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STUDIES ON THE GRAFTING OF POLYMERS
ONTO CARBON BLACK SURFACE

(カーボンブラック表面へのポリマーのグラフト反応に関する研究)

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PREFACE

The research in this thesis was performed under the guidance by Associate Professor Norio Tsubokawa and former Professor Yasuo Sone at the Department of Material and Chemical Engineering, Faculty of Engineering, Niigata University.

The purpose of the present dissertation is to graft various polymers onto carbon black surface for its surface modification and functionalization.

I hope that the findings obtained through this research would give the valuable suggestions for new grafting methods with technical utility.

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CHAPTER 1

GENERAL INTRODUCTION

Recently, various kinds of inorganic powders are produced and used in composite materials in order to improve the mechanical properties and to evolve new properties. Carbon black is the most common in those powders and widely used industrially as pigments and fillers for polymers, especially the reinforcing filler for rubber.

With the exception of acetylene black, all commercially available carbon blacks are made from a hydrocarbon source, such as natural gas, oil, or a mixture of the two, by incomplete combustion or thermal decomposition of it in a limited supply of air at about 1000 °C. The major manufacturing processes that are used to produce commercial carbon blacks are as follows.

(1) Channel Process. In this process carbon black particles are produced by the incomplete oxidation of natural gas. Flames from the burning gas impinge on steel channels, where the carbon particles are deposited. These channels move over scrapers that remove the carbon black, which is collected in hoppers. The yield of carbon black obtained by the channel process is very low, running about 1-5%.

(2) Furnace Process. Aromatic residue oils from petroleum refineries are used for producing oil furnace blacks. In this process oil is heated to about 300 °C and then is atomized into the hot zone of the furnace (maintained at about 1400 °C by auxiliary gas burners), where the particles of carbon black are formed by the thermal decomposition of the oil. Yields of 35-65% are obtained by this process.

(3) Thermal Process. The thermal decomposition of hydrocarbon gases in the absence of a flame provides the reaction for the

production of thermal blacks. In a typical process the reactor, called generator, is heated at 1300 °C by burning a stoichiometric mixture of fuel and air and then injected with natural gas to produce the thermal black. The yields obtained by this process are about 40-50%. Acetylene blacks, which are obtained by pyrolysis of acetylene typically above 1800 °C, are considered to be a class of thermal black.

Carbon black is the ultrafine particle of 10-400 nm diameter. Its crystal structure appears to consist of concentric crystallites which are made up of turbostratic structure of 3-5 carbon-hexagonal-layer planes (approximately 1.7 nm diameter and 0.35 nm interplanar spacing). (See Figure 1-1.)¹⁻⁹⁾ Carbon black particles aggregate each other, and this aggregate is so called "Structure".¹⁰⁾

From a chemical point of view, carbon black is composed of 90-99% carbon, 0.1-10% oxygen, 0.2-1% hydrogen, and small amount of sulfur and ash.⁶⁾ Though the carbon atoms inside the crystallite are joined by covalent bonds, the unsatisfied valences of them on the edge sites of the layer planes at the surface can be saturated by oxygen, for example. Therefore, carbon black has oxygen containing groups such as carboxyl, phenolic hydroxyl, and quinonic oxygen groups on the surface (See Figure 1-2).^{6,11-14)} These functional groups on the surface can undergo normal organic reactions.

In general, dispersing inorganic powders uniformly into a polymer or an organic solvent is very difficult. In addition, the properties of inorganic powder-polymer composites are considered to depend on not only the mechanical properties of the polymer matrix, but also the properties of interfacial

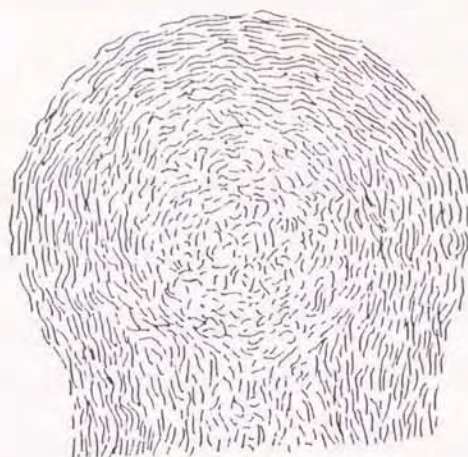


Figure 1-1

Microstructural model of carbon black particle according to Harling [Reprinted from K. Kinoshita, *Carbon*, John Wiley & Sons, New York, 1988, p 27.]

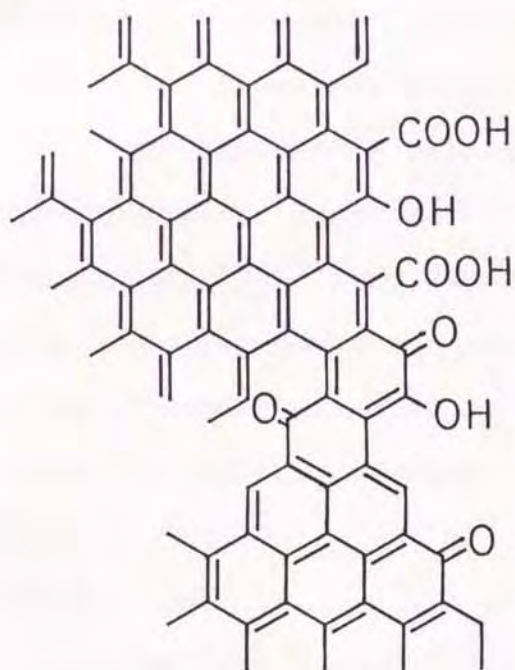


Figure 1-2

Schematic representation of the oxygen containing groups on the carbon black surface

regions between the powder surface and the matrix polymer.

The chemical and physical modification of inorganic powder surfaces, therefore, has been extensively studied. For example, oxidation, surface grafting, treatment by surfactant or coupling agent, plasma treatment, and sputtering are representative.¹⁵⁾ In those treatments, the surface grafting of polymers, namely, chemical binding of polymers onto the powder surface, interests us in designing new functional powders which have both properties of grafted polymers and powders, such as conductivity, heat resistivity, and ferromagnetism: for instance, by the grafting of unsaturated polyester onto the carbon black surface, a conductive polymer which can be crosslinked is obtained.

As mentioned above, carbon black has functional groups on the surface, and the other inorganic powders such as silica, ferrite, and titanium oxide also have reactive hydroxyl groups on their surfaces.¹⁶⁾ Our laboratory has reported the surface grafting of various polymers such as vinyl polymer,¹⁷⁻¹⁹⁾ polyester,^{20,21)} polyether,²²⁻²⁴⁾ polyamide,^{25,26)} and polysiloxane^{27,28)} onto inorganic powders using these functional groups, and many experimental attempts by other researchers also have been made to graft polymers onto these powder surfaces.^{16,29-33)}

Grafting reaction can be roughly classified into the following three principles (See Figure 1-3):^{16,34,35)}

- (1) the termination of the polymerization onto the powder surface which can deactivate growing polymer chains,
- (2) the reaction of a functional polymer with the powder surface where reactive groups are introduced, and

(1) Termination of polymerization onto the powder surface



(2) Reaction of the functional polymer with the powder surface



(3) Initiation of polymerization from the powder surface



Figure 1-3 Principles of grafting reactions onto powder surfaces
(Asterisk indicates activated species.)

(3) the initiation of the polymerization from the powder surface using initiating groups introduced onto the surface.

By the process (1) polymer-grafted powder with a higher percentage of grafting can not be obtained because of the preferential formation of ungrafted polymer.

Process (2) enables us to control the molecular weight and the number of grafted polymer chains onto powder surfaces. The percentage of grafting by this process, however, are limited to 30-40% because the grafted polymer chains on the surface mask the reactive groups on the surface.

The process (3) is most favorable for grafting polymers effectively onto powder surfaces. For instance, to obtain polymer-grafted carbon black with a higher percentage of grafting, the anionic grafting of polymers initiated by lithium phenolate^{18,25,36)} or alkali metal carboxylate^{20,37,38)} groups and metallized aromatic rings^{39,40)} on the surface of the carbon black has been investigated. Furthermore, the cationic grafting of polyether,^{22,41)} polyester,^{42,43)} and polyacetal⁴⁴⁾ has been achieved by use of acylium perchlorate groups introduced onto the carbon black surface. The radical grafting from the carbon black surface, however, has been scarcely investigated.⁴⁵⁾

It is well known that carbon black itself has unpaired electrons;^{46,47)} these unpaired electrons, however, have no ability to initiate the radical polymerization because they are stabilized by the polycondensed aromatic rings of the carbon black.^{47,48)} Accordingly, the introduction of active radicals onto the carbon black surface is required for the radical grafting from carbon black.

From this point of view, the present research has been carried out for investigating the radical grafting from the carbon black surface initiated by initiating groups introduced onto the surface.

In chapter 2, the radical graft polymerization of vinyl monomers from the carbon black surface initiated by peroxyester groups or azo groups introduced onto the surface is discussed. Furthermore, effect of e -value of vinyl monomers on the graft polymerization is also investigated.

Chapter 3 deals with the radical grafting from carbon black initiated by a redox system consisting of ceric ions and reducing groups introduced onto the surface.

In chapter 4, the graft polymerization of vinyl monomers to grafted polymer chains on the carbon black surface is described with a view to obtaining polymer-grafted carbon black with a higher percentage of grafting.

Concluding remarks are presented in chapter 5.

The contents of this thesis are composed of the following papers.

- (1) Radical Grafting from Carbon Black by Carbon Black Having Hydroxy Methyl Group/Ceric Ion Redox System

Norio Tsubokawa, Kazuhiro Fujiki, and Yasuo Sone

J. Polym. Sci., Polym. Chem. Ed., 24, 191-194 (1986).

- (2) Polymer-Grafted Carbon Black with a Higher Percentage of Grafting: Graft Polymerization of Vinyl Monomers onto Unsaturated Polyester-Grafted Carbon Black Surfaces

Norio Tsubokawa, Kazuhiro Fujiki, and Yasuo Sone

Kobunshi Ronbunshu, 44, 605-612 (1987).

- (3) Radical Grafting from Carbon Black. Graft Polymerization of Vinyl Monomers Initiated by Peroxyester Groups Introduced onto Carbon Black Surface
Norio Tsubokawa, Kazuhiro Fujiki, and Yasuo Sone
Polym. J., 20, 213-220 (1988).
- (4) Graft Polymerization of Vinyl Monomers onto Carbon Black by Use of the Redox System Consisting of Ceric Ions and Carbon Black Carrying Alcoholic Hydroxyl Groups
Norio Tsubokawa, Kazuhiro Fujiki, and Yasuo Sone
J. Macromol. Sci.-Chem., A25, 1159-1171 (1988).
- (5) Effect of e -Value of Vinyl Monomers on the Radical Graft Polymerization from Carbon Black Surface
Kazuhiro Fujiki, Norio Tsubokawa, and Yasuo Sone
Tanso, No.140, 234-240 (1989).
- (6) Radical Grafting from Carbon Black. Graft Polymerization of Vinyl Monomers Initiated by Azo Groups Introduced onto Carbon Black Surface
Kazuhiro Fujiki, Norio Tsubokawa, and Yasuo Sone
Polym. J., 22, 661-670 (1990).
- (7) Grafting onto Carbon Black Having Few Functional Group 5. Introduction of Amino and Methylol Groups onto Carbon Black by Use of Electrophilic Substitution Reaction and Utilization of These Groups for Grafting of Polymers onto the Surface
Kazuhiro Fujiki, Katsuaki Magara, Norio Tsubokawa, and Yasuo Sone
Nippon Gomu Kyokaishi, 64, (1991)
(accepted for publication).

CHAPTER 2

GRAFT POLYMERIZATION OF VINYL MONOMERS INITIATED BY PEROXYESTER OR AZO GROUPS INTRODUCED ONTO CARBON BLACK SURFACE

2.1 ABSTRACT

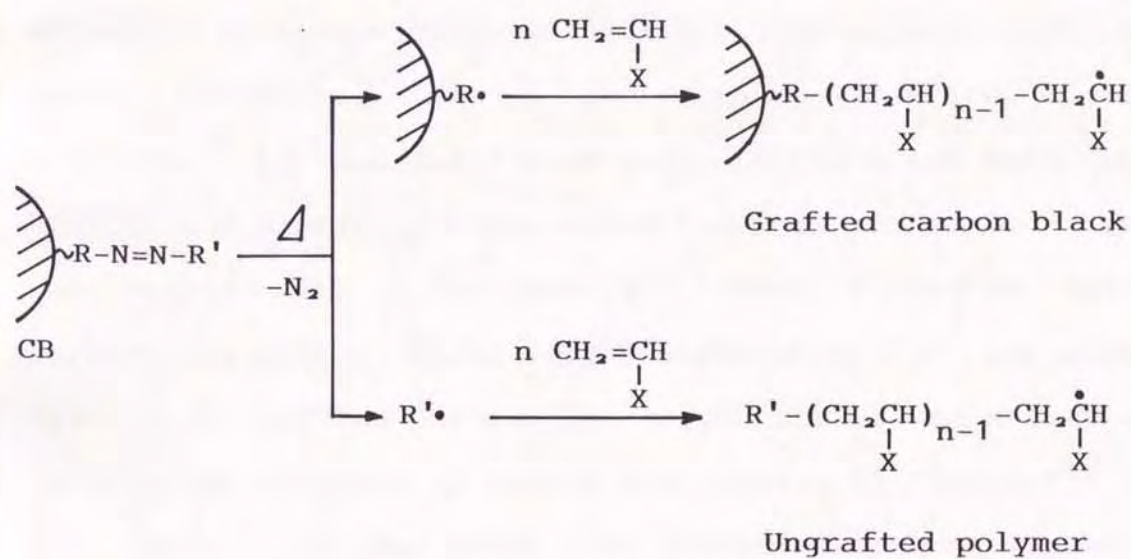
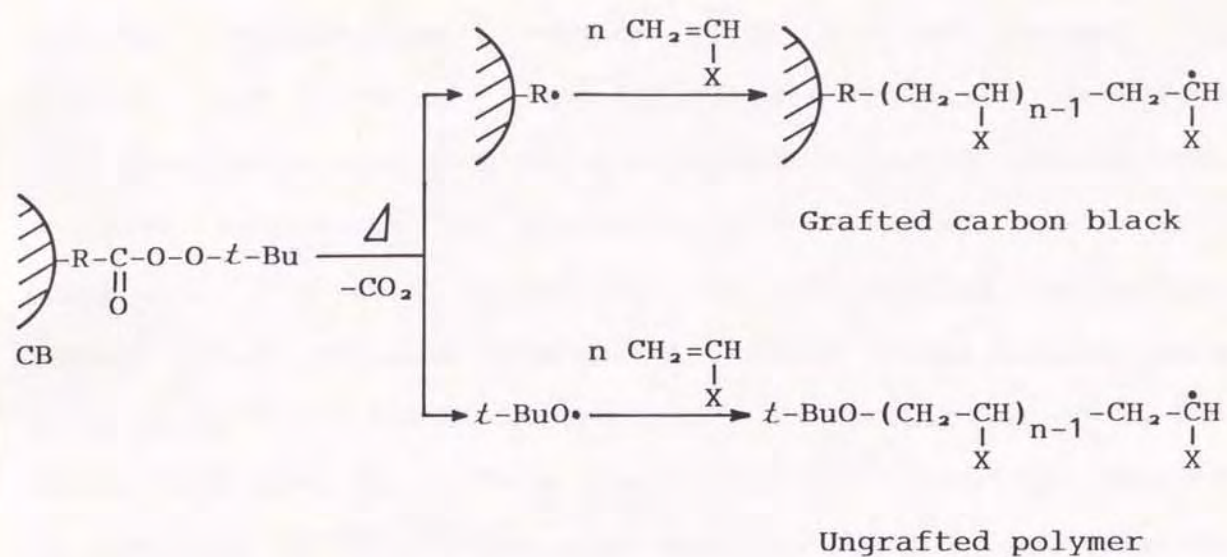
The radical graft polymerization of vinyl monomers from carbon black initiated by peroxyester or azo groups introduced onto the surface was investigated. Carbon black having peroxyester groups was able to initiate the graft polymerization of methyl methacrylate, and poly(methyl methacrylate) was effectively grafted onto the surface by propagating the polymer from the radical produced on the surface. The polymerization of vinyl monomers such as methyl methacrylate and styrene was also initiated by azo groups introduced onto the carbon black surface. During the polymerization, the corresponding polymer was effectively grafted onto the carbon black surface through the propagation of the polymer from the radical produced on the surface by the decomposition of the azo groups. Furthermore, the effect of e -value of vinyl monomers on the graft polymerization was investigated. The carbon black having azo groups initiated the polymerization of vinyl monomers to give polymer-grafted carbon black regardless of the e -value of monomers. On the other hand, carbon black having peroxyester groups was capable of initiating the polymerization of vinyl monomers with positive e -value, but incapable of that with negative e -value.

2.2 INTRODUCTION

The grafting of various polymers onto carbon black has been widely investigated. For instance, polymer-grafted carbon black can be easily obtained when the polymerization of vinyl monomers is initiated by radical,¹⁷⁾ anionic,⁴⁹⁾ and cationic⁵⁰⁾ initiators in the presence of carbon black. The percentage of grafting of polymer and grafting efficiency, however, are less than 10% because the carbon black surface reacts with initiators in preference to growing polymer radicals.

Therefore, it is necessary to initiate the polymerization from active sites introduced onto the surface of the carbon black to obtain the polymer-grafted carbon black with a higher percentage of grafting.^{34,35)} From this point of view, we reported the grafting of various polymers onto carbon black by the anionic grafting from alkali metal carboxylate groups on carbon black^{37,38)} and by the cationic grafting from acylium perchlorate groups on carbon black.^{41,51)} The radical grafting from carbon black, however, has been scarcely investigated.

In this chapter, the introduction of peroxyester or azo groups onto the surface of the carbon black and the graft polymerization of vinyl monomers initiated by these initiating groups on the surface were discussed (Scheme 2-1). In addition, the effect of e -value of vinyl monomers on the graft polymerization was investigated.



Scheme 2-1

2.3 EXPERIMENTAL

2.3.1 Materials

The carbon black samples used were of furnace and channel type. Furnace black Philblack O (Phillips Petroleum Co.) was extracted with chloroform before use to remove the resinous substances on the surface.⁵⁾ Channel black Neospectra II (Columbian Carbon Co.) was used without extraction because of no resinous substances. These carbon blacks were dried in vacuo at 110 °C before use. The properties of carbon blacks (BET specific surface area, pH,^{6,52,53)} and the content of carboxyl (COOH),⁵⁴⁾ phenolic hydroxyl (OH),⁵⁵⁾ and quinonic oxygen (C=O)^{56,57)} groups) are shown in Table 2-1.

Methyl methacrylate (MMA) was washed with a 10% aqueous solution of sodium hydrogensulfite, a 5% aqueous solution of sodium hydroxide, and a 20% aqueous solution of sodium chloride. It was dried over sodium sulfate and then calcium hydride and distilled twice under reduced pressure. Styrene was washed with a 10% aqueous solution of sodium hydroxide followed by water, dried over calcium chloride, and distilled twice under reduced pressure. Acrylonitrile was washed with a 5% aqueous solution of sodium hydroxide, 5% phosphoric acid, and water. It was dried over potassium carbonate and then distilled in the presence of carbon black. *N*-Vinyl-2-pyrrolidone, glycidyl methacrylate, 4-vinylpyridine, acrylic acid, and 2-hydroxyethyl methacrylate were distilled under reduced pressure in the presence of hydroquinone. Vinyl acetate and methyl vinyl ketone were distilled twice.

tert-Butyl hydroperoxide (*t*-BuOOH) and *tert*-butyl peroxy-

Table 2-1 Properties of carbon blacks used

Carbon black	BET surface area/m ² g ⁻¹	pH	COOH mmol g ⁻¹	OH mmol g ⁻¹	C=O mmol g ⁻¹
Neospectra II ^a	906	3.0	0.40	0.24	0.92
Philblack O ^b	79.6	8.7	0	0.02	0.18

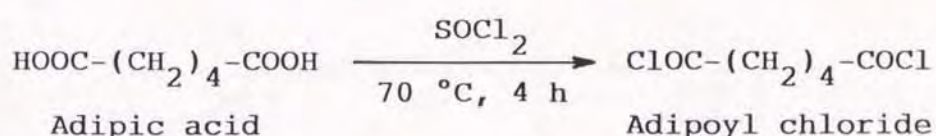
^aChannel black.

^bFurnace black.

benzoate (BPOB) obtained from Nippon Oil & Fats Co., Ltd. were purified by distillation under reduced pressure. Tolylene 2,4-diisocyanate (TDI) obtained from Wako Pure Chemical Co., Ltd. was distilled under reduced pressure just before its use. 4,4'-Azobis(4-cyanovaleric acid) (ACV) obtained from Otsuka Chemical Co., Ltd. and 2,2'-azobis(2-cyano-*n*-propanol) (ACP) obtained from Wako Pure Chemical Co., Ltd. were dried in vacuo at room temperature before use.

Dioxane, benzene, and tetrahydrofuran (THF) were refluxed over sodium and distilled twice. Dimethyl sulfoxide (DMSO) was dried over calcium hydride with stirring for two days and then distilled twice under reduced pressure. Chloroform was washed with concentrated sulfuric acid, an aqueous solution of sodium hydroxide, and water. It was dried over potassium carbonate and then distilled. Other solvents and reagents were used without further purification.

Adipoyl chloride was prepared by the reaction of adipic acid with thionyl chloride by the ordinary method (Scheme 2-2).



Scheme 2-2

2.3.2 Introduction of Carboxyl Groups onto Carbon Black

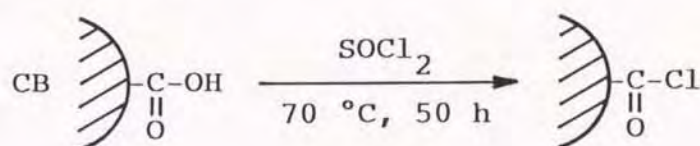
Carbon black which consists of polycondensed aromatic rings has high reactivity to free radicals. For instance, it has been reported that in the reaction of 2,2'-azobisisobutyronitrile (AIBN) with carbon black, 1-cyano-1-methyl-ethyl radicals were fixed onto the surface.^{13,58-60)}

Therefore, the introduction of carboxyl groups onto carbon black was achieved by the reaction of carbon black with 3-carboxy-1-cyano-1-methylpropyl radicals which formed by the thermal decomposition of ACV (Scheme 2-3).

