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Grafting onto carbon black by the reaction of reactive carbon black having acyl chloride group with several polymers

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SUMMARY

Acyl chloride group introduced onto carbon black rapidly lost its activity by the moisture in air. However, the decrease of acyl chloride group content in vacuum was negligibly small. By the reaction of the acyl chloride group with several polymers having hydroxyl or amino group, such as polyethylene glycol (PEG), poly(vinyl alcohol)(PVA), and polyethyleneimine (PEI), these polymers were found to be effectively grafted onto carbon black; for instance, the grafting ratio of PEG ($Mn=8.2x10^3$), PVA ($Mn=2.2x10^4$), and PEI ($Mn=2.0x10^4$) was 18.5%, 32.9%, and 45.8%, respectively. The number of polymer grafted onto carbon black decreased with an increase of its molecular weight.

INTRODUCTION

The grafting of various kinds of polymers onto carbon black surface has been investigated in our laboratory with a view to obtaining carbon black which is to be easily dispersed in various polymers (1,2). In the series of our papers, we have reported the grafting by the reaction of functional group on carbon black with polymers. For instance, phenolic hydroxyl and carboxyl groups on carbon black were found to react with prepolymer having a terminal isocyanate group to give polymer-grafted carbon black (3,4).

Furthermore, it was demonstrated that the reactive carbon black having isocyanate (5), acyl azide (5), and masked isocyanate group (6) reacts with functional polymers having hydroxyl, carboxyl, and amino groups and that polymer-grafted carbon black is readily obtained.

On the other hand, Boehm has reported that acyl chloride group is easily introduced onto carbon black surface by the reaction of carboxyl group with thionyl chloride (7). It is well known that acyl chlorides react with active hydrogen compounds. Therefore, it is expected that acyl chloride group on carbon black reacts with various polymers having active hydrogen group to give polymer-grafted carbon black.

In the present paper, the introduction of reactive acyl chloride group onto carbon black by the reaction of thionyl chloride with carboxyl group on the carbon black and its stability upon storage were examined. Moreover, the grafting onto carbon black by the reaction of its acyl chloride group on carbon black with several polymers having hydroxyl or amino group will be discussed (Eq.1).

$$\text{CB-COOH} \xrightarrow{SOCl_2} \text{CB-COCl}$$

$$\text{CB-COCl} + \text{HR}\sim\sim\sim\sim\text{P} \longrightarrow \text{CB-COR}\sim\sim\sim\sim\text{P} + \text{HCl} \qquad \text{(Eq.1)}$$

$$\text{(HR: HO-, } H_2N\text{-, and -NH-)}$$

EXPERIMENTAL

Materials

Carbon black used was color channel black Neospectra II (Columbian Carbon Co., specific surface area; 906 m^2/g). It was dried in vacuo at 110°C before use. The content of carboxyl group of the carbon black is 0.40 mmol/g.

Thionyl chloride obtained from Tokyo Kasei Kogyo Co.,Inc. (Japan) was used without further purification.

Benzene was refluxed over sodium and distilled. Dimethyl sulfoxide (DMSO) was dried over CaH_2 for three days and distilled twice under reduced pressure. All other solvents and reagents were used after ordinary purifications.

Polymers

Diol-type polypropylene glycol (PPG; $Mn=2.0x10^3$), polyethylene glycol (PEG; $Mn=8.2x10^3$), and poly(vinyl alcohol)(PVA; $Mn=2.2x10^4$ and $6.6x10^4$) were obtained from Wako Pure Chemical Co.,Ltd. (Japan) and used without further purification.

Diol-type polybutadiene glycol (PBG; $Mn=1.0x10^3$ and $2.0x10^3$), and polyethyleneimine (PEI; $Mn=1.8x10^3$ and $2.2x10^4$) were obtained from Nippon Soda Co.,Ltd. (Japan) and Nippon Shokubai Kagaku Kogyo Co. (Japan), respectively.

Silicone diol (SDO; $Mn=5.6x10^3$) and silicone diamine (SDA; $Mn=3.0x10^3$) were obtained from Shin-Etsu Chemical Co.,Ltd. (Japan).

All of these polymers were dried in vacuo at below 80°C before use.

