

Grafting of Functional Polymers onto Reactive Carbon Black Having Chlorotriazinyl Groups

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ABSTRACT: The grafting of various polymers onto reactive carbon black, based on the reaction of chlorotriazinyl groups introduced onto the surface with functional polymers, was investigated. The introduction of chlorotriazinyl groups onto carbon black was achieved by the reaction of 2,4,6-trichloro-1,3,5-triazine with phenolic hydroxyl groups on the surfaces of carbon blacks. The amount of chlorotriazinyl groups introduced onto carbon black Neospectra II was determined to be 0.12 meq g^{-1} . This value corresponds to about 50% of the phenolic hydroxyl groups on the carbon black. The chlorotriazinyl groups easily reacted with polypropylene glycol (PPG), silicone diol (SDO), silicone diamine (SDA) and polyethyleneimine (PEI) to give polymer-grafted carbon blacks. The percentage of grafting of PPG ($\bar{M}_n = 2.0 \times 10^3$) and PEI ($\bar{M}_n = 1.8 \times 10^3$) was estimated to be 23.6% and 45.7%, respectively. The percentage of grafting of polymers increased with an increase in molecular weight, but the number of grafted polymer chains decreased. The polymer-grafted carbon black obtained from the reaction gave a stable colloidal dispersion in tetrahydrofuran.

KEY WORDS Reactive Carbon Black / Grafting / Chlorotriazinyl Group / 2,4,6-Trichloro-1,3,5-triazine / Phenolic Hydroxyl Group / Polypropylene Glycol / Silicone Diol / Silicone Diamine / Polyethyleneimine / Stability of Dispersion /

The grafting of polymers onto carbon black has been achieved by the polymerization of various monomers initiated by active sites, such as peroxyester, potassium carboxylate, and acylium perchlorate groups, introduced onto the surface.¹ Although the polymer was effectively grafted from carbon black in the polymerizations, it was generally difficult to control the molecular weight of grafted polymer on carbon black. On the contrary, grafting by the reaction of reactive carbon blacks with polymers enabled us not only to control the molecular weight of grafted polymer chains but also to graft various commercial available functional polymers.

In our preceding papers, we reported the preparation of some reactive carbon blacks having acyl chloride,² acyl azide,^{3,4} or blocked

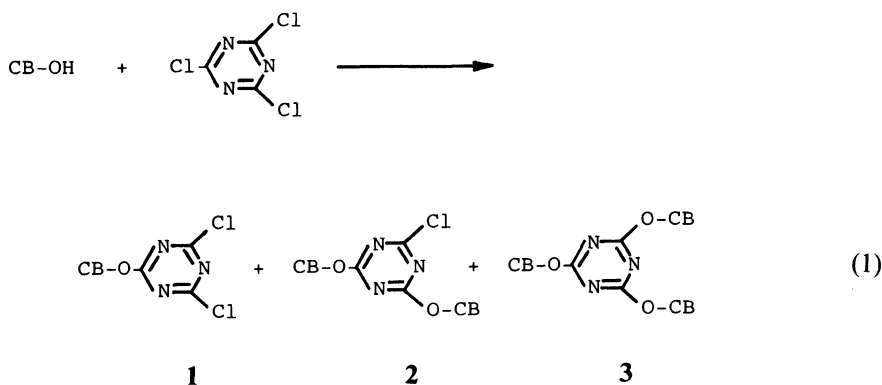
isocyanate groups on the surfaces.⁴ These reactive carbon blacks reacted with functional polymers having hydroxyl, carboxyl, or amino group to give polymer-grafted carbon blacks.²⁻⁴ Furthermore, it has been demonstrated that the percentage of grafting increased with an increase of molecular weight of the polymer, but the number of polymer chains decreased.⁴

On the other hand, cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) readily reacts with hydroxyl and amino compounds. For instance, cyanuric chloride has been used to immobilize enzymes to water-insoluble supports for affinity chromatography.^{5,6} It has been reported that cyanuric chloride can be used as a linking agent for the attachment of hydroxymethylferrocene to a pyrolytic graphite electrode.⁷ No

attempt, however, was made to use cyanuric chloride as a linking agent for the grafting of polymer onto carbon black.