Into a 500 mL flask, 6.0 g of carbon black, 0.40 g of ACV, and 100 mL of benzene were charged. The reaction mixture was stirred at 60 °C under nitrogen. Then 0.40 g of ACV was added to the reaction mixture every 8 h interval of the reaction and the reaction was allowed to continue for 56 h (total ACV used for the treatment was 2.8 g). The resulting carbon black was purified by Soxhlet extraction with acetone and dried in vacuo. The amount of carboxyl groups introduced onto carbon black was determined by nitrogen analysis.⁶¹⁾

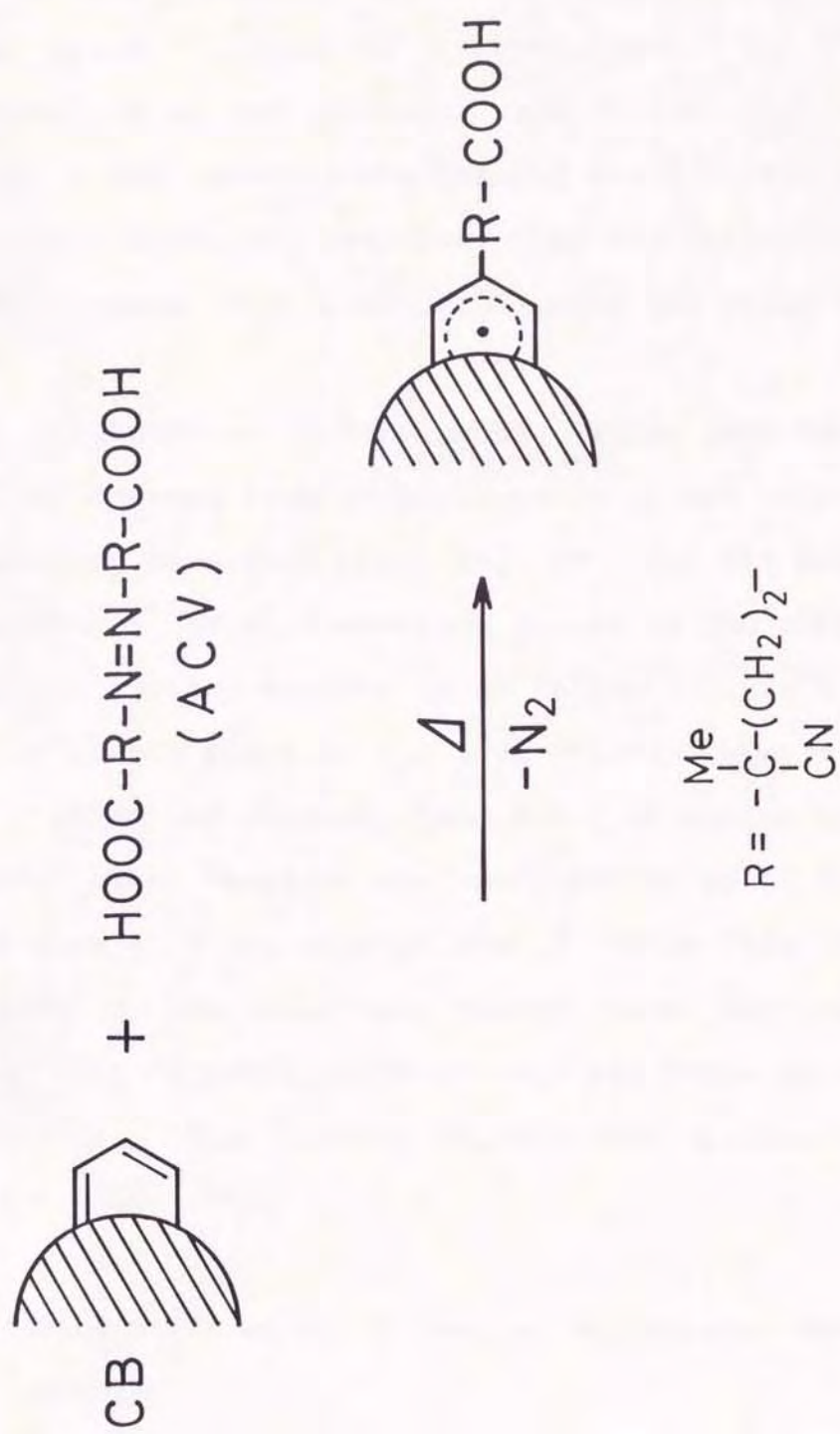
2.3.3 Introduction of Acyl Chloride Groups onto Carbon Black

(1) Carbon black having acyl chloride groups was prepared by the reaction of carboxyl groups on the surface with thionyl chloride (Scheme 2-4).^{51,62)}



Scheme 2-4

The procedures are as follows: Into a 300 mL flask, 0.6 g of carbon black, 60 mL of absolute benzene, a large excess (30 mL) of thionyl chloride were charged. The mixture was refluxed with stirring for 50 h. After the reaction, benzene and unreacted thionyl chloride were distilled away under reduced pressure and then the resulting carbon black was dried in vacuo at 110 °C. The treated carbon black was stored in



Scheme 2-3

vacuo at room temperature.

(2) In addition, the introduction of acyl chloride groups onto carbon black by the reaction of phenolic hydroxyl groups with adipoyl chloride was carried out as follows: Into a 100 mL flask, 2.0 g of carbon black, 1.0 mL of adipoyl chloride, 30 mL of dioxane, and 0.1 mL of pyridine were charged. The mixture was stirred at 50 °C for 24 h under dry nitrogen. After the reaction, the resulting carbon black was filtered, washed with absolute dioxane and dried in vacuo.

2.3.4 Introduction of Peroxyester Groups onto Carbon Black

The introduction of peroxyester groups onto carbon black (preparation of carbon black 1P, 2P, and 3P) was achieved by the reaction of acyl chloride groups on the surface with *t*-BuOOH. A typical example is as follows: Into a 100 mL flask, 2.0 g of carbon black having acyl chloride groups, 1.0 mL of *t*-BuOOH, 20 mL of dioxane, and 0.1 g of sodium hydroxide were charged. The reaction was conducted at 20 °C for 12 h under stirring with a magnetic stirrer. After the reaction, the resulting carbon black was poured into methanol, filtered, washed with methanol and acetone, and dried in vacuo at room temperature. The treated carbon black was stored in the dark at below 0 °C.

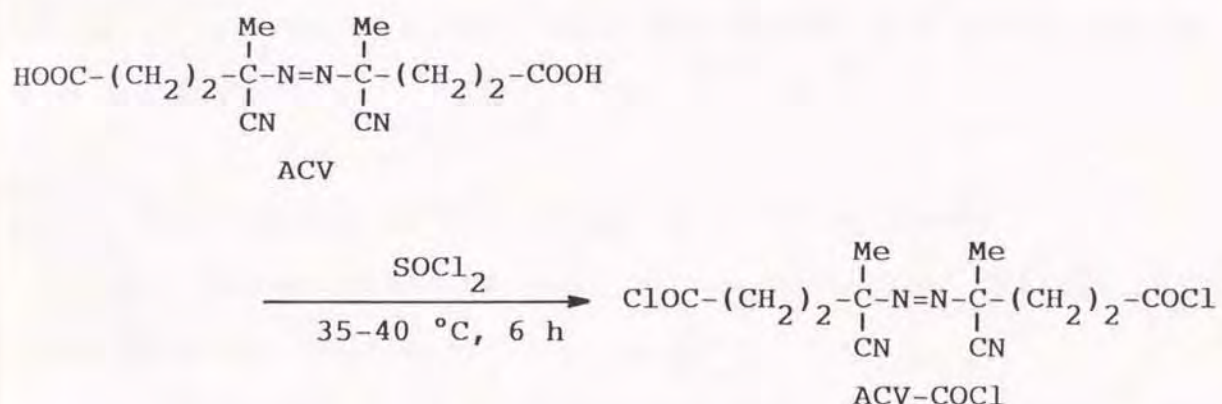
2.3.5 Determination of Content of Peroxyester Groups on Carbon Black

Carbon black having peroxyester groups was stirred with excess of an aqueous solution of KI (0.01 molL^{-1}) at room temperature for 3 h. Then excess of KI was titrated with an

aqueous AgNO_3 solution (0.01 molL^{-1}) and an aqueous KSCN solution (0.01 molL^{-1}) according to the method of Volhard.⁶³⁾ The content of peroxyester groups on carbon black was calculated from the amount of KI consumed by the carbon black.

2.3.6 Preparation of 4,4'-Azobis(4-cyanovaleryl chloride)

4,4'-Azobis(4-cyanovaleryl chloride) (ACV-COCl) was prepared by the reaction of ACV with thionyl chloride (Scheme 2-5).⁶⁴⁾



Scheme 2-5

Into a 100 mL flask, 30 mL of thionyl chloride was charged. Then 10 g of ACV was added gradually into the flask, and the reaction was continued with stirring for 6 h at 35-40 °C under dry nitrogen. After the reaction, unreacted thionyl chloride was distilled away under reduced pressure, and the reaction product was recrystallized from chloroform. The prepared ACV-COCl was dried in vacuo at room temperature and stored in the dark below 0 °C.

2.3.7 Introduction of Hydroxyl Groups onto Carbon Black

The introduction of hydroxyl groups onto the carbon black

surface was carried out by the reaction of carboxyl, phenolic hydroxyl, and quinonic oxygen groups on the surface with *n*-butyllithium (BuLi). (Scheme 2-6.)⁶⁵⁾ The procedures were as follows: Into a 200 mL flask, 6.0 g of carbon black, 10 mL of BuLi (about a 15% hexane solution), and 60 mL of THF were charged. The mixture was stirred with a magnetic stirrer for 2 h at 25 °C under dry nitrogen. After the reaction, the resulting carbon black was filtered, washed with distilled water until the filtrate was neutral, and dried in vacuo at 110 °C. The treated carbon black was stored in a desiccator at room temperature.

2.3.8 Introduction of Azo Groups onto Carbon Black

The introduction of azo groups onto the surface was achieved by the following three methods.

(1) Preparation of Carbon Black 1A: Carbon black 1A was prepared by the reaction of acyl chloride groups on the surface with ACP. Into a 200 mL flask, 6.0 g of carbon black having acyl chloride groups, 1.0 g of ACP, 80 mL of dioxane, and α -picoline were charged. Then the reaction mixture was stirred with a magnetic stirrer for 8 h at 25 °C under dry nitrogen. After the reaction, the resulting carbon black was repeatedly washed with methanol and dried in vacuo at room temperature. The treated carbon black was stored in the dark below 0 °C.

(2) Preparation of Carbon Black 2A: Carbon black 2A was prepared by the reaction of isocyanate groups on the surface with ACV. A typical example was as follows. Into a 200 mL flask, 5.0 g of carbon black, 130 mL of DMSO, 1.0 mL of TDI, and α -picoline were charged.^{66,67)} The mixture was stirred

with a magnetic stirrer at 60 °C under dry nitrogen, and after the reaction for 4 h, the flask was cooled to room temperature. Then 4.0 g of ACV was added into the flask and the reaction was continued with stirring for 8 h at 25 °C. Subsequent procedures of washing and drying of the resulting carbon black were performed in the same manner as described above.

(3) Preparation of Carbon Black 3A: Carbon black 3A was prepared by the reaction of hydroxyl groups on the surface with ACV-COCl. A typical example was as follows. Into a 200 mL flask, 6.0 g of carbon black, 0.6 g of ACV-COCl, 80 mL of dioxane, and α -picoline were charged. When the BuLi-treated carbon black was used, 4.9 g of ACV-COCl was reacted. Then the reaction mixture was stirred with a magnetic stirrer for 8 h at 25 °C under dry nitrogen. Subsequent procedures of washing and drying were performed in the same manner as described above.

2.3.9 Polymerization Procedures

A typical example is as follows. Into a glass tube, 0.30 g of carbon black and 10 mL of monomer were charged. In the polymerization initiated by peroxyester groups on carbon black, 0.50 g of carbon black was used. Then the tube was cooled, thawed three times with nitrogen, and sealed under vacuum. The sealed tube was heated at a definite temperature with shaking. After a definite time, the contents of the tube were poured into a large excess of a precipitant for the polymer. The precipitate was filtered and dried in vacuo at 40 °C.

When *N*-vinyl-2-pyrrolidone and acrylic acid were used as monomer, the polymerization was stopped by adding hydroquinone and then unreacted monomer was removed by distillation under

reduced pressure. The residue was dried in vacuo at 40 °C.

The conversion was calculated by the following equation:

$$\text{Conversion (\%)} = \frac{\text{Precipitate obtained (g)} - \text{Carbon Black (g)}}{\text{Monomer used (g)}} \times 100$$

2.3.10 Determination of Percentage of Grafting and Grafting Efficiency

The reaction product was dispersed in a solvent for the polymer with stirring, and the dispersion was centrifuged at 1.2×10^4 rpm until the carbon black was precipitated completely in order to separate ungrafted polymer from the reaction product that contained polymer-grafted carbon black. The carbon black precipitated was extracted with a solvent for the polymer using a Soxhlet extractor until no more polymer could be detected in the refluxing solvent. The percentage of grafting and grafting efficiency were determined by the following equations:

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

$$\text{Grafting efficiency (\%)} = \frac{\text{Polymer grafted (g)}}{\text{Total polymer formed (g)}} \times 100$$

The amount of grafted polymer was determined from the increment in weight of carbon black after the graft polymerization.

2.3.11 Stability of Dispersion of Poly(methyl methacrylate)-Grafted Carbon Black

PMMA-grafted carbon black (1.0 g) was dispersed in 100 mL of THF and the dispersion was allowed to stand at room temperature. After a definite time, 5.0 mL of dispersion liquid was taken out with a pipet and the content of the carbon black was determined. The stability of dispersion was estimated by the content of the carbon black in dispersion.

Stability of dispersion (%)

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

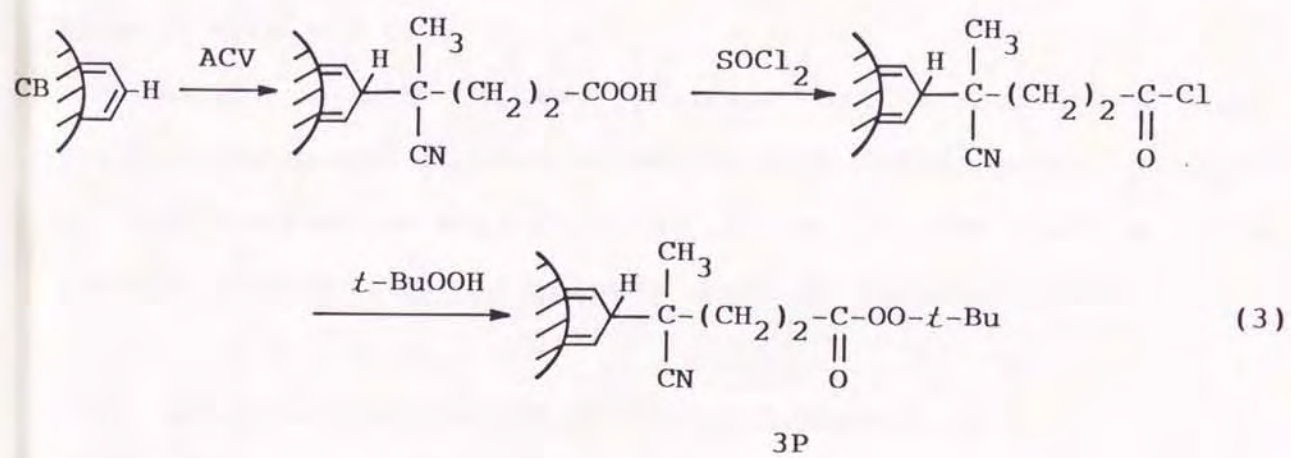
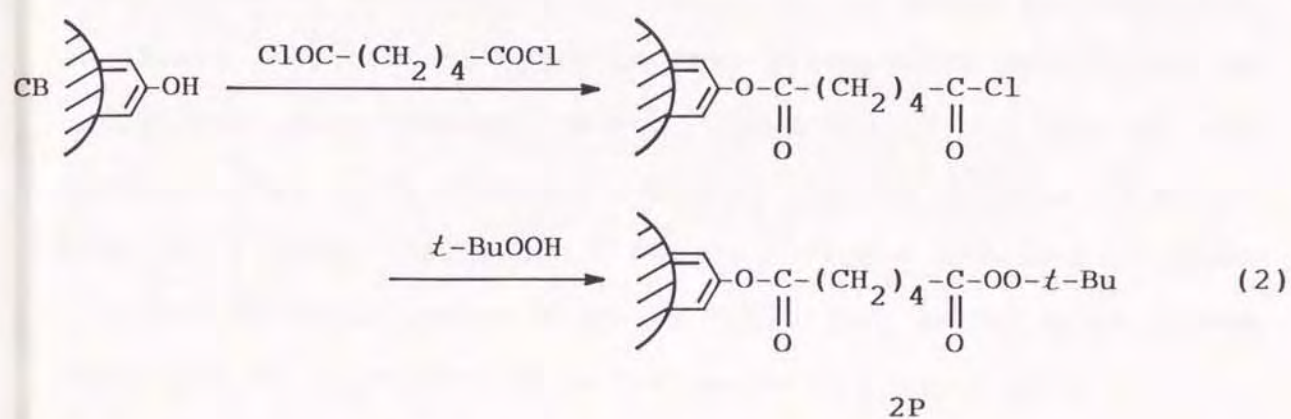
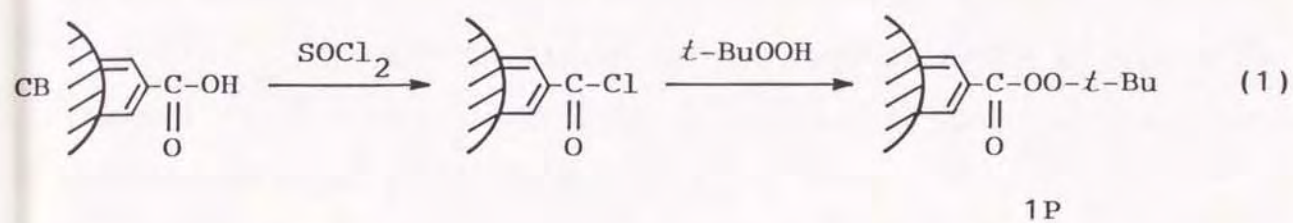
2.4 RESULTS AND DISCUSSION

2.4.1 Graft Polymerization of Vinyl Monomers Initiated by Peroxyester Groups Introduced onto Carbon Black Surface

(1) Introduction of Peroxyester Groups onto Carbon Black

It has been reported that peroxyester groups can be introduced onto a polymer chain by the reaction of acyl chloride groups on the polymer with *t*-BuOOH.⁶⁸⁻⁷⁰ Therefore, the introduction of peroxyester groups onto carbon black by the reaction of acyl chloride groups on the surface with *t*-BuOOH was examined.

The introduction of acyl chloride groups onto carbon black was achieved by the following three methods (Scheme 2-7): (1) the reaction of carboxyl groups on carbon black with thionyl chloride (Eq. 1), (2) the reaction of phenolic hydroxyl groups



Scheme 2-7

on carbon black with adipoyl chloride (Eq. 2), and (3) the reaction of 3-carboxy-1-cyano-1-methylpropyl groups, introduced by the reaction of ACV with carbon black, with thionyl chloride (Eq. 3). These carbon blacks having acyl chloride groups were treated with excess of *t*-BuOOH in dioxane in the presence of sodium hydroxide at 20 °C for 12 h.

The amount of peroxyester groups introduced onto carbon black surface, determined by titration, is shown in Table 2-2. In Table 2-2, it is apparent that peroxyester groups can be introduced onto channel black Neospectra II by use of its carboxyl (Eq. 1) or phenolic hydroxyl (Eq. 2) groups. However, because original Philblack O has no carboxyl groups and fewer phenolic hydroxyl groups shown in Table 2-2, peroxyester groups could not be introduced onto the surface by Eq. 1 or 2.

Therefore, the introduction of peroxyester groups onto Philblack O was achieved by use of Philblack O previously treated with ACV (Eq. 3).

Based on the above results, it is concluded that peroxyester groups can be introduced onto carbon black surface by the reaction of acyl chloride groups on the surface with *t*-BuOOH according to the methods shown in Eqs. 1, 2, and 3.

(2) Graft Polymerization of Methyl Methacrylate

Graft Polymerization of MMA Initiated by Carbon Black 1P

The polymerization of MMA was carried out in the presence of carbon black 1P at 70 °C and the initiating activity was examined. Table 2-3 shows the results of the polymerization of MMA initiated by carbon black 1P.

As shown in Table 2-3, thermal polymerization of MMA

Table 2-2 Peroxyester groups introduced onto
carbon black surface

Carbon black	$\frac{\text{COOH}}{\text{mmol g}^{-1}}$	$\frac{\text{OH}}{\text{mmol g}^{-1}}$	Introduction reaction	No.	Peroxyester group/ mmol g^{-1}
Neospectra II	0.40	0.24	—	—	0
Neospectra II	0.40	0.24	Eq. 1	1P	0.20
Neospectra II	0.40	0.24	Eq. 2	2P	0.18
Philblack O	0	0.02	Eq. 1	—	0
Philblack O	0	0.02	Eq. 2	—	0
Philblack O ^a	0.20	0.02	Eq. 3	3P	0.15

^aCarboxyl groups were introduced by the treatment with ACV.

proceeded even in the absence of initiator, whereas the rate of the polymerization was negligibly small. On the contrary, both in the presence of untreated carbon black and in the presence of carbon black 1P, the polymerization of MMA was completely inhibited.

These phenomena suggest that in the presence of untreated carbon black, thermal polymerization is inhibited by oxygen containing groups on carbon black surface such as phenolic hydroxyl and quinonic oxygen groups. On the other hand, in the presence of carbon black 1P, *tert*-butyl peroxyester groups are considered to decompose to give phenyl radical and *tert*-butyloxy radical (Eq. 4).⁶⁹⁾ The phenyl radical seems to be stabilized by polycondensed aromatic rings of carbon black and has no ability to initiate the polymerization. Furthermore, the *tert*-butyloxy radical may possibly react with the carbon black surface in preference to the monomer.^{17,60)} (A detailed discussion about this phenomenon is described at section 2.4.3-(3) in this chapter.) Although the *tert*-butyloxy radical initiates the polymerization of MMA, the growing polymer radical may be immediately trapped by the quinonic oxygen groups on the surface.

Therefore, it is apparent that the graft polymerization of vinyl monomers is unable to initiate by carbon black 1P.

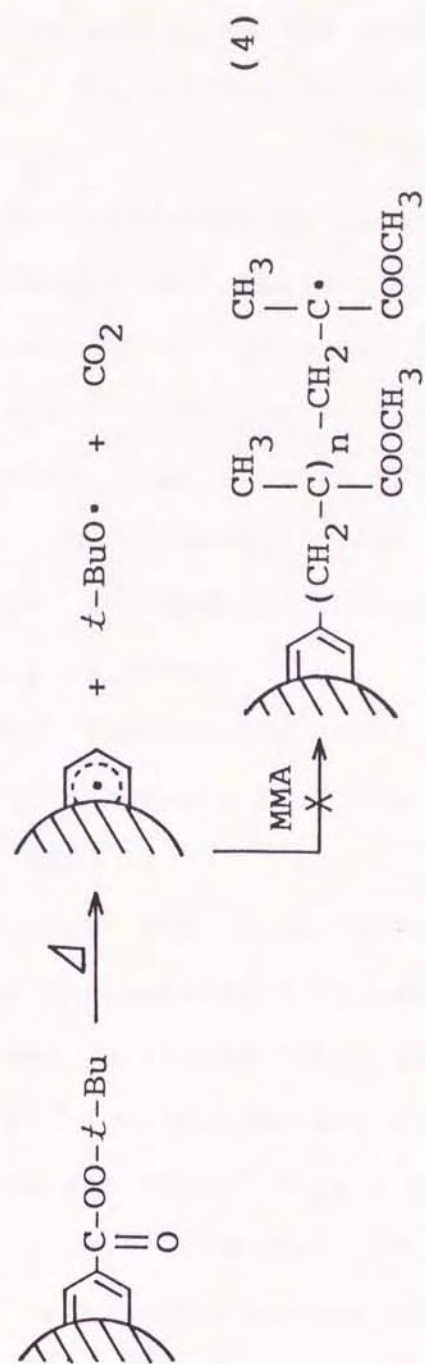
Graft Polymerization of MMA Initiated by Carbon Black 2P

The graft polymerization of MMA from carbon black was examined by use of carbon black 2P as an initiator. Different from carbon black 1P, carbon black 2P was expected to generate *tert*-butyloxy radical and alkyl radical that have initiating

Table 2-3 Graft polymerization of MMA initiated by
carbon black 1P

Carbon black	Conversion %
None	0.7
Neospectra II	0
<i>l</i> -BuOOCO-Neospectra II (1P)	trace

Carbon black, 0.50 g; MMA, 10 mL; 70 °C; 6 h.



Scheme 2-8

activity of polymerization.

The results are shown in Table 2-4. As mentioned above, in the presence of untreated carbon black, no polymerization could be detected at all. On the contrary, in the presence of carbon black **2P**, the polymerization of MMA was found to be initiated at 70 °C.

To ensure the initiation by peroxyester groups on carbon black **2P**, the initiating ability of *t*-BuOOH-adsorbed Neospectra II was evaluated. As shown in Table 2-4, *t*-BuOOH-adsorbed carbon black failed to initiate the polymerization of MMA. This suggests that *t*-BuOOH adsorbed on carbon black surface during the treatment for the introduction of peroxyester groups is removed completely by washing with methanol and drying in vacuo.

These results lead to the conclusion that carbon black having peroxyester groups, **2P**, has ability to initiate the polymerization of MMA.

