

Accounts

Functionalization of Carbon Material by Surface Grafting of Polymers

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Recent advances in surface grafting of polymers onto carbon materials, such as carbon black, graphite powder, and carbon fiber, and the application of polymer-grafted carbon materials as a novel functional materials have been mainly reviewed. The grafting of polymers onto the surface was achieved by (1) grafting onto process, (2) grafting from process, (3) polymer reaction process, and (4) stepwise growth by dendrimer synthesis methodology. For the grafting, surface functional groups, such as carboxyl and phenolic hydroxy groups, were used as grafting sites. For example, in the living cationic polymerization initiated by carbon black/$ZnCl_2$ system, carboxyl groups on the surface acted as initiating site and grafting site. In the surface grafting, polycondensed aromatic rings of carbon materials could be used as grafting sites by using ligand exchange reaction of polymers containing ferrocene moieties. It was demonstrated that, by the grafting of polymers onto carbon black surface, the dispersibility in solvent and the surface wettability were readily controlled by pH and temperature. By postgrafting of hydrophilic polymer to grafted hydrophobic chain on carbon black, amphiphilic carbon black was obtained. The applications of crystalline polymer-grafted carbon black as a novel gas sensor material and a positive temperature coefficient material are summarized.

Carbon black, graphite, and carbon fiber are well known as one of the industrially important and commercially available carbon materials.[1–3] Carbon black and graphite have excellent properties, such as heat, chemical and weather resistance, light weight, electro-conductivity, and low thermal expansion. In addition, carbon black is used industrially as a deep black pigment for polymer materials and especially as a conducting and reinforcing filler for rubber. Graphite powder and plates are widely used as an electrode of various electric cells and as conducting filler of polymer composite for an electric resistor and a heater.

On the other hand, carbon fiber has the desirable properties of high temperature resistance, high modulus, extremely high strength, low density, and chemical resistance. Therefore, carbon fiber is widely used as a reinforcing fiber of fiber reinforced plastics (FRP).

In general, dispersing fine carbon particles, such as carbon black and graphite powder, uniformly into a polymer or an organic solvent is very difficult because of aggregation of the powder. In addition, the mechanical properties of FRP are considered to depend on not only the mechanical properties of the polymer matrix, but also on the properties of interfacial regions between the carbon fiber and the matrix polymer.

The chemical and physical modifications of carbon black and carbon fiber surfaces, therefore, have been extensively studied. The chemical modification of surfaces is permanent, but physical modification is temporary. Among the permanent chemical modifications, the surface grafting of polymers, namely, chemical binding of polymers onto carbon black and carbon fiber surfaces, interests us for use in designing new functional carbon materials which have the excellent properties both of carbon black and graphite, such as electro-conductivity, heat-resistance, and chemical-resistance, and of grafted polymers, such as photosensitivity, curing ability, bioactivity, and pharmacological activity.[4–6]

Carbon black is classified into the following classes: channel black, furnace black, acetylene black, and thermal black. Channel black is produced by the incomplete oxidation of natural gas through impinging flames of the burning gas on a steel channel. Furnace black is produced by the thermal decomposition of aromatic residue oils in a furnace. Thermal black is produced by the thermal decomposition of hydrocarbon gases in the absence of a flame.

Carbon blacks typically contain about 90–99% elemental carbon, with oxygen and hydrogen as the other constituents.[7] Heteroatoms, mainly oxygen, are retained or bonded at the edges and corners of the polycondensed aromatic ring (hexagonal plane) or to carbon atoms in defect positions of the hexagonal plane. Therefore, carbon black has oxygen-containing groups, such as carboxyl, phenolic hydroxy, lactone, and quinonic oxygen groups on the surface.[7–9]

Graphite and carbon fiber also have surface functional groups, oxygen-containing groups, but the content is known to be small. The average particle size, specific surface area, and

Table 1. Properties of Carbon Black, Graphite Powder, and Carbon Fiber

Carbon Material	Surface area	Particle size	Functional group/mmol g^{-1}		
	$m^2\ g^{-1}$	nm	OH	COOH	CO
Philblack O[a)]	79.6	29.4	0.02	0	0.18
Neospectra II[b)]	906	15	0.24	0.40	0.92
Denkablack[c)]	65.0	65.0	0.02	0	0.01
Graphite powder	—	4000	0.01	0	0.08
Carbon fiber	—	6900[d)]	0.03	0.03	—

a) Furnace black, b) Channel black, c) Acetylene black, d) Fiber diameter.

functional group content of several carbon blacks, graphite powder, and carbon fiber are shown in Table 1. The content of phenolic hydroxy, carboxyl, and quinonic oxygen groups was determined by use of 2,2-diphenyl-1-picrylhydrazyl,[10] sodium bicarbonate,[11] and sodium borohydride.[12]

We have reported the grafting of various polymers such as vinyl polymer,[13,14] polyester,[15,16] polyether,[17,18] poly(organophosphazene),[19] and poly(dimethysiloxane)[20] onto carbon black surface using carboxyl and phenolic hydroxy groups as grafting sites. Furthermore, many experimental attempts by other researchers also have been made to graft polymers onto carbon black surface.[21,22] In comparison with carbon black, the surface grafting of polymers onto graphite powder and carbon fiber surface was rarely achieved, because graphite and carbon fiber have few functional groups as grafting sites, as shown in Table 1. In general, surface grafting onto graphite and carbon fiber must be achieved after the introduction of functional groups using conventional organic reactions, such as oxidation and electrophilic substitution reaction to polycondensed aromatic rings of the surface.[23,24]

In this account, our recent research topics on the surface grafting of polymers onto carbon materials, such as carbon black, graphite powder, and carbon fiber, and the application of the polymer-grafted forms of these carbons as the functional materials are mainly presented.

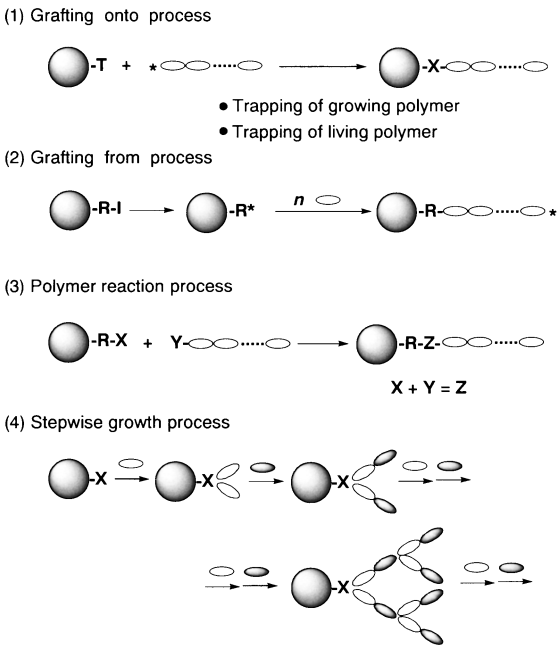
1. Methodology of Surface Grafting of Polymers

Several methodologies of the surface grafting of polymers onto powder and fiber have been developed for the preparation of graft copolymers. These methodologies can be applied to the preparation of polymer-grafted particle and fiber surfaces. In general, one of the following principles (Scheme 1) may be applied to prepare polymer-grafted carbon black, graphite, and carbon fiber.[4]

(1) Grafting onto process: the termination of growing polymer radical, cation, and anion, formed during the polymerization of various monomers initiated by conventional initiator in the presence of particle and fiber, and the deactivation of living polymer chain ends with functional groups on the particle and fiber surface.

(2) Grafting from process: the initiation of graft polymerization of various monomers from radical and ionic initiating groups previously introduced onto the particle and fiber surfaces.

(3) Polymer reaction process: the reaction of surface functional groups on particles and fibers with polymers having functional groups, such as hydroxy, carboxyl, and amino groups.



Scheme 1. Grafting of polymers onto carbon material surface.

(4) Stepwise growth process: the grafted polymer chains are grown from surface functional groups by repeated reaction of low molecular compounds by dendrimer synthesis methodology.

By process (1), although polymer-grafted particles can be obtained, the percentage of grafting onto particles is less than 10%, because of the preferential formation of ungrafted polymers. On the contrary, by use of living polymer, polymers with well defined molecular weight and narrow molecular weight distribution can be grafted onto the particle and fiber surface.

Process (2) is the one most favorable for the preparation of polymer-grafted particle and fiber with a high percentage of grafting. It is difficult, however, to control the molecular weight and number of grafted polymer chains.

An important characteristic of process (3) is that not only are the molecular weight and the number of grafted chains on the particle and fiber surface easily controlled, but also commercially available polymers having a well defined structure can be grafted.

In addition, by process (4), although dendrimer with theoretical structure was not easily grafted, hyperbranched polymers having a large number of terminal functional groups can

be grafted onto the surface.

2. Grafting of Polymers from Initiating Groups on the Surface of Carbon Black

We have achieved the anionic, cationic, and radical graft polymerization of various monomers onto carbon black initiated by azo[13] or peroxyester,[14] potassium carboxylate,[15,16] and acylium perchlorate groups[17,18] introduced onto the surface, respectively. The grafting of polymers onto graphite and carbon fiber surfaces from initiating groups on the surface has been also reported.[6,25,26]

For coverage of the above topics, readers are referred to review papers[4–6,27] and the references cited therein. This section singles out for consideration just a few topics of current interest.

In this account, the percentage of grafting is defined as the percentage of grafted polymer to carbon black and determined by the following Eq. 1:

$$\text{Grafting } (\%) = (A/B) \times 100, \quad (1)$$

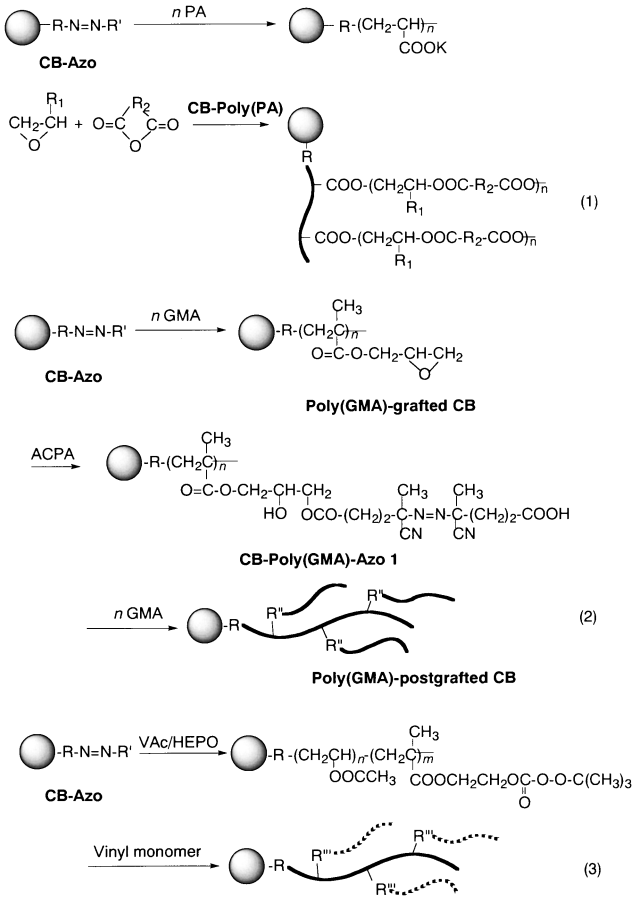
where A is weight of grafted polymer on carbon black surface and B is weight of carbon black: the weight of grafted polymer on the surface was estimated from weight loss when polymer-grafted carbon black was heated at 500 °C by a thermal analyzer.

2.1 Postgrafting from Pendant Initiating Groups of Grafted Chain on Carbon Black Surface. To prepare branched polymer-grafted carbon black with higher percentage of grafting, we have investigated on the grafting of polymers having pendant initiating groups, such as potassium carboxylate,[28] azo,[29] and peroxycarbonate groups,[30] onto the carbon black surface and the postgraft polymerization of vinyl monomers initiated by these pendant initiating groups of polymer chains grafted onto the surface as shown in Schemes 2 (1), (2), and (3), respectively.

The grafting of branched polymers onto carbon black surface is very interesting, because the surface properties of carbon black can be widely controlled from hydrophobic to hydrophilic (see Section 8.3 and 8.4).

2.1.1 Postpolymerization from Pendant Potassium Carboxylate Groups. The grafting of polymers having pendant potassium carboxylate groups was achieved by the radical polymerization of potassium acrylate (PA) initiated by azo groups previously introduced onto the surface.[28] The anionic alternating ring-opening copolymerization of epoxides with cyclic acid anhydrides was initiated by poly(PA)-grafted carbon black; branched polymers having polyester branches were effectively grafted onto the surface, as shown in Scheme 2 (1).

