

Surface Grafting of Polymers onto Carbon Thin Film

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SYNOPSIS

The surface grafting of polymers onto carbon thin film deposited on a glass plate was achieved by two methods: the graft polymerization initiated by initiating groups introduced onto the surface; and the trapping of polymer radicals by surface aromatic rings of the thin film. It was found that the radical and cationic graft polymerization of vinyl monomers are initiated by azo and acylium perchlorate groups introduced onto the surface, respectively, and the corresponding polymers are grafted onto the surface: the surface grafting of polymers were confirmed by the contact angle of the surface with water. In addition, the anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides was found to be initiated by potassium carboxylate groups on the carbon thin film to give the corresponding polyester-grafted carbon thin film. On the other hand, polymer radicals formed by the decomposition of azo polymer, such as poly(polydimethylsiloxane-azobiscyanopentanoate) and poly(polyoxyethylene-azobiscyanopentanoate), were successfully trapped by the surface aromatic rings of carbon thin film and polydimethylsiloxane and polyoxyethylene were grafted onto the surface. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

We have reported that carboxyl and phenolic hydroxyl groups present on carbon black surfaces undergo chemical reactions and can be readily converted to reactive functional groups.^{1,2} For example, potassium carboxylate,^{3,4} acylium perchlorate,^{5,6} and azo⁷ and peroxyester groups⁸ introduced onto the surface have an ability to initiate the anionic, cationic, and radical graft polymerization, respectively. In the polymerization, polymer-grafted carbon black with a high percentage of grafting was obtained, because the grafted chains are propagated from surface initiating groups.

Recently, we also reported that polymer radicals formed by the decomposition of azo polymers, which contain an azo bond in the main chain, are effectively trapped by polycondensed aromatic rings of carbon black to give the corresponding polymer-grafted carbon black.⁹ This method enabled the effective surface grafting of polymers onto carbon black having few functional groups.

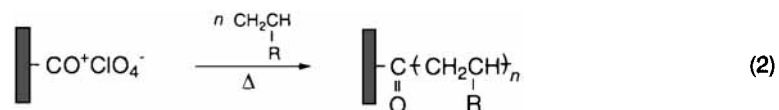
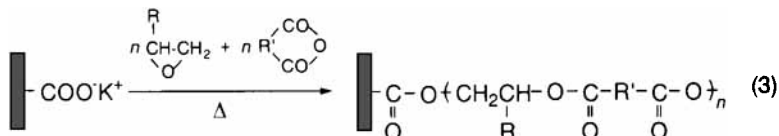
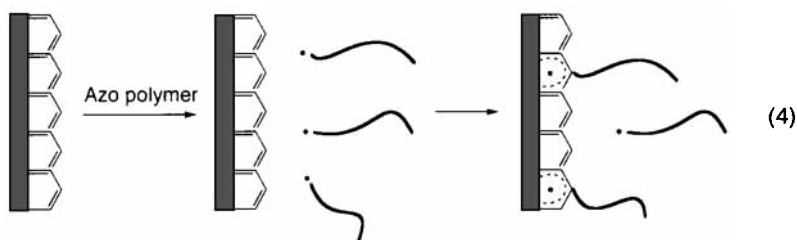
To modify the carbon thin film deposited on a glass plate, the grafting of polymers onto the surface was investigated. The surface grafting of carbon thin film was achieved by two methods: the radical, cationic, and anionic graft polymerization initiated by azo [Eq. (1)], acylium perchlorate [Eq. (2)], and potassium carboxylate groups [Eq. (3)] introduced onto the surface, respectively; and the trapping of polymer radicals, which formed by the decomposition of azo polymers, by aromatic rings of the surface [Eq. (4)].

EXPERIMENTAL

Carbon Thin Film

Carbon thin film, which was prepared by the evaporation of carbon onto a glass plate (10 × 15 × 1 mm) according to a sputtering method, was provided from Mitsubishi Chemical Co. Ltd. The thickness of the thin film was 3 × 10⁻⁶ cm. Carbon thin film was washed with chloroform and dried *in vacuo* before use.