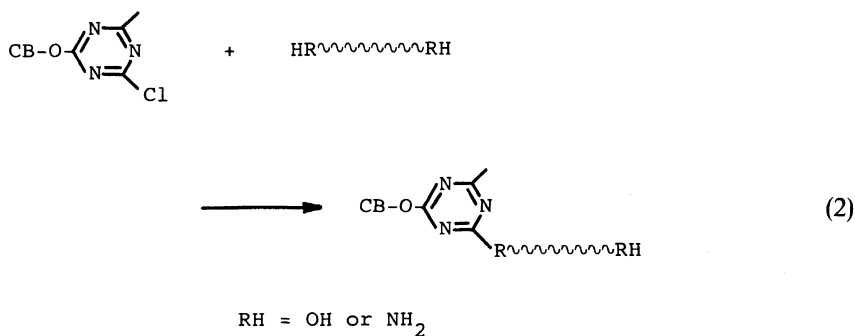
The reactive carbon black having chlorotriazinyl groups has the following advantages: (1) the introduction of chlorotriazinyl groups onto carbon black can be achieved by one-step reaction. (2) phenolic hydroxyl groups on carbon black can be used for the attachment of

the reactive group. (3) although the possibility of the formation of **2** and **3** besides **1** shown in Equation 1 is present in the reaction of carbon black with cyanuric chloride, if **1** can be preferentially obtained by the control of the reaction conditions, one chlorotriazinyl group has two active chlorine atoms whose reactivity corresponds to acyl chloride groups.



In the present paper, we wish to report on the grafting of various polymers by use of reactive carbon black having chlorotriazinyl

groups as shown in eq 2. Moreover, the effect of molecular weight on the grafting is discussed.



EXPERIMENTAL

Materials

Channel blacks Neospectra II (Columbian Carbon Co.; BET specific surface area, $906 \text{ m}^2 \text{ g}^{-1}$) and FW 200 (Degussa A.G.; $460 \text{ m}^2 \text{ g}^{-1}$) were dried *in vacuo* at 110°C be-

fore use. Furnace black Philblack O (Philips Petroleum Co.; $79.6 \text{ m}^2 \text{ g}^{-1}$) was extracted with benzene by a Soxhlet apparatus to remove resinous substances present on the surface and also dried *in vacuo* at 110°C before use.

Cyanuric chloride obtained from Tokyo Kasei Kogyo Co., Ltd., Japan was recrystallized from carbon tetrachloride. Dioxane

and tetrahydrofuran (THF) were refluxed over sodium and distilled twice.

n-Butyllithium (BuLi) (about 5% hexane solution) and 2,4-dinitrofluorobenzene obtained from Wako Pure Chemical Industries Ltd., Japan, were used without further purification. Other reagents and solvents were used after ordinary purification.

Polymers

Diol-type polypropylene glycol (PPG; $\bar{M}_n = 2.0 \times 10^3$) was obtained from Wako Pure Chemical Industries Ltd. Polyethyleneimine (PEI; $\bar{M}_n = 1.8 \times 10^3$) was obtained from Nippon Shokubai Kagaku Kogyo Co., Ltd., Japan. Silicone diol (SDO; $\bar{M}_n = 1.0 \times 10^3$, 1.8×10^3 , 3.2×10^3 , and 5.6×10^3) and silicone diamine (SDA; $\bar{M}_n = 1.7 \times 10^3$) were obtained from Shin-Etsu Chemical Industries Co., Ltd., Japan. All the polymers were dried *in vacuo* below 80°C before use.