2.1.2 Postpolymerization from Pendant Azo Groups. The azo group pendant to grafted polymer on carbon black were introduced by the reaction of the pendant glycidyl (2,3-epoxypropyl) groups of grafted poly(glycidyl methacrylate) [poly(GMA)] with 4,4′-azobis(4-cyanopentanoic acid) (ACPA), as shown in Scheme 2 (2).[29] The contents of azo groups introduced onto poly(GMA)-postgrafted carbon black were determined to be 0.23 mmol/g by elemental analysis. This indicates that 9.2% of pendant glycidyl groups of grafted poly(GMA) on carbon black reacted with ACPA. The carbon



Scheme 2. Postgrafting from pendant initiating groups of grafted chain on carbon black surface.

black was abbreviated as CB-Poly(GMA)-Azo **1**.

It was confirmed that the postpolymerization of GMA is initiated by radicals formed by the decomposition of pendant azo groups of grafted poly(GMA) chain on carbon black to give branched poly(GMA)-grafted carbon black: by postgraft polymerization, the poly(GMA) grafting increased from 35% to 50%.[29] During the postpolymerization, no formation of gel was observed. This suggests that the coupling reaction between the growing polymer radicals from the grafted polymer on carbon black surface does not proceed, because the growing polymer radicals from the grafted polymer on the surface are fixed on the solid (carbon black).

It is well known that in the radical polymerization, the polymerization rate has a 0.5 order dependence on the initiator concentration because of bimolecular termination of growing polymer radicals. The effect of concentration of CB-Poly(GMA)-Azo **1** on the postpolymerization rate (Rp) was investigated. The result is shown in Fig. 1. It was found that the postpolymerization rate has 0.85 order dependence on the CB-Poly(GMA)-Azo **1** concentration. The value is larger than that of ordinary radical polymerization system. The same tendency was observed in radical graft polymerizations initiated by azo and peroxide groups introduced onto carbon black surfaces[13,14] and by the system consisting of cerium(IV) ion and alcoholic hydroxy groups on inorganic particle surfaces.[31]

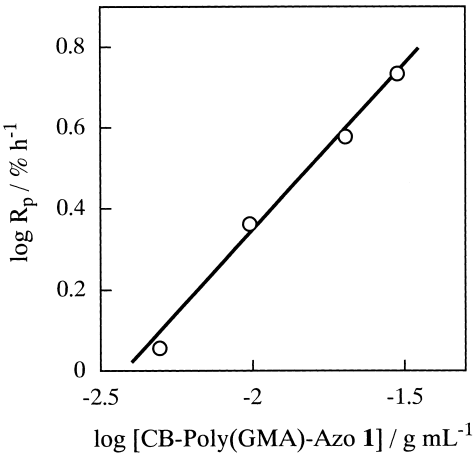


Fig. 1. Relationship between postpolymerization rate (Rp) and CB-Poly(GMA)-Azo **1** concentration ([CB-Poly (GMA)-Azo **1**]).

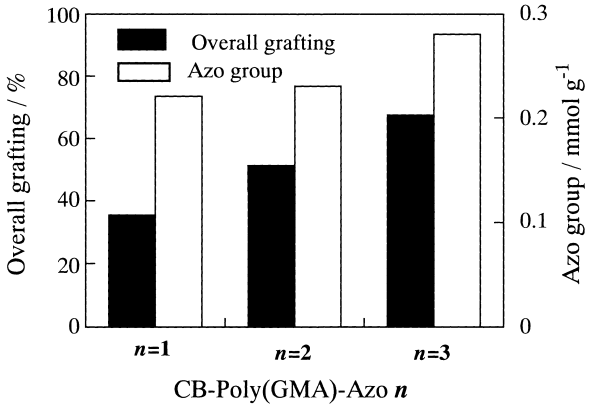


Fig. 2. Repeating postpolymerization of GMA initiated by azo groups introduced onto branched polymer-grafted carbon black (CB-Poly(GMA)-Azo ***n***). CB-Poly(GMA)-Azo ***n***, 0.30 g; GMA, 10.0 mL; 70 °C; 30 min.

These results suggest that unimolecular termination of growing polymer radicals from the grafted polymer chains of polymer-grafted carbon black proceeded in the initial stage of the polymerization. This may be due to the fact that the bimolecular termination of polymer radicals is inhibited, because the growing polymer radicals on the surface are fixed on the carbon black surface as mentioned above.

The introduction of azo groups to pendant glycidyl groups of branched poly(GMA)-postgrafted carbon black was repeated and repeating postpolymerization was investigated.[29] Branched poly(GMA)-postgrafted carbon black having pendant azo groups in the grafted branched poly(GMA), i.e., CB-Poly(GMA)-Azo **2**, was also prepared by the reaction of ACPA with pendant glycidyl groups of branched poly(GMA)-grafted carbon black obtained from the above postpolymerization using CB-Poly(GMA)-Azo **1.**

The repeating postpolymerization of GMA was found to be initiated by CB-Poly(GMA)-Azo **2** to give branched polymer-grafted carbon black: the overall grafting increased from 50% to 70%. The relationship between CB-Poly(GMA)-Azo ***n*** and overall grafting (the amount of azo groups introduced to grafted poly(GMA) on carbon black) is shown in Fig. 2. The percentage of overall grafting indicates the values after the repeating postpolymerization of GMA in the presence of CB-Poly(GMA)-Azo ***n***.

The percentage of overall grafting and the amount of azo groups increased with increasing repetitions of introduction of azo groups to grafted poly(GMA) on carbon black and the postpolymerization of GMA. These results suggest that the polymerization of GMA is initiated in the presence of poly(GMA)-grafted carbon black having pendant azo groups and that hyperbranched polymers are grafted onto the surface. However, the increase of azo groups introduced onto grafted polymer chain became small with increasing repeating times. This may be due to the fact that pendant glycidyl groups of branched poly(GMA) on the surface were blocked by grafted polymer chains with increasing repeating times of the postpolymerization.[29]

2.1.3 Postpolymerization from Pendant Peroxycarbonate Groups. Recently, we have investigated the grafting of polymers having pendant peroxycarbonate groups onto carbon black surface by the copolymerization of vinyl acetate (VAc) with *O*,*O*-*t*-butylperoxy *O*-2-(methacryloyloxy)ethyl monoperoxycarbonate (HEPO) initiated by azo groups introduced onto the surface, We have studied the postgraft polymerization of vinyl monomers initiated by the pendant peroxycarbonate groups of poly(VAc-*co*-HEPO)-grafted carbon black as shown in Scheme 2 (3).[30]

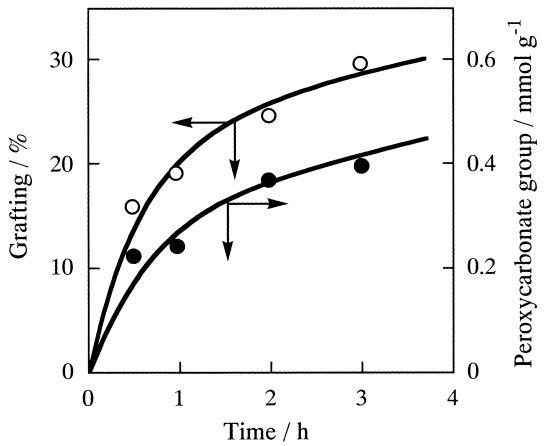


Fig. 3. Copolymerization of VAc with HEPO initiated by carbon black having azo groups. CB, 0.30 g; HEPO = VAc = 25 mmol; 80 °C.

Since the 10 h half-life temperature of HEPO is 104.3 °C,[32] the copolymerization of VAc with HEPO initiated by CB having azo groups was carried out at 80 °C: little thermal decomposition of HEPO was considered to occur at 80 °C. It was found that, in the copolymerization of VAc with HEPO initiated by CB-Azo, the percentage of grafting and the amount of peroxycarbonate groups of grafted polymer on carbon black increased with progress of the copolymerization and became constant about 28% and 0.40 mmol/g after 3 h, respectively (Fig. 3).

Table 2 shows the results of the postgraft polymerizations of

Table 2. Postpolymerization of Several Vinyl Monomers Initiated by Poly(VAc-*co*-HEPO)-Grafted Carbon Black

Vinyl monomer	*e*-Value	Time	Conversion	Postgrafting
		min	%	%
MMA	0.40	30	15.6	43.0
GMA	0.57	15	14.2	34.3
HEMA	0.20	30	1.4	63.9
Styrene	−0.80	120	0	0
VAc	−0.22	120	0	0
NVPD	−1.14	120	0.3	0

Poly(VAc-*co*-HEPO)-grafted CB (Grafting = 24.3%), 0.20 g; vinyl monomer, 80 mmol; 100 °C.

various vinyl monomers initiated by pendant peroxycarbonate groups of poly(VAc-*co*-HEPO)-grafted carbon black. It was found that the postpolymerization of vinyl monomers with positive *e*-value, such as methyl methacrylate (MMA), glycidyl methacrylate (GMA), and 2-hydroxyethyl methacrylate (HEMA) is successfully initiated by poly(VAc-*co*-HEPO)-grafted carbon black to give the corresponding polymer-postgrafted carbon black, but the poly(VAc-*co*-HEPO)-grafted carbon black has no ability to initiate the postpolymerization of vinyl monomers with negative *e*-value, such as styrene, VAc, and *N*-vinyl-2-pyrrolidone (NVPD).

The same behavior was reported during the polymerization of vinyl monomers in the presence of carbon black using peroxides, such as benzoyl peroxide, as an initiator.[33,34] These results are explained as follows. The radicals formed by the decomposition of peroxides have abilities to abstract hydrogen atoms from carbon black to give surface active radicals. The surface active radicals on carbon black readily capture the growing polymer radicals with negative *e*-value, but not those with positive *e*-value.[33,34] Therefore, the polymerization of vinyl monomers with negative *e*-value in the presence of carbon black using peroxides as initiator is markedly retarded, whereas that with positive *e*-value is not much retarded.

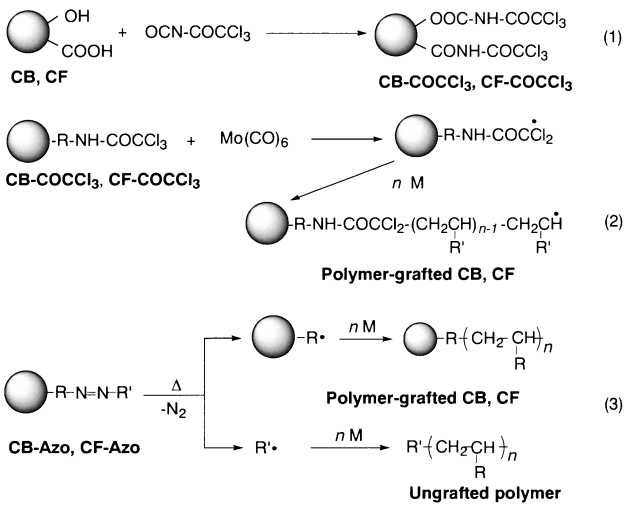
2.2 Effective Radical Grafting Initiated by the System Consisting of Trichloroacetyl Groups on the Surface and $Mo(CO)_6$. Bamford et al. have reported that a system consisting of haloalkyl compounds and transition metal carbonyl derivatives, such as $Mo(CO)_6$ and $Mn_2(CO)_{10}$, has the ability to initiate the radical polymerization of vinyl monomers.[35–38]

Therefore, the polymerization of vinyl monomers initiated by the system consisting of carbon black and carbon fiber having trichloroacetyl groups (CB-$COCCl_3$ and CF-$COCCl_3$) and $Mo(CO)_6$ system was investigated (Scheme 3 (2)).[39–41] The introduction of trichloroacetyl groups onto the surface was achieved by the reaction of surface carboxyl and phenolic hydroxy groups with trichloroacetyl isocyanate (Scheme 3 (1)).

Table 3 shows the results of the graft polymerization of vinyl monomers onto carbon fiber and carbon black initiated by CF-$COCCl_3$/$Mo(CO)_6$ and CB-$COCCl_3$/$Mo(CO)_6$ systems. The polymerizations of MMA, styrene, GMA, and HEMA successfully proceeded and the corresponding polymer was grafted onto carbon fiber and carbon black surfaces.

The grafting efficiency (the proportion of grated polymer to total polymer formed) in the graft polymerization of MMA initiated by the system consisting of CB-$COCCl_3$ (CF-$COCCl_3$) and $Mo(CO)_6$ was compared with that in the graft polymerization initiated by azo groups introduced onto carbon black (CB-Azo)[13] and carbon fiber surface (CF-Azo).[42] It was found that the grafting efficiency in the graft polymerization initiated by the system consisting of trichloroacetyl groups and $Mo(CO)_6$ was higher than that initiated by azo groups on the surface.