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Radical Graft Polymerization**Cationic Graft Polymerization****Anionic Graft Polymerization****Grafting by Trapping of Polymer Radicals****Reagents**

Methyl methacrylate (MMA) was washed with a 10% aqueous solution of sodium sulfate, aqueous alkali, and an aqueous solution of sodium chloride, dried over anhydrous sodium sulfate, and distilled under reduced pressure. Styrene was washed with a 10% aqueous solution of sodium hydroxide and water, dried over barium oxide, and distilled under reduced pressure. *N*-Methyl-2-pyrrolidone (NVPD) was dried over sodium hydroxide and distilled under reduced pressure. Acrylic acid (AA) and perfluorohexylethyl acrylate (PFHEA) were distilled under reduced pressure. *N*-Vinylcarbazole (NVC) was recrystallized from *n*-hexane. Potassium acrylate (PA) was recrystallized from pure water. Styrene oxide (SO) and 3-perfluorohexyl-1,2-epoxypropane (PFHEP) were dried over calcium hydride and distilled. Phthalic anhydride (PAn) was recrystallized and sublimed under reduced pressure.

4,4'-Azobis(4-cyanopentanoic acid) (ACPA) was obtained from Wako Pure Chemical Co. and recrystallized from methanol. *t*-Butylperoxy-2-methacryloyloxyethyl carbonate (HEPO) obtained from Nippon Oil and Fats Co. Ltd., guaranteed reagent-

grade silver perchlorate obtained from Kojima Chemical Co. Ltd., 18-crown-6, and *N*-phenyl- β -naphthylamine were used without further purification. Toluene-2,4-diisocyanate (TDI) was distilled before use.

Azo polymer was prepared by the polycondensation of hydroxyl terminated polydimethylsiloxane (or polyoxyethylene) with 4,4'-azobis(4-cyanopentanoic chloride) according to the method of Ueda and Nagai.¹⁰ Dimethyl sulfoxide (DMSO) was dried over calcium hydride and distilled. Other solvents and reagents were used after ordinary purification.

Introduction of Carboxyl Groups onto Carbon Thin Film

The introduction of carboxyl and phenolic hydroxyl groups onto the surface was achieved by flame treatment.¹¹ The carbon thin film was passed through the flame of a gas burner several times. The introduction of carboxyl and phenolic hydroxyl groups onto the thin film was also achieved by treatment with 35% nitric acid at 110°C for 5 h.¹²

Introduction of Azo Groups onto Carbon Thin Film

The introduction of azo groups onto the surface was achieved by the reaction of isocyanate groups, which were introduced by the treatment with TDI, with ACPA.⁷ A typical example is as follows. Carbon thin film was treated with a small excess of TDI in DMSO at 60°C for 4 h. After cooling to room temperature, a small excess of ACPA was added to the mixture and the reaction was continued at room temperature in the dark for 8 h. The resulting carbon thin film was repeatedly washed with methanol and dried *in vacuo*.

Introduction of Acylium Perchlorate Groups onto Carbon Thin Film

The introduction of acylium perchlorate groups onto the carbon thin film, that is, pretreatment, was achieved by the reaction of silver perchlorate with surface acyl chloride groups, which were introduced by the treatment with thionyl chloride.^{5,6} The carbon thin film was treated with an excess of thionyl chloride in benzene at 70°C for 50 h. After the reaction, the thin film was washed with absolute THF and dried *in vacuo*. Then the resulting film was treated with 0.10 g of silver perchlorate in 15.0 cm³ of nitrobenzene at room temperature for 48 h.

Introduction of Potassium Carboxylate Groups onto Carbon Thin Film

The introduction of potassium carboxylate groups onto the carbon thin film was carried out by the neutralization of carboxyl groups with aqueous potassium hydroxide.^{3,4} The carbon thin film was treated with an excess of 0.5% aqueous alkali at 60°C for 6 h. After the reaction the thin film was washed with pure water and dried *in vacuo*.

Procedures of Graft Polymerization

The radical graft polymerization of vinyl monomers initiated by azo groups introduced onto the thin film was carried out under high vacuum. A typical example is as follows. Into a glass ampule that contains a stirrer bar, 0.30 g of carbon thin film having surface azo groups, vinyl monomer, and solvent were charged. The ampule was cooled by liquid nitrogen, thawed three times, and sealed *in vacuo*. The reaction was carried out under stirring with a magnetic stirrer at 70°C.

The cationic graft polymerization was carried out as follows. After the pretreatment for the introduc-

tion of acyl perchlorate groups, 0.15 mol of monomer was added and the polymerization was conducted at 40°C under nitrogen.

The anionic graft polymerization of epoxides with PAN was carried out as follows. Into a glass tube that contained carbon thin film, 0.10 mol of PAN, 0.02 g of 18-crown-6, and 0.02 g of *N*-phenyl- β -naphthylamine, 0.10 mol of epoxides was added. The reaction mixture was stirred with a magnetic stirrer at 120°C under dry nitrogen.

After the anionic, cationic, and radical graft polymerization, the thin film was washed with THF repeatedly and dried *in vacuo*.