Preparation of Carbon Black Having Phenolic Hydroxyl Groups

To introduce hydroxyl groups onto the surfaces of carbon blacks, carbon blacks were treated with BuLi solution and then hydrolyzed with water.⁸ A typical example is as follows: Into a flask containing a mixture of 5.0 g of carbon blacks and 60.0 ml of THF, 10.0 ml of the BuLi solution were charged. The reaction mixture was stirred at a room temperature under dry nitrogen. After 2 h, the mixture was poured into a large amount of distilled water to hydrolyze the reacted carbon blacks. The carbon blacks were isolated by filtration, washed with distilled water until the filtrate was neutral, and finally dried *in vacuo* at 80°C. The content of hydroxyl groups of this sample was determined to be 1.09 meq/g according to the method previously reported.⁹

Treatment of Carbon Black with 2,4-Dinitrofluorobenzene

Phenolic hydroxyl groups on the surfaces of carbon black were blocked by reaction with

2,4-dinitrofluorobenzene.^{10,11} The resultant carbon blacks were inactive to the reaction with cyanuric chloride. Into a flask, 5.0 g of Neospectra II, 60.0 ml of *N,N*-dimethylformamide, 30.0 ml of aqueous solution of NaHCO₃ (3.0%), and 2.5 ml of 2,4-dinitrofluorobenzene were charged. The reaction mixture was stirred at a room temperature for 24 h. After filtration, the resulting carbon black was extracted with methanol for 50 h and then water for 50 h using a Soxhlet apparatus.

Preparation of Reactive Carbon Blacks

Into a flask, 5.0 g of the carbon black with phenolic hydroxyl groups, 1.0 g cyanuric chloride, 0.5 ml of pyridine, and 60.0 ml of dioxane were charged. The reaction mixture was stirred with a magnetic stirrer under nitrogen at 80°C for 24 h. After the mixture was filtered, the obtained crude reactive carbon blacks were extracted with THF using a Soxhlet apparatus to remove unreacted cyanuric chloride. The reactive carbon blacks having chlorotriazinyl groups were dried *in vacuo* at 110°C and stored in the dark *in vacuo*.

Chlorine and nitrogen atoms on carbon blacks were determined by a Vorhard method¹² and a semi-micro-Kjeldahl procedure,¹³ respectively.

Grafting Reactions of Reactive Carbon Black with Polymers

Reactions of reactive carbon black with polymers, such as PPG, SDO, PEI, and SDA, were carried out in the absence of solvents. A typical example is as follows: Into a flask, 0.30 g of reactive carbon black, 2.5 mmol of the polymers, and 0.1 ml of pyridine were charged. The reaction mixture was stirred with a magnetic stirrer at 80°C under nitrogen.

Determination of Percentage of Grafting

After the grafting reaction, 10.0 ml of methanol were added to the reaction mixture and stirred at about 30°C for 24 h to block the

unreacted active chlorines of chlorotriazinyl groups on the grafted carbon black. The grafted carbon blacks were dispersed in THF and the dispersion was centrifuged at 1.0×10^4 rpm, because the grafted carbon blacks passed through filter paper. The carbon black precipitated was heated at 100°C for 24 h to aggregate the carbon black particles. Subsequently, it was extracted with benzene using a Soxhlet apparatus to remove the unreacted polymer and dried *in vacuo* at 100°C . As dispersing and extracting solvents for PEI, methanol was used. The percentage of grafting was calculated by the following equation:

Percentage of grafting (%)

$$= \frac{\text{Polymer-grafted carbon black (g)} - \text{Carbon black used (g)}}{\text{Carbon black used (g)}} \times 100$$

Sedimentation of Polymer-Grafted Carbon Black

Polymer-grafted carbon black (0.30 g) was dispersed in 100 ml of THF with a magnetic stirrer and the dispersion was allowed to stand at a room temperature. After a definite time, 5.0 ml of dispersion liquid were taken out with a pipet and the content of carbon black dispersed was determined. The stability of dispersion was determined by the following equation:

Stability of dispersion (%)

$$= \frac{\text{Carbon black dispersed after standing (g)}}{\text{Carbon black dispersed before standing (g)}} \times 100$$