We have reported that the grafting efficiency in the graft po-

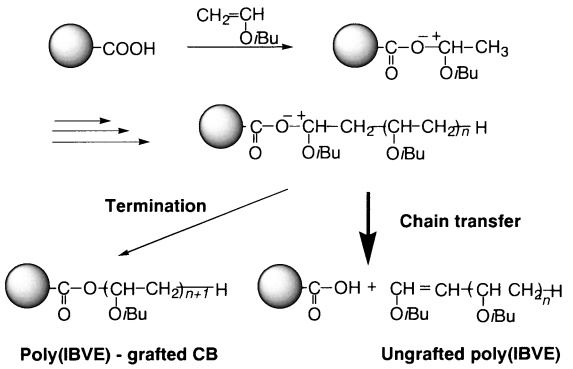


Scheme 3. Radical graft polymerization initiated by (1) CB-$COCCl_3$/$Mo(CO)_6$ system and (2) CB-Azo.

Table 3. Graft Polymerization of Vinyl Monomers Initiated by CF-$COCCl_3$/$Mo(CO)_6$ and CB-$COCCl_3$/$Mo(CO)_6$ System

Carbon	Monomer	Time	Grafting
		h	%
CF-$COCCl_3$	MMA	12	6.3
	Styrene	12	3.0
	GMA	1	2.3
	HEMA	0.25	3.6
CB-$COCCl_3$	MMA	4	38.8
	NVC	2	44.2

CF-$COCCl_3$ (CB-$COCCl_3$), 0.10 g; $Mo(CO)_6$, 0.01 g; monomer, 80 mmol; 70 °C.

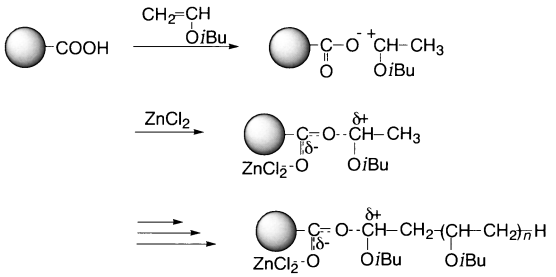


Scheme 4. Cationic polymerization of IBVE initiated by carboxyl groups on carbon black.

lymerization initiated by azo groups on the particle surface was about 50% at the initial stage of the polymerization, but decreased to few percent at the middle and the last stage of polymerization.[13,14,42–44] This indicates that, at the initial stage of the polymerization, both the propagation of polymer chains from surface radicals and the formation of ungrafted polymer by fragment radicals formed by the decomposition of azo groups on the surface proceed. However, the formation of ungrafted polymer by fragment free radicals (Scheme 3 (3)) and chain transfers of the growing polymer radicals from the surface preferentially proceed with progress of the polymerization.

On the other hand, in the initiating system consisting of trichloroacetyl groups on the surface and $Mo(CO)_6$, the propagation of polymer chains from the surface seems to preferentially proceed, because of the absence of formation of initiator fragments which produce ungrafted polymer. Therefore, the grafting efficiency in the graft polymerization initiated by the system consisting of trichloroacetyl groups and $Mo(CO)_6$ was considerably higher than that in the polymerization initiated by azo groups on the surface.

2.3 Living-like Cationic Polymerization Initiated by Carboxyl Groups on Carbon Black and $ZnCl_2$ System. We have pointed out that carboxyl groups present on carbon black and carbon fiber surfaces have the ability to initiate the cationic polymerization of vinyl monomers, such as isobutyl vinyl ether (IBVE), *N*-vinylcarbazole, and α-methylstyrene.[45–48] During such polymerization, a part of polymer was grafted onto the surface, but the percentage of grafting onto carbon black and carbon fiber was less than 10%. The rate of the polymerization was slow and the number average molecular weight (M_n) of poly(IBVE) was very small: M_n = 1000–4000. The molecular weight distribution of poly(IBVE) became broad with progress of the polymerization. These results indicate that the cationic polymerization is initiated by proton addition from surface carboxyl groups to IBVE and that the propagation proceeds with carboxylate anion as counter anion, as shown in Scheme 4. The M_n of polymer became small because of preferential chain transfer reaction of propagating cation. On the other hand, the grafting of polymer onto carbon black is considered to be due to ester formation between the propagating cation and the carboxylate anion (Scheme 4). In such polymerization, however, ungrafted polymer was formed



Scheme 5. Living cationic polymerization initiated by carbon black/$ZnCl_2$ system.

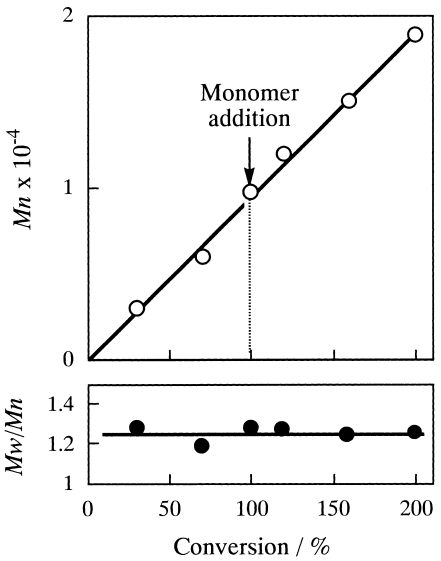


Fig. 4. Conversion vs M_n and M_w/M_n curves in the cationic polymerization of IBVE initiated by the carbon black/$ZnCl_2$ system. Carbon black, 0.10 g; IBVE, 4.0 mmol; $ZnCl_2$, 0.20 mmol; total volume (toluene), 9.0 mL; 0 °C.

in preference to grafting onto carbon black. Therefore, it is considered that poly(IBVE) with lower molecular weight and broad molecular weight distribution is obtained in the cationic polymerization initiated by carboxyl groups on carbon black and carbon fiber surfaces.

It has been recently reported that living cationic polymerization of vinyl ethers can be achieved by stabilization of a growing carbocation with a suitably nucleophilic counteranion.[49–52] For example, the cationic living polymerization of IBVE was reported to be initiated by nitro-substituted benzoic acid/$ZnCl_2$[51] and $CF_3COOH/ZnCl_2$ systems.[52] In the polymerization, a growing carbocation was considered to be stabilized by a binary counter anion, $RCOO^-\cdots ZnCl_2$. Therefore, the effect of $ZnCl_2$ addition on the cationic polymerization of IBVE initiated by carboxyl groups on carbon black surfaces was investigated (Scheme 5).[53]

Figure 4 shows the relationship between conversion and M_n of poly(IBVE) obtained from the above polymerization. The M_n of poly(IBVE) was found to be directly proportional to monomer conversion. These results suggest that each propagating carbocation was stabilized by suitably nucleophilic counter anion, $CB\text{-}COO^-\cdots ZnCl_2$, and the polymerization of

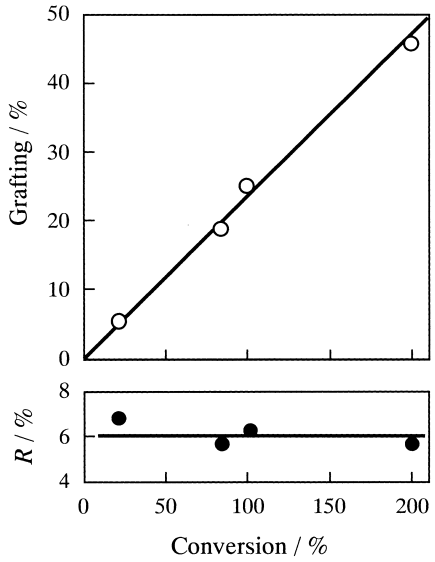
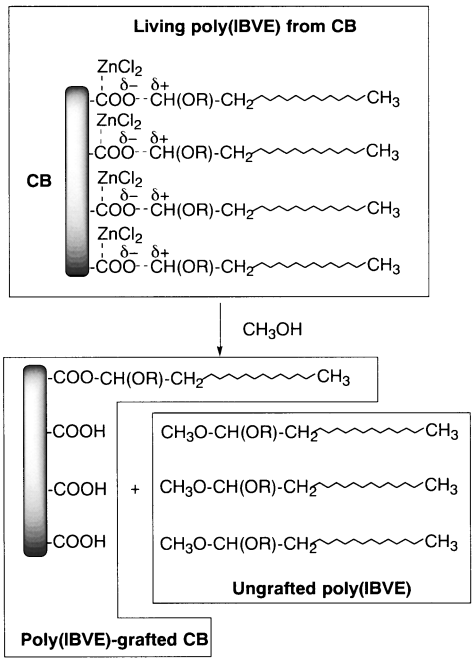


Fig. 5. Conversion vs percentage of grafting and R in the cationic polymerization of IBVE initiated by the carbon black/$ZnCl_2$. Reaction conditions are given in Fig. 4. R; percentage of carboxyl groups used for the termination of living poly(IBVE).



Scheme 6. Grafting of poly(IBVE) onto carbon black during the living cationic polymerization initiated by carbon black/$ZnCl_2$ system.

IBVE initiated by carbon black in the presence of $ZnCl_2$ shows the living nature of the polymerization.

The living nature of the IBVE polymerization initiated by carbon black/$ZnCl_2$ system was further demonstrated by a so-called "monomer addition" experiment. As shown in Fig. 4, the added IBVE feed was smoothly polymerized at nearly the same rate as the first charge was. After the monomer addition, the M_n of poly(IBVE) further increased in direct proportion to monomer conversion as it did in the first stage. This result indicates that long-lived poly(IBVE) was formed.

The M_n of poly(IBVE) obtained was in excellent agreement with the value calculated by assuming the poly(IBVE) chain forms per unit carboxyl group on carbon black surfaces. The molecular weight distribution of poly(IBVE) obtained from the initiating system was narrower (M_w/M_n = 1.20∼1.30) than that obtained from the polymerization initiated by carbon black alone.

These results suggest that, in the presence of $ZnCl_2$ with its strong electron-withdrawing nature, carbon black induces living cationic polymerization by stabilization of growing carbocation with counter anion (CB-$COO^-\cdots ZnCl_2$), as shown in Scheme 5.

It has been reported that poly(IBVE) obtained from living polymerization initiated by benzoic acid/$ZnCl_2$ system, which was quenched with methanol, has both ester and acetal terminal groups.[51] Therefore, it is expected that the grafting of poly(IBVE) onto carbon black surface proceeds after the quenching of living polymer formed in the polymerization initiated by carbon black/$ZnCl_2$ system. Figure 5 shows the relationship between conversion and percentage of poly(IBVE) grafting onto carbon black surface. The percentage of grafting was found to be directly proportional to conversion.

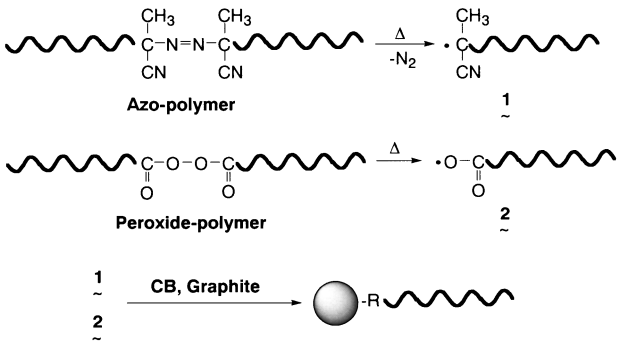
In addition, Fig. 5 also shows the relationship between conversion and R, percentage of carboxyl groups used for the termination of living poly(IBVE) (grafting efficiency). The result indicates that during the polymerization, in spite of conversion, about 6% of living ends of poly(IBVE) were terminated with ester bonds to give poly(IBVE)-grafted carbon black and a large amount (about 94%) of living ends were terminated with acetal bonds to give ungrafted poly(IBVE) when the living polymerization was quenched with methanol, as shown in Scheme 6.

The M_n values and molecular weight distributions of grafted and ungrafted poly(IBVE) are considered to be equal, because the polymerization of (IBVE) is started instantaneously from all carboxyl groups on carbon black surface and the grafted and ungrafted poly(IBVE) are formed when the polymerization is quenched with methanol. Little evidence of ester bond of grafted poly(IBVE) was obtained by spectroscopic methods. However, the grafted poly(IBVE) on carbon black surface was able to be removed from the surface by the treatment with methanol solution of potassium hydroxide. This indicates that poly(IBVE) is grafted onto the surface with ester bonds.

We have also reported that the living-like cationic polymerization of IBVE was readily initiated by carboxyl groups on carbon black/$EtAlCl_2$ system in the presence of 1,4-dioxane as an added base.[54] The M_n of poly(IBVE) obtained from the above polymerization system was also directly proportional to monomer conversion and the M_n of poly(IBVE) was inversely proportional to carboxyl group content of carbon black surface. The percentage of poly(IBVE) grafting onto the surface also reached 40–50%.

3. Grafting of Polymers by Radical Trapping

Carbon black is well known as a strong radical scavenger.[55,56] Therefore, the radical polymerization in the presence



Scheme 7. Grafting of polymers onto carbon materials by trapping of polymer radicals formed by the thermal decomposition of azo-polymer and peroxide-polymer.

of carbon black was inhibited and/or retarded, because of the trapping of growing polymer radical and initiating radical by carbon black surface. During the polymerization, a part of the polymer formed was grafted onto the surface, but the percentage of grafting was less than 5–10%, because of preferential trapping of low molecular primary radicals formed by the decomposition of initiator.[33,34]

Therefore, it is expected that polymer radicals formed by the decomposition of macro-initiators, such as azo-polymer and peroxide-polymer, will be successfully trapped by carbon black surface because of the absence of low molecular weight radicals.