Contact Angle of Polymer-Grafted Carbon Thin Film

The contact angle of polymer-grafted carbon thin film with pure water was determined by the method in the literature.¹³

RESULTS AND DISCUSSION

Radical Graft Polymerization onto Carbon Thin Film

We have reported that the radical graft polymerizations of vinyl monomers are initiated by azo groups introduced onto the carbon black surface to give the corresponding polymer-grafted carbon black with high percentage of grafting.⁷ Therefore, the introduction of azo groups onto carbon thin film by the reaction of ACPA with isocyanate groups, which were introduced by the treatment with TDI, and the radical graft polymerization initiated by the surface azo groups were investigated. Table I shows the contact angle of variously treated carbon thin films with pure water.

Table I Contact Angle of Treated Carbon Thin Film with Water

Carbon Thin Film	Contact Angle (°)
Untreated	57
HNO ₃ treated	27
Flame treated	< 10
ACPA treated ^a	51
ACPA treated ^b	64
KOH treated ^c	21

^a Treated with ACPA after HNO₃ treatment.

^b Treated with ACPA after flame treatment.

^c Treated with KOH after flame treatment.

Table II Contact Angle of Carbon Thin Film with Water after Radical Graft Polymerization

Carbon Thin Film	Contact Angle (°)
PSt grafted ^a	80
PMMA grafted ^a	68
PNVC grafted ^b	71
PPFHEA grafted ^a	87
PAA grafted ^c	59
PNVPD grafted ^d	52

^a Monomer, 0.15 mol; benzene, 5.0 cm³; 80°C; 8 h.

^b NVC, 0.02 mol; benzene, 5.0 cm³; 80°C; 8 h.

^c AA, 0.15 mol; MeOH, 5.0 cm³; 80°C; 1.5 h.

^d NVPD, 0.19 mol; 80°C; 8 h.

The contact angle of the untreated carbon thin film with pure water, that is, 57°, was almost equal to that of the graphite surface.¹⁴ By the oxidation of the carbon thin film surface, the contact angle was decreased, especially remarkably by the flame treatment. These results clearly show that oxygen containing groups, such as carboxyl and phenolic hydroxyl, were introduced onto the carbon thin film surface by the above treatments.¹⁴

The contact angle increased to 51–64° by the treatment of carbon thin film with TDI followed by ACPA, indicating the introduction of azo groups onto the surface. The contact angle of azo group introduced carbon thin film prepared after flame treatment is larger than that after nitric acid treatment. This suggests that the azo group content of the former is larger than that of latter. Therefore, hereafter flame-treated carbon thin film was used for the graft polymerization.

The radical graft polymerizations of styrene, MMA, NVC, PFHEA, AA, and NVPD were carried out using surface azo groups introduced onto carbon thin film. The results are summarized in Table II.

It was found that the contact angle of carbon thin film after the polymerization of styrene, MMA, NVC, and PFHEA increased and reached those of the corresponding polymer film. For example, the contact angle of carbon thin film obtained from the polymerization of MMA and styrene was almost equal to that of the polyMMA (PMMA) and polystyrene (PSt) surface, respectively. On the other hand, the contact angle of carbon thin film obtained from the polymerization of NVPD and AA was decreased, indicating the increase of the hydrophilic nature of the surface.

It is interesting to note that the contact angle of polyAA (PAA)-grafted carbon thin film decreases from 59° to 45° with the treatment with a dilute

aqueous solution of potassium hydroxide; and then with the treatment with dilute acid solution, the contact angle returns to that of the original PAA-grafted carbon thin film. This indicates that pendant carboxyl groups of surface grafted PAA chains are reversibly converted between carboxyl and potassium carboxylate groups.

Figure 1 shows the relationship between the contact angle after the polymerization of styrene and NVPD and polymerization time. The contact angle of carbon thin film during the polymerization of styrene increased with progress of the polymerization, but decreased during the polymerization of NVPD. The contact angle no longer increased after 10 h in both polymerizations. This indicates that the grafted polymer chains on the surface interfere with the propagation of polymers from neighboring azo groups.

Based on the above results, it is concluded that azo groups introduced onto carbon thin film have an ability to initiate the radical polymerization and the grafted chains are propagated from the surface.

