxyl-capped or amino-capped polymers to give polymer-grafted carbon black.

In the present paper we report the grafting of various polymers onto carbon black by the reaction of acyl chloride-capped polymers with phenolic hydroxyl groups on the surface: acyl chloride-capped polymers were prepared by the reaction of polymers having terminal hydroxyl groups with adipoyl dichloride or isophthaloyl dichloride. Furthermore, the reaction of amino or imidazoline groups introduced onto the carbon black surface with acyl chloride-capped polymers was investigated.

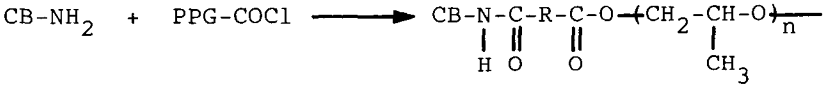


$$\mathrm{HO{+}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}O{+}_n H \;+\; 2\,Cl{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}Cl \longrightarrow Cl{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}O{+}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}O{+}_n\underset{\displaystyle O}{\underset{\|}{C}}{-}R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}Cl} \qquad (1)$$

PPG-COCl



$$\mathrm{CB{-}OH \;+\; PPG{-}COCl \longrightarrow CB{-}O{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}O{+}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}O{+}_n} \qquad (2)$$



$$CB\text{-}NH_2 + PPG\text{-}COCl \longrightarrow CB\text{-}\underset{H}{N}\text{-}\underset{O}{\overset{}{C}}\text{-}R\text{-}\underset{O}{C}\text{-}O\text{+}CH_2\text{-}\underset{CH_3}{CH}\text{-}O\text{+}_n \qquad (3)$$

PPG-COCl (I) : R= $-(CH_2)_4-$

PPG-COCl (II): R=

EXPERIMENTAL

Materials

The carbon black used was channel black Neospectra II (Columbian Carbon Co.). Its specific surface area (BET) was 906 m^2/g. The determination of the content of functional groups present on the carbon black surface was independently reported by several authors, such as Studebaker [10], Boehm [11], Rivin [12], and Donnet [13]. The content of phenolic hydroxyl [14], carboxyl [12], and quinonic oxygen [10] groups was determined to be 0.24, 0.40, and 0.92 meq/g, respectively. The carbon black was dried *in vacuo* at 120°C before use.

Adipoyl dichloride and isophthaloyl dichloride were prepared by the reaction of thionyl chloride with the corresponding carboxylic acid according to a usual method.

2,2′-Azobis[2-(2-imidazoline-2-yl)propane] (AIP) was obtained from Wako Pure Chemical Industries, Ltd., Japan, and recrystallized from methanol.

All other reagents and solvents were purified by the usual methods.

Polymers

Diol-type poly(propylene glycol)s (PPG) ($\bar{M}_n = 1.0 \times 10^3$, 2.0×10^3, and 3.0×10^3) were obtained from Wako Pure Chemical Industries, Ltd. Poly(ethylene glycol) (PEG) ($\bar{M}_n = 6.0 \times 10^3$) was obtained from Kanto Chemical Co. Ltd., Japan. Silicone diol (SDO) ($\bar{M}_n = 1.8 \times 10^3$) was obtained from Shin-Etsu Chemical Industries Co. Ltd., Japan. All the polymers were dried *in vacuo* below 80°C before use.

Preparation of Acyl Chloride-Capped Polymers

Acyl chloride-capped polymers were prepared by the reaction of polymers having terminal hydroxyl groups with adipoyl dichloride or isophthaloyl dichloride. A typical example was as follows. Into a 100-mL flask equipped with a dropping funnel, a reflux condenser, and a nitrogen inlet, 0.01 mol polymer was charged. Then 0.02 mol adipoyl dichloride was added dropwise to the flask under stirring with a magnetic stirrer. The reaction was conducted at 50°C for 3 h in a stream of nitrogen. The resulting polymer was dried *in vacuo* at 50°C.