3.1 Trapping of Polymer Radicals Formed by the Decomposition of Macro-Initiators. We have reported that the polymer radicals formed by the decomposition of azo-polymer[20] and peroxide-polymer[57] are successfully trapped by polycondensed aromatic rings of the surface to give the corresponding polymer-grafted carbon black and graphite, as shown in Scheme 7. It was noted that the surface grafting by the polymer radical trapping is very effective for the grafting of carbon black and graphite with a few functional groups as grafting sites.

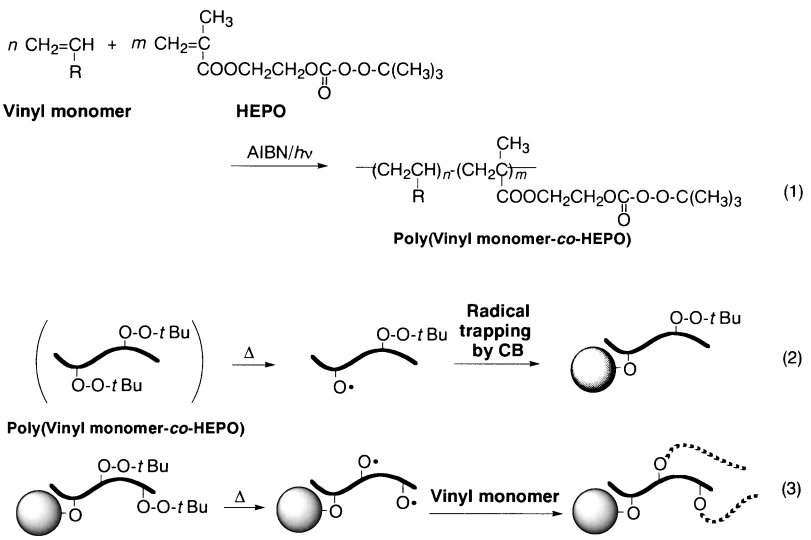
The preparation of azo-polymers is achieved by the polycondensation of azo initiators having acyl chloride or carboxyl with functional polymers having hydroxy or amino groups.[58] On the other hand, we reported the preparation of peroxide polymers having peroxide groups in the main chain by the cationic polymerization of styrene and ring-opening polymerization of THF and ε-caprolactone (CL) in the presence of 3,3′-(dioxydicarbonyl)bisbenzylium diperchlorate, which was prepared by the reaction of bis[(3-chloromethyl)benzoyl] peroxide with silver perchlorate.[57]

We have also prepared the peroxide polymers by the copolymerization of vinyl monomers with HEPO initiated by the photodecomposition of 2,2′-azobisisobutyronitrile (AIBN) at room temperature, as shown in Scheme 8 (1).

Table 4 shows the results of grafting reactions of various carbon blacks with poly(MMA-*co*-HEPO), poly(St-*co*-HEPO), and poly(VAc-*co*-HEPO).[59] It became apparent that, by use of peroxide polymers having pendant peroxycarbonate groups, the corresponding polymers are effectively grafted onto the surface (Scheme 8 (2)). The percentage of grafting onto carbon black obtained from the reaction with poly(VAc-*co*-HEPO) having the highest molecular weight was larger than that from the reaction with poly(MMA-*co*-HEPO) and poly(styrene-*co*-HEPO), but the number of grafted polymer chains (G_n) was smallest. This may be due to carbon black surfaces being shielded by neighboring grafted chains. This effect on the grafting reaction was enhanced with increasing molecular weight of the peroxide polymers.

It is interesting to note that even after the grafting reaction, a part of pendant peroxycarbonate groups remains on poly(MMA-*co*-HEPO)-grafted carbon black obtained from the above reaction. Therefore, the postpolymerization of vinyl monomers were initiated by the poly(MMA-*co*-HEPO)-grafted carbon black to give branched polymer grafted carbon black (Scheme 8 (3)).[59]

3.2 Trapping of Polymer Radicals Formed by γ-Ray Irradiation of Polymer Radiation grafting of polyethylene (PE) onto carbon black was carried out by γ-ray irradiation of

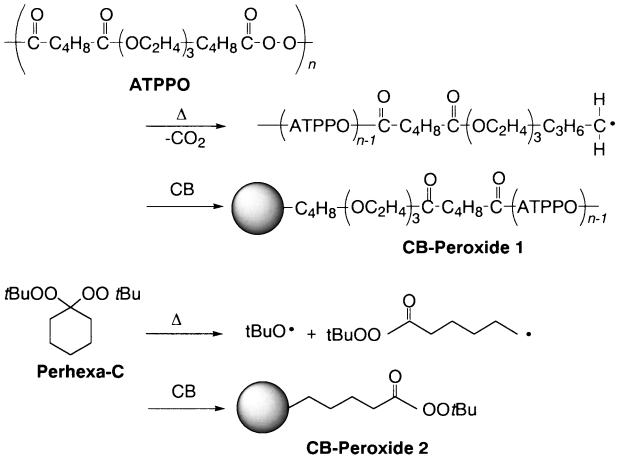


Scheme 8. Grafting of polymers having pendant peroxycarbonate groups onto carbon black and postgraft polymerization.

Table 4. Grafting of Poly(vinyl monomer-*co*-HEPO) with Several Carbon Blacks[a)]

CB	Grafted polymer	$M_n \times 10^{-3}$	Grafting/%	G_n[b)]/10^{19}No. g^{-1}
Neospectra II	Poly(MMA-*co*-HEPO)	7.0	30.2	2.59
Philblack O	Poly(MMA-*co*-HEPO)	7.0	22.2	2.43
Denkablack	Poly(MMA-*co*-HEPO)	7.0	20.9	1.80
Neospectra II	Poly(St-*co*-HEPO)	9.6	51.6	3.24
Philblack O	Poly(St-*co*-HEPO)	9.6	29.8	1.87
Neospectra II	Poly(VAc-*co*-HEPO)	29.8	88.2	1.78
Philblack O	Poly(VAc-*co*-HEPO)	29.8	49.7	1.01

a) CB, 0.60 g; polymer, 2.00 g; toluene, 40.0 mL; 100 °C; 10 h.
b) Number of grafted polymer.



Scheme 9. Introduction of peroxide groups onto carbon black by use of polymeric peroxide and bis-peroxide.

PE-adsorbed carbon black. At low irradiation temperature, the percentage of grafting was very small in spite of the higher irradiation dose. On the contrary, at high temperatures near or above the melting point of PE, the grafting of PE onto the carbon black surface proceeded and the percentage of grafting exceeded 90% when the irradiation dose reached 200 kGy.[60]

Such results indicate that polymer radicals formed by the γ-ray irradiation of PE were successfully trapped by carbon black surfaces. The decomposition temperature of the grafted PE on the surface was higher than both free PE and adsorbed PE on the carbon black surface, indicating that there is a covalent bond between the carbon black and PE molecules.

3.3 Introduction of Initiating Groups by Radical Trapping. Polymeric peroxide, such as poly[(triethylene glycol)-*per*-(adipic acid)-*per*-(monoperoxy adipic acid)] (ATPPO), and bis-peroxide, such as 1,1-bis(*t*-butyldioxy)cyclohexane (Perhexa-C), are commercially available and can be used for the preparation of polymers having peroxide groups by the polymerization of vinyl monomers.[32,61] As mentioned above, polycondensed aromatic rings of carbon black surface are known to act as a strong radical trapping agent.[53,54] Therefore, the introduction of peroxide groups onto carbon black surfaces through the trapping of peroxide radicals formed by the decomposition of ATPPO and Perhexa-C was investigated, as shown in Scheme 9.[62]

Carbon black was heated with ATPPO and Perhexa-C in toluene for 10 h at several temperatures. The results are shown in Figs. 6 (a) and (b), respectively. It was found that peroxide groups are successfully introduced onto carbon black surface by the reaction of ATPPO and Perhexa-C with carbon black. The amount of peroxide groups introduced onto carbon black surfaces using ATPPO increased with increasing reaction temperature, but decreased above 60 °C: the temperature is almost equal to the 10 h half-life temperature of ATPPO. On the contrary, the maximum point of peroxide group content using Perhexa-C was observed at 70 °C: the temperature is considerably lower than the 10 h half-life temperature of Perhexa-C.

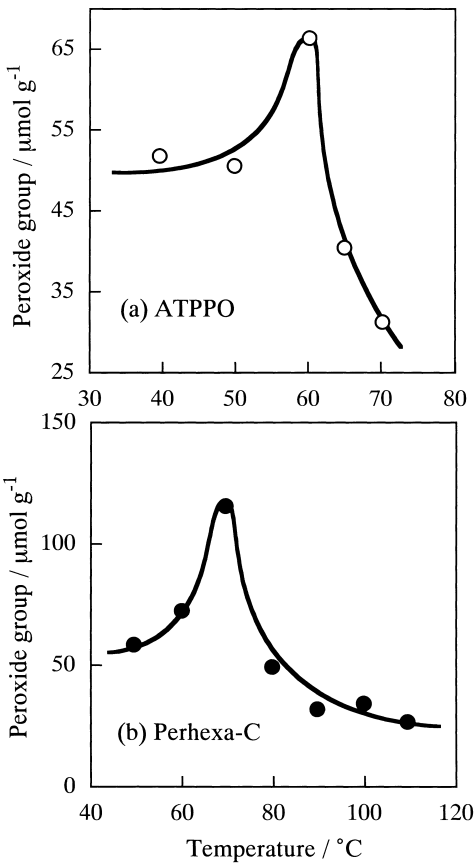


Fig. 6. Effect of temperature on the introduction of peroxide groups onto carbon black by the reaction with (a) ATPPO and (b) Perhexa-C. CB, 0.10 g; ATPPO, 0.50 g (Perhexa-C, 1.00 mL); toluene, 50.0 mL; 10 h.

These results are explained as follows. In the case of

Table 5. Polymerization of Several Vinyl Monomers Initiated by CB-Peroxide **1** and **2**

CB	Monomer	*e*-Value	Temperature	Time	Conversion	Grafting
			°C	min	%	%
CB-Peroxide **1**	MMA	0.40	70	80	6.9	68.3
	HEMA	0.20	70	40	6.4	191.1
	Styrene	−0.80	70	80	4.2	7.5
	VAc	−0.22	70	80	0	0
CB-Peroxide **2**	MMA	0.40	90	120	3.1	69.3
	HEMA	0.20	90	180	6.1	34.7
	Styrene	−0.80	90	180	3.4	4.8
	VAc	−0.22	90	180	0	0

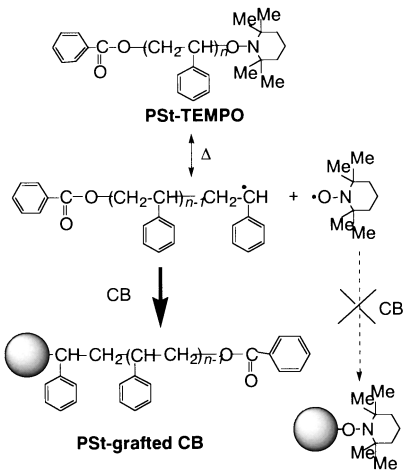
CB-Peroxide, 0.10 g; monomer, 0.10 mL.

ATPPO, even if the decomposition of peroxide groups on CB proceeded during the introduction reaction, surface peroxide groups are regenerated on the surface, because ATPPO is a polymeric peroxide, as shown in Scheme 7. In the case of Perhexa-C, however, the peroxide groups introduced onto carbon black are deactivated by the decomposition of surface peroxide groups. Therefore, in the case of Perhexa-C, the maximum peroxide group content is considered to be observed at a lower temperature than its 10 h half-life temperature.