Figure 2-1 shows the time-conversion curves of the polymerization of MMA initiated by carbon black **2P** at 70 and 90 °C. As is seen in Figure 2-1, the polymerization was of a dead-end type and conversion did not increase even if the polymerization time was extended up 6 h.

Smets et al. have reported that in the presence of carboxyl groups, peroxyester groups in a polymer chain decompose very rapidly.⁶⁸⁾ Therefore, it is considered that in the polymerization initiated by carbon black **2P**, peroxyester groups on carbon black rapidly decompose by the action of carboxyl groups on the surface. In addition, since carbon black **2P** has phenolic hydroxyl and quinonic oxygen groups on the surface,

Table 2-4 Graft polymerization of MMA initiated by
carbon black 2P

Carbon black	Conversion	Grafting
	%	%
None	0.7	—
Neospectra II	0	—
λ -BuOOH-adsorbed Neospectra II	0	—
λ -BuOOCO-Neospectra II (2P)	3.8	45.5

Polymerization conditions are given in Table 2-3.

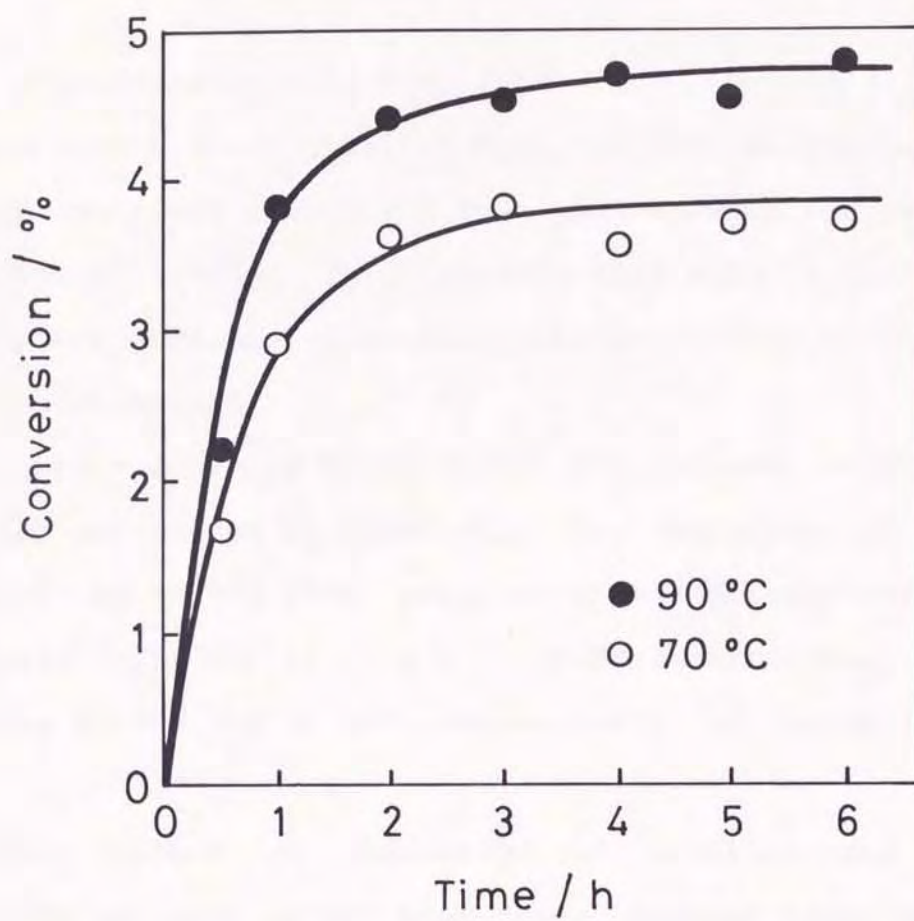


Figure 2-1

Graft polymerization of MMA
initiated by carbon black 2P

Carbon black, 0.50 g; MMA, 10 mL.

resulting *tert*-butyloxy radical and the growing polymer radical probably react with phenolic hydroxyl and quinonic oxygen groups, respectively. As a result, the polymerization of MMA initiated by carbon black 2P seems to become the dead-end type.

Proof of Grafting from Carbon Black

The carbon black obtained from the polymerization produced a stable colloidal dispersion in a good solvent for poly(methyl methacrylate) (PMMA). This suggests that PMMA is grafted from carbon black surface. Therefore, the percentage of grafting of PMMA was determined.

Figure 2-2 shows the relationship between polymerization time and percentage of grafting. The percentage of grafting increased up to 40% with progress of the polymerization, but no longer increased after 2 h. Grafting efficiency at 70 and 90 °C was 62-70% and 46-53%, respectively, as shown in Figure 2-3.

These values of percentage of grafting and grafting efficiency are much larger than those obtained from the polymerization in the presence of carbon black using benzoyl peroxide as an initiator.¹⁷⁾ This may be due to the fact that PMMA is propagated from the radical produced on the surface by the decomposition of peroxyester groups.

Graft Polymerization of MMA Initiated by Carbon Black 3P

The initiating activity of the graft polymerization of MMA for furnace black 3P was examined. The results are shown in Figure 2-4. It is apparent that carbon black 3P also has ability to initiate the polymerization of MMA. Although

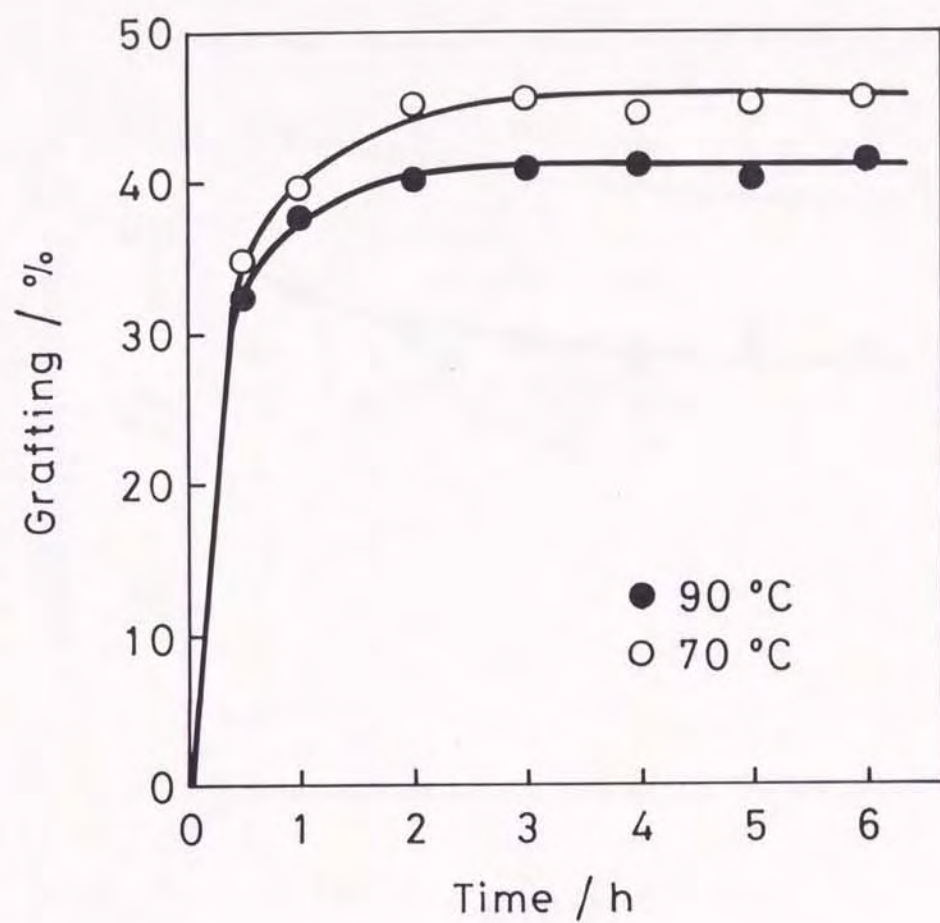


Figure 2-2

Relationship between polymerization time
and percentage of grafting using
carbon black 2P as an initiator

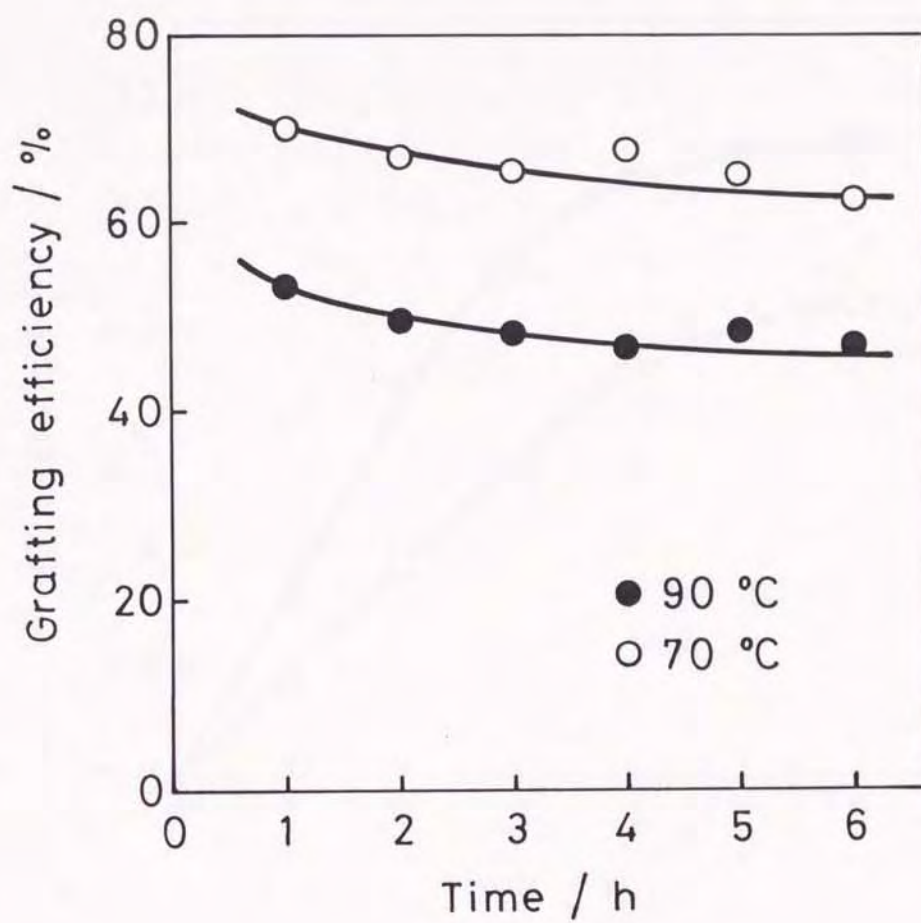


Figure 2-3

Relationship between polymerization time
and grafting efficiency using
carbon black 2P as an initiator

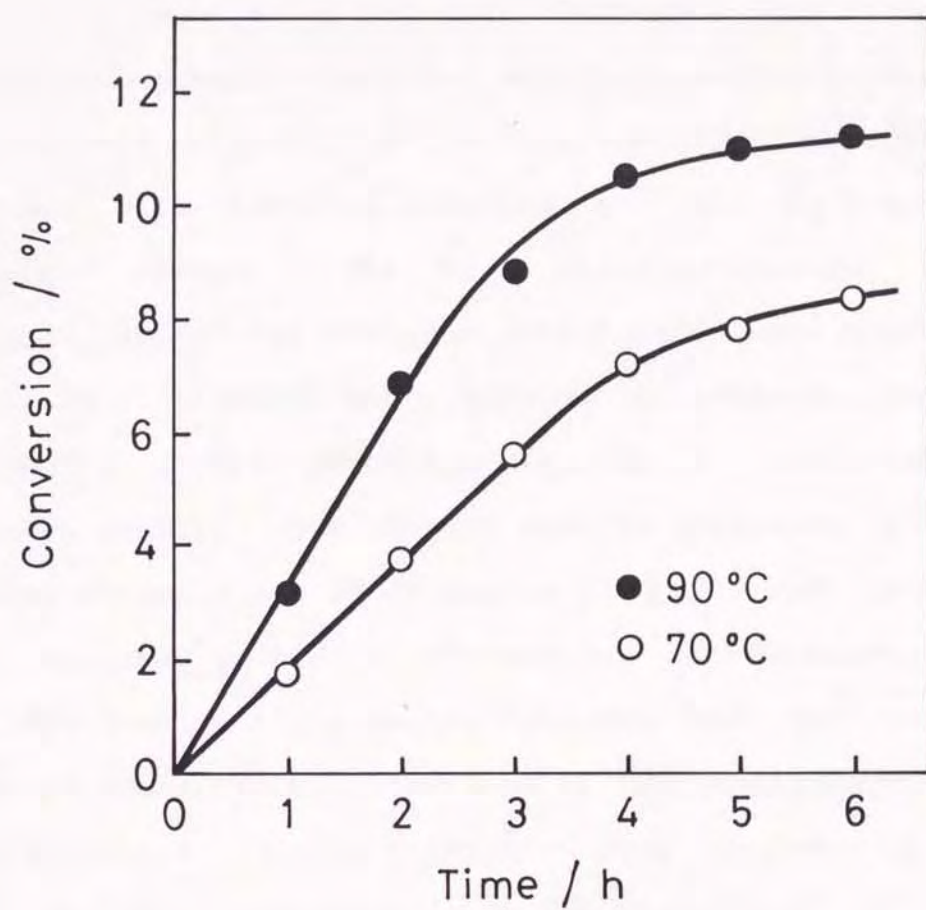


Figure 2-4

Graft polymerization of MMA
initiated by carbon black 3P

Polymerization conditions are
given in Figure 2-1.

the rate of the polymerization initiated by carbon black 3P is somewhat less than that of carbon black 2P, conversion increased up to 11% after 6 h at 90 °C.

As mentioned above, carboxyl groups accelerate the decomposition of peroxyester groups. Different from carbon black 2P, carboxyl groups introduced onto furnace black were almost quantitatively transferred to acyl chloride groups by the treatment with thionyl chloride for the introduction of peroxyester groups. The acyl chloride groups remaining unchanged during the reaction with *t*-BuOOH were treated with methanol to give methyl ester groups. Accordingly, the content of carboxyl groups of carbon black 3P is considered to be negligibly small. The results seem to show that peroxyester groups on carbon black 3P decompose gradually and the polymerization proceeds to higher conversion. Furthermore, furnace black 3P has little phenolic hydroxyl and quinonic oxygen groups on the surface. The lack of the reaction of the *tert*-butoxy radical or the growing polymer radical with these groups is also considered to be the reason for not becoming dead-end type of the polymerization.

Figure 2-5 shows the effect of the amount of carbon black 3P on the polymerization of MMA. The rate of the polymerization increased with an increase of the amount of carbon black 3P as an initiator.

The percentage of grafting of PMMA obtained from the polymerization initiated by carbon black 3P is shown in Figure 2-6. The percentage of grafting increased up to 80% with progress of the polymerization. This may be due to the propagation of PMMA from the radical produced by the decomposi-

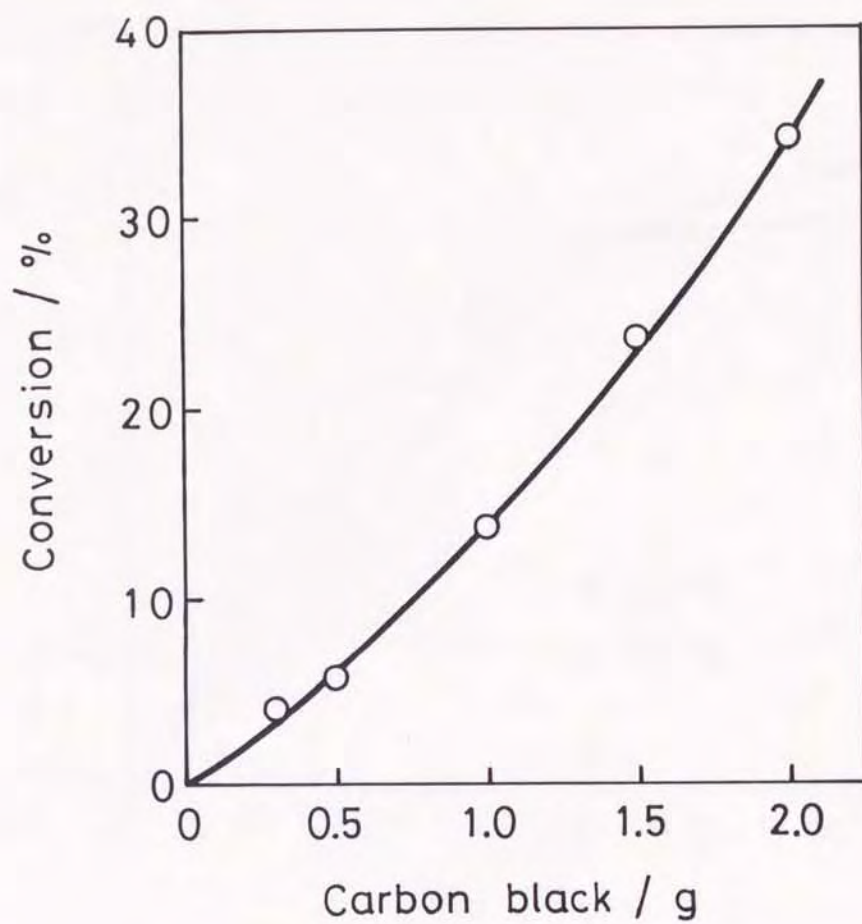


Figure 2-5

Effect of the amount of carbon black 3P
on the graft polymeriza-tion of MMA

MMA, 10 mL; 70 °C; 3 h.

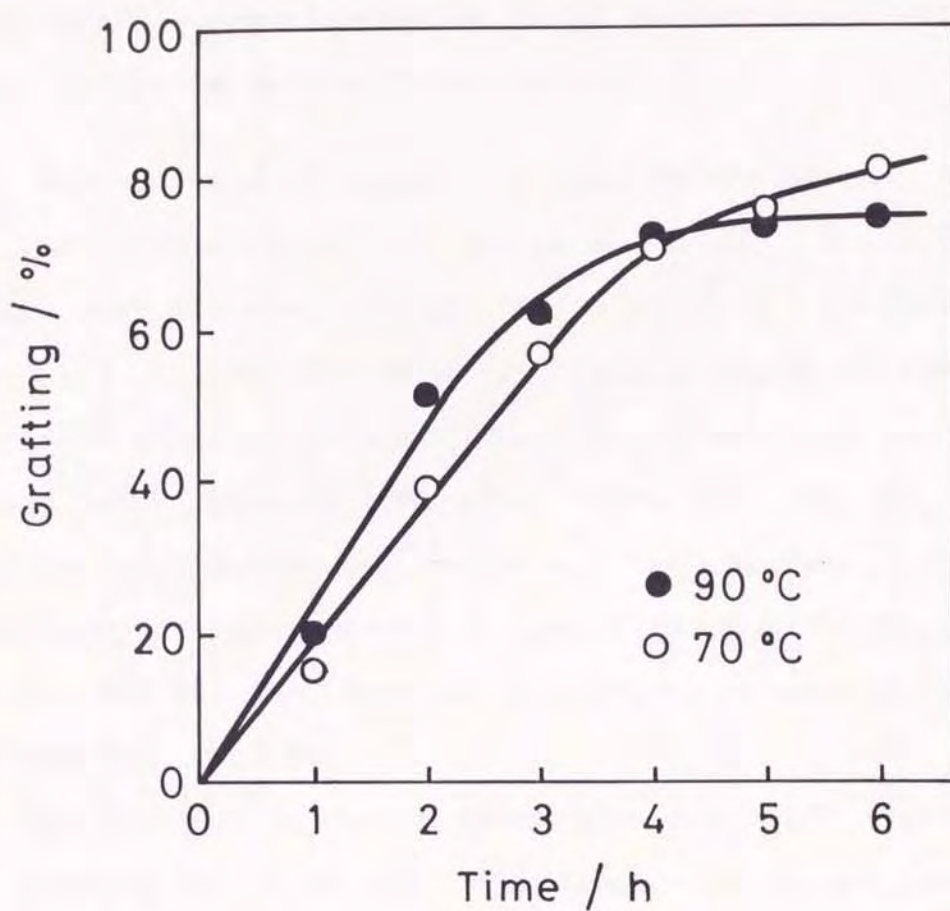


Figure 2-6

Relationship between polymerization time
and percentage of grafting using
carbon black 3P as an initiator

tion of peroxyester groups on carbon black 3P. Therefore, it is apparent that PMMA is effectively grafted onto the surface by use of carbon black 3P as an initiator.

2.4.2 Graft Polymerization of Vinyl Monomers Initiated by Azo Groups on Carbon Black Surface

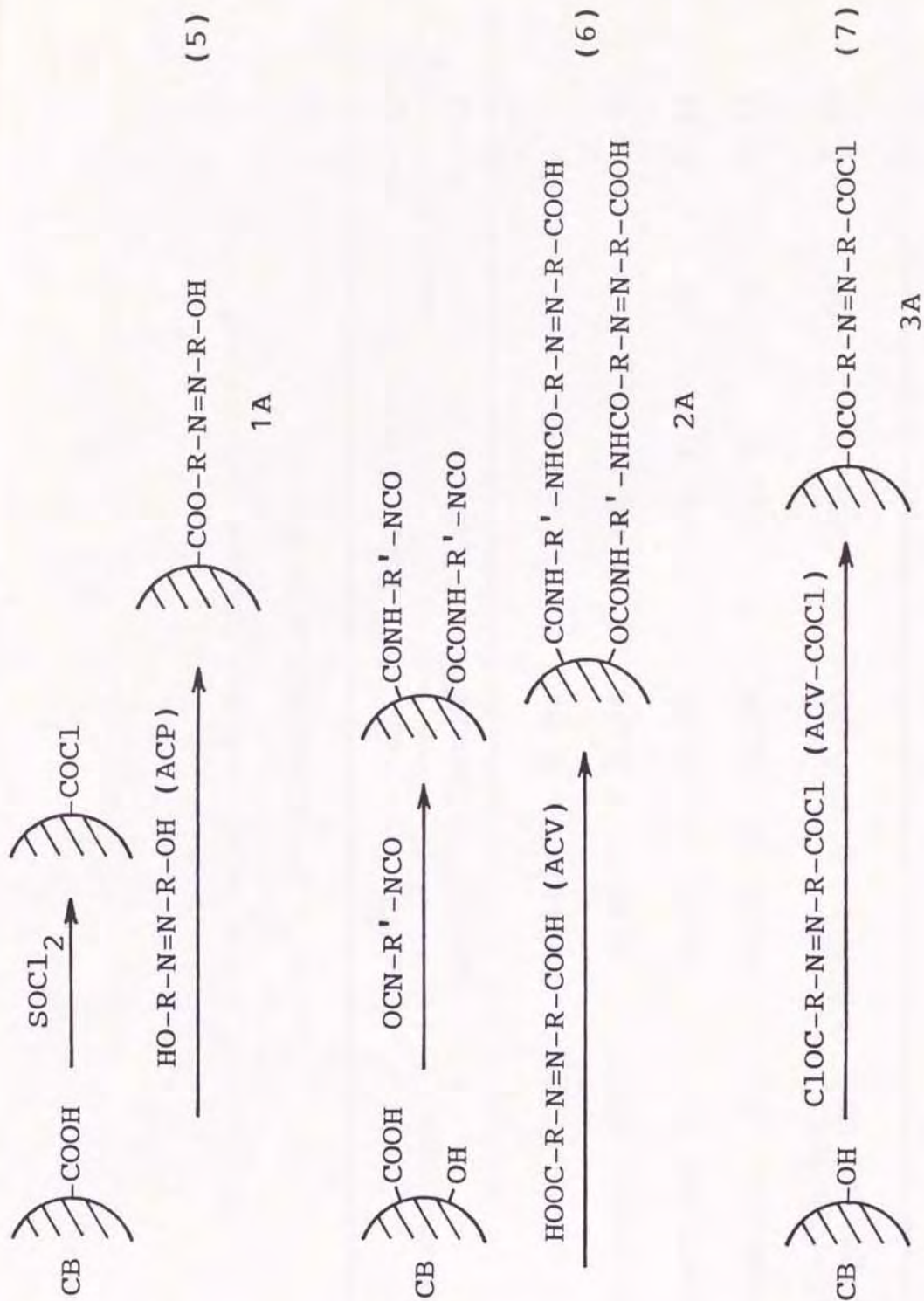
(1) Introduction of Azo Groups onto Carbon Black

The introduction of azo groups onto the carbon black surface was achieved by the following three methods (Scheme 2-9): (1) the reaction of acyl chloride groups on the surface, which were introduced by the reaction of carboxyl groups on the surface with thionyl chloride, with ACP (Eq. 5), (2) the reaction of isocyanate groups on the surface, which were introduced by the treatment of carbon black with TDI, with ACV (Eq. 6), and (3) the reaction of hydroxyl groups on the surface with ACV-COCl (Eq. 7).