Introduction of Acyl Chloride Group onto Carbon Black

Introduction of acyl chloride group onto carbon black was achieved by the treatment of carbon black with thionyl chloride (7). A typical example was as follows. Into a flask equipped with a reflux condenser, 7.0g of Neospectra II, 20ml of thionyl chloride and 50ml of benzene were charged. The mixture was refluxed for 50h under stirring with a magnetic stirrer. After the reaction, benzene and unreacted thionyl chloride were distilled off under reduced pressure. Subsequently, the resulting carbon black was dried in vacuo at 90°C for 48h and stored in vacuo (13.3 Pa) at room temperature.

Determination of Acyl Chloride Group on Carbon Black

Acyl chloride group on carbon black was hydrolyzed with water at room temperature for 5h and hydrogen chloride liberated was titrated with 0.01N aqueous solution of potassium hydroxide using phenolphthalein as an indicator.

Reaction of Carbon Black Having Acyl Chloride Group with Polymers Having hydroxyl or Amino Group

The reaction of carbon black having acyl chloride group (CB-COCl) with PPG, PEG, PBG, SDO, and SDA was carried out in bulk. Into a flask that contained 0.35g of CB-COCl, 2.5mmol of polymer and 1.0mmol of triethylamine were added. The mixture was stirred with a magnetic stirrer at a given temperature under nitrogen. On the other hand, the reaction of CB-COCl with PEI and PVA was carried out in solution using DMSO (7.0ml) as solvent.

Determination of Grafting Ratio

After the reaction, the carbon black reacted with PPG, PEG, and PEI was dispersed in methanol and the dispersion was centrifuged at 1.2×10^4 rpm. The carbon black precipitated was extracted with methanol using a Soxhlet apparatus to remove unreacted polymer and dried in vacuo at 100°C. The dispersing and extracting solvent for PBG, SDO, and SDA were benzene and those for PVA were water. The grafting ratio of polymer onto carbon black was calculated by the following equation.

$$\text{Grafting ratio(\%)} = \frac{\text{Weight of polymer grafted(g)}}{\text{Weight of carbon black used(g)}} \times 100$$

RESULTS AND DISCUSSION

Stability of Acyl Chloride Group on Carbon Black

It has been reported that acyl chloride group is able to introduce onto carbon black by the reaction of thionyl chloride with carboxyl group (7). In our study, the amount of acyl chloride group introduced onto channel black Neospectra II was found to be 0.38 meq/g. This value corresponds to about 95% against carboxyl group on carbon black.

Generally, acyl chloride group is known to be a moisture-sensitive group. Therefore, the stability of acyl chloride group introduced onto carbon black upon storage was investigated. Carbon black having acyl chloride group was allowed to stand in a vacuum desiccator (1.33 Pa) or in contact with air at room temperature and then the content of acyl chloride group on carbon black was determined at given intervals. The results are shown in Figure 1.

It became apparent from Figure 1 that CB-COCl left in air loses its activity rapidly and the content of acyl chloride group decreased to about one third of its initial value after 3 days. On the contrary, the decrease of acyl chloride group content was scarcely observed even after 1 month upon storage

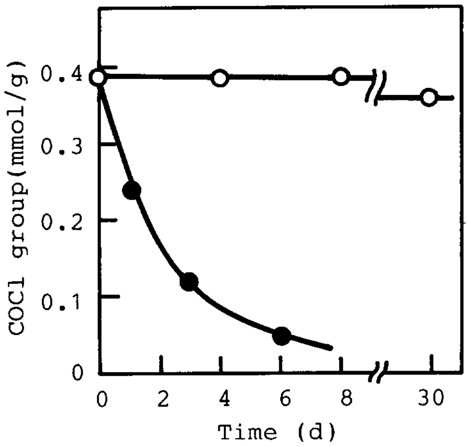


Figure 1. Stability of acyl chloride group on carbon black during storage at room temperature.

(○): stored in vacuo.
(●): stored in air.

in vacuo. Therefore, it was found that CB-COCl can be stored in vacuo without the loss of its activity.

Effect of Triethylamine on the Grafting Reaction

In general, a base such as triethylamine and pyridine is used in the reaction of acyl chlorides with active hydrogen compounds to scavenge hydrogen chloride liberated. Therefore, the effect of triethylamine on the grafting by the reaction of CB-COCl with SOD and SDA was investigated. The results are shown in Table I.

As shown in Table I, it is apparent that in the reaction with SDO, the grafting ratio considerably increased by the addition of triethylamine. Therefore, in such grafting reaction, it is necessary to scavenge hydrogen chloride liberated by the reaction. However, in the grafting of SDA, the effect of the addition of triethylamine was not observed. This may be due to the fact that SDA itself acts as a base. Furthermore, 1.0mmol of triethylamine was found to suffice for the removal of hydrogen chloride.