The carbon black treated with ATPPO at 60 °C and with Perhexa-C at 70 °C was abbreviated as CB-Peroxide **1** and CB-Peroxide **2**, respectively. Table 5 shows the results of the graft polymerization of MMA, HEMA, styrene, and VAc initiated by CB-Peroxide **1** and CB-Peroxide **2**. CB-Peroxide **1** and CB-Peroxide **2** have an ability to initiate the graft polymerization of MMA and HEMA with positive *e*-value to give the corresponding polymer-grafted carbon black: the percentage of poly(HEMA) grafting reached 191%, indicating 1.91 g of polymer was grafted onto 1 g of carbon black. However, these carbon blacks failed to initiate the polymerization of styrene and VAc with negative *e*-value. The same tendency was observed in the postpolymerization of vinyl monomers initiated by pendant peroxycarbonate groups of poly(VAc-*co*-HEPO)-grafted carbon black as mentioned above.[30]

Based on the above results, we conclude that the polymerization of vinyl monomers with positive *e*-value is initiated by the surface radicals formed by the decomposition of peroxide groups introduced onto carbon black surface to give the corresponding polymer-grafted CB.[62]

3.4 Trapping of Living Polymer Radical. 2,2,6,6-Tetramethyl-1-piperidin-1-oxy (TEMPO) is known as a stable radical and is used as spin label and radical trapping agent of unstable radicals. Recently, it has been reported that the living radical polymerization of styrene was successfully achieved by use of benzoyl peroxide (BPO) as an initiator in the presence of TEMPO.[63–65] The resultant TEMPO-terminated polystyrenes (PSt-TEMPO) have terminal dissociative C–O–N bonds. Therefore, when the PSt-TEMPO is heated in the presence of vinyl monomers beyond the dissociation temperature of C–O–N bond, AB-type block copolymer was synthesized by initiation of polymerization from the polystyryl radicals.[65–67] Furthermore, it has been reported that fullerene-end capped polystyrene was synthesized by reaction of fullerene with polystyryl radicals formed by the thermal dissociation of PSt-TEMPO.[68,69]



Scheme 10. Grafting of polymers onto carbon black by trapping of living polymer radical.

Therefore, the grafting reaction of carbon black surface with polystyryl radicals formed by the thermal decomposition of PSt-TEMPO was examined (Scheme 10).[70]

Table 6 shows the results of the grafting reaction of PSt-TEMPO ($M_n = 1.2 \times 10^4$; $M_w/M_n = 1.20$) with carbon black in *m*-xylene at 125 °C. When PSt having no TEMPO moiety was heated with carbon black in *m*-xylene, polystyrene retained by carbon black surfaces after Soxhlet extraction with THF was less than 5% (Run 1); this may be due to physical adsorption of polystyrene by carbon black. When PSt-TEMPO was reacted with carbon black at 30 °C, at which the dissociation of C–O–N bond is negligibly small, the amount of polystyrene retained by carbon black after the reaction was almost equal to that adsorbed (Run 2). On the contrary, it was found that polystyrene with narrow molecular weight distribution is grafted onto the surface by the heating of PSt-TEMPO with carbon black at 125 °C (Runs 3 and 4); the percentage of grafting onto carbon black surface was 10–16%. Furthermore, it was found that polystyrene was grafted onto carbon black by direct addition of carbon black into living radical polymerization system without isolation of PSt-TEMPO (Run 5).

Based on the above results, we conclude that polystyryl radicals formed by the thermal dissociation of C–O–N bond of

Table 6. Grafting of PSt-TEMPO with Carbon Black Surface

Run	Polymer	M_n / 10^3	Temperature / °C	Grafting / %
1	PSt[a)]	11.4	125	5.0
2	PSt-TEMPO[b)]	11.2	30	4.5
3	PSt-TEMPO[b)]	11.2	125	9.2
4	PSt-TEMPO[b)]	3.2	125	16.0
5	Living PSt radical[c)]	10.0	125	11.5

a) Philblack I, 0.10 g; PSt, 90 μmol; *m*-xylene, 10.0 mL; 12 h.
b) Philblack I, 0.10 g; PSt-TEMPO ($M_n = 1.2 \times 10^4$; $M_w/M_n = 1.02$), 90 μmol; *m*-xylene, 10.0 mL; 12 h.
c) St, 48.0 mmol; BPO, 0.495 mmol; TEMPO, 0.50 mmol; 69 h.

PSt-TEMPO are successfully captured by carbon black surfaces.[70] On the other hand, little TEMPO formed by the dissociation of C–O–N bond of PSt-TEMPO bonded to carbon black surfaces because of the stability and steric hindrance of TEMPO radical, as shown in Scheme 10.

4. Grafting of Polymers by the Reaction with Surface Functional Groups

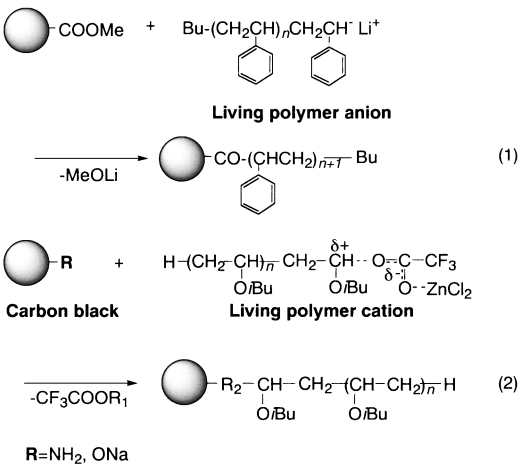
We have pointed out that various polymers with well defined molecular weights and structures can be grafted onto carbon black surfaces by the reaction of surface reactive groups,[71] such as acyl azide,[72] acyl chloride,[73] and epoxide,[74] with hydroxy or amino-capped polymers. The grafting of polymers was also achieved by the reaction of surface functional groups on carbon black with reactive polymers having terminal reactive groups, such as isocyanate,[75] acyl chloride,[76,77] and oxazoline groups.[78] Wu et al. have reported the grafting reaction of isocyanate-terminated polyurethane onto carbon fiber with surface functional groups on the surface.[79]

In addition, conventional functional polymers were grafted onto carbon black and carbon fiber surfaces by the condensation of surface functional groups with polymers in the presence of a condensing agent.[80,81]

In this section, some recent topics on the grafting of polymers by polymer reactions with surface functional groups in the absence of condensing agent and by the reaction with living polymer cations are summarized.

4.1 Grafting Reaction of Functional Polymers with Surface Functional Groups by Simple Impregnation Method. Lin et al. have reported the grafting of polyethylene glycol (PEG) onto carbon black surfaces having carboxyl groups by a simple impregnation method.[82] For a typical run, carbon black was mixed with a desired amount of PEG dissolved in water. The mixture was stirred at room temperature for a few minutes and finally dried in an oven at 100 °C overnight. The percentage of PEG grafting was determined to be 78%. The surface acidity decreased with progress of the grafting reaction, indicating that the acidic groups, such as carboxyl groups, play an important role in the grafting reaction.

4.2 Reaction with Living Polymers. The grafting of polymers with controlled molecular weight and narrow molecular weight distribution onto carbon black is required for the preparation of high-performance carbon black/polymer nanocomposite and functionalization of carbon black by the surface grafting of polymers. There are few reports on the control of molecular weight and molecular weight distribution of grafted polymer on carbon black and carbon fiber. Donnet and his coworkers have reported the grafting of polystyrene by the termination of living polymer anion with surface ester groups introduced onto carbon black, as shown in Scheme 11 (1).[83,84]



Scheme 11. Grafting of polymers onto carbon black by termination of living polymers.

It has been reported that by the termination of living poly(IBVE) cation with nucleophiles having functional groups such as sodium salts of malonic ester and amines, poly(IBVE) having terminal functional groups can be obtained.[85–87] Living poly(2-methyl-4,5-dihydroxazole) (poly(MeOZO)) cation is also very sensitive to nucleophiles such as amines.[88] Therefore, we have examined the grafting of poly(IBVE) and poly(MeOZO) onto carbon black surfaces by the termination of living polymer cation with surface amino and sodium phenolate groups on carbon black, as shown in Scheme 11 (2).[89] The introduction of amino groups onto the surface was achieved by the reduction of nitro groups, which were introduced by the nitration of polycondensed aromatic rings of carbon black surface.[23] On the other hand, sodium phenolate groups were introduced by the reaction of phenolic hydroxy groups with sodium hydroxide.

The grafting reaction of living poly(IBVE) cation ($M_n = 5.0 \times 10^3$; $M_w/M_n = 1.10$) with nucleophilic groups introduced onto various carbon blacks was carried out at 25 °C under several conditions. The results are summarized in Table 7. By the reaction of untreated carbon black with living poly(IBVE) cat-

Table 7. Grafting of Living Poly(IBVE) and Poly(MeOZO) Cation with Nucleophilic Groups Introduced onto Carbon Black Surface[a)]

Carbon black	Polymer		Grafting	$R^{d)}$
	Poly(IBVE)[b)]	Poly(MeOZO)[c)]	%	%
Untreated	living		trace	—
CB-NH_2	quenched		trace	—
CB-NH_2	living		16.2	5.3
CB-ONa	living		23.5	7.2
CB-NH_2		living	32.9	24.5
CB-ONa		living	31.8	22.5

a) CB, 0.01 g; living polymer, 1.2 mmol; toluene, 10.0 mL; 25°C; 1 h.
b) $M_n = 5.0 \times 10^3$, $M_w/M_n = 1.10$.
c) $M_n = 2.2 \times 10^3$, $M_w/M_n = 1.22$.
d) Percentage of nuclerophilic groups used for the grafting reaction.

ion, no grafting onto the surface was observed. In addition, after the quenching of living poly(IBVE) cation with ammoniacal methanol, the polymer did not react with carbon black having amino groups. On the contrary, poly(IBVE) was found to be grafted onto carbon black surface by the reaction of the living poly(IBVE) cation with amino and sodium phenolate groups introduced onto carbon black. The percentage of amino groups used for the grafting reaction (R) with living poly(IBVE) cation was only 5–7%. This indicates that surface amino groups are readily blocked by the neighboring grafted polymer chains. In addition, it was found that the grafting reaction of living poly(MeOZO) ($M_n = 2.2 \times 10^3$; $M_w/M_n = 1.22$) with carbon blacks having nucleophilic groups successfully proceeded. The value of R on poly(MeOZO) was larger than that of poly(IBVE) because of the low molecular weight of poly(MeOZO).

Based on the above results, we concluded that the living polymer cation can be successfully terminated with surface nucleophilic groups introduced onto carbon black; polymer with narrow molecular weight distribution and well defined molecular weight is grafted onto the surface.[89]

The effect of molecular weight of living polymer cations on the grafting reaction with carbon black having amino groups is shown in Fig. 7. It is interesting to note that the percentage of grafting and the mole number of grafted chain (G_n) decreased with increasing molecular weight of living polymers. This may be due to surface amino groups of carbon black being shielded by neighboring grafted polymer chains. This effect on the grafting was enhanced with an increase of molecular weight of the living polymer. The same tendency was observed on the grafting reaction of surface reactive groups on carbon black with amino or hydroxy terminated functional polymers.[71]

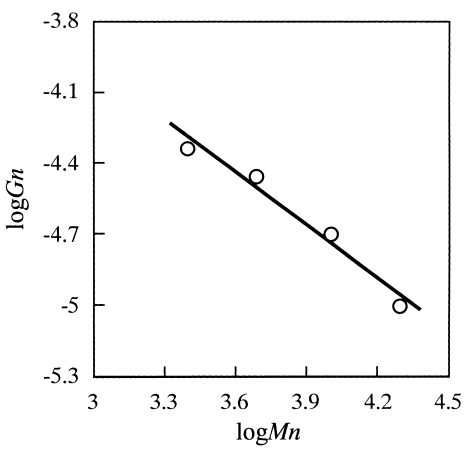


Fig. 7. Relationship between log M_n and log G_n in the grafting of living poly(IBVE) cation onto carbon black having amino groups.

We have pointed out that the relationship between *G*n of grafted polymer on carbon black and the molecular weight (M_n) of the grafted polymer is given by the following Eq. 2:

$$G_n = K \times M_n^{\alpha}, \tag{2}$$

where K and α are constants.[71]

As shown in Fig. 7, a plot of log G_n vs log *M*n gave a straight line. Such a result suggested the relationship between G_n and M_n for the reaction of amino groups on carbon black with living poly(IBVE) cation was given by the following Eq. 3:

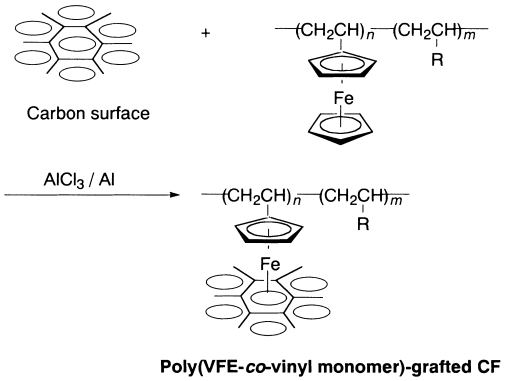
$$G_n = 0.02 \times M_n^{-0.74} \tag{3}$$

The grafting of poly(IBVE) and poly(MeOZO) onto carbon fiber was also achieved by use of carbon fiber having amino groups.[90]

5. Grafting of Polymers by Ligand Exchange Reaction with Aromatic Rings of the Surface

As mentioned above, for the grafting of graphite and carbon fiber with few functional groups, the grafting method which uses the polycondensed aromatic rings on the surface is desirable. Recently, we have succeeded in a novel grafting method which uses the polycondensed aromatic rings as grafting sites.