The reaction of carbon black with ACP, ACV, or ACV-COCl was carried out at 25 °C. Therefore, it is not necessary to take into account for the decomposition of the azo compounds during the reaction, because the half-lives of them are reported to be more than 10000 min.⁷¹⁾

The amount of azo groups introduced onto the surface of the carbon black was determined by elemental (nitrogen) analysis. The results are summarized in Table 2-5.

As shown in Table 2-5, it is apparent that azo groups can be introduced onto the carbon black surface by the reaction according to the methods 1, 2, and 3 (Eqs. 5, 6, and 7). The azo group content of carbon black increased, depending on the introduction method, in the following order: $3 < 1 < 2$. This



Scheme 2-9

Table 2-5 The amount of azo groups introduced onto
carbon black surface

Carbon black	$\frac{\text{COOH}}{\text{mmolg}^{-1}}$	$\frac{\text{OH}}{\text{mmolg}^{-1}}$	Introduction reaction	No.	$\frac{\text{Azo group}}{\text{mmolg}^{-1}}$
Neospectra II	0.40	0.24	—	—	0
Neospectra II	0.40	0.24	Eq. 5	1A	0.18
Neospectra II	0.40	0.24	Eq. 6	2A	0.33
Neospectra II	0.40	0.24	Eq. 7	3A	0.13
BuLi-treated Neospectra II	0	1.96	Eq. 7	4A	0.48

order agreed with increasing amount of starting functional groups used for the introduction of azo groups: the functional groups used for the introduction of azo groups by the method 3, 1, and 2 are phenolic hydroxyl groups (0.24 mmolg^{-1}), carboxyl groups (0.40 mmolg^{-1}), and carboxyl and phenolic hydroxyl groups ($0.40 + 0.24 = 0.64 \text{ mmolg}^{-1}$), respectively.

To increase the azo group content of carbon black, hydroxyl groups were introduced onto carbon black. The introduction of hydroxyl groups was achieved by the hydrolysis of phenoxy and alkoxy lithium groups, which were introduced by the reaction of BuLi with phenolic hydroxyl, carboxyl, and quinonic oxygen groups on the surface (See Scheme 2-6 at section 2.3.7).⁶⁵⁾ By the treatment the hydroxyl group content of the carbon black increased to 1.96 mmolg^{-1} . Carbon black **4A** was prepared by the reaction of hydroxyl groups on the treated carbon black with ACV-COCl. The amount of azo groups introduced onto carbon black **4A** increased to 0.48 mmolg^{-1} as shown in Table 2-5.

The above results make us conclude that azo groups can be introduced onto the carbon black surface according to the reaction as shown in Eqs. 5, 6, and 7.

(2) Confirmation of Initiating by Azo Groups Introduced onto Carbon Black

The polymerization of MMA was carried out in the presence of carbon black **2A** at 70°C and the initiating ability of the azo groups on the surface was examined. The results are summarized in Table 2-6.

As shown in Table 2-6, the thermal polymerization of MMA

proceeded slightly even in the absence of initiator, whereas the rate of polymerization was negligibly small. In the presence of untreated carbon black, however, no polymerization of MMA was observed at all. On the contrary, the polymerization of MMA was found to be initiated in the presence of carbon black 2A and PMMA was grafted onto the surface.

To ensure initiation by the azo groups on the surface, the initiating activity of ACV-adsorbed carbon black was evaluated. ACV-adsorbed carbon black was prepared by the treatment of untreated carbon black with ACP in a manner similar to the introduction of azo groups. As shown in Table 2-6, ACV-adsorbed carbon black had no ability to initiate the polymerization. This suggests that ACV adsorbed on the carbon black surface during the treatment for the introduction of azo groups is completely removed by washing with methanol after the treatment.

On the basis of the above results, we can conclude that the polymerization of MMA is initiated by azo groups introduced onto the surface of the carbon black.

(3) Graft Polymerization of Methyl Methacrylate

Graft Polymerization of MMA Initiated by Carbon Black 1A

The graft polymerization of MMA onto carbon black was examined by use of carbon black 1A as an initiator. Figure 2-7 shows the time-conversion curves of the polymerization of MMA at 50 and 70 °C.

As seen in Figure 2-7, it is apparent that carbon black 1A also has ability to initiate the polymerization of MMA. The polymerization was of the dead end type and the conversion did

Table 2-6 Initiating activity of azo groups introduced onto
carbon black surface

Carbon black	Conversion	Grafting
	%	%
None	0.7	—
Untreated	0	—
ACV-adsorbed	0	—
Carbon black 2A	4.6	40.0

Carbon black, 0.30 g; MMA, 10 mL; 70 °C; 6 h.

not increase even if the polymerization time was extended to 6 h. This may be due to a low content of azo groups.

The carbon black obtained from the polymerization gave a stable colloidal dispersion in a good solvent for PMMA: the precipitation of the carbon black particles from the dispersion of the carbon black obtained from the polymerization was scarcely observed even after 30 days. This suggests that PMMA is grafted from the carbon black surface.

Figure 2-8 shows the relationship between the polymerization time and percentage of grafting using carbon black 1A as an initiator. The percentage of grafting increased to 40% as the polymerization proceeded, where the grafting efficiency at 50 °C and 70 °C was 44-45% and 38-50%, respectively, as shown in Figure 2-9. Although PMMA was grafted onto the carbon black during the polymerization of MMA initiated by AIBN in the presence of untreated carbon black, the percentages of grafting and grafting efficiency were less than 10% and 1.0%, respectively. Therefore, the percentages of grafting and grafting efficiency in the polymerization initiated by azo groups on the surface were much larger than those obtained from the polymerization in the presence of untreated carbon black using AIBN as an initiator. This is due to that PMMA is propagated from the radical produced on the surface by the decomposition of the azo groups. The formation of ungrafted PMMA was considered to be attributable to the propagation from another initiator fragment.

Graft Polymerization of MMA Initiated by Carbon Black 2A

As shown in Table 2-5, the azo group content of carbon

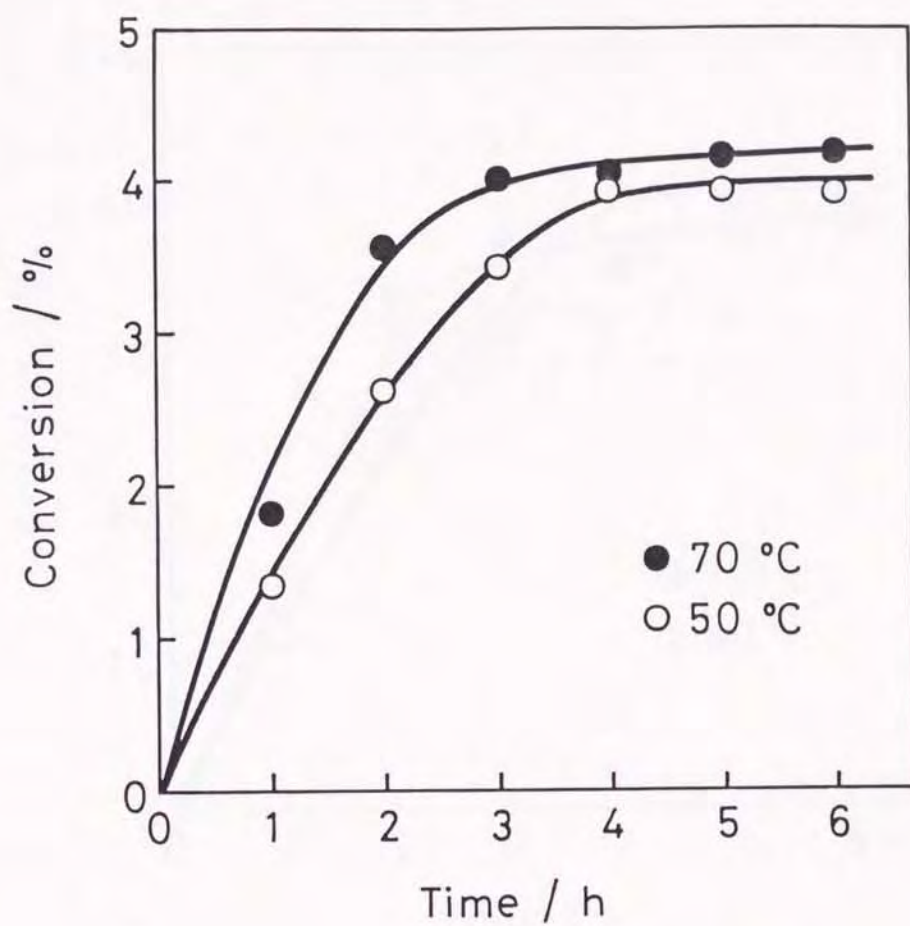


Figure 2-7

Graft polymerization of MMA
initiated by carbon black 1A

Carbon black, 0.30 g; MMA, 10 mL.

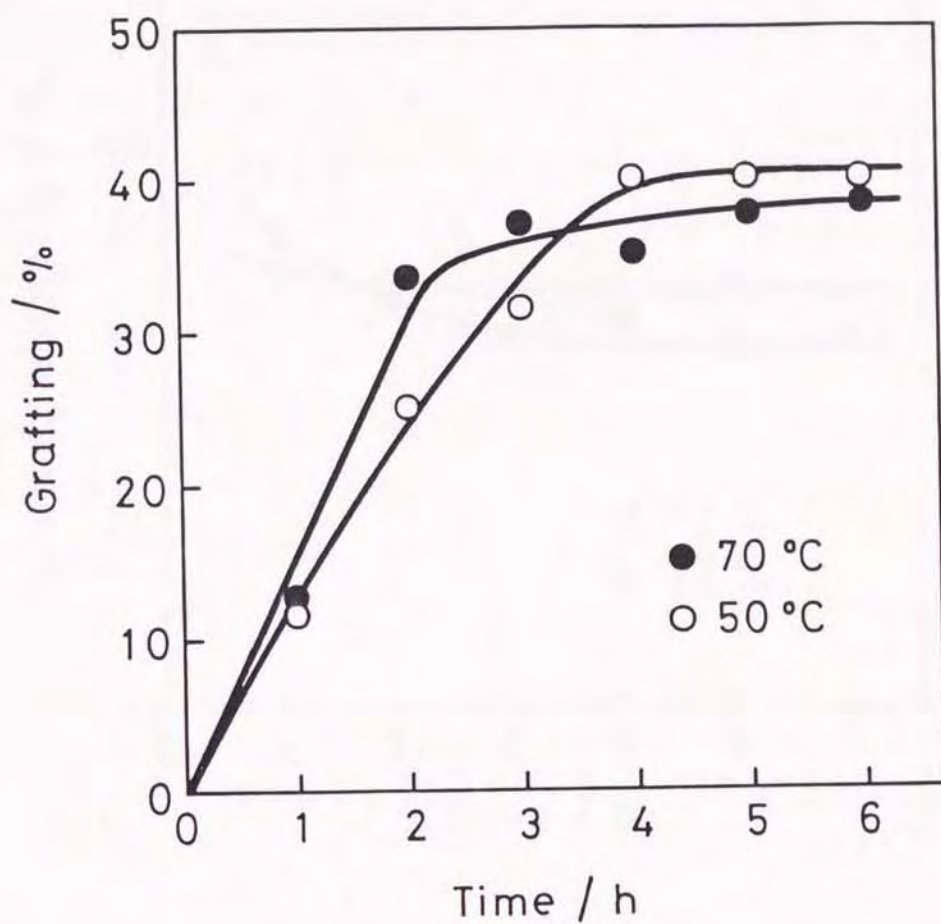


Figure 2-8
Relationship between polymerization time
and percentage of grafting using
carbon black 1A as an initiator

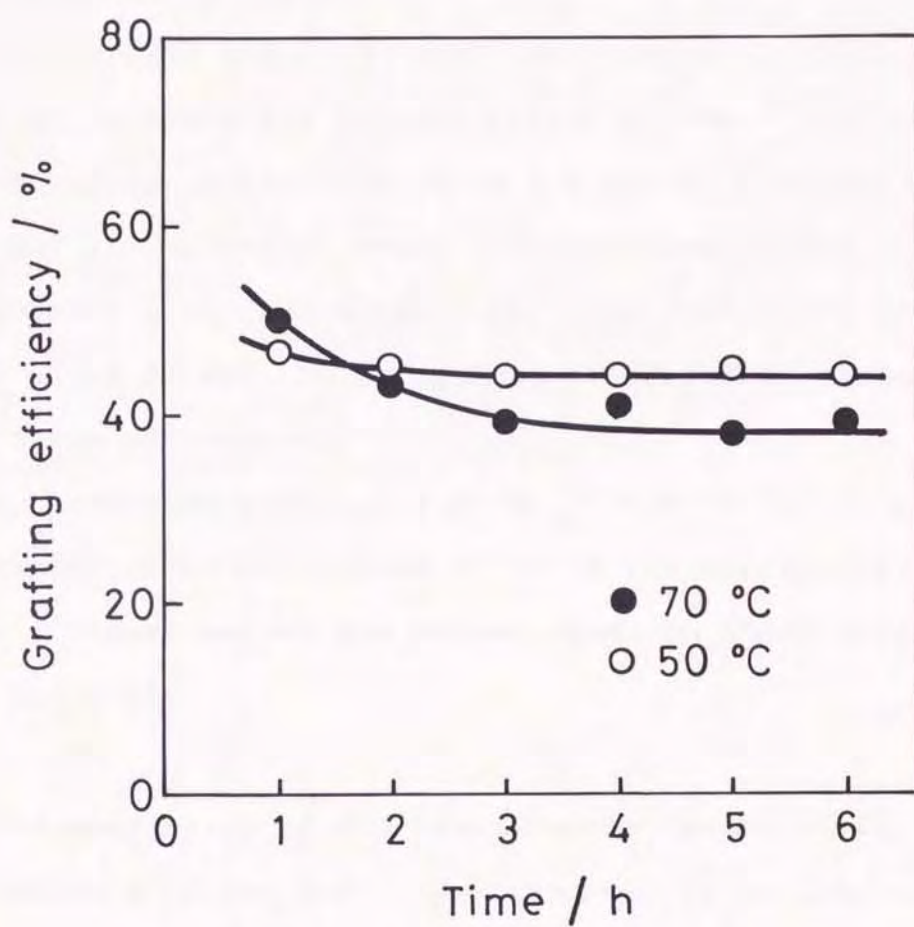


Figure 2-9

Relationship between polymerization time
and grafting efficiency using
carbon black 1A as an initiator

black 2A was larger than that of carbon black 1A. Therefore, the initiating activity of carbon black 2A for the graft polymerization of MMA was examined. The results are shown in Figures 2-10 and 2-11.

Figures 2-10 and 2-11 show that carbon black 2A also has ability to initiate the polymerization of MMA. The conversion and percentage of grafting after 6 h in the presence of carbon black 2A are slightly larger than those of carbon black 1A. In comparison with carbon black 1A, the initiating activity of carbon black 2A and the percentage of grafting, however, are not so large as expected.

The grafting efficiency at 50 °C and 70 °C in the graft polymerization was determined to be 45-58% and 40-50%, respectively. These values are almost equal to those initiated by carbon black 1A.

Graft Polymerization of MMA Initiated by Carbon Black 3A

Figures 2-12 and 2-13 show the results of graft polymerization of MMA initiated by carbon black 3A. From these results, it is concluded that the graft polymerization of MMA is initiated by carbon black 3A to give PMMA-grafted carbon black. The initiating activity and percentage of grafting, however, were lower than those of carbon black 1A or 2A, because of the lowest content of azo groups.

Graft Polymerization of MMA Initiated by Carbon Black 4A

As shown in Table 2-5, by the reaction of the BuLi-treated carbon black with ACV-COCl, carbon black 4A with the highest azo group content was obtained: its azo group content increased

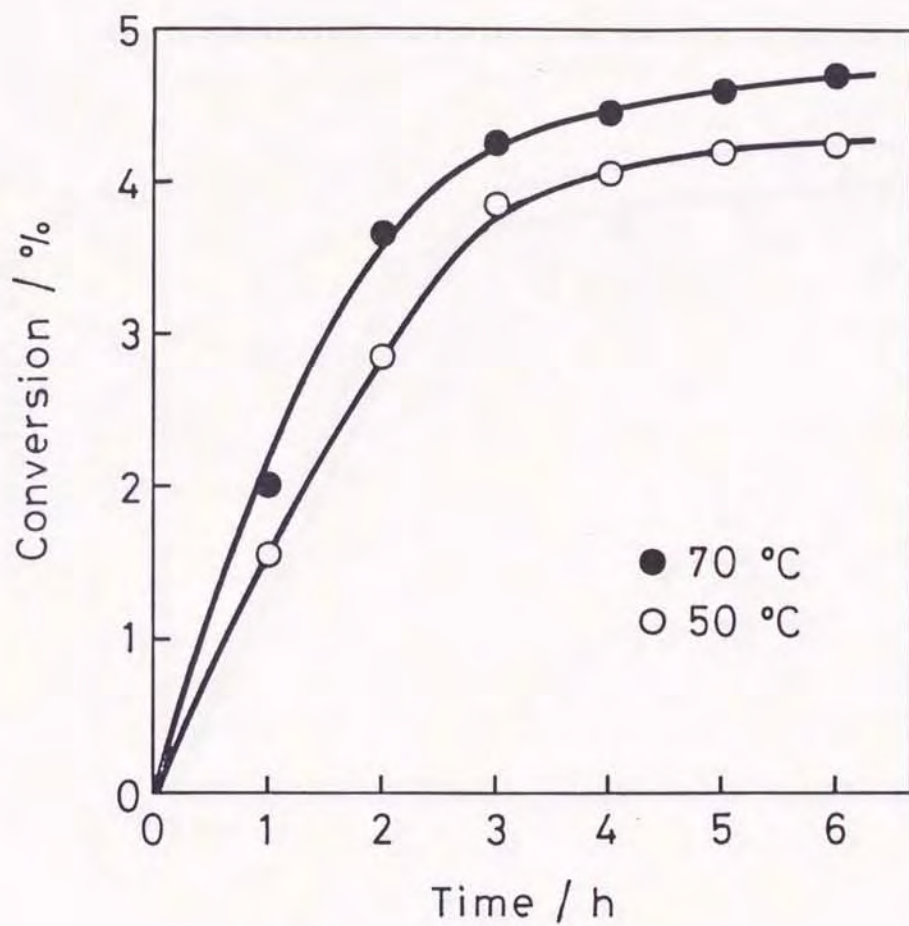


Figure 2-10

Graft polymerization of MMA
initiated by carbon black 2A

Polymerization conditions are
given in Figure 2-6.

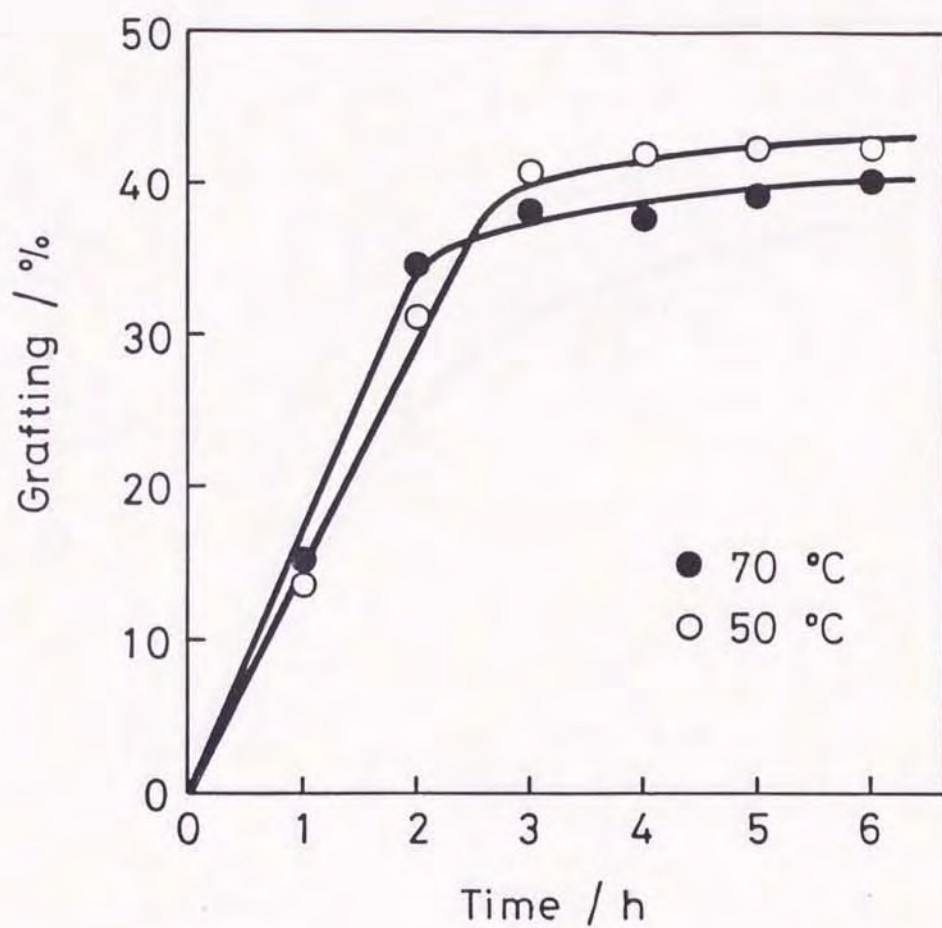


Figure 2-11

Relationship between polymerization time and percentage of grafting using carbon black 2A as an initiator

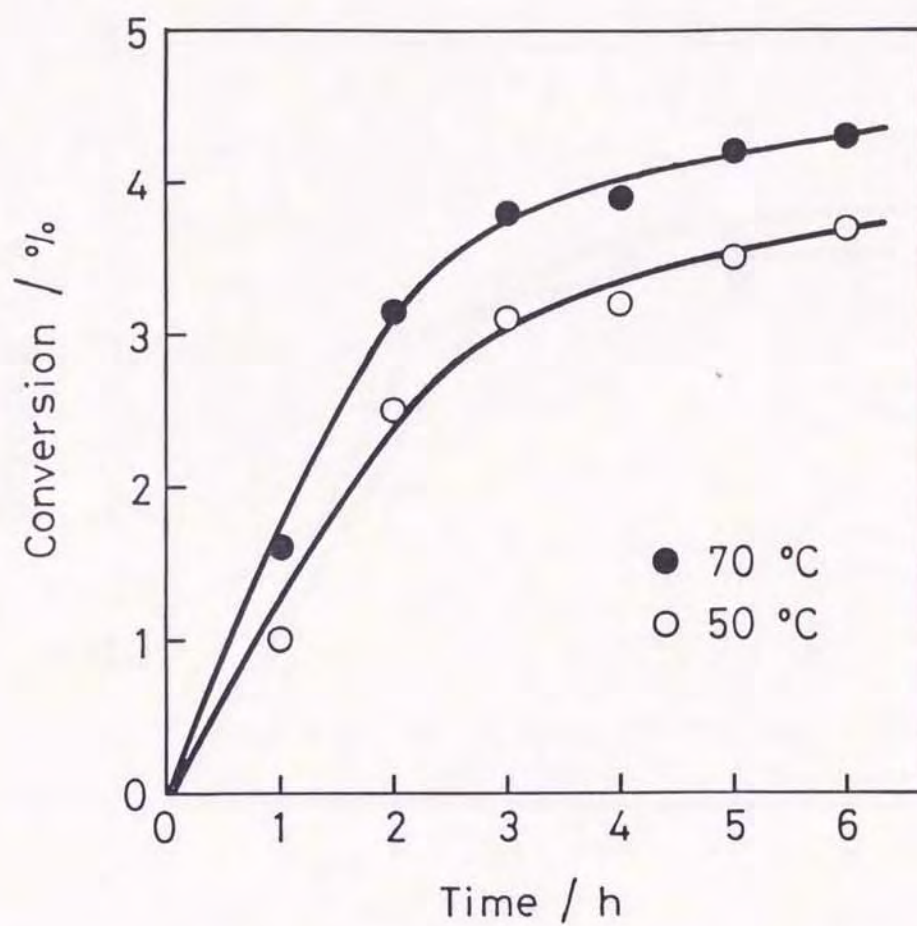


Figure 2-12

Graft polymerization of MMA
initiated by carbon black 3A

Polymerization conditions are
given in Figure 2-6.