Introduction of Amino Groups onto Carbon Black

The introduction of amino groups onto carbon black was achieved by the reduction of nitrated carbon black. The nitration of the polycondensed aromatic ring of carbon black was carried out as follows [15]. To a suspension of 3.0 g carbon black in 120 mL of acetic anhydride, 30 mL fuming nitric acid was added under stirring with a magnetic stirrer at below 5°C for 5 h. Then the reaction was continued at room temperature for 5 h. Following the reaction, the content of the flask was poured into 1 L of ice-cooled water. The supernatant solution was removed by decantation, and the carbon black precipitated was washed with distilled water until the filtrate was neutral.

The reduction of nitro groups on carbon black was carried out as follows. Into a 200-mL flask that contained 3.0 g nitrated carbon black, 12 mL 30% ammonia water, and 50 mL distilled water, 80 mL of 15% sodium hydrosulfite aqueous solution was added. The reaction mixture was stirred at room temperature for 24 h. Following the reaction, carbon black was filtered and washed with distilled water until the filtrate was neutral.

Introduction of Imidazoline Groups onto Carbon Black

The introduction of imidazoline groups onto carbon black was carried out by the reaction of carbon black with the 2-(2-imidazoline-2-yl)propane radical which formed by the thermal decomposition of AIP [16]. A typical example was as follows. Into a 300-mL flask that contained 3.0 g carbon black and 50 mL benzene, 0.2 g AIP was added every 8 h. The reaction was conducted with stirring under nitrogen at 70°C. After the reaction was run for 96 h (the total amount of AIP added was 2.4 g), the resulting carbon black was extracted with acetone and dried *in vacuo*. The amount of imidazoline group introduced onto carbon black was determined by nitrogen analysis.

Treatment of Carbon Black with Diazomethane

The treatment of carbon black with diazomethane was carried out by the method reported by Studebader [17] to block phenolic hydroxyl and carboxyl groups with methylation.

The Reaction of Carbon Black with Acyl Chloride-Capped Polymer

The reaction of carbon black with acyl chloride-capped polymers was carried out in bulk. Into a 100-mL flask that contained 0.30 g carbon black, 5.0 g acyl chloride-capped polymer and 0.1 mL triethylamine were added. The reaction mixture was stirred at 80–120°C under nitrogen. After the reaction was completed, the product was dispersed in tetrahydrofuran and the dispersion was centrifuged at 1.0×10^4 rpm. The carbon black, completely precipitated after 1 h, was extracted with tetrahydrofuran until polymer was no longer detected in the extract. The percentage of grafting was estimated by the following equation:

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

Stability of Dispersion of Polymer-Grafted Carbon Black

Polymer-grafted carbon black (0.30 g) was dispersed in 100 mL tetrahydrofuran with a magnetic stirrer, and the dispersion was allowed to stand at room temperature. After a definite time, 5.0 mL dispersion liquid was removed with a pipet, and the content of carbon black dispersed in the tetrahydrofuran was determined. The stability of dispersion was estimated by the carbon black content of the dispersion:

$$\text{content of carbon black in dispersion (\%)} = \frac{\begin{array}{c}\text{carbon black dispersed}\\ \text{after standing (g)}\end{array}}{\begin{array}{c}\text{carbon black dispersed}\\ \text{before standing (g)}\end{array}} \times 100$$

RESULTS AND DISCUSSION

Characterization of Acyl Chloride-Capped Polymers

Figure 1 shows the infrared spectra of PPG and adipoyl chloride-capped PPG (PPG-COCl (I)) which was prepared by the reaction of 1 mol PPG ($\bar{M}_n = 2.0 \times 10^3$)