Nesmeyanov et al. have reported that the η^6-benzene-η^5-cyclopentadienyl-iron (I) cation could be readily prepared by ligand exchange reaction of ferrocene with benzene in the presence of $AlCl_3$ and aluminum powder.[91,92] They have also demonstrated that the ligand exchange reaction proceeds with not only benzene but also with other arenes.[93–96] Furthermore, Miyake et al. reported that ligand exchange reaction of fer-



Scheme 12. Grafting of polymers by ligand exchange reaction of ferrocene containing polymer with polycondensed aromatic rings of carbon materials.

rocene was successfully applied to the introduction of functional groups to hexagonal-plane of various carbon materials, such as active carbon fiber and carbon black.[97] Therefore, we have examined the grafting of polymers by use of ligand exchange reaction of ferrocene with carbon materials.

5.1 Ligand Exchange Reaction with Polymer Containing Ferrocene Moieties. It has been reported that the copolymerization of various vinyl monomers and vinylferrocene (VFE) was successfully initiated by AIBN as an initiator to give the corresponding copolymer.[98,99]

We have reported the grafting reaction of poly(VFE-*co*-vinyl monomer) onto carbon fiber surface by ligand exchange reaction between ferrocene moieties of the copolymer and polycondensed aromatic rings of carbon fiber, as shown in Scheme 12.[100]

Table 8 shows the results of the reaction of poly(VFE-*co*-MMA), $M_n = 2.1 \times 10^4$, and poly(VFE-*co*-St), $M_n = 4.2 \times 10^4$, with carbon fiber surface by ligand exchange reaction between ferrocene moieties of the copolymer and polycondensed aromatic rings of carbon fiber. Even if carbon fiber was heated with poly(VFE-*co*-MMA) in dioxane in the absence of $AlCl_3$, no grafting of the copolymer onto carbon fiber surface was observed (Run 1). In addition, little grafting of the copolymer onto the carbon fiber surface was observed in the presence of aluminum powder alone (Run 2).

On the contrary, the grafting reaction considerably proceeded in the presence of $AlCl_3$ (Run 3). In the coexistence of $AlCl_3$ and aluminum powder, poly(VFE-*co*-MMA) was successfully grafted onto the carbon fiber surface and the percentage of grafting reached 27.6% after 24 h at 80 °C. The percentage of grafting was much higher than that obtained from the radical graft polymerization initiated by the system consisting of carbon fiber having trichloroacetyl groups and $Mo(CO)_6$[41] and by azo groups on the surface.[42] In addition, poly(VFE-*co*-St) was also grafted onto carbon fiber surface by the ligand exchange reactions shown in Table 8 (Run 5).

Table 8. Grafting of Poly(VFE-*co*-vinyl monomer) onto Carbon Fiber by Ligand Exchange Reaction under Various Conditions

Run	Copolymer	$AlCl_3$	Al	Grafting
		mmol	mmol	%
1	Poly(VFE-*co*-MMA)	—	—	trace
2	Poly(VFE-*co*-MMA)	—	0.17	trace
3	Poly(VFE-*co*-MMA)	0.65	—	4.4
4	Poly(VFE-*co*-MMA)	0.65	0.17	27.6
5	Poly(VFE-*co*-St)	0.65	0.17	18.9

CF, 0.10 g; poly(VFE-*co*-vinyl monomer), 0.10 g; 1,4-dioxane, 20 mL; 80 °C; 24 h.

The SEM aspects of poly(VFE-*co*-MMA)-grafted carbon fiber and untreated carbon fiber are shown in Fig. 8. It was found that carbon fiber surface was covered with poly(VFE-*co*-MMA).

The grafting of poly(VFE-*co*-vinyl monomer) by the ligand exchange reaction was also successfully applied for the grafting onto graphite and carbon black surface.[101]

The above results suggest that the grafting of copolymers containing VFE onto carbon fiber surface proceed by the ligand exchange reaction between ferrocene moieties of the copolymer and polycondensed aromatic rings of carbon fiber, as shown in Scheme 12. The surface grafting by the ligand exchange reaction between ferrocene moieties of the copolymer and the polycondensed aromatic rings of carbon materials is very effective to obtain polymer-grafted carbon materials with higher percentage of grafting.

5.2 Introduction of Carboxyl Groups by Ligand Exchange Reaction. It is possible to introduce carboxyl groups onto carbon fiber, graphite, and carbon black surface by the

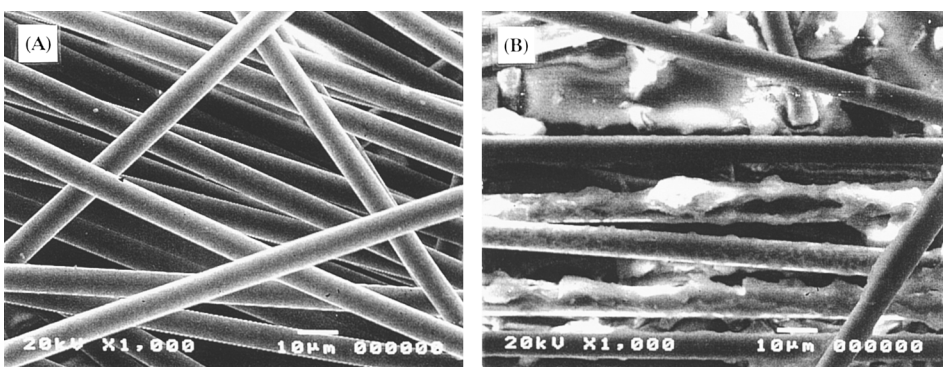
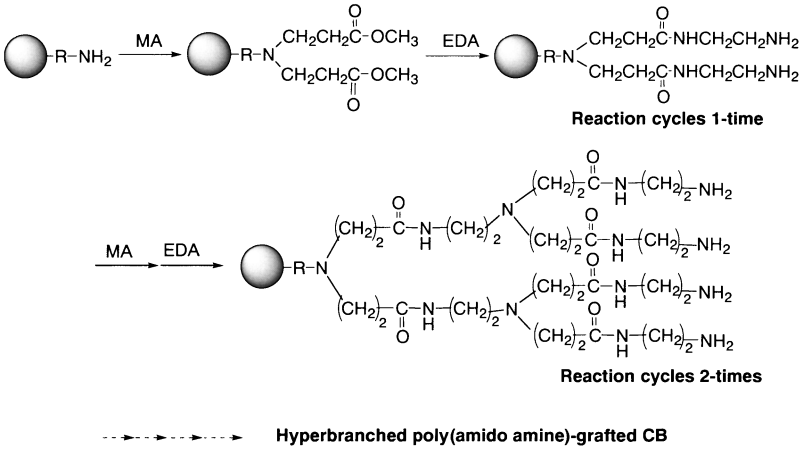


Fig. 8. SEM aspects of (A) untreated and (B) poly(VFE-*co*-MMA)-grafted carbon fiber.

Table 9. Grafting of Poly(amido amine) onto Carbon Black Surface

Reaction Cycles	Amino group/mmol g^{-1}		Grafting/%	
	Obsd	Calcd	Obsd	Calcd
3-times	1.3	4.8	25.5	95.8
5-times	2.1	19.2	48.6	424.0
7-times	3.1	76.8	68.3	1737.4
10-times	6.6	614.4	96.2	13994.6

Amino groups of initiator site (0.6 mmol/g).



Scheme 13. Grafting of hyperbranched poly(amido amine) onto carbon black by dendrimer synthesis methodology.

ligand exchange reaction of 1,1′-ferrocenedicarboxylic acid (Fer-COOH), as shown in Fig. 9. The carboxyl groups introduced onto the surface were used as grafting sites of hydroxy terminated polymers.[102]

6. Grafting of Hyperbranched Poly(amido amine) by Dendrimer Synthesis Methodology

Attention has been focused recently on "Dendrimer", because the dendrimers have the fundamental building blocks, controlled molecular weight, controlled branching, and versatility in modification of terminal groups.[103–105] For example, poly(amido amine) dendrimer was synthesized by repeating two processes: (1) Michael addition of methyl acrylate (MA) to ammonia as an initiator core and (2) amidation of the resulting ester moieties with ethylenediamine (EDA). In this section, the grafting of hyperbranched poly(amido amine) onto the carbon black surface by using the dendrimer synthesis methodology is presented.

The introduction of amino groups was achieved by the reduction of nitrated carbon black surface with aqueous solution of sodium hydrosulfite as mentioned above.[23] The treatment of MA and EDA was repeated for *n* times to obtain hyperbranched poly(amido amine)-grafted carbon black. It is considered that hyperbranched poly(amido amine)s grow from surface amino groups and are grafted onto carbon black surfaces as shown in Scheme 13.[106]

Table 9 shows the amino group content of carbon black after the grafting reaction of poly(amido amine) when carbon black having 0.60 mmol/g of amino groups was used as an initiator site. The amount of amino groups of the resulting carbon black increased with increase of the number of reaction cycles.

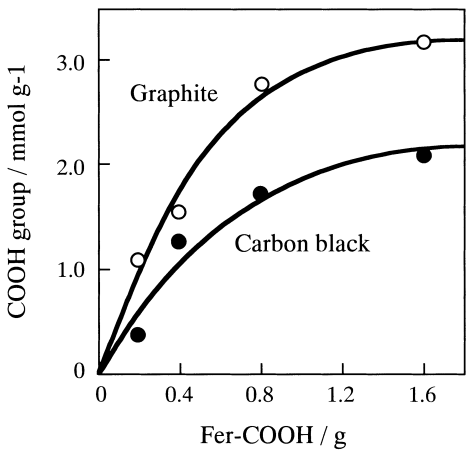


Fig. 9. Introduction of carboxyl groups onto graphite and carbon black surface by ligand exchange reaction. Carbon, 0.8 g; $AlCl_3$:Al = 4:1; 1,4-dioxane, 50 mL; 80 °C; 24 h.

On the other hand, when untreated carbon black was used, no increase of surface amino groups was observed. These results indicate that poly(amido amine) grows from the surface amino groups of carbon black. However, the amount of amino groups of poly(amido amine)-grafted carbon black was much smaller than that calculated.

Table 9 also shows the percentage of poly(amido amine) grafting onto carbon black obtained from the above reaction. It was found that the percentage of grafting of poly(amido amine) onto carbon black surface increased with increase of the number of reaction cycles. However, the grafting in every reaction cycle was much smaller than that calculated. The IR

Table 10. Pencil Scratch Hardness of Carbon Black/Alumina Gel Composite

Polymer-grafted CB/g		Heating at 40 °C/h	Scratch hardness
None	0	48	9H
Untreated[a)]	0.20	48	—[b)]
Untreated[a)] + Poly(MeOZO)[c)]	0.20	48	—[b)]
Poly(MeOZO)-grafted[a)]	0.38	48	8H
Poly(NVPD)-grafted[a)]	0.28	48	8H
Poly(MeOZO)-grafted[a)]	0.38	96[d)]	8H
Poly(NVPD)-grafted[a)]	0.28	96[d)]	8H

a) Net weight of CB, 0.20 g; 4% AIP aqueous solution, 125 g.
b) Thin film was hardly obtained.
c) Poly(MeOZO), 1.67 g.
d) In the absence of nitric acid.

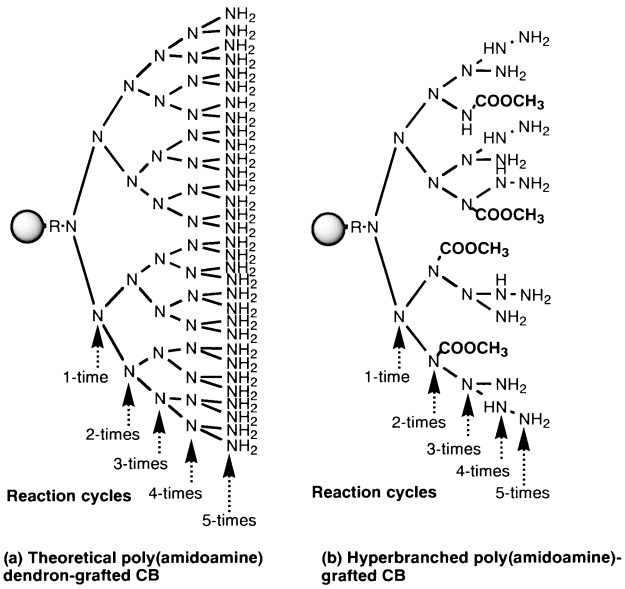


Fig. 10. Schematic description of theoretical and experimental structure of poly(amido amine) dendron-grafted carbon black.

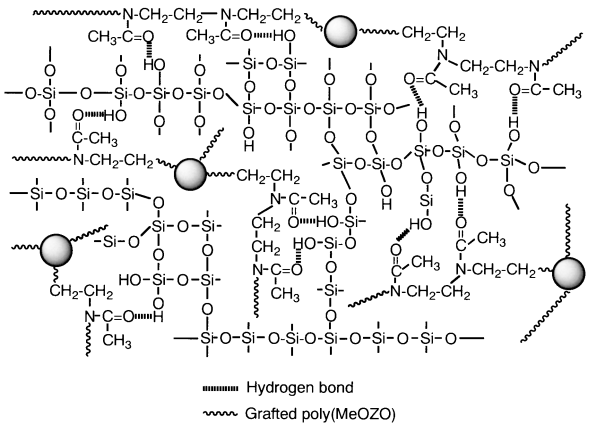


Fig. 11. Schematic representation structure of silica gel/poly(MeOZO)-grafted carbon black composite.

spectra of poly(amido amine)-grafted carbon black showed a absorption at 1715 cm^{-1}, which is characteristic of ester bond, indicating the incomplete amidation with EDA.