RESULTS AND DISCUSSION

Reactions of Cyanuric Chloride with Phenolic Hydroxyl Groups on Carbon Black

Phenolic hydroxyl groups on carbon black are capable of undergoing chemical reaction.¹⁴ Therefore, the reaction of cyanuric chloride with carbon black Neospectra II was carried out at 80°C in the presence of pyridine and the

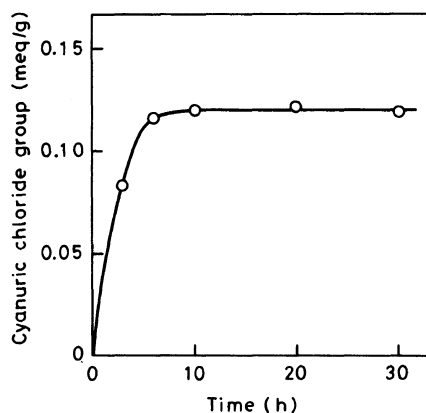


Figure 1. Introduction of chlorotriazinyl groups onto the surface of carbon black. Neospectra II, 5.0 g; cyanuric chloride, 1.0 g; dioxane, 60.0 ml; pyridine, 0.5 ml; 80°C .

chlorotriazinyl groups introduced onto the surface were determined by nitrogen analysis. The results are shown in Figure 1.

Figure 1 clearly shows that by the reaction of cyanuric chloride with Neospectra II, chlorotriazinyl groups can be introduced onto the surface. The number of chlorotriazinyl groups increased rapidly at the initial stage of the reaction, but not after 10 h. Thus, the reaction at 80°C for 10 h is required for the introduction of chlorotriazinyl groups onto carbon black.

To clarify the reaction site on carbon black, the reaction of cyanuric chloride with various carbon blacks was carried out and the chlorotriazinyl groups introduced were compared with the content of the phenolic hydroxyl groups of those carbon blacks. The results are shown in Table I.

Table I clearly shows that chlorotriazinyl groups can be introduced onto not only channel black but also furnace black. The number of chlorotriazinyl groups introduced onto the surface increased with content of phenolic hydroxyl groups. The number of chlorotriazinyl groups introduced onto BuLi- H_2O -treated Neospectra II,⁸ whose hydroxyl group content was increased by about 4.5 times,

Table I. Chlorotriazinyl groups introduced onto various carbon blacks^a

Carbon black	OH meq g ⁻¹	Chlorotriazinyl group/meq g ⁻¹
Neospectra II	0.24	0.12
FW 200	0.10	0.06
Philblack O	0.02	0.01
Treated-Neospectra II ^b	1.09	0.35
Treated-Neospectra II ^c	trace	trace

^a Carbon black, 5.0 g; cyanuric chloride, 1.0 g; dioxane, 60.0 ml; pyridine, 0.5 ml; 80°C; 24 h.

^b Treated with BuLi followed by H₂O.

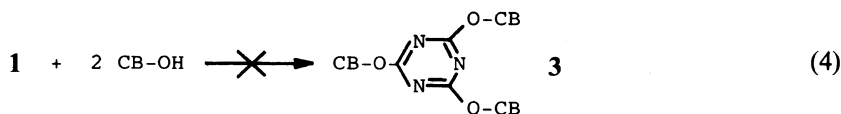
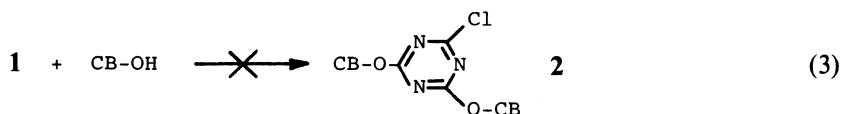
^c Treated with 2,4-dinitrofluorobenzene.

increased to 3 times that of untreated Neospectra II.