Postgrafting of Polymers from Pendant Peroxycarbonate Groups of Surface Grafted Polymer Chain

The postgraft polymerization initiated by pendant peroxycarbonate groups of surface grafted polymer on carbon thin film was investigated [Eq. (5)]. The grafting of polymer having pendant peroxycarbonate groups onto the thin film was achieved by the copolymerization of MMA with HEPO initiated by azo groups introduced onto the surface at 80°C; the decomposition of pendant peroxycarbonate groups

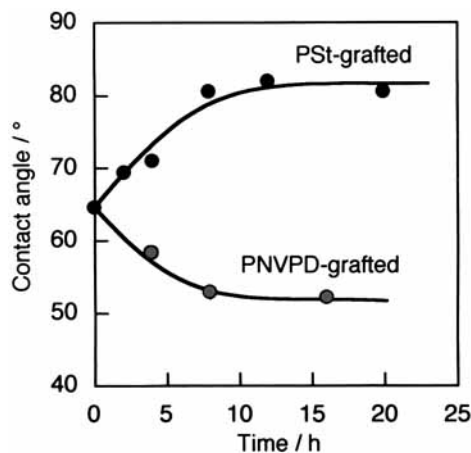
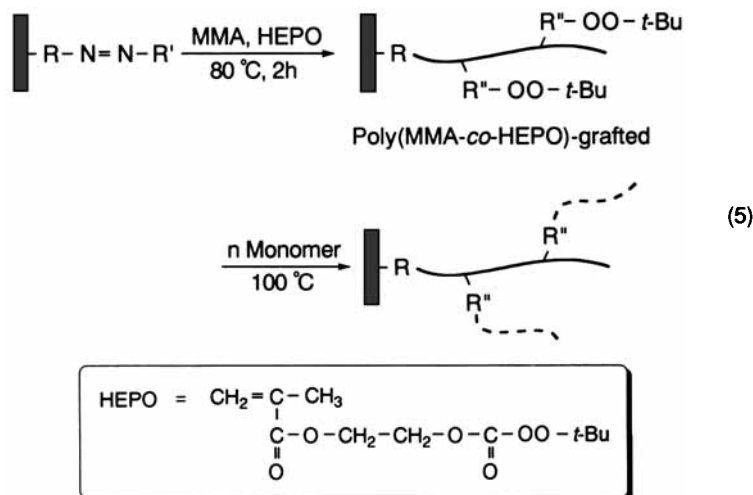


Figure 1 Relationship between polymerization time and contact angle of carbon thin film with water in the radical grafting of PSt and polyNVPD (PNVPD).



at 80°C is reported to be considerably small.¹⁵ The results are shown in Table III.

The increase of the contact angle of carbon thin film after the graft copolymerization of MMA with HEPO was relatively small. This may be due to the hydrophilic nature of HEPO moieties in poly(MMA-co-HEPO).

The postpolymerization of styrene and PFHEA was carried out by use of grafted poly(MMA-co-HEPO) on carbon thin film at 100°C. The results are also shown in Table III. It was found that the postpolymerization of styrene and PFHEA is successfully initiated by pendant peroxy carbonate groups of grafted poly(MMA-co-HEPO) and polystyrene or polyPFHEA (PPFHEA) is postgrafted onto the surface. The contact angle of PPFHEA-postgrafted carbon thin film surface was almost equal to that of poly(tetrafluoroethylene).

Cationic Graft Polymerization onto Carbon Thin Film

It has been reported that surface acylium perchlorate groups on carbon black, which were introduced by the reaction of surface acyl chloride groups with silver perchlorate, have an ability to initiate the cat-

ionic graft polymerization of various monomers to give polymer-grafted carbon black.^{5,6} Therefore, the cationic graft polymerization of styrene and NVPD initiated by surface acylium perchlorate groups introduced by the reaction of silver perchlorate with surface acyl chloride groups was investigated. Figure 2 shows the relationship between polymerization time and contact angle of carbon thin film obtained from the cationic polymerization of styrene and NVPD.

It was found that the contact angle of carbon thin film during the polymerization of styrene increased with progression of the polymerization, but decreased during the polymerization of NVPD. This indicated that the cationic graft polymerizations of styrene and NVPD are successfully started from surface acylium perchlorate groups and the corresponding polymers are grafted onto the surface.