Grafting onto Carbon Black by the Reaction of Acyl Chloride Groups with Several Functional Polymers

The reaction of acyl chloride group on carbon black sur-

TABLE I
Effect of Triethylamine on the Reaction of CB-COCl with SDO and SDA

TEA	Grafting ratio (%)	
(mmol)	SDO(Mn=5.6x10^3)	SDA(Mn=1.8x10^3)
0	9.4	40.9
1.0	21.4	40.7
8.0	21.0	40.9

CB-COCl, 0.35g; polymer, 2.5mmol; 80°C; 20h.

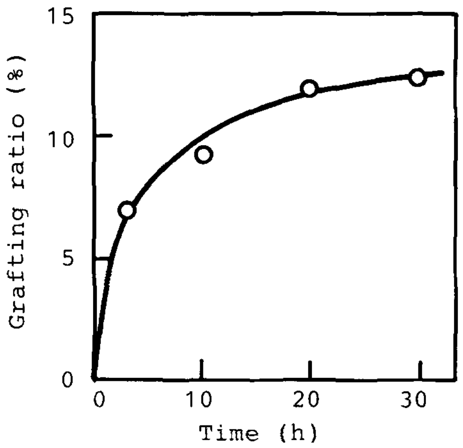


Figure 2. Grafting of PPG by the reaction of CB-COCl with PPG.

Neospectra II-COCl,0.35g; PPG (Mn=2.0x10^3), 2.5mmol; triethylamine, 1.0mmol; 130°C.

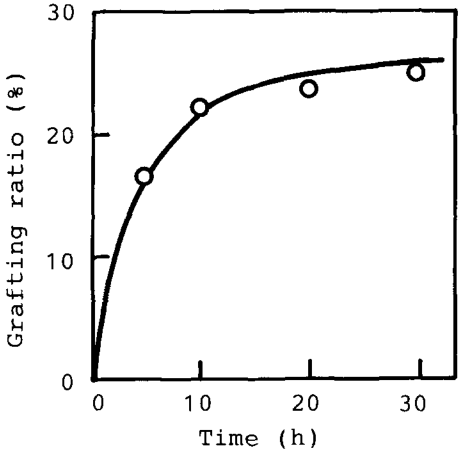


Figure 3. Grafting of PEI by the reaction of CB-COCl with PEI.

Neospectra II-COCl,0.35g; PEI (Mn=1.8x10^3), 2.5mmol; triethylamine, 1.0mmol; DMSO,7.0 ml; 80°C.

face with several polymers having functional groups such as hydroxyl group and amino group was carried out and the relationship between reaction time and the grafting ratio of these polymer onto carbon black was investigated. Figure 2 shows the results of the reaction of CB-COCl with PPG (Mn=2.0x10^3).

As shown in Figure 2, the grafting ratio after heating at 130°C for 30h was determined to be 13.5%. The adsorption ratio of PPG onto carbon black, which is determined after the Soxhlet extraction of PPG-adsorbed carbon black, was less than 5.0%. Therefore, it is concluded that acyl chloride group on carbon black reacts with terminal hydroxyl group of PPG to give PPG-grafted carbon black.

Figure 3 shows the result of the reaction of CB-COCl with PEI. Figure 3 clearly shows that PEI is effectively grafted onto carbon black by use of CB-COCl.

Further the application to graft various kinds of functional polymer was examined. Table II shows that PEG, PBG, PVA, SDO, SDA, and PEI are able to graft onto carbon black by the reaction of acyl chloride group with those functional groups of

TABLE II
Grafting onto Carbon Black by the Reaction of CB-COCl with Several Functional Polymers[a]

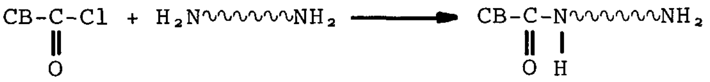
Polymer	$Mn \times 10^{-3}$	DMSO (ml)	Temp. (°C)	Grafting ratio(%)	Polymer grafted (μmol/g)
PPG	2.0	-	130	11.2	560
PEG	8.2	-	130	18.5	22.6
PBG	1.0	-	80	27.2	272
PBG	2.0	-	80	16.7	83.5
PVA	22.0	7.0	130	32.9[b]	15.0
PVA	66.0	7.0	130	41.6[b]	6.3
SDO	5.6	-	130	20.4	36.4
SDA	3.0	-	80	40.7	136
PEI	1.8	7.0	80	23.5	131
PEI	20.0	7.0	80	45.8	22.9

[a] CB-COCl, 0.35g; polymer, 2.5mmol; triethylamine, 1.0mmol;20h.
[b] CB-COCl, 0.25g; polymer, 0.015mmol; triethylamine, 1.0mmol; 20h.