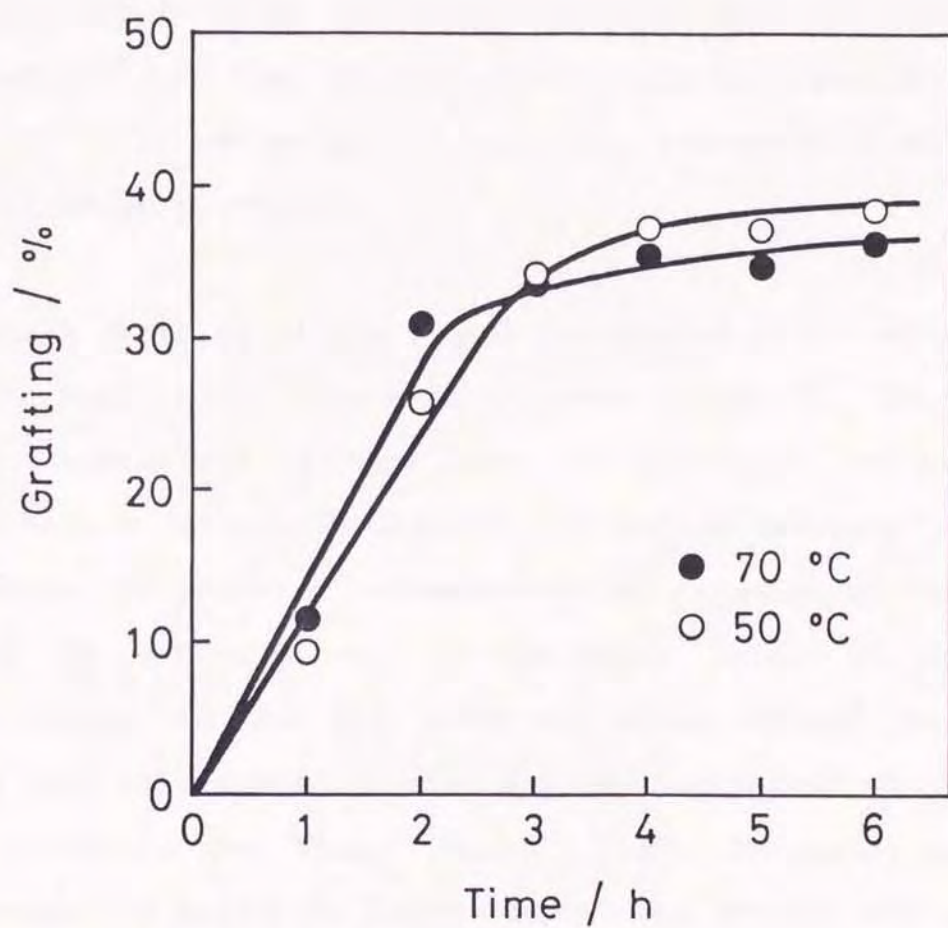


Figure 2-13

Relationship between polymerization time
and percentage of grafting using
carbon black 3A as an initiator

to 0.48 mmol g^{-1} . Figure 2-14 shows the time-conversion curves of the polymerization of MMA initiated by carbon black 4A.

As shown in Figure 2-14, the rate of the polymerization and conversion after 6 h were found to increase remarkably compared with those of carbon black 1A, 2A, or 3A.

Figure 2-15 shows the relationship between the percentage of grafting and the polymerization time initiated by carbon black 4A. The percentage of grafting increased to 80% as the polymerization proceeded.

Initiating Activity of Azo Groups Introduced onto Carbon Black

The initiating activities of carbon black 1A, 2A, 3A, and 4A were summarized in Table 2-7. It was found by comparing carbon black 3A and 4A that the initiating activity and the percentage of grafting increase with an increase of azo group content of carbon black. On the other hand, by comparing carbon black 1A and 3A, whose azo group content is almost equal, the initiating activity and the percentage of grafting were found to be almost equal. This suggests that the difference of half-life for decomposition between ACP and ACV is decreased by the bonding onto the carbon black surface. This may be due to that both ACP and ACV are bonded onto the carbon black surface with ester bonds. Further detailed investigation is now undertaken to estimate the relationship between the structure and initiating activity of azo groups introduced onto the surface.

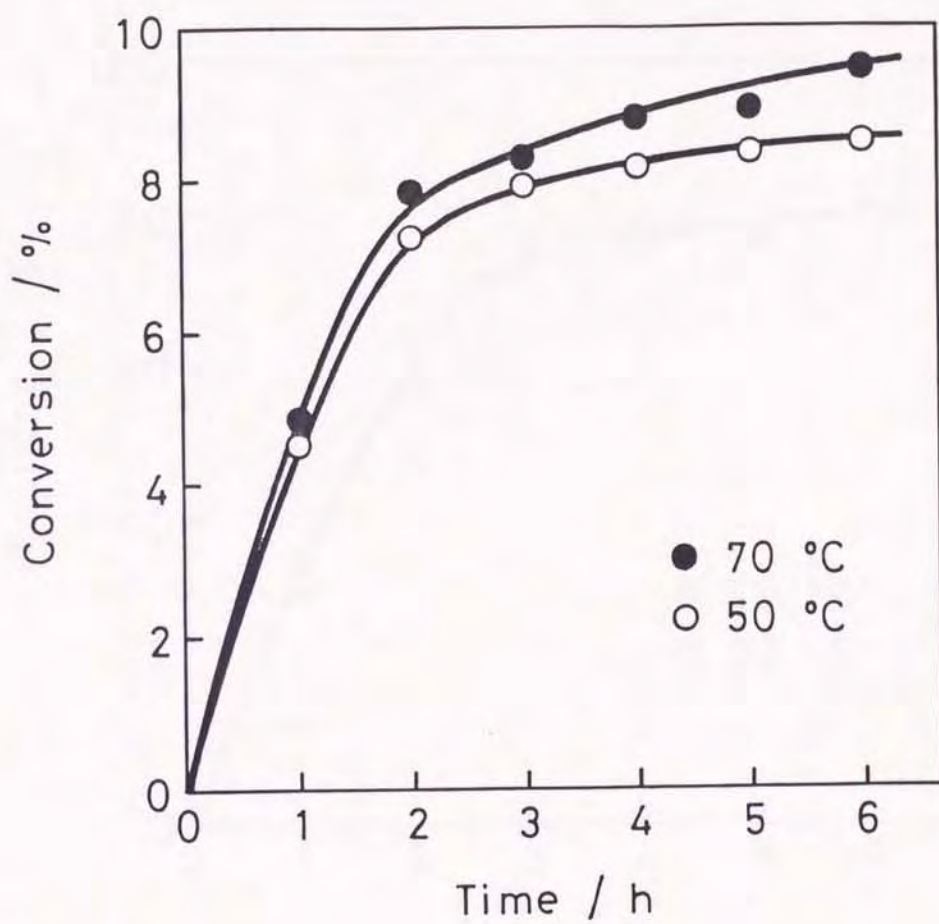


Figure 2-14

Graft polymerization of MMA
initiated by carbon black 4A

Polymerization conditions are
given in Figure 2-6.

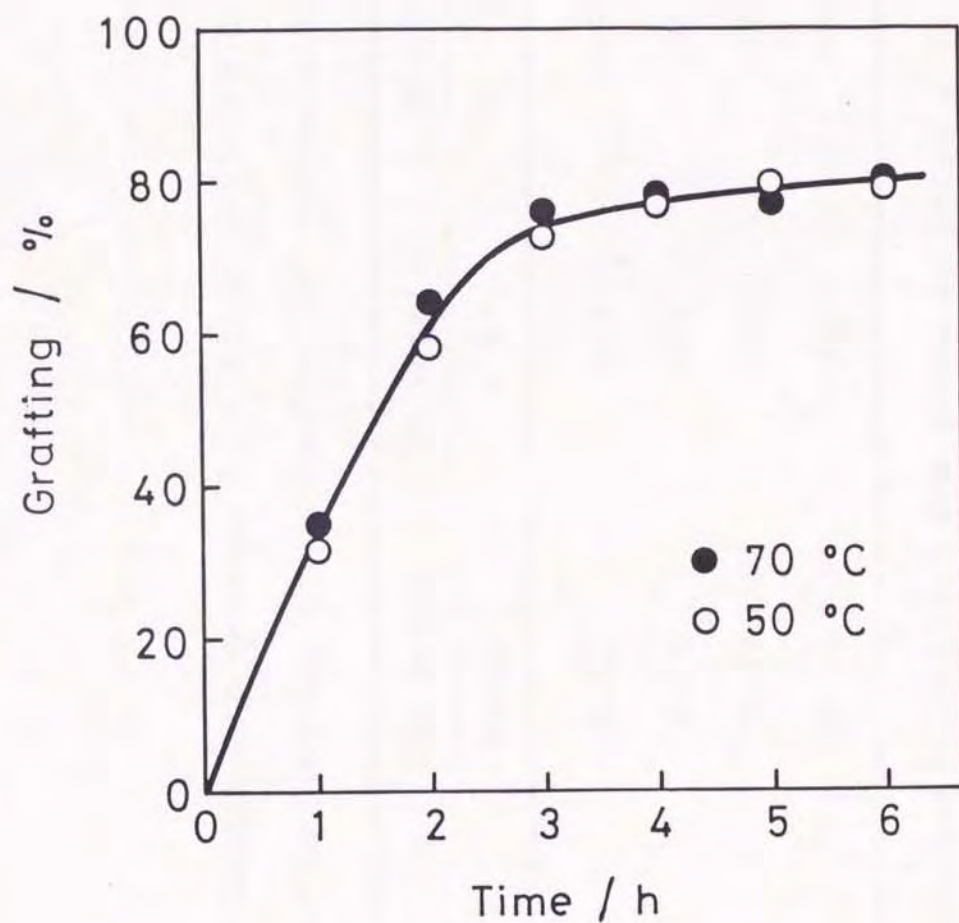


Figure 2-15

Relationship between polymerization time and percentage of grafting using carbon black 4A as an initiator

Table 2-7 Relationship between initiating activity of the polymerization and azo group content of carbon black

Carbon black	Azo group mmolg^{-1}	Conversion %	Grafting %
3A	0.13	3.8	35.9
1A	0.18	4.1	38.5
2A	0.33	4.6	40.0
4A	0.48	9.5	80.0

Polymerization conditions are given in Table 2-6.

2.4.3 Effect of e -Value of Vinyl Monomers on the Graft Polymerization

(1) Graft Polymerization of Vinyl Monomers Using Carbon Black Having Peroxyester Groups

It has been reported that the radical graft polymerization of vinyl monomers with negative e -value in the presence of carbon black was remarkably retarded but that with positive e -value was not retarded when peroxides such as benzoyl peroxide were used as initiators.^{17,60,72)} Therefore, I investigated the effect of e -value of vinyl monomers on the graft polymerization initiated by peroxyester groups attached on the carbon black surface.

As shown in Figure 2-16, the graft polymerization of MMA, with positive e -value, was initiated by carbon black 2P, and PMMA was effectively grafted from the surface: the percentages of grafting and grafting efficiency increased to 45 and 70%, respectively.

I investigated also the polymerization of MMA, initiated by BPOB the amount of which is equivalent to the peroxyester group content on carbon black 2P, in the presence of untreated carbon black and compared the results with that in the absence of carbon black. The results are shown in Figure 2-17. The rate of the polymerization in the presence of carbon black after an induction period was found to be almost equal to that in the absence of carbon black. The percentages of grafting and grafting efficiency, however, were 15 and 0.5%, respectively. These values were much lower than those obtained from the polymerization initiated by carbon black 2P as an initiator. Therefore, it seems that most of the formed PMMA

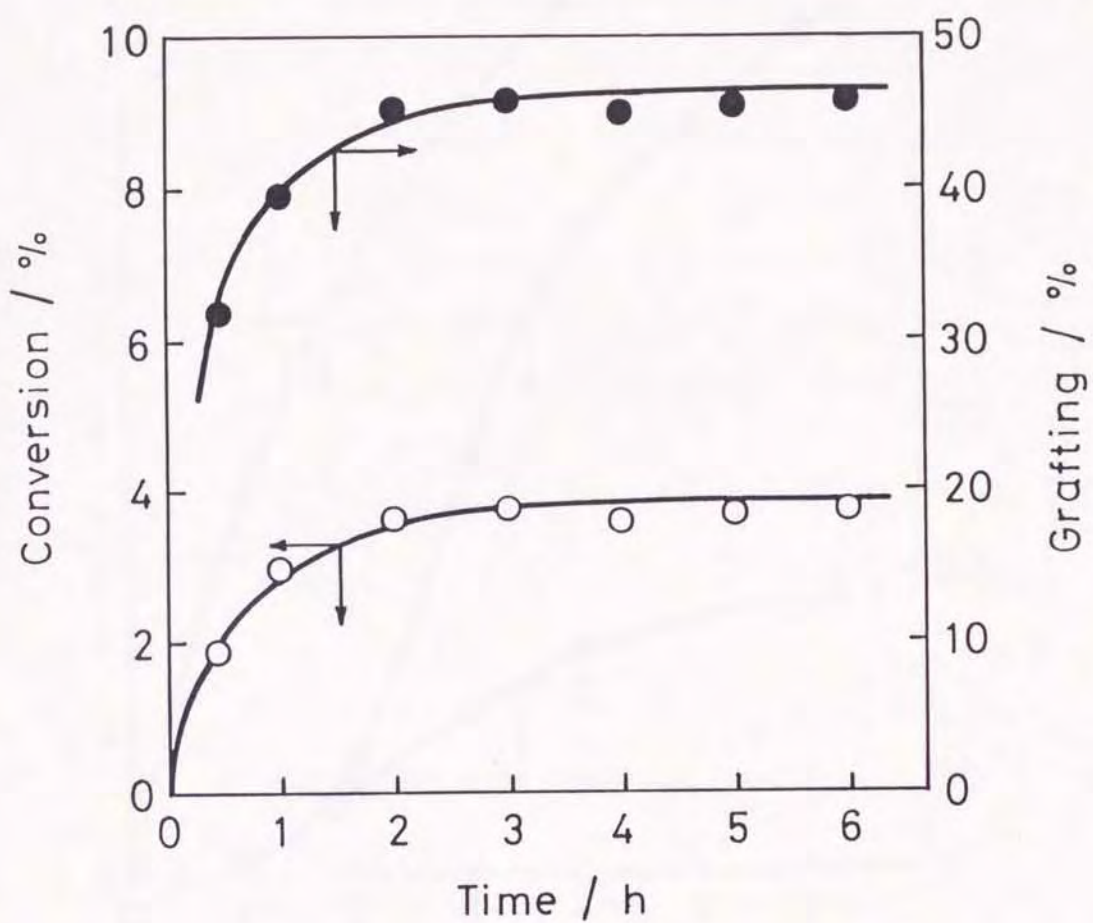


Figure 2-16

Graft polymerization of MMA
initiated by carbon black 2P

Carbon black, 0.30 g; MMA, 10 mL; 70 °C.

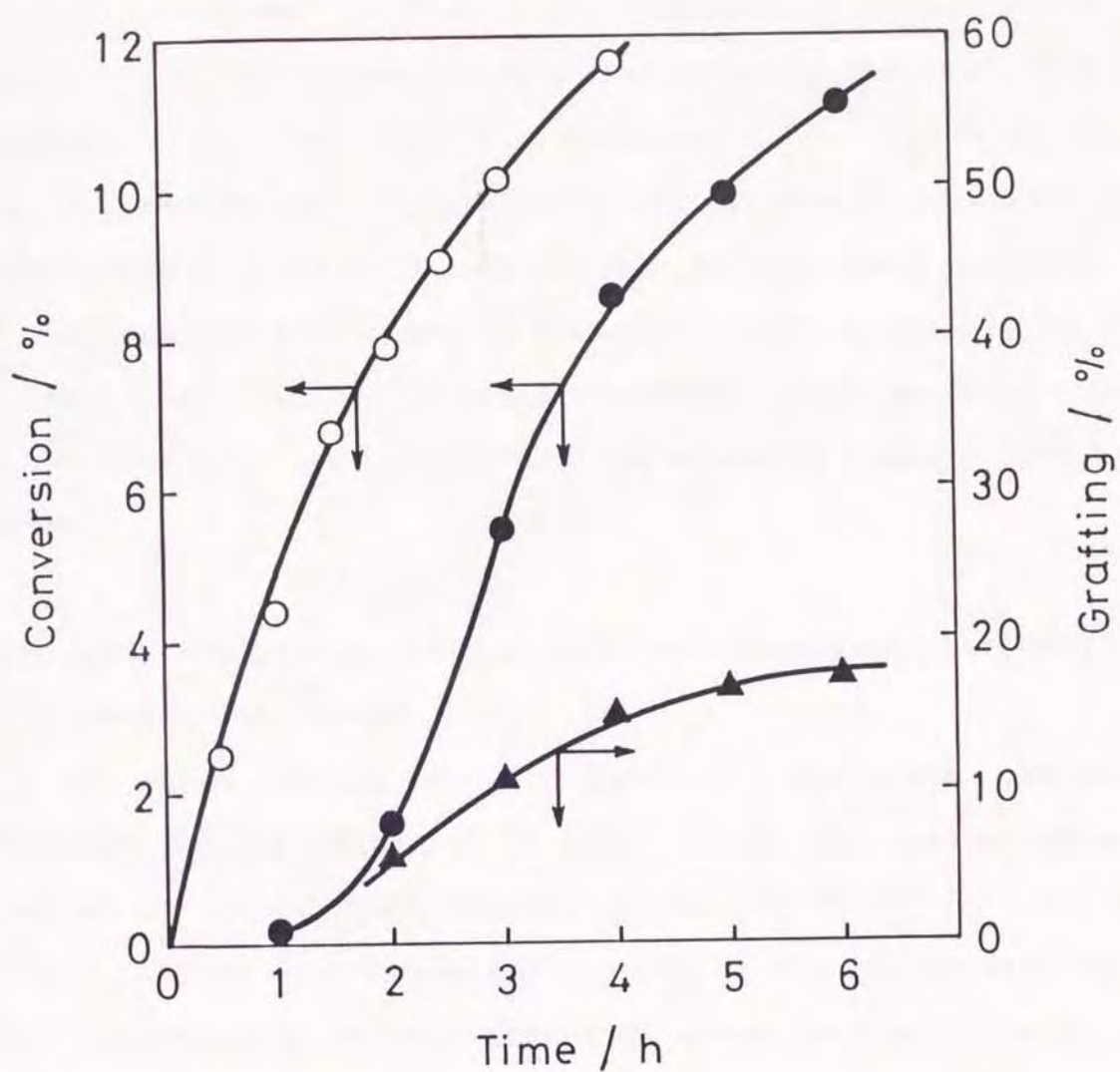


Figure 2-17

Polymerization of MMA initiated by BPOB
in the presence of untreated carbon black

Carbon black, 0.30 g; MMA, 10 mL;
BPOB, 0.054 mmol; 70 °C.

(O): in the absence of carbon black
(●,▲): in the presence of carbon black

are ungrafted polymers.

The results of the graft polymerization of styrene, with negative e -value, initiated by carbon black 2P are shown in Figure 2-18. The polymerization was markedly retarded, and the conversion was less than 1% even after 10 h. The results of the polymerization of styrene in the presence of untreated carbon black using BPOB as an initiator are shown in Figure 2-19 and compared with those in the absence of carbon black. The polymerization in the presence of carbon black was also found to be retarded, and polystyrene was scarcely grafted onto the surface.

(2) Graft Polymerization of Vinyl Monomers Using Carbon Black Having Azo Groups

As shown in Figures 2-10 and 2-11, the graft polymerization of MMA was initiated by carbon black 2A: the percentages of grafting and grafting efficiency reached 40 and 50%, respectively. Figure 2-20 shows the results of the polymerization of MMA, initiated by ACV the amount of which is equivalent to the azo groups on carbon black 2A, in the presence or in the absence of untreated carbon black. Though the polymerization was retarded in the presence of carbon black, a part of formed polymer was grafted onto the surface. This result suggests that initiator fragments and growing polymer radicals competitively react to the surface of the carbon black.⁶⁰⁾

The graft polymerization of styrene initiated by carbon black 2A was also investigated. The results are shown in Figure 2-21. Though the conversion was not high, polystyrene was effectively grafted onto the surface. The values of

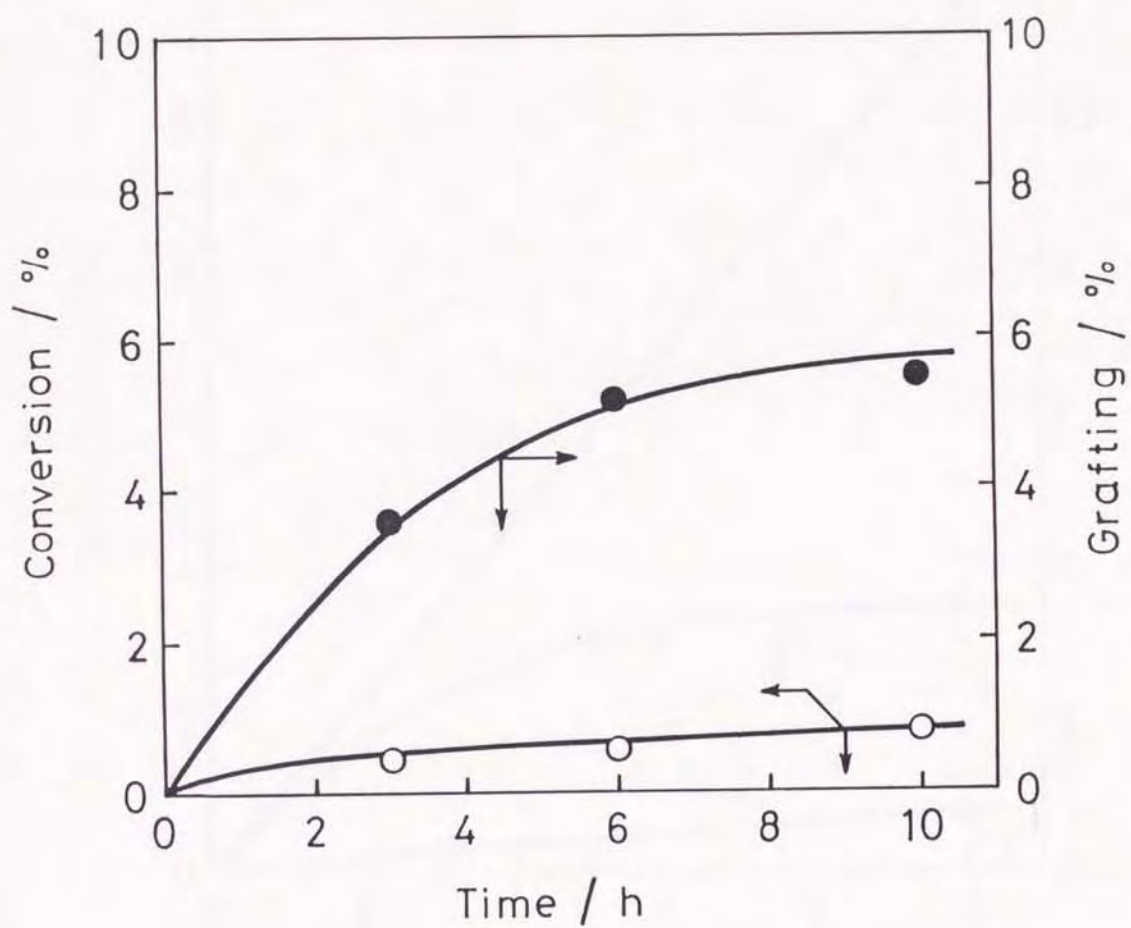


Figure 2-18

Graft polymerization of styrene
initiated by carbon black 2P

Carbon black, 0.30 g; styrene, 10 mL; 70 °C.