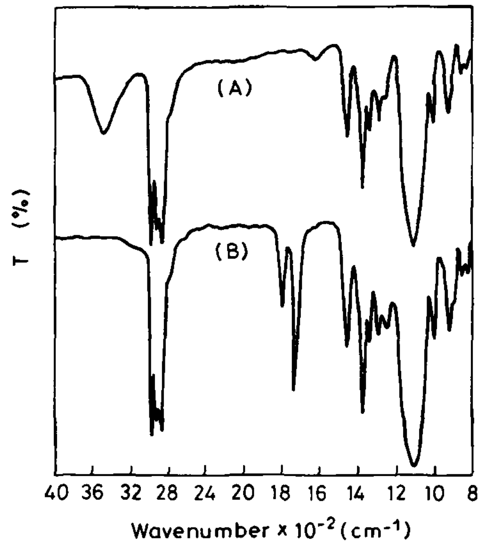


FIG. 1. Infrared spectra of PPG (A) and adipoyl chloride-capped PPG (B).

with 2.0 mol adipoyl dichloride. The absence of unreacted adipoyl dichloride in PPG-COCl (I) was confirmed by its size exclusion chromatogram: the chromatogram shows only one sharp peak. As shown in Fig. 1, the absorption of the hydroxyl group of PPG at 3500 cm^{-1} completely disappeared due to the reaction with adipoyl dichloride. Furthermore, the infrared spectra of PPG-COCl (I) exhibited new absorptions at 1800 and 1740 cm^{-1} besides the one observed in PPG. The absorptions at 1800 and 1740 cm^{-1} are characteristic of the acyl chloride group and the ester bond, respectively. Other adipoyl chloride- and isophthaloyl-capped polymers prepared from PPG, PEG, and SDO were also identified by infrared spectra.

Table 1 shows the molecular weight of acyl chloride-capped PPG, PEG, and SDO as determined by vapor pressure osmosis. These values closely agreed with the theoretical molecular weights.

Grafting by the Reaction of PPG-COCl with Carbon Black

Table 2 shows the results of the reaction of PPG-COCl (I) ($\bar{M}_n = 2.4 \times 10^3$) with carbon black under different conditions. As shown in Table 2, when carbon black

TABLE 1. Molecular Weight of Adipoyl Chloride-Capped Polymers[a]

Polymer	$\bar{M}_n \times 10^{-3}$	COCl-capped polymer, $\bar{M}_n \times 10^{-3}$
PPG	1.0	1.3
PPG	2.0	2.4
PPG	3.0	3.2
PEG	6.0	6.1
SDO	1.8	2.0

[a] Determined by vapor pressure osmosis.

TABLE 2. Reaction of PPG-COCl (I) with Carbon Black under Different Conditions[a]

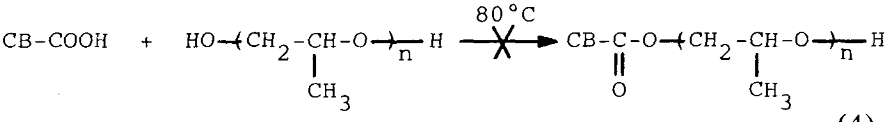
Carbon black	Polymer	Temperature, °C	Percentage of grafting
Untreated	PPG	20	9.8
Untreated	PPG	80	10.0
Untreated	PPG-COCl	80	27.7
Untreated	PPG-COOMe[b]	80	10.1
CH_2N_2-treated[c]	PPG-COCl	80	9.8

[a] Carbon black, 0.30 g; polymer, 5.0 g; triethylamine, 0.1 mL; 20 h.

[b] Terminal acyl chloride groups were blocked with methanol.