Anionic Graft Polymerization onto Carbon Thin Film

We have reported that the anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides is initiated by potassium carboxylate groups introduced onto the carbon black surface and

Table III Contact Angle of Carbon Thin Film with Water Before and After Postgrafting

Carbon Thin Film	Monomer	Contact Angle (°)	
		Before Postgrafting	After Postgrafting
Poly(MMA-co-HEPO) grafted	Styrene	67	96
	PFHEA	67	111

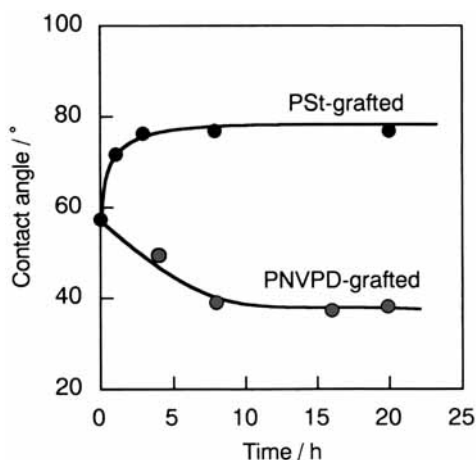


Figure 2 Relationship between polymerization time and contact angle of carbon thin film with water in the cationic grafting of PSt and PNVPD.

the corresponding copolymers, polyesters, are effectively grafted onto the surface.⁴ Therefore, the grafting of polyesters by the anionic ring-opening alternating copolymerization of epoxides with PAn initiated by surface potassium carboxylate groups was investigated. The introduction of potassium carboxylate groups onto carbon thin film was achieved by the neutralization of surface carboxyl groups: when treating carbon thin film with KOH, the contact angle decreased to 21° as shown in Table I.

The results of the copolymerization of SO or PFHEP and PAn using surface potassium carboxylate groups are shown in Table IV. In the polymerization, 18-crown-6 and *N*-phenyl- β -naphthylamine were added to accelerate the polymerization and to inhibit the thermal polymerization, respectively.⁴

In the presence of untreated and flame-treated carbon thin film, the grafting of polyester was scarcely observed because of no change of contact angle after the polymerization. On the contrary, the contact angle of carbon thin film after the copoly-

Table IV Contact Angle of Carbon Thin Film with Water after Anionic Ring Opening Copolymerization of Epoxides with Phthalic Anhydride

Carbon Thin Film	Contact Angle (°)
Poly(SO- <i>co</i> -PAn) grafted	67
Poly(PFHEP- <i>co</i> -PAn) grafted	97

Epoxide = PAn = 0.1 mol; 18-crown-6-ether, 0.02 g; *N*-phenyl- β -naphthylamine, 0.02 g; 120°C; 6 h.

Table V Contact Angle of Carbon Thin Film with Water after Treatment with Azo Polymer

Carbon Thin Film	Contact Angle (°)
Poly(DMS) grafted	86
Poly(PEG) grafted	39

Azopolymer, 1.5 g; benzene, 20 cm³; 70°C; 6 h.

merization of SO with PAn and PFHEP with PAn increased from 21° to 67° and 97°, respectively.

These results indicate that the anionic ring-opening copolymerization of epoxides with PAn was initiated by potassium carboxylate groups introduced onto the surface and grafted polyester chains were propagated from the surface.

Trapping of Polymer Radical by Carbon Thin Film Surface

Carbon blacks (surface polycondensed aromatic rings) are known to act as an effective radical trapping agent, because the reactivity of radicals to aromatic compounds increased with an increase in the number of aromatic rings.^{16,17} In the previous article, we demonstrated that polymer radicals formed by the decomposition of azo⁹ and peroxide polymers¹⁸ are effectively trapped by the carbon black surface to give polymer-grafted carbon black with a high percentage of grafting. Therefore, the grafting of polymers onto the carbon thin film surface by the reaction of azo polymer, poly(polydimethylsiloxane-azobiscyanopentanoate) [poly(DMS-ACPA): $M_n = 4.5 \times 10^3$] or poly(polyoxyethylene-azobiscyanopentanoate) [poly(PEG-ACPA): $M_n = 5.1 \times 10^3$], with carbon thin film in toluene was examined. The results are summarized in Table V.

By the treatment with poly(DMS-ACPA), the contact angle of carbon thin film increased to 86°: this value is almost equal to that of polydimethylsiloxane. On the other hand, the contact angle after the treatment with poly(PEG-ACPA) decreased, because of the hydrophilic nature of the PEG. These results indicate the grafting of polydimethylsiloxane and PEG onto the carbon thin film surface are successfully preceded by the trapping of the corresponding polymer radicals.

CONCLUSIONS

1. The radical, cationic, and anionic graft polymerizations were initiated by azo, acylium

perchlorate, and potassium carboxylate groups introduced onto carbon thin film, respectively, and the corresponding polymers were grafted onto the surface.

2. The postpolymerization of styrene and PFHEA were successfully initiated by pendant peroxy carbonate groups of poly (MMA-co-HEPO) grafted onto the carbon thin film and branched polymers were grafted onto the surface.
3. Polymer radicals formed by the decomposition of azo polymers were successfully trapped by the carbon thin film surface to give the corresponding polymer-grafted carbon thin film.

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