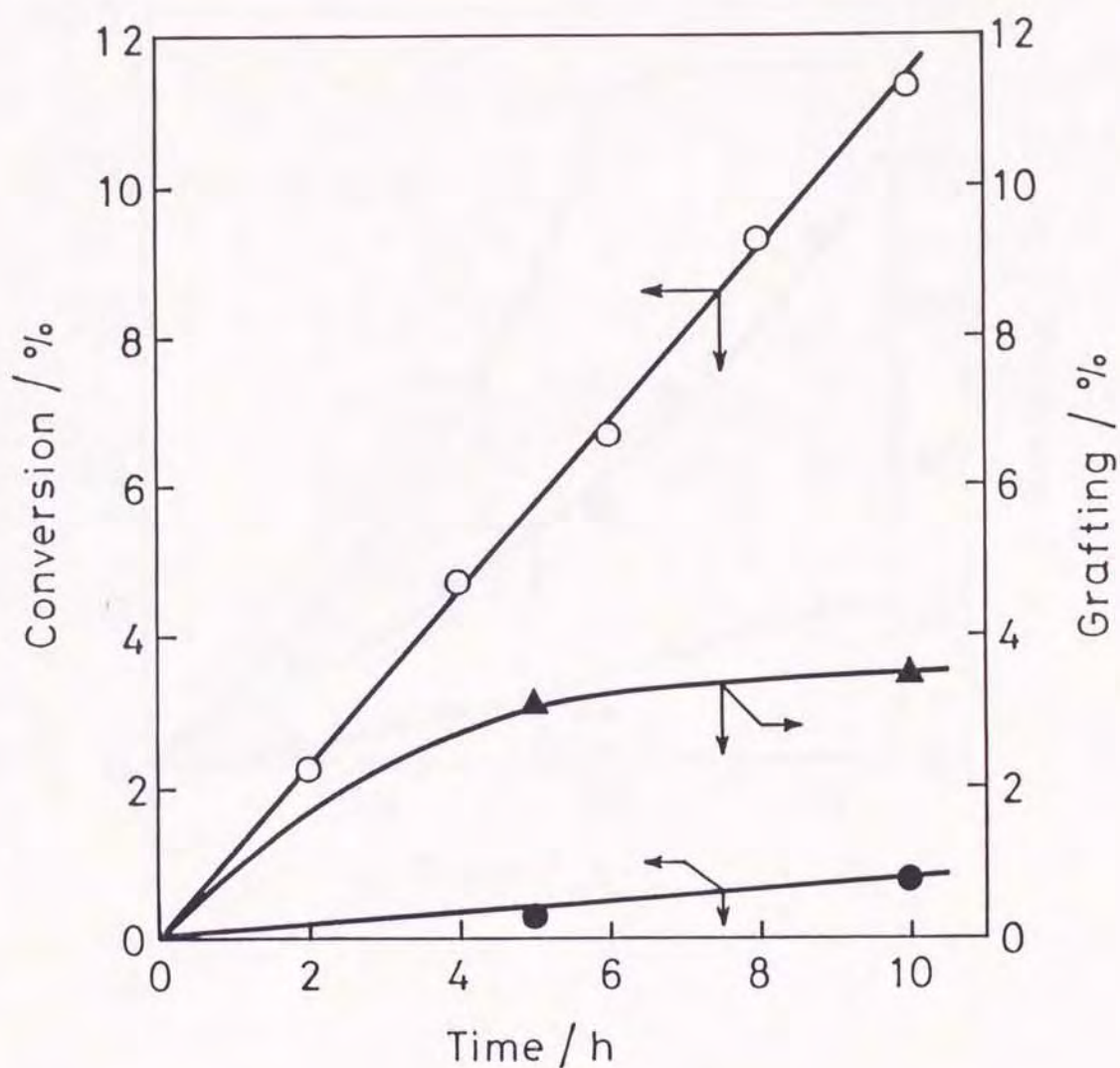


Figure 2-19

Polymerization of styrene initiated by BPOB
in the presence of untreated carbon black

Carbon black, 0.30 g; styrene, 10 mL;
BPOB, 0.054 mmol; 70 °C.

(O): in the absence of carbon black
(●,▲): in the presence of carbon black

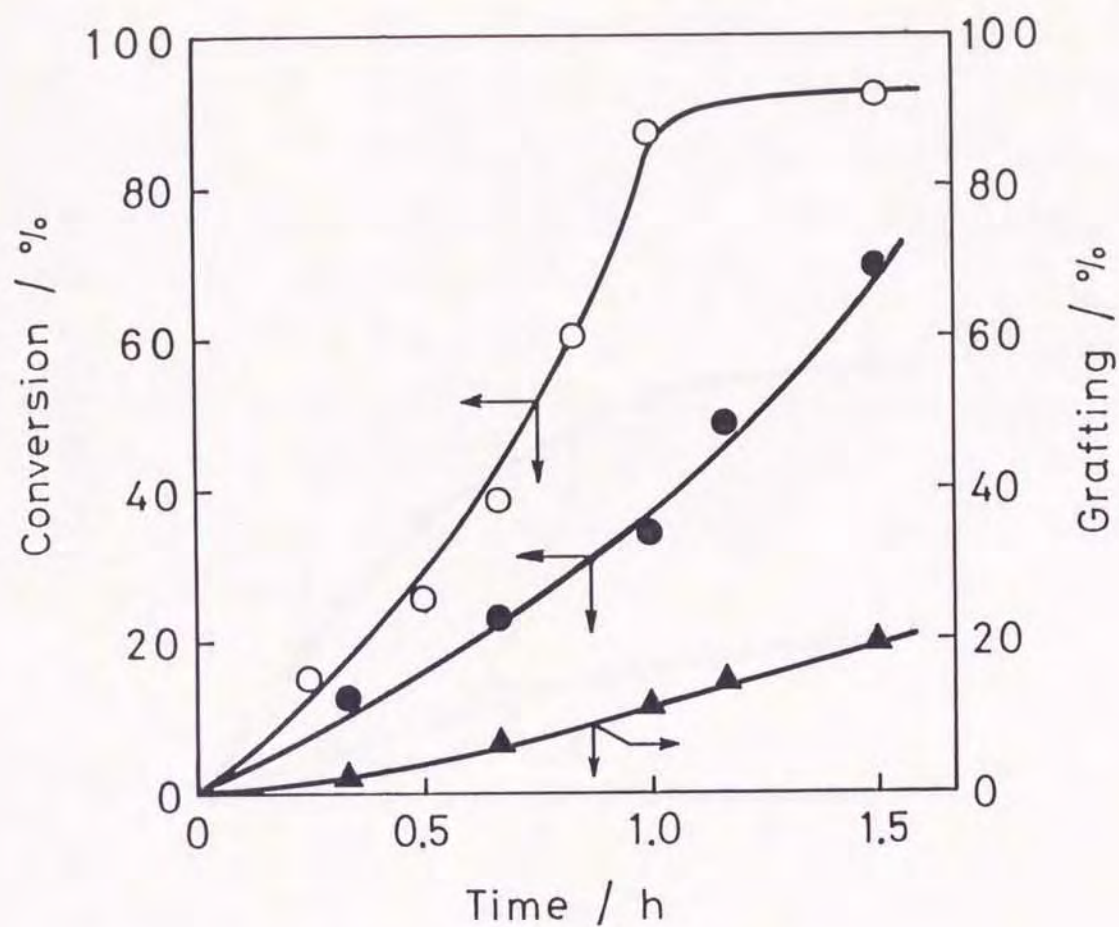


Figure 2-20

Polymerization of MMA initiated by ACV
in the presence of untreated carbon black

Carbon black, 0.30 g; MMA, 10 mL;
ACV, 0.099 mmol; 70 °C.

(O): in the absence of carbon black
(●,▲): in the presence of carbon black

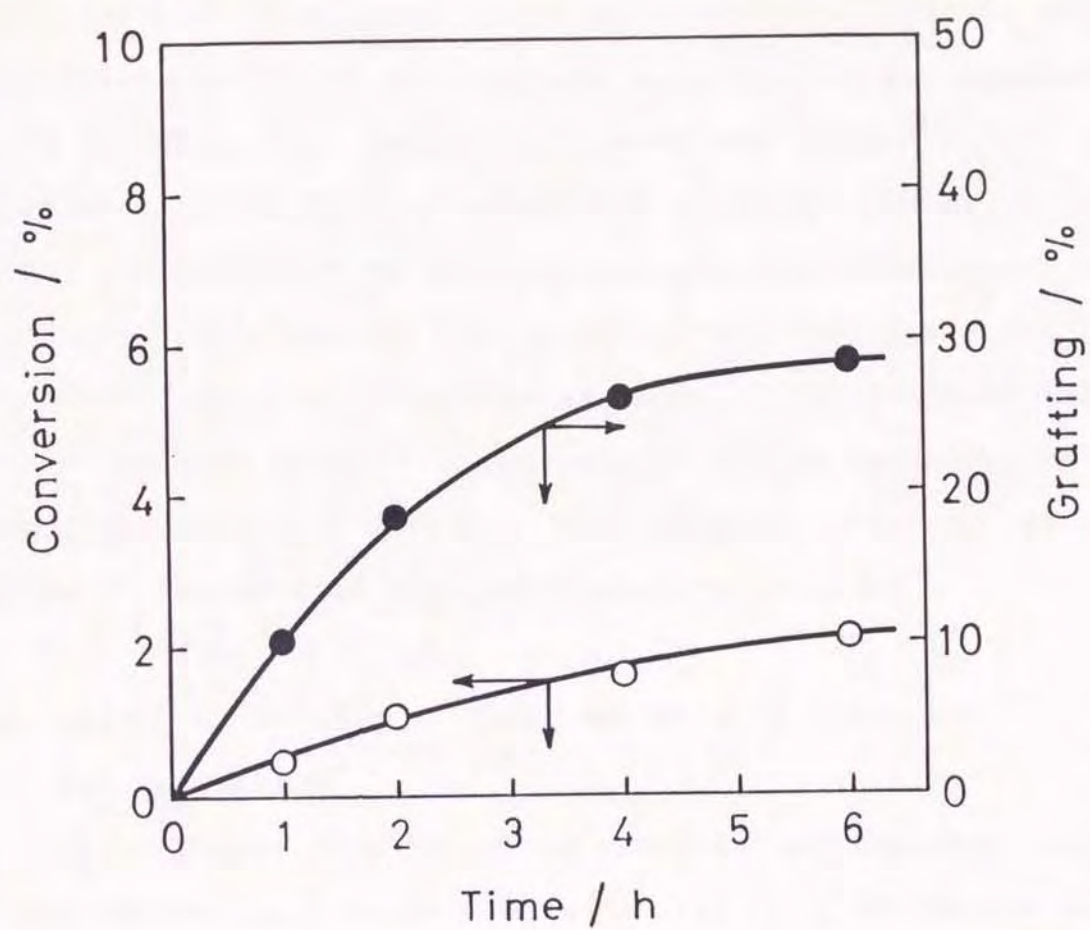


Figure 2-21

Graft polymerization of styrene
initiated by carbon black 2A

Carbon black, 0.30 g; styrene, 10 mL; 70 °C.

percentage of grafting and grafting efficiency increased to 30 and 45%, respectively, as the polymerization proceeded. The polymerization of styrene in the presence of untreated carbon black initiated by ACV are compared with that in the absence of carbon black. The results are shown in Figure 2-22. The polymerization was similarly retarded by carbon black, but the values of percentage of grafting and grafting efficiency were 10 and 4%, respectively. These values are very different from those using peroxyester groups as shown in Figures 2-18 and 2-20. It is also found that the retardation by carbon black in the polymerization of styrene, with negative e -value, is more prominent than that of MMA, with positive e -value.

(3) Effect of e -Value of Vinyl Monomers on the Graft Polymerization

As is evident from the above results, peroxyester groups on the carbon black surface have ability to initiate the graft polymerization of MMA with positive e -value but have no ability to do that of styrene with negative e -value. On the other hand, both the graft polymerization of MMA and styrene were initiated by azo groups introduced onto the carbon black surface though the graft polymerization of styrene was liable to be more retarded than that of MMA. In order to elucidate the effect of e -value of vinyl monomers on the graft polymerization, I examined the graft polymerization of a variety of vinyl monomers using carbon black having peroxyester or azo groups on the surface.

Table 2-8 shows the results of the graft polymerization of various vinyl monomers initiated by carbon black 2P. It is

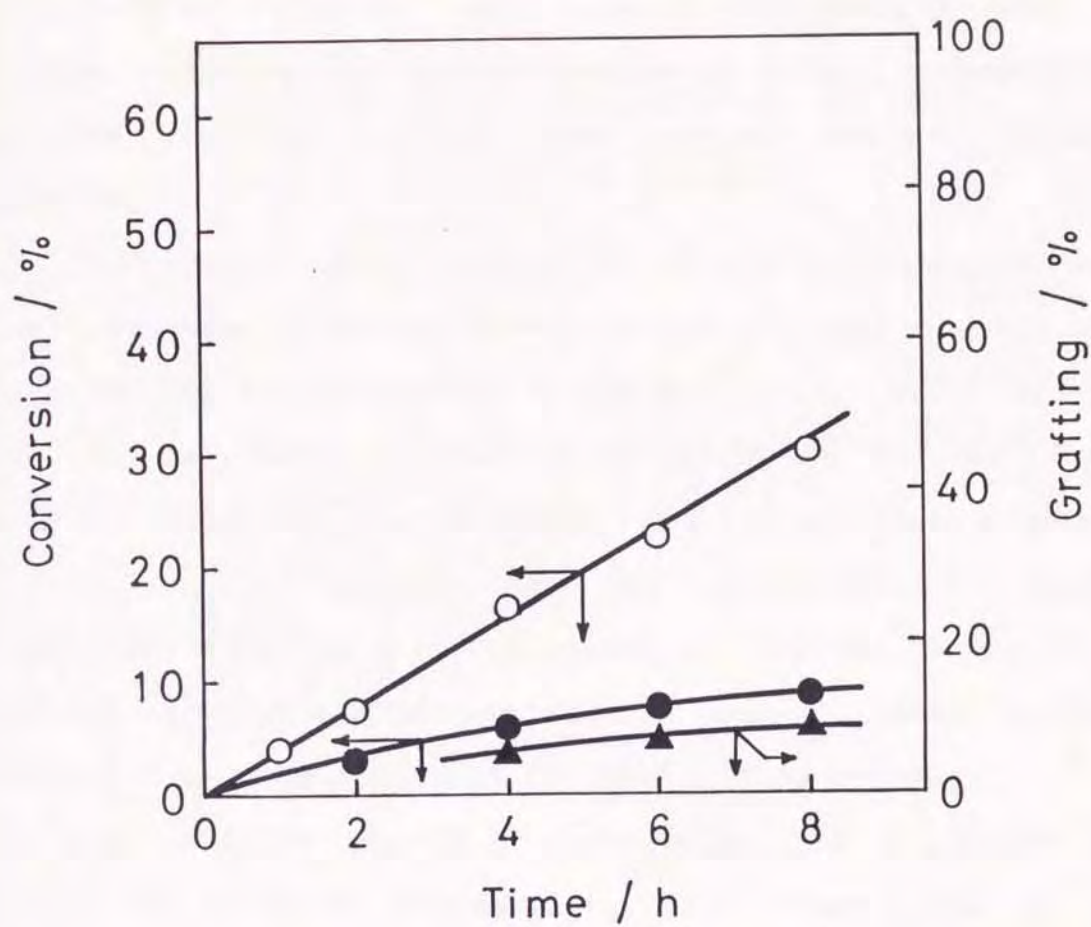


Figure 2-22

Polymerization of styrene initiated by ACV
in the presence of untreated carbon black

Carbon black, 0.30 g; styrene, 10 mL;
ACV, 0.099 mmol; 70 °C.

(O): in the absence of carbon black
(●,▲): in the presence of carbon black

apparent that carbon black 2P has ability to initiate the polymerization of vinyl monomers with positive e -value, and the corresponding polymers are effectively grafted onto the surface. The graft polymerization of vinyl monomers with negative e -value, however, were scarcely initiated by carbon black 2P.

Furthermore, the results of the graft polymerization of vinyl monomers initiated by azo groups attached on the carbon black surface are summarized in Table 2-9. As shown in Table 2-9, it is apparent that carbon black 2A has ability to initiate the graft polymerization of vinyl monomers regardless of the e -value of monomers, and the corresponding polymers are effectively grafted onto the surface. All the carbon blacks obtained from these polymerizations made a stable colloidal dispersion in a good solvent for the grafted polymer.

The radicals formed by decomposition of peroxides have ability to abstract hydrogen atoms from carbon black to give surface active radicals. The surface active radicals on carbon black, which are formed by the reaction of initiator fragments with carbon black, readily capture the growing polymer radicals with negative e -value, but not with positive e -value.^{17,60,72} (See Scheme 2-10.) 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 scarcely retarded.

On the contrary, the radicals formed by decomposition of azo initiators do not have much ability to abstract hydrogen atoms from the carbon black surface. Consequently, when azo

Table 2-8 Effect of e -value of vinyl monomers on the graft polymerization initiated by carbon black 2P

Monomer	e -value	Conversion	Grafting
		%	%
<i>N</i> -Vinyl-2-pyrrolidone	-1.14	0.9	9.8
Styrene	-0.80	0.5	5.2
4-Vinylpyridine	-0.28	0.9	7.6
Vinyl acetate	-0.22	0.2	2.3
2-Hydroxyethyl methacrylate	0.20	2.7	36.9
Methyl methacrylate	0.40	3.8	45.6
Glycidyl methacrylate	0.57	5.6	86.7
Methyl vinyl ketone	0.68	2.4	33.4
Acrylic acid	0.77	20.9	124.4
Acrylonitrile	1.20	10.8	77.5

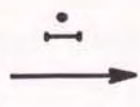
Carbon black 2P, 0.30 g; monomer, 10 mL; 70 °C.

Table 2-9 Effect of e -value of vinyl monomers on the graft polymerization initiated by carbon black 2A

Monomer	e -value	Conversion	Grafting
		%	%
<i>N</i> -Vinyl-2-pyrrolidone	-1.14	2.6	74.3
Styrene	-0.80	2.0	28.5
4-Vinylpyridine	-0.28	10.3	79.9
Vinyl acetate	-0.22	2.3	20.5
2-Hydroxyethyl methacrylate	0.20	1.7	24.0
Methyl methacrylate	0.40	4.7	40.0
Glycidyl methacrylate	0.57	10.6	87.5
Methyl vinyl ketone	0.68	4.6	35.2
Acrylic acid	0.77	6.2	64.8
Acrylonitrile	1.20	13.1	76.2

Carbon black 2A, 0.30 g; monomer, 10 mL; 70 °C.

CB Monomer

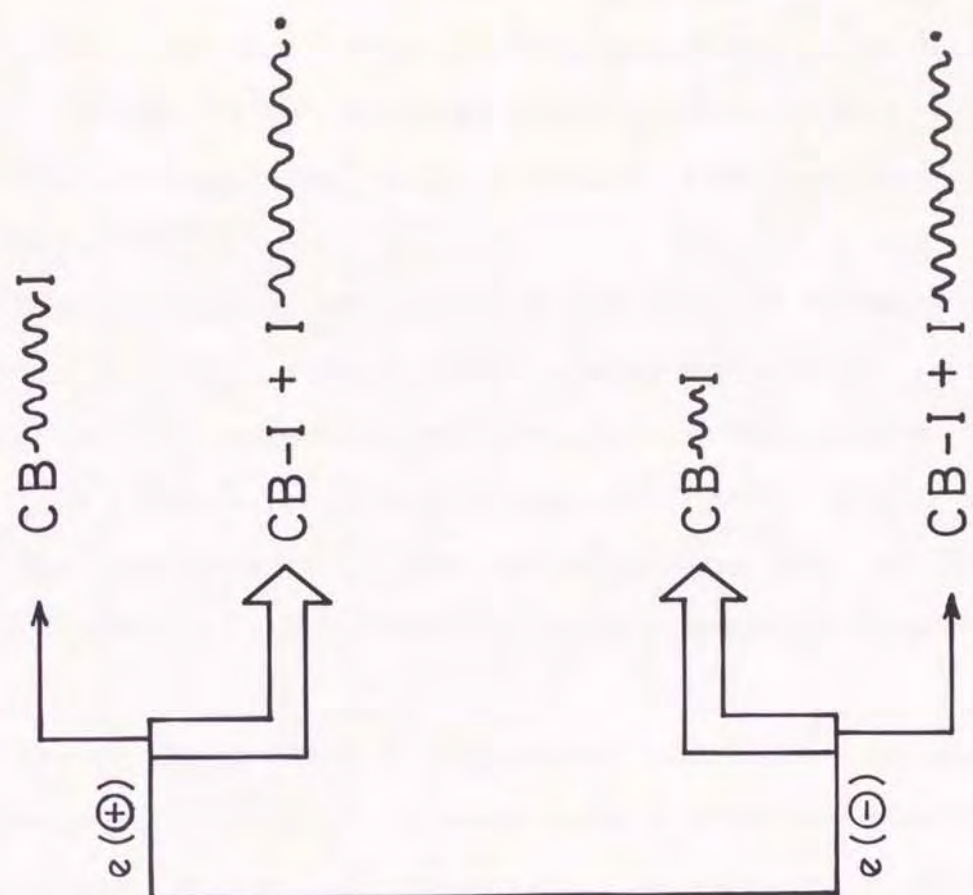


CB \cdot + I~
Surface active
radical

I~
Growing polymer
radical

—(*)—

(*), Competitive reaction of $I\cdot$ and
I~ to $CB\cdot$.



Scheme 2-10

initiators are used, remarkable retardation or inhibition by carbon black is not observed regardless of e -value of vinyl monomers because the surface active radicals are scarcely produced.^{17,60,72)}

The results shown in Tables 2-8 and 2-9 suggest that the radicals (t -BuO \cdot) formed by the decomposition of peroxyester groups on the carbon black produce surface active radicals (CB \cdot) by hydrogen abstraction from the carbon black surface, but the radicals ($\cdot R'$) from azo groups on the carbon black have little ability to produce surface active radicals (Scheme 2-11).

Accordingly, it is concluded that the radical graft polymerization of vinyl monomers from carbon black initiated by peroxyester groups introduced onto the surface is limited to vinyl monomers with positive e -value, but that initiated by azo groups introduced onto the carbon black surface proceeds regardless of e -value of vinyl monomers to give polymer-grafted carbon black with a higher percentage of grafting.

2.4.4 Stability of Dispersion of Poly(methyl methacrylate)-Grafted Carbon Black

The dispersibility of PMMA-grafted carbon black (the percentage of grafting value is 40.0%) in THF was compared with that of untreated and PMMA-adsorbed ones. The results are shown in Figure 2-23. Though untreated carbon black precipitated completely within 1 day, PMMA-grafted carbon black gave a stable colloidal dispersion in THF, a good solvent for grafted PMMA. The stability of dispersion of the carbon black was scarcely improved by adsorption of PMMA onto the surface.