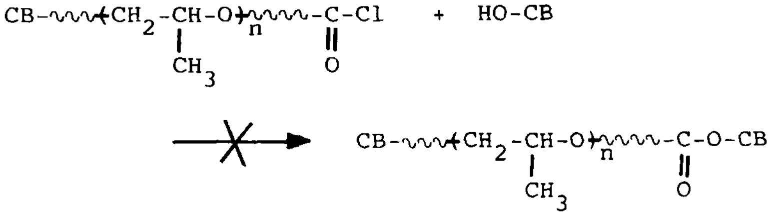
[c] Surface carboxyl and phenolic hydroxyl groups were blocked by methylation.

was mixed with PPG at 20°C, PPG was retained on the carbon black surface even after extraction with tetrahydrofuran. Even if PPG was heated with carbon black at 80°C, the amount of PPG retained on the surface did not increase. This indicates that no direct esterification of carboxy groups on the surface with PPG proceeds (Eq. 4). Furthermore, due to blocking of the COCl group with methanol (PPG-$COOCH_3$), no grafting of the polymer was observed.



$$\text{CB-COOH} + \text{HO}\!-\!\!\left(\text{CH}_2\text{-}\underset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{-O}\right)_{\!n}\!\!-\text{H} \;\overset{80\,^\circ\text{C}}{\not\longrightarrow}\; \text{CB-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-O}\!-\!\!\left(\text{CH}_2\text{-}\underset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{-O}\right)_{\!n}\!\!-\text{H} \qquad (4)$$

On the contrary, it was found that when carbon black was reacted with PPG-COCl (I), the amount of PPG-COCl (I) retained on the surface was much larger than PPG. These results suggest that PPG-COCl (I) was grafted onto carbon black by the reaction of an acyl chloride group of PPG-COCl (I) with a phenolic hydroxyl group on the surface. The carbon black obtained from the reaction was completely dispersed in tetrahydrofuran, and no carbon-polymer gel was observed. This indicates that the terminal acyl chloride group of the grafted polymer chain no longer reacted with carbon black (Eq. 5). This may be because the carbon black reacted with a large excess of PPG-COCl.



$$\mathrm{CB}\sim\!\sim\!\sim\!\Big(\mathrm{CH_2{-}}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{{-}O}\Big)_n\!\sim\!\sim\!\sim\!\sim\mathrm{{-}}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}Cl} \;+\; \mathrm{HO{-}CB} \qquad (5)$$

$$\not\longrightarrow \;\mathrm{CB}\sim\!\sim\!\sim\!\Big(\mathrm{CH_2{-}}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{{-}O}\Big)_n\!\sim\!\sim\!\sim\!\sim\mathrm{{-}}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}O{-}CB}$$

Diazomethane-treated carbon black, whose phenolic hydroxyl group was blocked by methylation, was unable to react with PPG-COCl (I) (Table 2).

Figure 2 shows the infrared spectra of untreated carbon black and PPG-grafted carbon black (percentage of grafting = 27.7%). The infrared spectra of untreated carbon black exhibited a broad, weak absorption at 1610 cm^{-1}. On the contrary, the infrared spectra of PPG-grafted carbon black exhibited absorption at 1740 and 1110 cm^{-1}, characteristic of ester and ether bonds, respectively. Furthermore, other absorptions in PPG-grafted carbon black agreed with those of PPG-COCl (I).

To remove the grafted PPG chains on carbon black, the PPG-grafted carbon black was hydrolyzed by a dilute methanol solution of potassium hydroxide. The infrared spectra of hydrolyzed and of ungrafted carbon black completely agreed. It is therefore concluded that PPG is grafted onto carbon black with an ester bond by the reaction of PPG-COCl with the phenolic hydroxyl group on the surface.

Effect of Temperature on the Grafting

Figure 3 shows the effect of temperature on the grafting of PPG-COCl onto carbon black by the reaction of PPG-COCl (I) ($\bar{M}_n = 2.4 \times 10^3$) with the phenolic hydroxyl group on the carbon black surface.