Based on the above results, it was concluded that the theoretical propagation of poly(amido amine) dendrimer from carbon black surface (Fig. 10 (a)) was not achieved, but hyperbranched poly(amido amine)-grafted carbon black with higher percentage of grafting can be obtained (Fig. 10 (b)).[106] This may be due to the fact that the Michael addition and especially amidation were carried out in heterogeneous system and the grafted chains on the surface interfere with the growth of poly(amido amine) from the surface because of steric hindrance.

7. Carbon Black/Metal Oxide Gel Composite by Sol-Gel Process

One of the important extensions of the sol-gel process is the preparation of organic/inorganic hybrid materials consisting of an organic polymer and a metal oxide, such as silica gel and alumina gel, with molecular-level dispersion. Polymers, such as polyamide,[107] poly(oxyethylene),[108] poly(ether ketone),[109] and poly(MeOZO)[110,111] have been successfully incorporated into inorganic network matrices by the sol-gel process.

We have succeeded in the preparation of a novel composite of carbon black/metal oxide gel, such as silica gel and alumina gel, in which carbon black particles are dispersed uniformly, by the sol-gel reaction in the presence of polymer-grafted carbon black (Fig. 11).[112–114]

Table 10 shows pencil scratch hardness values of thin films of carbon black/alumina gel composite obtained from the sol-gel reaction of aluminum isopropoxide (AIP) in the presence of polymer-grafted carbon blacks. In the presence of untreated carbon black, a thin film of alumina gel composite was hard to obtain even in the presence of ungrafted poly(MeOZO), because aggregated carbon black particles were formed during the sol-gel reaction. On the contrary, in the presence of polymer-grafted carbon black, a deep black thin film of alumina gel, in which carbon blacks were uniformly incorporated, was readily obtained, because these polymer-grafted carbon blacks uniformly dispersed in the reaction mixture during the sol-gel reaction. The scratch hardness of the poly(MeOZO)-grafted and poly(NVPD)-grafted carbon black/alumina gel composite was determined to be 8H. On the other hand, the scratch hardness of thin film of alumina gel obtained from sol-gel reaction of AIP in the absence of carbon black was 9H. Therefore, the scratch hardness of the polymer-grafted carbon black/alumina

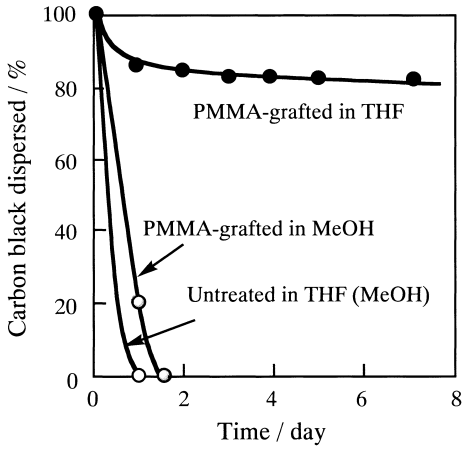


Fig. 12. Dispersibility of poly(MMA)-grafted carbon black in THF and methanol.

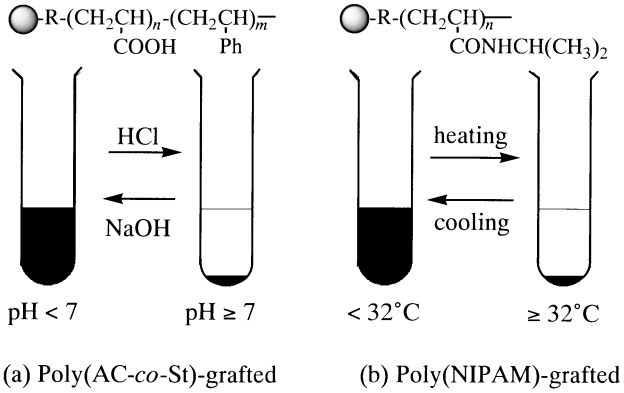


Fig. 13. Dispersibility control of carbon black in water by pH and temperature of dispersant.

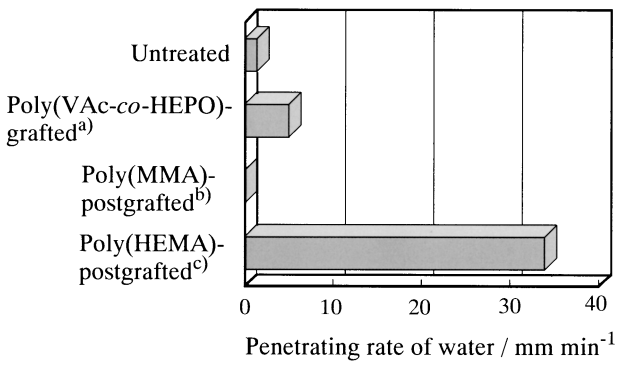


Fig. 14. Penetrating rate of water through the column packed with polymer-grafted carbon black. (a), poly(VAc-*co*-HEPO)-grafted (Grafting = 33.0%) (b), poly(MMA)-postgrafted (Overall grafting = 51.7%) (c), poly(HEMA)-postgrafted (Overall grafting = 123.8%).

gel composite was liable to decrease, but to still be rather firm due to the effect of grafted polymer chains on the carbon black surface, as polymer-grafted carbon blacks were incorporated.[113]

The IR absorption band of carbonyl groups of poly(MeOZO)-grafted carbon black/alumina gel composite was compared with that of poly(MeOZO). The absorption of carbonyl stretching band of the alumina gel composite shifted to lower wavenumbers than that of the polymer itself: from 1634 cm^{-1} to 1614 cm^{-1}.

The result suggests that carbon black is incorporated into alumina gel by hydrogen bonds between carbonyl groups of the grafted poly(NVPD) and poly(MeOZO) chains on the surface and residual hydroxy groups in the alumina gel. The same tendency was reported by Saegusa et al. in the case of hybrids of silica gel with polymers having alkyl amide groups.[110,111]

8. Properties of Polymer-Grafted Carbon Materials

8.1 Dispersibility. Figure 12 shows the comparison of dispersibility of poly(MMA)-grafted carbon black in THF and methanol with that of untreated carbon black. Untreated carbon black completely precipitated within 1 day in THF and methanol. On the contrary, poly(MMA)-grafted carbon black gave a stable colloidal dispersion in THF, which is a good solvent for grafted poly(MMA). However, even the poly(MMA)-grafted carbon black precipitated in methanol, which is not a solvent of poly(MMA).

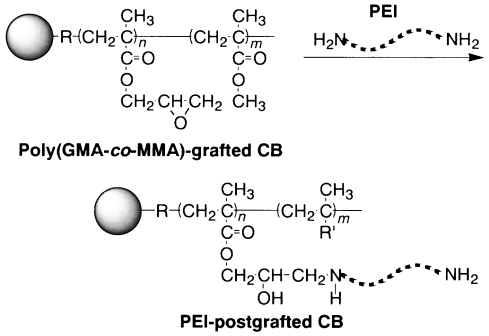
This suggests that polymer chains grafted onto carbon black lose the ability to interfere with the aggregation of carbon black when the carbon black is dispersed in a poor solvent for the grafted polymer. Accordingly, it seems that grafted polymer chains spread out from the carbon black surface in a good solvent for the grafted polymer, but shrink onto the surface in a poor one.

Therefore, one expects that the dispersibility of carbon black in water can be controlled by pH or temperature of dispersant by the grafting of polymers, whose solubility in solvent changes with pH or temperature.

8.2 Control of Dispersibility by pH and Temperature. For example, copolymer of acrylic acid (AC) with styrene is known to be insoluble in acidic water, but to be soluble in alkaline water. Therefore, poly(AC-*co*-St)-grafted carbon black gave a stable colloidal dispersion in alkaline water, but immediately precipitated in acidic water, as shown in Fig. 13 (a).

In addition, it is well known that poly(*N*-isopropylacrylamide), poly(NIPAM), is soluble in water below the lower critical solution temperature of about 32 °C, but is insoluble in water above the temperature. Therefore, poly(NIPAM)-grafted carbon black gave a stable dispersion in water below 32 °C, but readily precipitated above the temperature, as shown in Fig. 13 (b). This is due to the fact that the solubility of the polymer in water turns from soluble to insoluble with increasing temperature.

8.3 Control of Surface Wettability. Figure 14 shows the penetrating rate of water through a column packed with untreated, poly(VAc-*co*-HEPO)-grafted, poly(MMA)-postgrafted, and poly(HEMA)-postgrafted carbon black. The results clearly show that untreated carbon black surface shows a hydrophobic nature, and such hydrophobic nature of carbon black surface was not much changed by the grafting of poly(VAc-*co*-HEPO). On the contrary, by the postgrafting of hydrophilic poly(HEMA), the carbon black surface shows an extremely hydrophilic nature, but by the postgrafting of poly(MMA), the carbon black surface turned extremely hydro-



Scheme 14. Postgrafting of hydrophilic PEI to hydrophobic polymer chain on carbon black.

phobic. Therefore, it is concluded that the wettability of carbon black surface can be controlled by the grafting and postgrafting of hydrophilic and hydrophobic polymers.

By the grafting of hyperbranched poly(amido amine) onto carbon black surface, the surface became to extremely hydrophilic and the ability for the adsorption of humidity by the carbon black surface extremely increases in comparison with the ability for such a adsorption by the untreated one.[115]

8.4 Amphiphilic Property. We have reported that poly(ethyleneimine) (PEI), can be successfully postgrafted to poly(GMA-*co*-MMA)-grafted carbon black by the reaction of amino and imino groups of PEI with pendant glycidyl groups of the grafted poly(GMA-*co*-MMA) on the surface to give branched polymer-grafted carbon black (Scheme 14).[116] The composition of grafted poly(GMA-*co*-MMA) used in this study was GMA:MMA = 44.5:55.5 and the percentage of grafting was 25.0%.

As mentioned above, the wettability of carbon black surface was readily controlled by the postgrafting of hydrophilic and hydrophobic polymers onto the surface. Therefore, the relationship between wettability of carbon black surface to water and PEI postgrafting onto poly(GMA-*co*-MMA) onto carbon black was examined.[117]

Figure 15 shows the relationship between percentage of PEI-postgrafting and penetrating rate of water through the column packed with PEI-postgrafted carbon black. It was found that the penetrating rate of water increased with increasing percentage of postgrafting of PEI. The surface of PEI-postgrafted carbon black, whose PEI-postgrafting is 0–3.0%, shows hydrophobic nature. On the contrary, PEI-postgrafted carbon black surface shows hydrophilic nature when PEI-postgrafting exceeded 9.5%. It is interesting to note that the surface of PEI-postgrafted carbon black, whose PEI-postgrafting is 3.0–9.5%, shows amphiphilic nature.[117]

Therefore, it is concluded that hydrophobic and hydrophilic nature of carbon black surface can be controlled by the postgrafting of hydrophilic PEI to poly(GMA-*co*-MMA) grafted on the surface.

The dispersibility of PEI-postgrafted carbon black in binary mixture (toluene/water) was examined. Polymer-grafted carbon black was added into a toluene/water binary mixture; this mixture was shaken vigorously and then allowed to stand. The results are shown in Fig. 16. Poly(GMA-*co*-MMA)-grafted carbon black dispersed in toluene phase only and no carbon

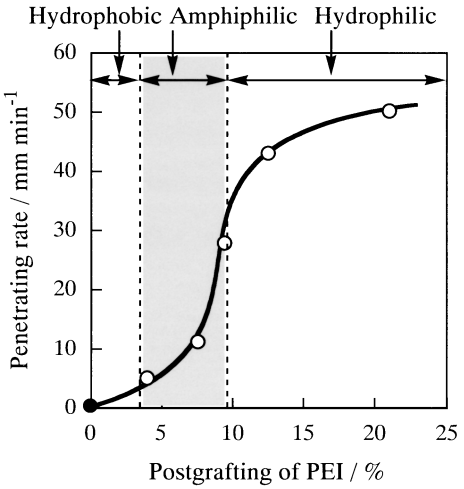


Fig. 15. Relationship between percentage of PEI postgrafting to poly(GMA-*co*-MMA)-grafted carbon black and penetrating rate of water through the column packed with PEI-postgrafted carbon black. Grafting, 25.0%; grafted copolymer, GMA:MMA = 44.5:55.5.