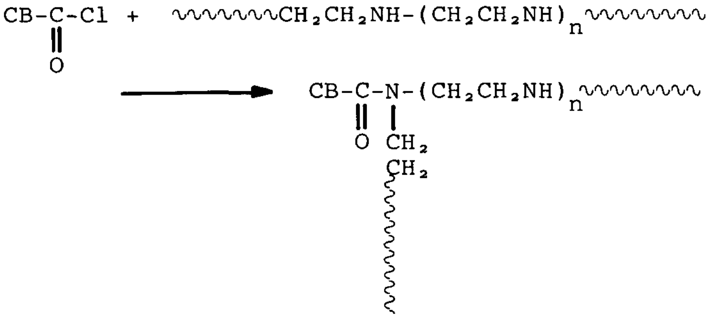
the polymers. These carbon blacks obtained from the reaction gave a stable colloidal dispersion in organic solvents.

Based on the above result, it is considered that by the reaction of CB-COCl with hydroxyl and with amino group of the polymers, these polymers are grafted with ester and amide bond, respectively (Eqs.2 and 3). Moreover, in the reaction of PEI, not only terminal amino group but also imino group in polymer chain probably react with acyl chloride group (Eq.4).

$$\mathrm{CB{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}Cl} + \mathrm{HO}\sim\sim\sim\sim\mathrm{OH} \longrightarrow \mathrm{CB{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O}\sim\sim\sim\sim\mathrm{OH} \qquad \text{(Eq.2)}$$



$$\mathrm{CB{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}Cl} + \mathrm{H_2N}\sim\sim\sim\sim\mathrm{NH_2} \longrightarrow \mathrm{CB{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}}\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}\sim\sim\sim\sim\mathrm{NH_2} \qquad \text{(Eq.3)}$$



$$\mathrm{CB{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}Cl} + \sim\sim\sim\mathrm{CH_2CH_2NH{-}(CH_2CH_2NH)_n}\sim\sim\sim \longrightarrow \mathrm{CB{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}}\underset{\underset{\underset{\sim\sim\sim}{\mathrm{CH_2}}}{\underset{\mathrm{CH_2}}{|}}}{\mathrm{N}}\mathrm{{-}(CH_2CH_2NH)_n}\sim\sim\sim \qquad \text{(Eq.4)}$$

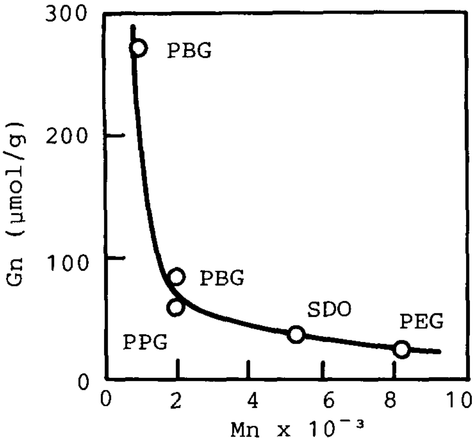


Figure 4. Relationship between the number of grafted polymer (Gn) and its molecular weight (Mn).

Effect of Molecular Weight on the Grafting Reaction

In order to clear the effect of molecular weight on the grafting onto carbon black, the relationship between average number molecular weight (Mn) of diol-type polymer (PPG, PBG, PEG, SDO) and the number of grafted polymer chain (Gn) was shown in Figure 4.

Figure 4 shows that the number of polymer molecules grafted onto carbon black extremely decrease with an increase of molecular weight of polymers. The result suggests that the reactivity of polymer of higher molecular weight with acyl chloride group on carbon black is lower than that of lower molecular weight. A similar tendency has been reported in the grafting by the reaction of silica with polystyrene having terminal chlorosilane group (8). Further investigation for the effect of molecular weight on the grafting is now in progress.

In conclusion, by the use of active carbon black having acyl chloride group, it became feasible to graft various kinds of functional polymers, having hydroxyl groups and amino groups, onto carbon black surface.

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