When phenolic hydroxyl groups on carbon black were blocked by treatment of 2,4-dinitrofluorobenzene,^{10,11} chlorotriazinyl groups

onto carbon black were hardly introduced. This suggests that the cyanuric chloride adsorbed on carbon black surface is almost removed by extraction with THF.

It is well known that cyanuric chloride reacts with hydroxy compounds, such as alcohols and phenols, in the presence of bases to give 2-alkoxy, 2,4-dialkoxy, and 2,4,6-trialkoxy triazine.^{15,16} Therefore, the possibility of the formation of **1**, **2**, and **3**. (Shown in eq 1) is present in the reaction of carbon black with cyanuric chloride. The chlorine analysis of cyanuric chloride-treated carbon black, however, indicates that preferential formation of **1**: the ratio of chlorine to nitrogen content was about 2:3. This suggests that active chlorine atoms of **1** no longer react with carbon black, because solid-solid phase reaction to give **2** or **3** hardly proceeds (eq 3 and 4).



Based on the above results, it is concluded that cyanuric chloride reacts with phenolic hydroxyl groups on a carbon black surface to give reactive carbon black having chlorotriazinyl groups (**1**).

Grafting of Polymers Using Reactive Carbon Blacks

The grafting of PPG and SDO onto carbon blacks, which is based on the reaction of these polymers with chlorotriazinyl groups on carbon blacks, was carried out at 80°C. Figure 2 shows the relationship between the percentage of grafting and reaction time.

As shown in Figure 2, the percentage of

grafting of both PPG and SDO increased rapidly at the initial stage of the reaction, but no longer increased after 10 h.

Table II shows the relationship between the amount of chlorotriazinyl groups and the percentage of grafting.

When untreated Neospectra II was mixed with PPG or SDO, 12–13% of the polymer was retained on the surface even after Soxhlet extraction with benzene. But the percentage of grafting onto carbon black obtained from the reaction with reactive carbon black was larger than that of polymer retained on the untreated carbon black. The percentage of grafting of PPG and SDO was found to increase with

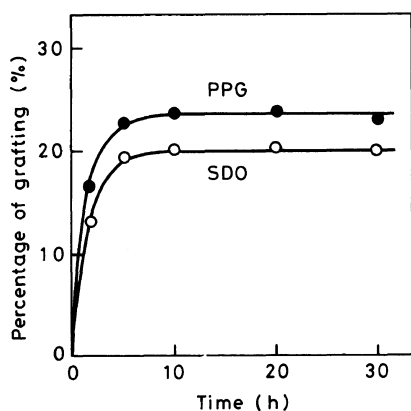


Figure 2. Grafting of PPG or SDO by reactive carbon black having chlorotriazinyl groups. Neospectra II, 0.30 g; polymer, 2.5 mmol; pyridine, 0.1 ml; 80°C.

Table II. Grafting of PPG or SDO by reactive carbon black having chlorotriazinyl groups^a

Carbon black	Chlorotriazinyl groups/meq g ⁻¹	Percentage of grafting/%	
		PPG	SDO
Untreated Neospectra II	0	13.0 ^b	12.8 ^b
FW 200	0.06	15.2	16.4
Neospectra II	0.12	23.6	20.4
Neospectra II	0.35	26.6	23.2

^a Carbon black, 0.30 g; polymer, 2.5 mmol; pyridine, 0.1 ml; 80°C; 10 h.

^b Polymer retained on the surface.

content of chlorotriazinyl groups on the carbon black. Thus, chlorotriazinyl groups on carbon black react with polymers having hydroxyl groups to give polymer-grafted carbon black.

The grafting of various polymers having hydroxyl or amino groups onto the reactive carbon black was carried out as shown in Table III.

Polymers such as PPG, SDO, PEI, and SDA

Table III. Grafting of various polymers by carbon black having chlorotriazinyl groups^a

Polymer ^b	$\bar{M}_n \times 10^{-3}$	Percentage of grafting/%	Number of grafted polymer/mmol g ⁻¹
PPG	2.0	23.6	0.12
SDO	1.8	20.4	0.11
PEI	1.8	45.7	0.25
SDA	1.7	33.6	0.20

^a Reaction conditions are given in Table II.