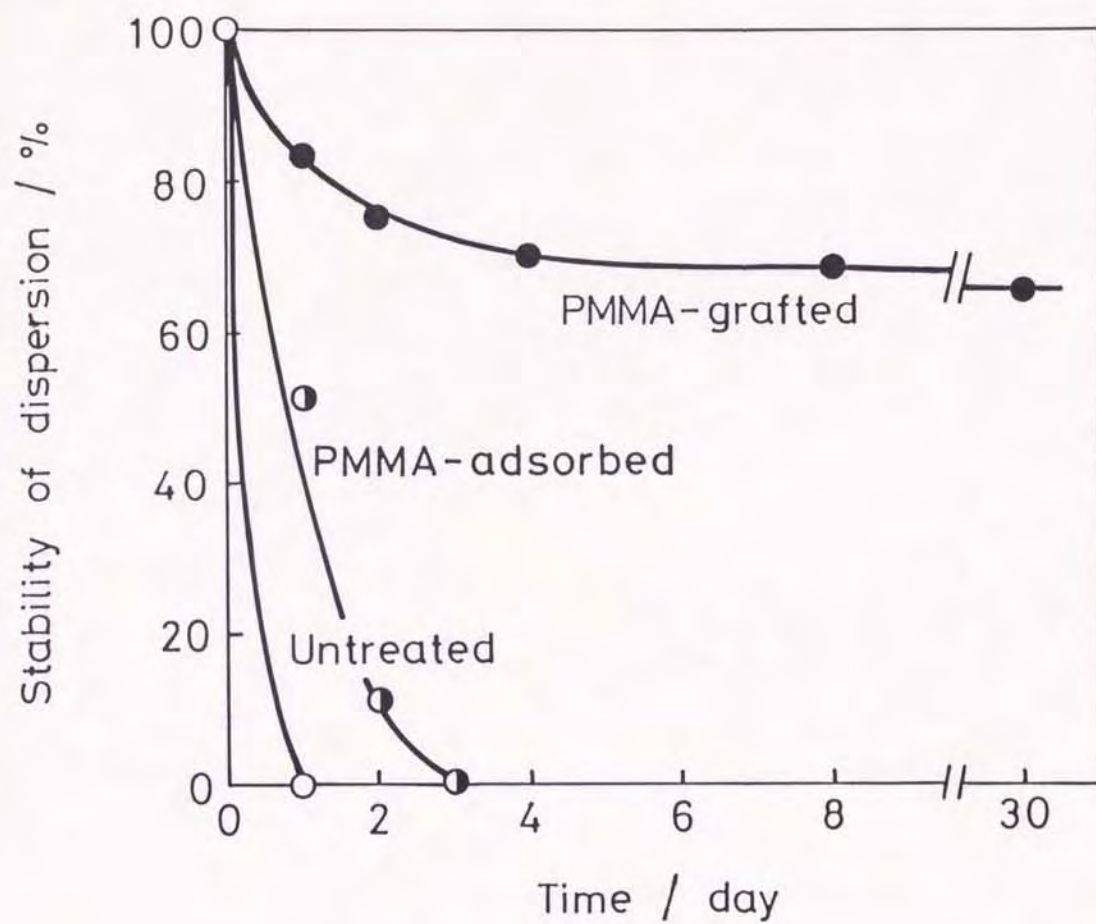


Figure 2-23

Stability of dispersion of PMMA-grafted
carbon black in THF

Percentage of grafting of PMMA, 40.0%;
room temperature.

These results suggest that PMMA chains grafted onto the carbon black surface interfere with the aggregation of carbon black particles. Accordingly, the dispersibility of the carbon black in an organic solvent was remarkably improved by the grafting of polymers onto the surface.

CHAPTER 3

GRAFT POLYMERIZATION OF VINYL MONOMERS INITIATED BY THE REDOX SYSTEM CONSISTING OF CERIC IONS AND REDUCING GROUPS ON CARBON BLACK SURFACE

3.1 ABSTRACT

Construction of a redox system attached on a surface of carbon black, which consisted of ceric ions and alcoholic hydroxyl or imidazoline groups, were tried. The introduction of hydroxymethyl groups onto the surface was achieved by the reaction of carbon black with formaldehyde using sodium hydroxide as a catalyst. The introduction of alcoholic hydroxyl groups onto the surface was carried out by the reaction of carbon black with hydroxyalkyl radicals which were formed by the reaction of benzoyl peroxide with the corresponding alcohol. Furthermore, *N*-(2-hydroxyethyl)carbamoyl or imidazoline groups were successfully introduced onto the surface by the reaction of carbon black with 2,2'-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] or with 2,2'-azobis[2-(2-imidazolin-2-yl)propane]. The graft polymerization of acrylamide was initiated by a redox system consisting of ceric ions and these reducing groups introduced onto the surface, and polyacrylamide was effectively grafted onto the surface. The percentage of grafting of polyacrylamide which was obtained from the polymerization initiated by Philblack O having hydroxymethyl groups/ceric ion redox system reached about 30%. Furthermore, the graft polymerization of several vinyl monomers was investigated.

3.2 INTRODUCTION

It has been reported that the radical polymerization of vinyl monomers are initiated by ceric ions in combination with reducing agents such as alcohols,^{73,74)} aldehydes,⁷⁵⁾ and acids.⁷⁶⁾ Particularly, ceric ion/alcohol systems have been used for the grafting of vinyl polymers to polymers having alcoholic hydroxyl groups, such as poly(vinyl alcohol) and cellulose.⁷⁷⁾

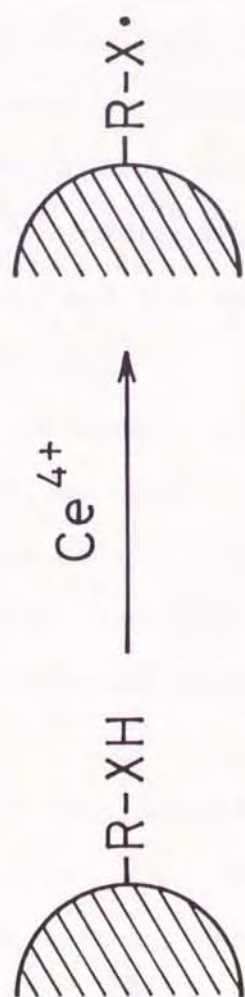
We succeeded in the radical graft polymerization of water-soluble vinyl monomers from carbon black initiated by a redox system consisting of ceric ions and hydroxymethyl groups introduced or poly(vinyl alcohol) grafted onto the surface of the carbon black.⁷⁸⁾ In this polymerization, polyacrylamide was effectively grafted onto the carbon black surface through the propagation of the polymer from radicals formed by the redox reaction of ceric ions with alcoholic hydroxyl groups on the surface.

This chapter is devoted to a discussion of graft polymerization of vinyl monomers initiated by a redox system consisting of ceric ions and reducing groups, such as alcoholic hydroxyl, and imidazoline groups, introduced onto the surface (Scheme 3-1).

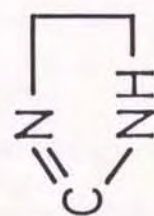
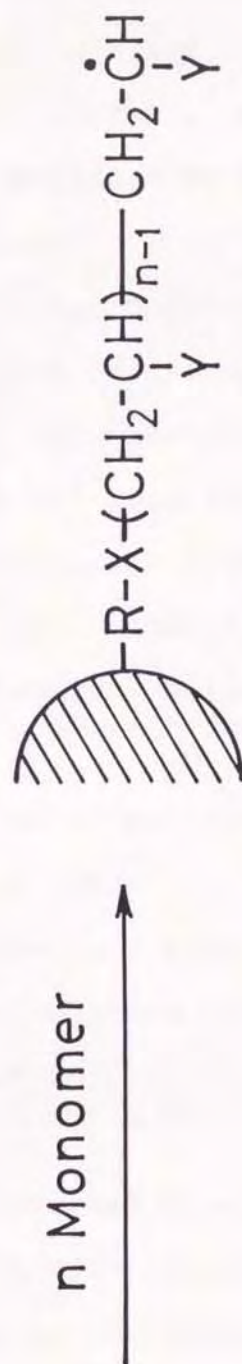
3.3 EXPERIMENTAL

3.3.1 Materials

The carbon black samples used in these experiments were



Carbon black



XH = CH₂OH ,

Scheme 3-1

channel black Neospectra II and furnace black Philblack O. The properties of these carbon blacks are shown in Table 2-1 (See 2.3.1 in chapter 2). These carbon blacks were dried in vacuo at 110 °C before use.

Acrylamide (AAm) was recrystallized from benzene and sublimed under reduced pressure. Acrylic acid, acrylonitrile, *N*-vinyl-2-pyrrolidone, vinyl acetate, methyl methacrylate, styrene, and chloroform were purified by the methods described at section 2.3.1 in chapter 2.

2,2'-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (AHP) and 2,2'-azobis[2-(2-imidazolin-2-yl)propane] (AIP) obtained from Wako Pure Chemical Co., Ltd. were dried in vacuo at room temperature before use. Benzoyl Peroxide (BPO) was dissolved in chloroform and then reprecipitated from ethanol.

Guaranteed-grade methanol, ethanol, 1-propanol, 2-propanol, and 1-octanol were dried over Molecular Sieves and then distilled.

Dioxane and benzene were refluxed over sodium and distilled twice. Guaranteed-grade ceric ammonium nitrate, nitric acid, and formaldehyde solution were used without further purification. Other solvents and reagents were also used without further purification.

3.3.2 Introduction of Hydroxymethyl Groups onto Carbon Black

The introduction of hydroxymethyl groups onto the carbon black surface was carried out by the electrophilic substitution reaction of aromatic rings of carbon black with formaldehyde in the presence of sodium hydroxide as the catalyst. Into a 200 mL flask, 5.0 g of carbon black, 150 mL of formaldehyde

solution (37% aqueous solution), and 1.2 g of sodium hydroxide were charged. The mixture was stirred with a magnetic stirrer for 24 h at 70 °C. After the reaction, the resulting carbon black was filtered, washed with distilled water until the filtrate was neutral, and dried in vacuo at 110 °C. The treated carbon black was stored in a desiccator at room temperature. The content of hydroxymethyl groups introduced onto the surface was determined by volumetrically measuring the amount of ethane evolved by the reaction with triethyl aluminum.^{79,80)}

3.3.3 Introduction of Alcoholic Hydroxyl or Imidazoline Groups onto Carbon Black

(1) Treatment of Carbon Black with Benzoyl Peroxide in Alcohol

The introduction of alcoholic hydroxyl groups onto carbon black was performed by the reaction of carbon black with hydroxyalkyl radicals which were formed by the reaction of BPO with the corresponding alcohol according to the method of Ohkita and Tajima.⁸¹⁾ A typical example is as follows: Under dry nitrogen, a mixture of 1.0 g of Philblack O, 1.0 g of BPO, and 40 mL of alcohol were heated at 45 °C with stirring. After the reaction for 50 h, the resulting carbon black was filtered, extracted with carbon tetrachloride to remove unreacted BPO, and dried in vacuo at 110 °C.

(2) Treatment of Carbon Black with Azo Compounds

The introduction of *N*-(2-hydroxyethyl)carbamoyl groups onto carbon black was achieved by the reaction of carbon black

with 1-*N*-(2-hydroxyethyl)carbamoyl-1-methylethyl radicals which were formed by the thermal decomposition of AHP in 1:1 mixture of water and dioxane as a solvent. The introduction of imidazoline groups was carried out by the reaction of carbon black with 1-(2-imidazolin-2-yl)-1-methylethyl radicals formed by the thermal decomposition of AIP using benzene as a solvent. The procedures were performed in the same manner as those of reaction of carbon black with ACV described at section 2.3.2 in chapter 2. The content of introduced reducing groups was determined by nitrogen analysis.

3.3.4 Polymerization Procedures

Into a 100 mL flask, 0.30 g of carbon black having hydroxymethyl groups and 9.0 mL of a 4.7 molL^{-1} aqueous solution of AAm were charged. After the deaeration of the mixture, 1.0 mL of 0.20 molL^{-1} solution of ceric ammonium nitrate in 1N nitric acid was added. The polymerization was conducted at 30 °C with stirring by a magnetic stirrer under dry nitrogen. When the carbon black treated with AHP or AIP was used, 0.80 molL^{-1} solution of ceric ammonium nitrate was added because of many more contents of the reducing groups.

After the definite time, the mixture was pored into excess of acetone to precipitate the polymer containing carbon black. The precipitant for polyacrylonitrile, poly(methyl methacrylate), and polystyrene was methanol. When *N*-vinyl-2-pyrrolidone and acrylic acid were used as monomer, unreacted monomer was removed under reduced pressure at 50 °C after the addition of *N*-phenyl- β -naphthylamine. The conversion was determined by the same equation described at section 2.3.4 in chapter 2.

3.3.5 Determination of Percentage of Grafting and Grafting Efficiency

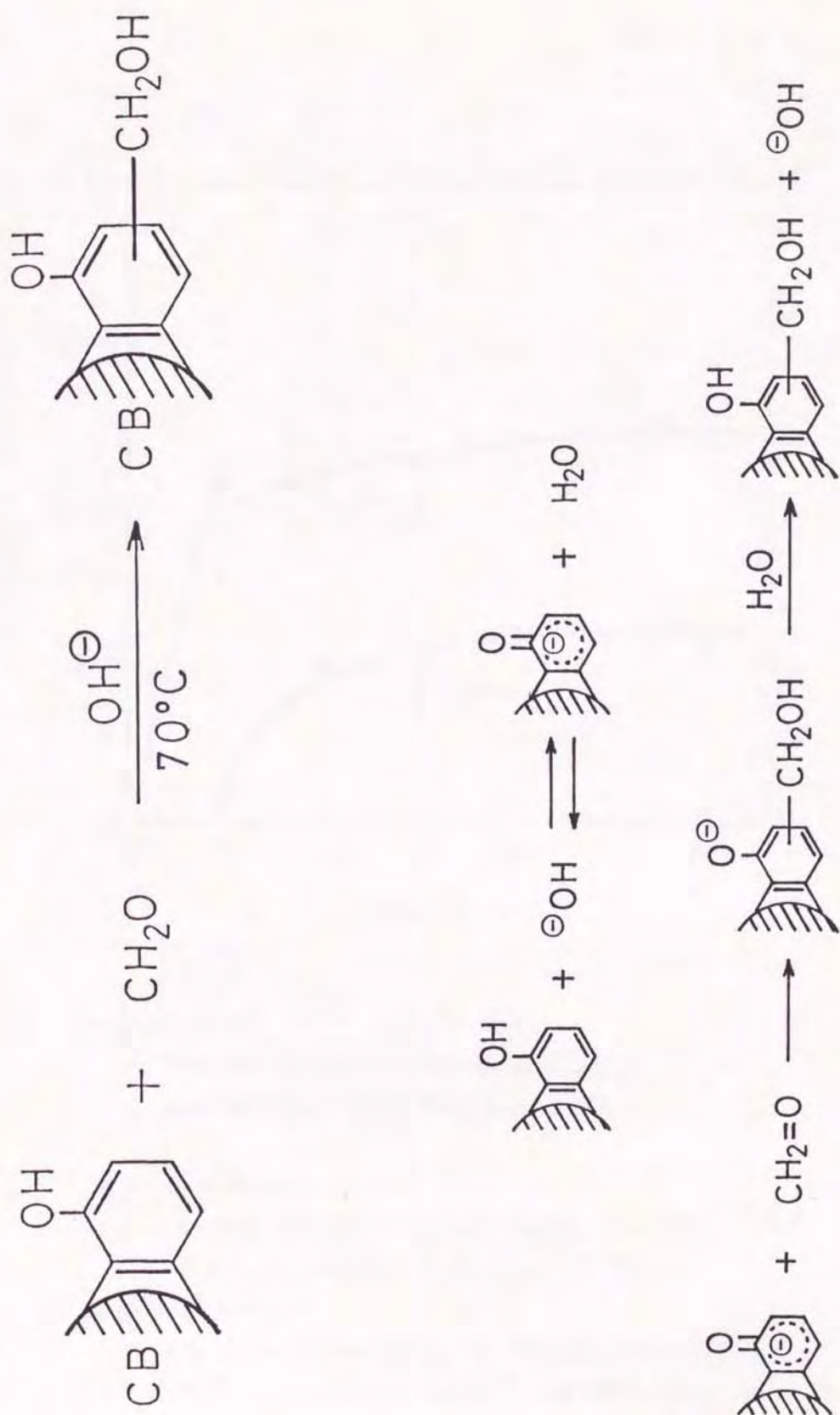
The percentage of grafting and grafting efficiency were determined by the same manner as described at section 2.3.10 in chapter 2.

3.4 RESULTS AND DISCUSSION

3.4.1 Introduction of Hydroxymethyl Groups onto Carbon Black

Hydroxymethylation of phenol under alkaline conditions is well known as an electrophilic substitution reaction in the reaction of phenol with formaldehyde to synthesize resol.^{82,83} Since carbon black has phenolic hydroxyl groups, its surface is also expected to undergo a similar reaction as above (Scheme 3-2).

Figure 3-1 shows the relation between formaldehyde-treatment time and the content of hydroxymethyl groups introduced onto Philblack O. Furthermore, the polymerization of AAm initiated by a redox system consisting of ceric ions and these formaldehyde-treated carbon blacks was examined. The relation between formaldehyde-treatment time and the conversion of AAm was also shown in Figure 3-1. From the results, it is apparent that hydroxymethyl groups are introduced onto the surface. The content of hydroxymethyl groups introduced onto the surface and the conversion increased to 0.12 mmol g^{-1} and 6.5%, respectively, and scarcely increased after 24 h. Figure 3-2 shows the relation between formaldehyde-treatment time and the content of hydroxymethyl groups introduced onto Neospectra II



Scheme 3-2

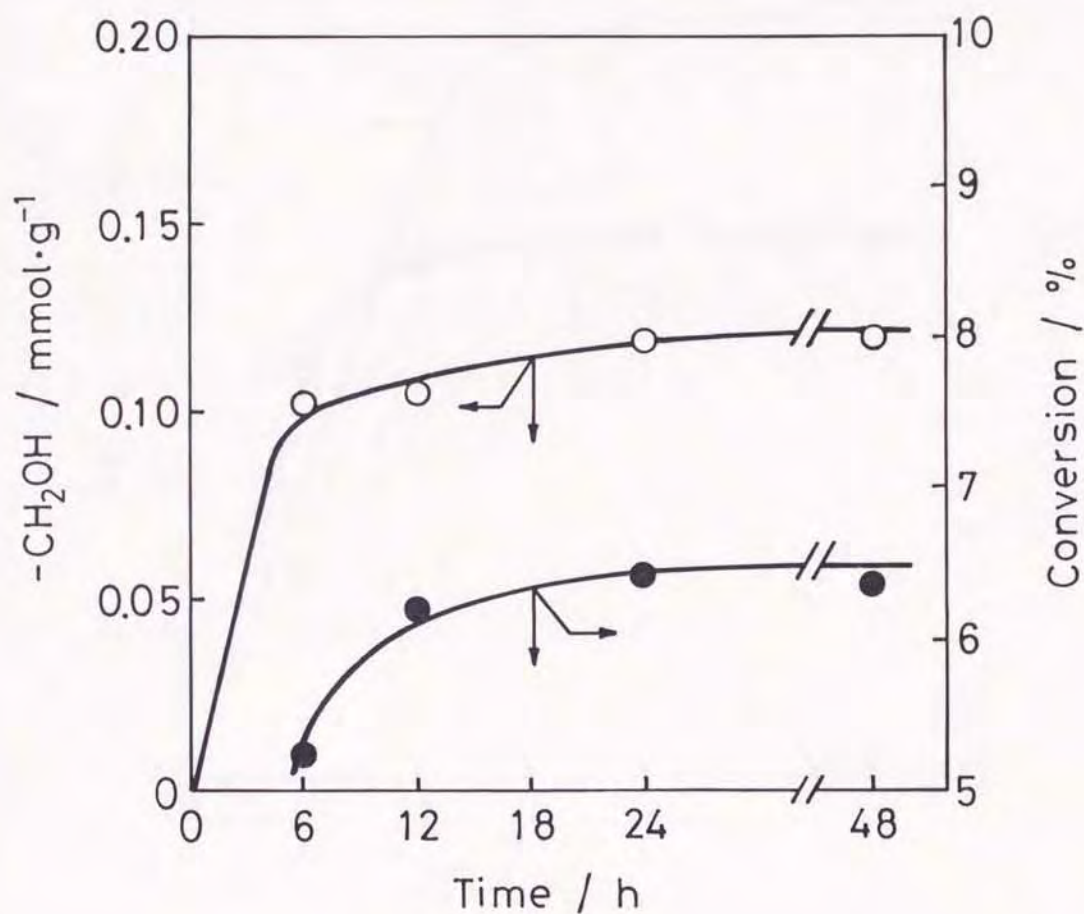


Figure 3-1

The content of CH₂OH groups
introduced onto Philblack O

CH₂O treatment:

carbon black, 5.0 g; NaOH, 1.2 g;
CH₂O aq. soln., 150 mL; 70 °C.

polymerization:

Philblack O-CH₂OH, 0.30 g; AAm, 3.0 g;
Ce⁴⁺ soln. (0.20 molL⁻¹ 1N-HNO aq. soln.),
1.0 mL; total vol. (H₂O), 10 mL; 30 °C; 1 h.

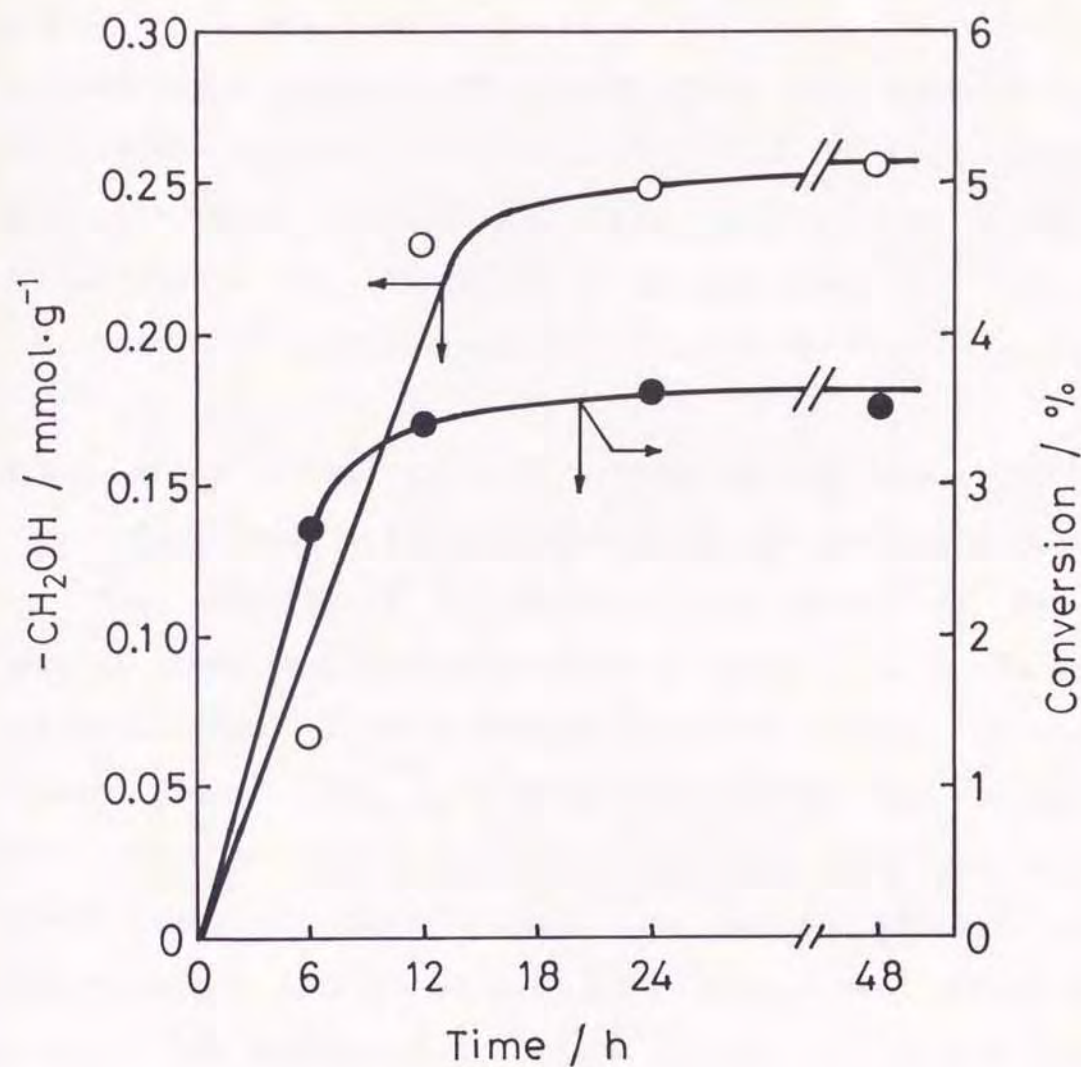


Figure 3-2

The content of CH₂OH groups
introduced onto Neospectra II

CH₂O treatment:

carbon black, 5.0 g; NaOH, 1.2 g;
CH₂O aq. soln., 150 mL; 70 °C.

polymerization:

Neospectra II-CH₂OH, 0.30 g; AAm, 3.0 g;
Ce⁴⁺ soln.(0.20 molL⁻¹ 1N-HNO aq. soln.),
1.0 mL; total vol.(H₂O), 10 mL; 30 °C; 1 h.

and the results of the polymerization of AAm initiated by these carbon blacks having hydroxymethyl groups/ceric ion redox system. It was also found that after 24 h, the content of hydroxymethyl groups introduced onto the surface and the conversion increased to 0.25 mmolg^{-1} and 3.5%, respectively. From the above results, the treatment of carbon black with formaldehyde, for 24 h at 70 °C is sufficient for the introduction of hydroxymethyl groups onto the surface.