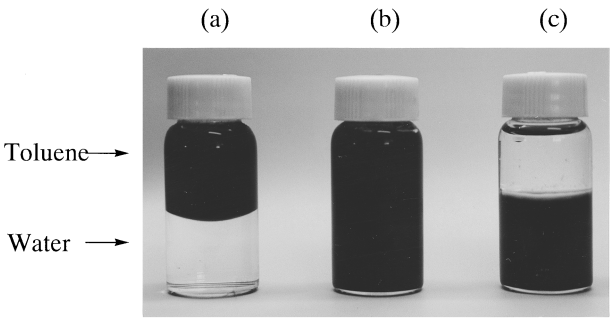


Fig. 16. Dispersibility of (a) poly(GMA-*co*-MMA)-grafted (grafting = 24.3%), (b) PEI-postgrafted (postgrafting = 3.9%), and (c) PEI-postgrafted carbon black (postgarfting = 13.7%) in binary mixture of toluene/water.

black in water phase was observed (Fig. 16 (a)), because of hydrophobic nature of the poly(GMA-*co*-MMA)-grafted carbon black. On the contrary, PEI-postgrafted carbon black, whose percentage of PEI postgrafting is 9.1% gave a stable dispersion in water, but not in toluene (Fig. 16 (c)). It is interesting to note that PEI-postgrafted carbon black, whose percentage of PEI postgrafting is 3.9%, suspended homogeneously in toluene/water mixture for a long time (Fig. 16 (b)).[114]

Furthermore, this solution was confirmed to be O/W (oil in water) type-emulsion by microscope observation. These results suggest that PEI-postgrafted carbon black whose percentage of postgrafting of PEI is 3.9% possesses surface activity. This may be due to the fact that PEI-postgrafted carbon black shows amphiphilic nature and has the most suitable value of the hydrophile-lipophile balance (HLB) to emulsify toluene and water. In addition, PEI-postgrafted carbon black particles were found to gather at the interface between toluene and water. Therefore, these carbon black particles are considered to arrange in the same manner as surfactant molecules on the basis of affinity of grafted poly(GMA-*co*-MMA) chains for toluene and of postgrafted PEI chains for water.[117]

Table 11. Electric Resistance of Composites from PEI and PEI-grafted Carbon Black in Dry Air and Methanol Vapor

Composite	$M_n \times 10^{-3}$	Electric resistance/Ω	
		Dry air	MeOH vapor
PEI(C) + Ungrafted CB	5.0	150k	140k
PEI(C) + PEI(C)-grafted CB	5.0	20	10k
PEI(A) + PEI(A)-grafted CB	1.8	400k	320k
PEI(A) + PEI(A)-grafted CB	30	2000k	1800k

Measuring temperature, 25.0 °C.

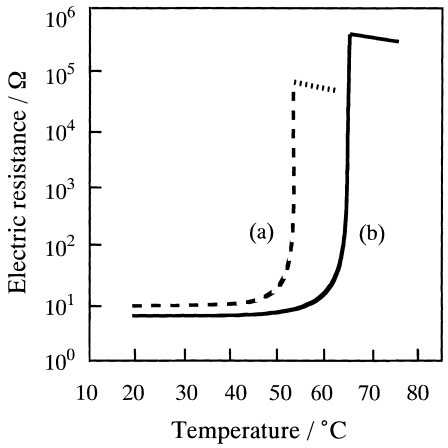


Fig. 17. Effect of temperature on the electric resistance of PEG-grafted carbon black. (a) $M_n = 1.5 \times 10^3$ (mp = 52 °C), (b) $M_n = 2.0 \times 10^4$ (mp = 63 °C).

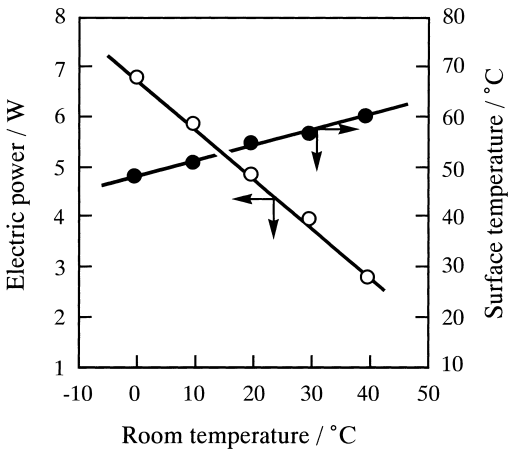


Fig. 18. Relationship between room temperature and electric power (surface temperature) of a heater prepared from PEG ($M_n = 2.0 \times 10^4$)-grafted carbon black.

8.5 PTC of Composite from Polymer-Grafted Carbon Black. It has been reported that vinyl polymer-grafted carbon black, which was crosslinked with a variety of crosslinking agents, shows a positive temperature coefficient of resistance, i.e., PTC, at temperatures near the glass transition temperature of the grafted polymer.[118–120]

We have reported the effect of temperature on the electric resistance of crystalline polymer-grafted carbon black.[121] Figure 17 shows the relationship between temperature and electric resistance of PEG-grafted carbon black: the M_n of PEG is 1.5×10^3 and 2.0×10^4. The electric resistance of the PEG-grafted carbon black drastically increases to values about 10^4–10^5 times the initial resistance at the melting point of PEG. This may be due to a widening of the gaps between the carbon black particles by melting of PEG.

Figure 18 shows the relationship between room temperature and electric power (surface temperature) of a plane heater made from PEG ($M_n = 2.0 \times 10^4$)-grafted carbon black. It was found that the surface temperature of the heater remains at about 60 °C, even if the room temperature changes from 0 °C to 60 °C. Therefore, a plane heater made from the composite, produced uniform heat at approximately 50 °C or 60 °C without any circuit for controlling temperature.[122] In addition, it is interesting to note that the electric power of the heater changes according to room temperature; the electric power decreased with increasing temperature.

8.6 Gas Sensing and Contamination Sensing in Solution. We have reported that composites prepared from crystalline polymer-grafted carbon black and crystalline polymer can be used as novel gas sensors.[123–128] Table 11 shows the electric resistance of composite prepared from PEI and PEI-grafted carbon black under dry air and methanol vapor.[123] PEI used was crystalline-type (PEI(C)) and amorphous-type (PEI(A)). It is interesting to note that the electric resistance of the composite prepared from PEI(C) and PEI(C)-grafted carbon black was much smaller than that of amorphous one, PEI(A). This may be due to the fact that the conductive circuit between carbon black particles in the composite prepared from PEI(C) is formed in the process of crystallization of PEI(C). On the other hand, even if PEI(C) was used, the electric resistance of composite from untreated carbon black was also larger than that from PEI(C)-grafted one. This may be due to the presence of aggregates of carbon black in the composite, because untreated carbon black does not disperse uniformly in PEI.

In addition, the electric resistance of composites from PEI(C) and PEI(C)-grafted carbon black in methanol vapor at 25 °C drastically increased, from 20 Ω to 10 kΩ. But the electric resistance of composite from PEI(A) and untreated carbon black scarcely changed: the resistance tends to decrease in methanol vapor. This indicates that crystalline structure of PEI in the composites plays an important role in the response ability of electric resistance of the composites.

Figure 19 shows the effect of various vapors on the electric resistance of composites from PEI(C) and PEI(C)-grafted carbon black at 25 °C.[123] It is interesting to note that the electric resistance of the composite drastically increased in methanol

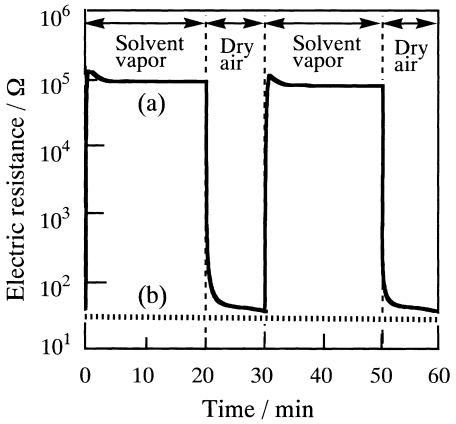


Fig. 19. Electric resistance of composite of PEI(C) and PEI(C)-grafted carbon black on the responsiveness to solvent vapor. (a) Methanol vapor; (b) toluene and hexane vapor.

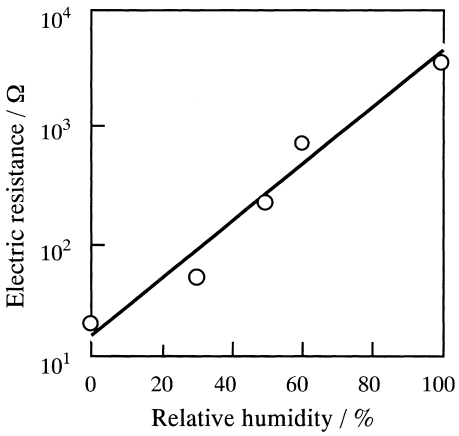


Fig. 20. Effect of relative humidity on the electric resistance of composite prepared from PEI(C) and PEI(C)-grafted carbon black.

(as shown in Fig. 19) and ethanol vapor, and in humidity, which are good solvents for PEI. On the contrary, the electric resistance changed little, in toluene and hexane vapor, which are not solvents of PEI. This is due to a slight change of gaps between carbon black particles based on the absorption of vapor of a good solvent by PEI(C). These results suggest the possibility of detection of a slight change of crystalline structure of PEI by the absorption of solvent as a large change of electric resistance of the composite.[123]

In addition, Fig. 19 shows that the electric resistance of these composites returns immediately to initial resistance when the composites are transferred in dry air. The responsiveness of electric resistance was reproducible even after 30 cycles of exposure to methanol vapor and dry air.

Figure 20 shows the relationship between electric resistance of the composite and relative humidity. It became apparent that the logarithm of electric resistance is linearly proportional to relative humidity. This indicates that the composite can applied as a sensor of humidity.[123]

We have prepared various sensor materials from PEG-grafted, PCL-grafted, poly(ethylene adipate) (PEA)-grafted, and polyethylene (PE)-grafted, PE-*block*-PEG-grafted carbon black and reported the response ability to various solvent vapors.[124–128]

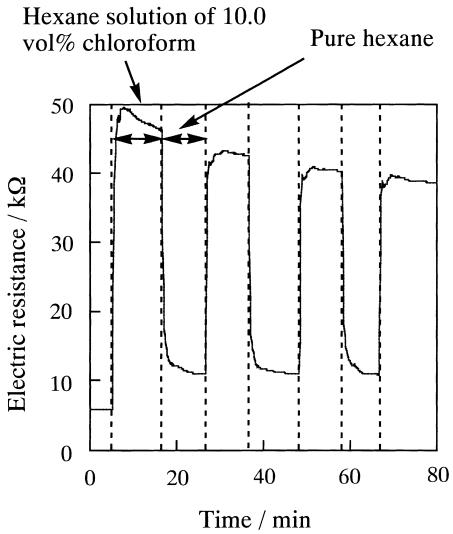


Fig. 21. Electric resistance of a composite from PCL-grafted carbon black in a hexane solution of 10.0 vol% chloroform at 20 °C.

The responses of the electric resistance of various composites prepared from the above types of crystalline polymer-grafted carbon black, such as PCL-grafted, PEG-grafted, and PEA-grafted, were investigated as a function of the contamination in hexane.[129] Figure 21 shows the electric resistance of the composite from PCL-grafted carbon black in hexane containing 10.0 vol% chloroform at 20 °C. The electric resistance of the composite prepared from PCL drastically increased in the hexane solution of chloroform, which is a good solvent for PCL, and immediately returned to a value close to the initial resistance when the composite was transferred into pure hexane, which is a non-solvent of PCL.

The logarithm of the electric resistance (the maximum resistance of third dipping) is linearly proportional to the chloroform concentration in hexane. This relation showed the good reproducibility. Therefore, it was found that the composite has the possibility of use as a cheap and a disposal contamination sensor in the industrial field.[129]

9. Concluding Remarks

In this account, recent studies are summarized on the functionalization of carbon materials, such as carbon black and carbon fiber, by grafting of polymers. The methodology for the surface grafting of polymers presented here can be applied for the grafting of polymers onto inorganic particles,[130–132] such as silica, titanium (IV) oxide, and ferrite, organic pigments,[133,134] and polymer powders.[132,133] In addition, the modification of inorganic and organic particles will become more and more important for the design of high performance plastics, composite materials, cosmetic materials, and paints. Furthermore, the carbon black surface-modified by grafting of polymers and carbon fiber has a large potential as a electrode material for fuel cell and a high performance nano-compoosite.

In general, the preparation of polymer-grafted carbon black and fine particles is carried out in solution. Therefore, the scale up synthesis of polymer-grafted fine particles is very difficult because of complicated procedures, such as filtration, centrifugation, and drying to remove by-products during the grafting reaction. These inhibit the application of polymer-grafted carbon black and carbon fiber as conventional industrial materials. Recently, we have succeeded in the scale-up synthesis of hyperbranched poly(amido amine) onto ultrafine silica surface in solvent-free dry system.[137] Therefore, the industrial applications of polymer-grafted carbon black will probably be expanded in the future.

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