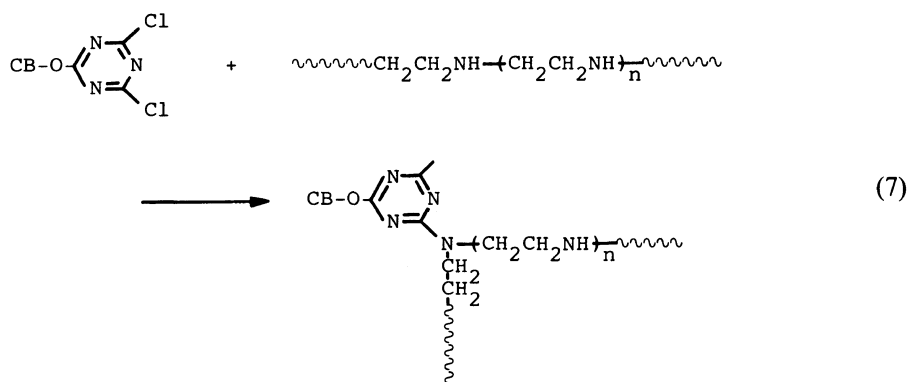
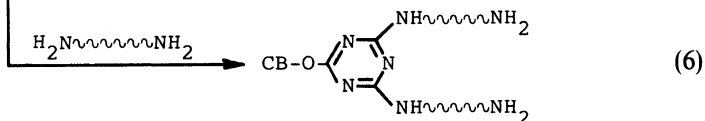
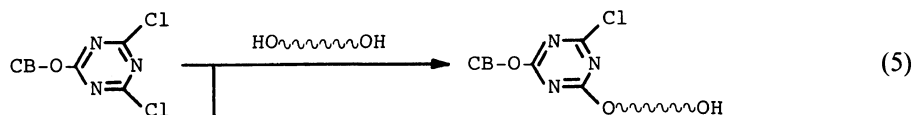
^b PPG, polypropylene glycol; SDO, silicone diol; PEI, polyethyleneimine; SDA, silicone diamine.

can be grafted onto the reactive carbon black by reaction of chlorotriazinyl groups on the surface with the hydroxyl or the amino groups of these polymers. The reactivities of PEI and SDA having amino groups was found to be larger than these of PPG or SDO, due to the high reactivity of amines to chlorotriazinyl groups.¹⁵

As mentioned above, one chlorotriazinyl group on carbon black has two reactive chlorine atoms. Therefore, the number of reactive chlorine atom on Neospectra II is calculated to be 0.24 meq g⁻¹, because the number of chlorotriazinyl groups introduced is 0.12 meq g⁻¹. As shown in Table III, the number of polymer grafted was 1.2–2.5 mmol g⁻¹. Accordingly, in the grafting of PPG and SDO, about 50% of the reactive chlorine atoms of chlorotriazinyl group was considered to remain unreacted after the grafting reaction. But in the grafting of PEI and SDA, 83–100% of the chlorine atom was consumed for the grafting.

The grafting schemes of these polymers having hydroxyl or amino groups are shown in eq 5 and 6. In the reaction of PEI, not only terminal amino groups but also imino groups in the polymer are considered to react with chlorotriazinyl groups (eq 7).

Grafting onto Reactive Carbon Black



Effects of Molecular Weight of Polymer on Grafting

Hamann *et al.* reported that in grafting by the reaction of chlorosilane-capped polystyrene with a silanol group on silica, the number of grafted polymer chains decreases with increase in the molecular weight of polymer.¹⁷ In a preceding paper, we reported that the number of grafted chains onto carbon black by reactions of acyl azide groups on the surface with polymers having hydroxyl groups decreased with increase in the molecular weight of these polymers.⁴ For purpose of confirming our previous result, the effects of molecular weight of polymers on the grafting by the reaction of reactive carbon black with SDO were investigated. Figure 3 shows the relationship between the molecular weight of SDO and percentage of grafting or number of polymer chains grafted onto carbon black.