Although the rate of grafting at 80°C is larger than at 40°C, the percentage of grafting after 10 h reached almost equal values. However, the percentage of grafting at 120°C is lower than that at 40 and 80°C. This suggests that steric

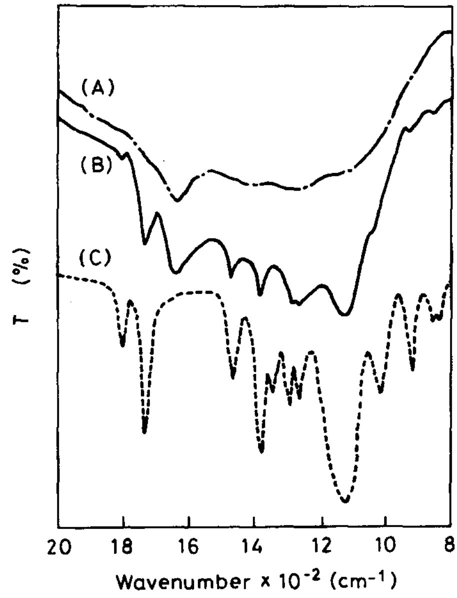


FIG. 2. Infrared spectra of carbon black (A), PPG-grafted carbon black (B), and PPG-COCl (C).

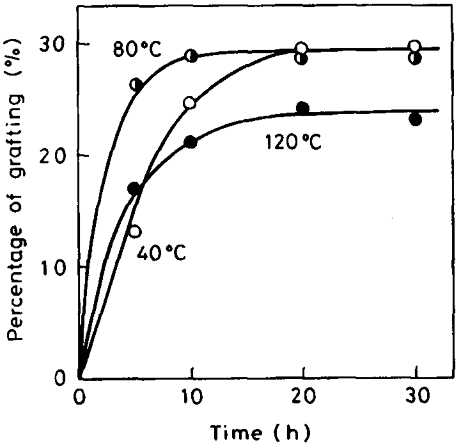


FIG. 3. Effect of temperature on the grafting of PPG by the reaction of PPG-COCl (I) ($\bar{M}_n$ = 2.4 × 10^3) with carbon black. Neospectra II, 0.50 g; PPG-COCl (I), 5.0 g; triethylamine, 0.1 mL.

hindrance increases with temperature. The same tendency was observed in the grafting reaction of carbon black with isophthaloyl chloride capped PPG-COCl (II) ($\bar{M}_n$ = 3.0 × 10^3) as shown in Fig. 4.

Effect of Molecular Weight of PPG-COCl on the Grafting

Table 3 shows the effect of molecular weight of PPG-COCl (I) on grafting onto carbon black. The percentage of grafting increased with an increase in the molecular weight of PPG-COCl (I). The number of PPG chains grafted onto the surface, however, decreased with an increase in the molecular weight. This may be due to the fact that phenolic hydroxyl groups are shielded by neighboring grafted chains. A similar result was reported in the reaction of the silanol group on silica with polystyrene containing a terminal chlorosilane group [18] and in the reaction of a reactive group on carbon black with functional polymers [8, 9].

Grafting of Various Polymers

The reaction of adipoyl chloride-capped various polymers with carbon black was examined. The results are summarized in Table 4. As shown in Table 4, acyl chloride-capped SDO and PEG react with phenolic hydroxy groups on carbon black to give polymer-grafted carbon black. The ratio of phenolic hydroxyl groups reacted with PPG-COCl was calculated to be 0.20–0.60.

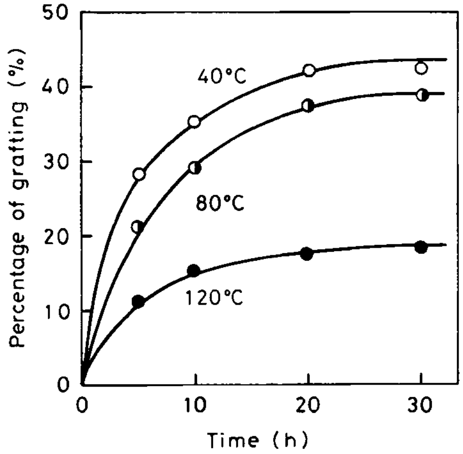


FIG. 4. Effect of temperature on the grafting of PPG by the reaction of PPG-COCl (II) ($\bar{M}_n$ = 3.0 × 10^3) with carbon black. Reaction conditions are shown in Fig. 3

TABLE 3. Effect of Molecular Weight of PPG-COCl (I) on Grafting onto Carbon Black[a]

$\bar{M}_n \times 10^{-3}$	Percentage of grafting	Number of grafted polymer, mmol/g
1.3	17.0	0.13
2.4	27.7	0.11
3.2	29.5	0.09

[a] Neospectra II, 0.30 g; PPG-COCl (I), 5.0 g; triethylamine, 0.1 mL; 80°C; 20 h.