The percentage of grafting increased with the molecular weight of SDO, but the number of grafted SDO chains decreased, due to the

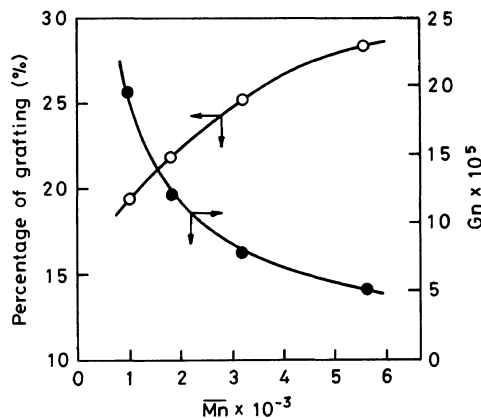


Figure 3. Relationship between molecular weight (\bar{M}_n) of SDO and percentage of grafting (the number of grafted polymer (G_n)).

fact that chlorotriazinyl groups are shielded by neighboring grafted chains. This is supported by the finding that the shielding effect on the grafting is enhanced with increase in the molecular weight of polymers.

Figure 4 shows the relationship between $\log \bar{M}_n$ and $\log G_n$ (G_n = the number of grafted

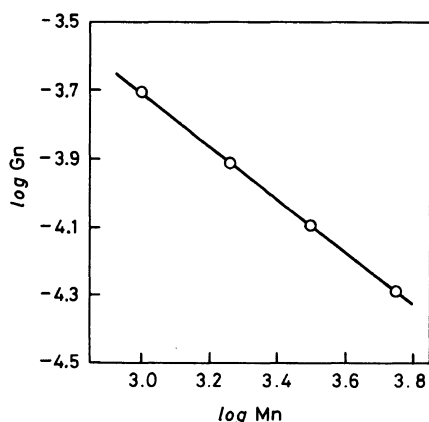


Figure 4. Relationship between $\log G_n$ and $\log \bar{M}_n$.

polymer chain). A plot of $\log \bar{M}_n$ vs. $\log G_n$ gave a straight line. The relationship between G_n and \bar{M}_n for SDO is thus given by the following equations:

$$G_n = 4.27 \times 10^{-2} \bar{M}_n^{-0.78}$$

This equation suggests that the number of grafted SDOs can be determined from its molecular weight. Furthermore, the equation is useful for the control of grafting of SDO onto carbon black.

Stability of Dispersion of PPG-Grafted Carbon Black

To clarify the properties of polymer-grafted carbon black, the stability of dispersion of PPG-grafted carbon black in THF was compared with that of untreated carbon black. The results are shown in Figure 5. Untreated carbon black in THF sedimented completely after 10 h. The stability of dispersion of carbon black in THF was scarcely improved by the adsorption of PPG onto carbon black and most of carbon black particles precipitated after 3 h. PPG-grafted carbon black, however, was found to give a stable colloidal dispersion in THF: the sedimentation of carbon black was no longer observed after 20 h.

The results indicate that the grafting of PPG is effective to improve the stability of dispersion of carbon black in organic solvents.

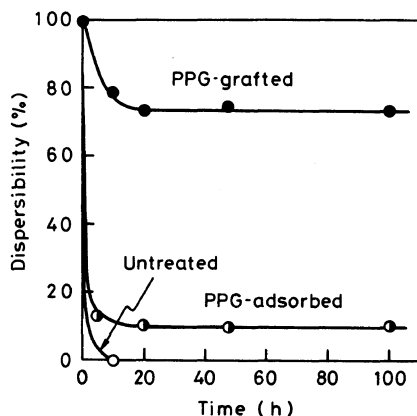


Figure 5. Stability of dispersion of PPG-grafted carbon black in THF at room temperature.

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