TABLE 4. Grafting Reaction of Isophthaloyl Chloride-Capped Polymers with Carbon Black[a]

Polymer	$\bar{M}_n \times 10^{-3}$	Percentage of grafting	R^b
PPG-COCl	3.0	29.0	0.40
PEG-COCl	6.9	35.5	0.21
SDO-COCl	2.0	29.3	0.60

[a] Neospectra II, 0.30 g; polymer, 5.0 g; triethylamine, 0.1 mL; 80°C; 10 h.

[b] $R = \dfrac{\text{grafted polymer (mmol/g)}}{\text{phenolic hydroxyl group (mmol/g)}}$.

Grafting onto Carbon Black Having Amino and Imidazoline Group

To obtain polymer-grafted carbon black with a higher percentage of grafting, grafting onto carbon black by the reaction of PPG-COCl (II) ($\bar{M}_n = 3.0 \times 10^3$) with the amino or imidazoline group introduced onto the surface was examined. The results are shown in Table 5.

It was found that PPG-grafted carbon black is also obtained by the reaction of PPG-COCl with an amino or imidazoline group on the surface. The percentage of grafting onto carbon black formed by the reaction of PPG-COCl with the amino groups on the surface was larger than that by the reaction with phenolic hydroxy groups on the surface. This may be due to the higher amino group content on the surface.

TABLE 5. Grafting Reaction of PPG-COCl (II) with Amino and Imidazoline Groups Introduced onto Carbon Black Surface[a]

Functional group	Content, meq/g	Percentage of grafting
Phenolic hydroxyl	0.24	29.0
Amino	0.44	55.3
Imidazoline	1.12	43.8

[a] Neospectra II, 0.30 g; PPG-COCl (II) ($\bar{M}_n$ = 3.0×10^3), 5.0 g; triethylamine, 0.1 mL; 80°C; 10 h.

Dispersibility of PPG-Grafted Carbon Black

The stability of a dispersion of PPG-COCl (II)-grafted carbon black, whose percentage of grafting is 29.0%, in tetrahydrofuran was compared with that of an untreated one. The results are shown in Fig. 5. As shown in Fig. 5, untreated carbon black immediately precipitated in tetrahydrofuran. On the contrary, PPG-grafted carbon black produced a stable colloidal dispersion in tetrahydrofuran: the sedimentation of carbon black particles was no longer observed after 1 d. This indicates that grafted polymer chains on a carbon black surface interfere with the aggregation of carbon black particles.

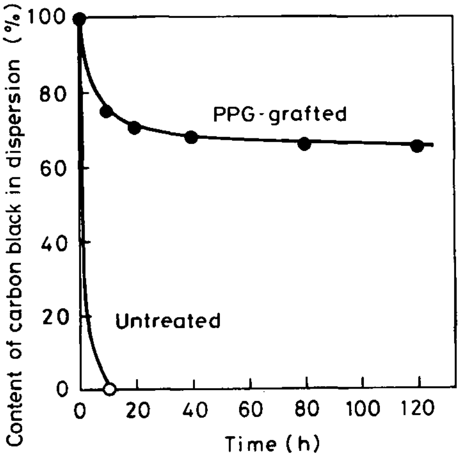


FIG. 5. Stability of dispersion of PPG-grafted carbon black (percentage of grafting = 29.0) in tetrahydrofuran at room temperature.

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