3.4.2 Proof of Initiation by a Redox System Consisting of Ceric Ions and Hydroxymethyl Groups on Carbon Black

The results of the graft polymerization of AAm under several conditions are summarized in Table 3-1. Though the polymerization of AAm proceeded slightly in the absence of carbon black, the rate of polymerization was considerably low. Neither system consisting of ceric ions and untreated carbon black nor that of ceric ions and formaldehyde-adsorbed carbon black had the ability to initiate the polymerization because the conversions of these systems were almost equal to the conversion in the absence of carbon black. Furthermore, the polymerization was not initiated by carbon black having hydroxymethyl groups alone. On the contrary, the polymerization of AAm was found to proceed with the coexistence of ceric ions and carbon black having hydroxymethyl groups and polyacrylamide (PAAm) was effectively grafted onto the surface. These results suggest that the polymerization is initiated by the radicals formed by the redox reaction of ceric ions with hydroxymethyl groups introduced onto the carbon black surface.

Table 3-1 Polymerization of AAm under several conditions

Carbon black	Ce^{4+} mL	Conversion		Grafting	
		%		%	
None	1.0	1.8	—	—	—
Untreated Philblack O	1.0	2.1	6.2	6.2	6.2
CH ₂ O-adsorbed Philblack O	1.0	2.2	7.5	7.5	7.5
Philblack O-CH ₂ OH	—	0	0	0	0
Philblack O-CH ₂ OH	1.0	6.4	33.1	33.1	33.1

Carbon black, 0.30 g; AAm, 3.0 g; Ce^{4+} soln. (0.20 molL⁻¹
 1N-HNO₃ aq. soln.), 1.0 mL; total vol. (H₂O), 10 mL; 30 °C; 1 h.

3.4.3 Effect of Ceric Ion Concentration on the Graft

Polymerization

By comparing Figures 3-1 and 3-2, it was found that the conversion of AAm by use of Neospectra II having hydroxymethyl groups was lower than that of Philblack O having hydroxymethyl groups though the content of hydroxymethyl groups introduced onto Neospectra II was more than that introduced onto Philblack O. The reason for this is considered to be that the polymerization is inhibited by oxygen containing groups such as phenolic hydroxyl and quinonic oxygen groups on the surface of Neospectra II, or ceric ions are consumed by the reaction with phenolic hydroxyl or carboxyl groups on the surface besides the reaction with hydroxymethyl groups introduced onto the surface.

Therefore, the effect of the concentration of ceric ions on the graft polymerization of AAm was investigated. Figure 3-3 shows the effect of ceric ion concentration on conversion of AAm and percentage of grafting in the graft polymerization of AAm using Philblack O having hydroxymethyl groups. The rate of polymerization increased with an increase of the ceric ion concentration. The formation of PAAm-gel containing carbon black was observed when the percentage of grafting exceeded 100%, that is, the ceric ion concentration was above 0.060 molL^{-1} . Accordingly, the ceric ion concentration for the graft polymerization using Philblack O having hydroxymethyl groups was determined to be 0.020 molL^{-1} to avoid the gelation of PAAm.

Figure 3-4 shows the results of the graft polymerization of AAm initiated by a redox system consisting of ceric ions and hydroxymethyl groups introduced onto Neospectra II. The

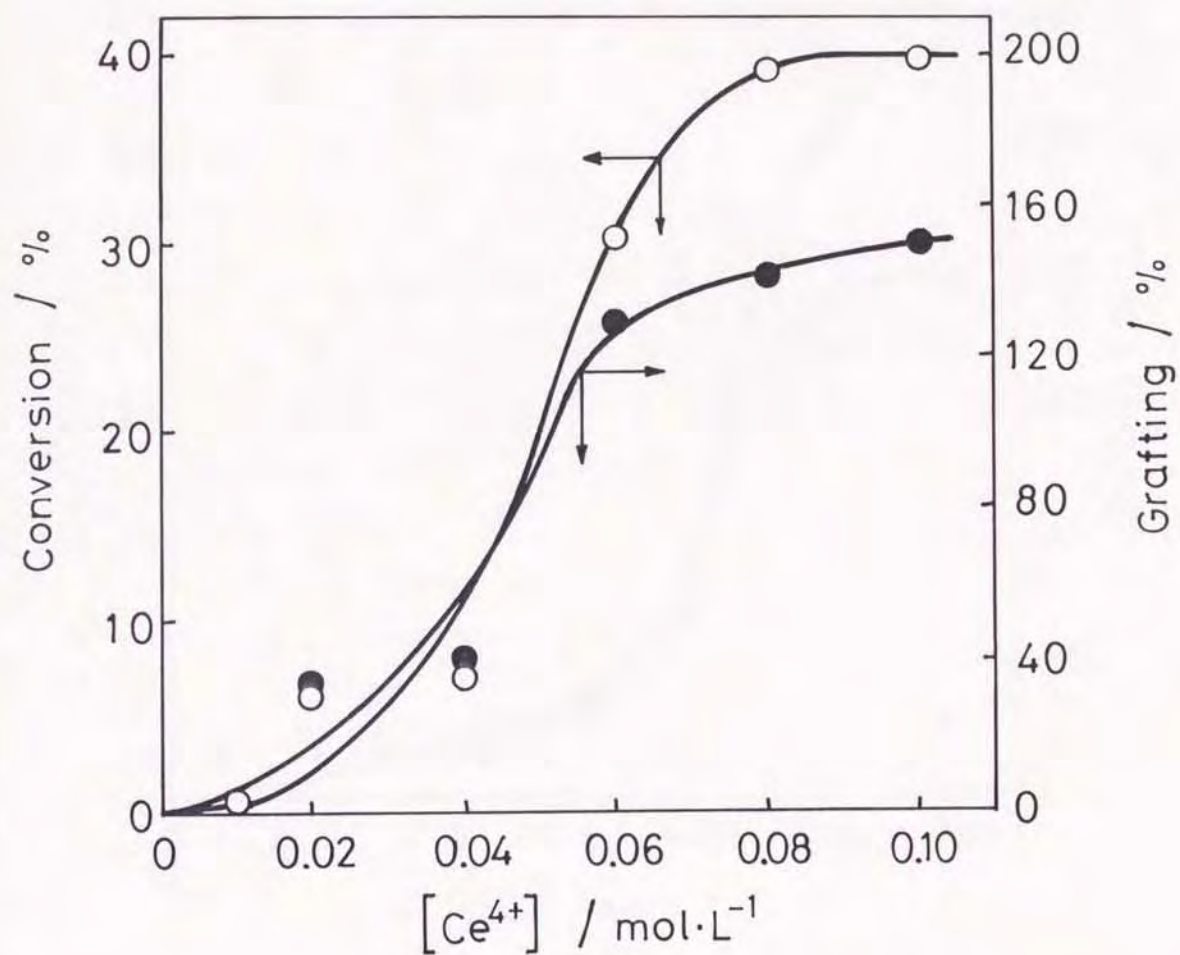


Figure 3-3

Effect of Ce^{4+} concentration on the polymerization of AAm initiated by Philblack O- $\text{CH}_2\text{OH}/\text{Ce}^{4+}$ redox system

Carbon black, 0.30 g; AAm, 3.0 g;
 Ce^{4+} soln., 1.0 mL; total vol. (H_2O),
 10 mL; 30 °C; 1 h.

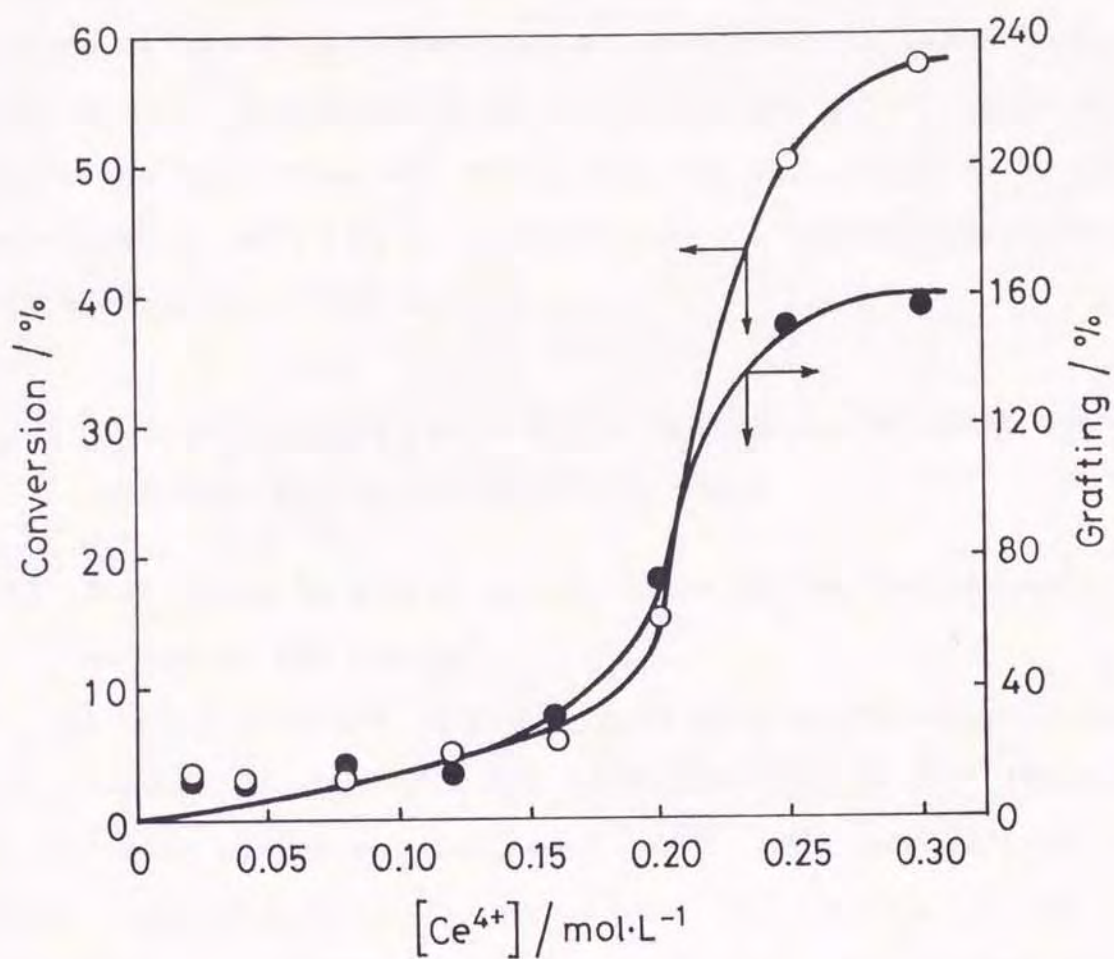


Figure 3-4

Effect of Ce^{4+} concentration on the polymerization of AAm initiated by Neospectra II- $\text{CH}_2\text{OH}/\text{Ce}^{4+}$ redox system

Carbon black, 0.30 g; AAm, 3.0 g;
 Ce^{4+} soln., 1.0 mL; total vol. (H_2O),
 10 mL; 30 °C; 1 h.

conversion and the percentage of grafting reached about 40 and 150%, respectively, as the ceric ion concentration increased. In case ceric ion concentration was above 0.25 molL^{-1} , gel containing carbon black was obtained. In the case of Neospectra II having hydroxymethyl groups/ceric ion redox system, about 4-fold concentration of ceric ions was necessary in order to get the same values of conversion and percentage of grafting in comparison with the case of Philblack O having hydroxymethyl groups/ceric ion redox system.

3.4.4 Initiation by a Redox System Consisting of Ceric Ions and Reducing Groups on Carbon Black

(1) Initiation by Use of Carbon Black Having Hydroxymethyl Groups on the Surface

Figure 3-5 shows the curves of time-conversion and time-percentage of grafting for the polymerization of AAm initiated by a redox system consisting of ceric ions and Philblack O having hydroxymethyl groups. Though the conversion was not high, the polymerization proceeded rapidly. The percentage of grafting reached about 30% after 1 h. This value of the percentage of grafting is much larger than that obtained from the polymerization in the presence of carbon black using a radical initiator. The reason for this is that PAAm is propagated from the radical produced on the surface by the redox reaction of ceric ions with hydroxymethyl groups.

The carbon black obtained from this polymerization formed a stable colloidal dispersion in water, a good solvent for grafted polyacrylamide. A little precipitation of carbon black particles from the dispersion was observed after 30 days.

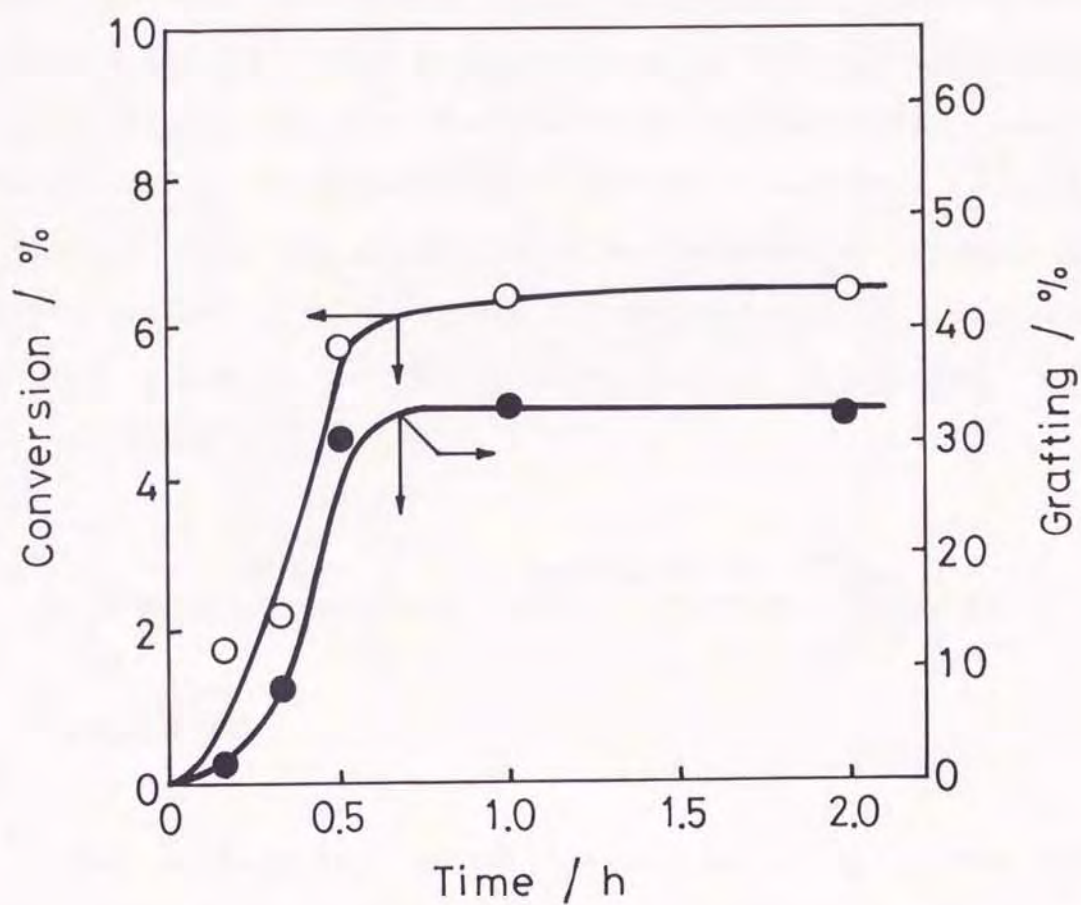


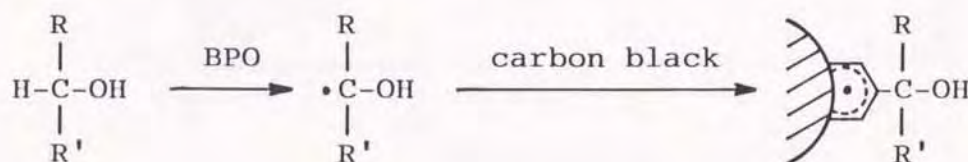
Figure 3-5

Polymerization of AAm initiated by
Philblack O-CH₂OH/Ce⁴⁺ redox system

Philblack O-CH₂OH, 0.30 g; AAm, 3.0 g;
Ce⁴⁺ soln. (0.20 molL⁻¹ 1N-HNO₃ aq. soln.),
1.0 mL; total vol. (H₂O), 10 mL; 30 °C; 1 h.

(2) Initiation by Use of Carbon Black Having Alcoholic Hydroxyl Groups on the Surface

Ohkita and Tajima reported⁸¹⁾ that during the reaction of carbon black with BPO in methanol, hydroxymethyl radicals which were produced by the reaction of methanol with benzoyloxy radicals formed by the decomposition of BPO were trapped by the carbon black surface in preference to the benzoyloxy radicals. Therefore, it is expected that alcoholic hydroxyl groups are introduced onto the carbon black surface by the reaction of the carbon black with hydroxyalkyl radicals which were produced by the reaction of BPO with the corresponding alcohol (Scheme 3-3).



Scheme 3-3

The polymerization of AAm initiated by redox systems consisting of ceric ions and various alcoholic hydroxyl groups introduced onto Philblack O was investigated. The results are shown in Figure 3-6. The alcoholic hydroxyl groups introduced onto the surface were hydroxymethyl (CH_2OH), 1-hydroxyethyl ($\text{CH}(\text{OH})\text{CH}_3$), 1-hydroxy-1-methylethyl ($\text{C}(\text{OH})\text{C}_2\text{H}_5$), 1-hydroxypropyl ($\text{CH}(\text{OH})\text{C}_2\text{H}_5$), and 1-hydroxyoctyl ($\text{CH}(\text{OH})\text{C}_7\text{H}_{15}$) groups.

Figure 3-6 clearly shows that the polymerization of AAm is initiated by these redox systems. The initiating activity of the redox system decreased, depending on the alcoholic hydroxyl groups introduced onto the surface, in the following order:

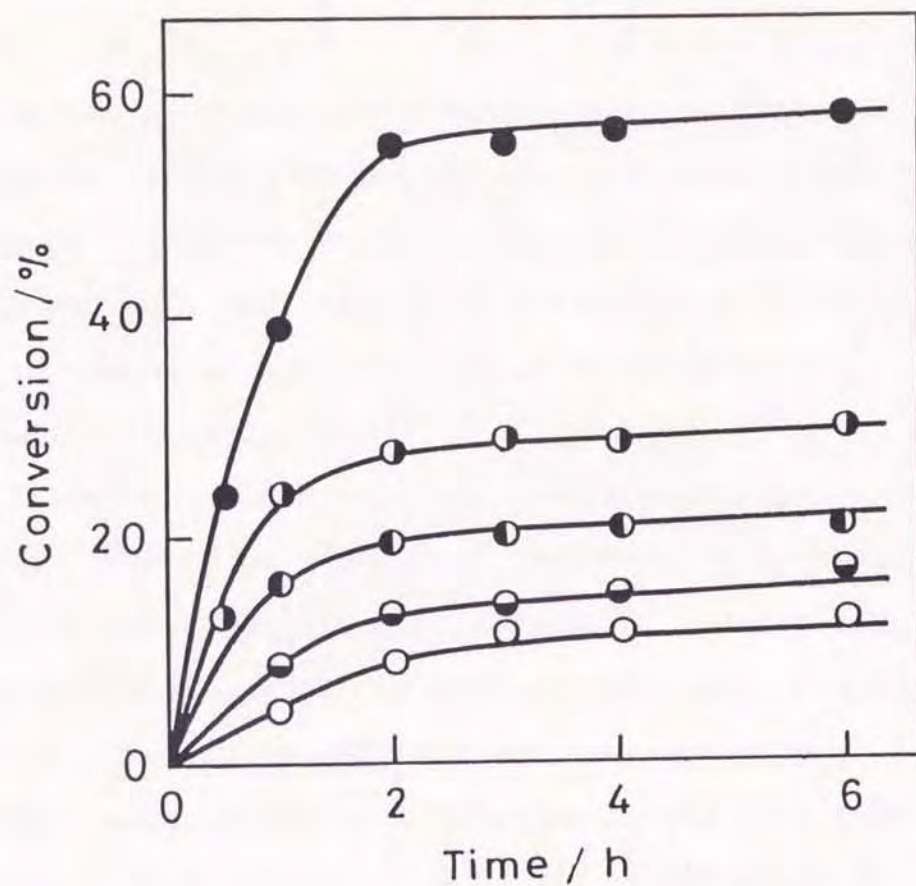
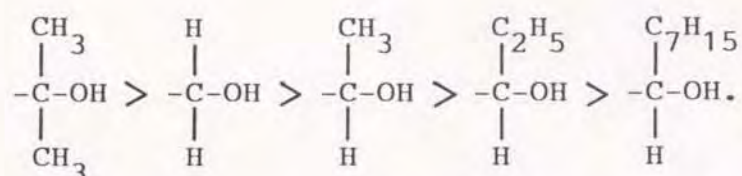


Figure 3-6

Polymerization of AAm initiated
by alcoholic hydroxyl groups on
carbon black/ceric ion redox system

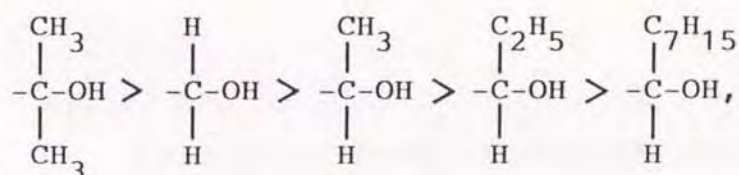
Carbon black, 0.30 g; AAm, 3.0 g;
Ce⁴⁺ soln. (0.20 molL⁻¹ 1N-HNO₃ aq. soln.),
1.0 mL; total vol. (H₂O), 10 mL; 30 °C.

- (●): 1-hydroxy-1-methylethyl group
- (◐): hydroxymethyl group
- (◑): 1-hydroxyethyl group
- (◒): 1-hydroxypropyl group
- (○): 1-hydroxyoctyl group



It seems that the initiating activity of these redox systems is affected by the amount of alcoholic hydroxyl groups introduced onto the surface. The hydroxymethyl group content introduced onto Philblack O by the reaction of Philblack O with BPO in methanol was reported to be 0.060 mmolg^{-1} by use of (^{14}C)methanol as tracer.⁸¹⁾

It was reported that the bond dissociation energy of α -hydrogen atom from 2-propanol, methanol, and ethanol is about 381, 385, 393 kJmol^{-1} , respectively.⁸⁴⁾ Increasing the bond dissociation energy of the alcohol will cause a decrease in the rate of the formation of the corresponding hydroxyalkyl radical, which leads to a decrease in the amount of alcoholic hydroxyl groups introduced onto the carbon black surface. The amount of alcoholic hydroxyl groups introduced onto the carbon black surface, therefore, was expected to decrease in the following order:



which is the same order as the decrease of the initiating activity by the redox system.

Figure 3-7 shows the relation between the percentage of grafting and the conversion for the graft polymerization of AAm. It can be seen from Figure 3-7 that the percentage of grafting increases with an increase in the conversion but is not influenced by the kind of alcoholic hydroxyl groups on the

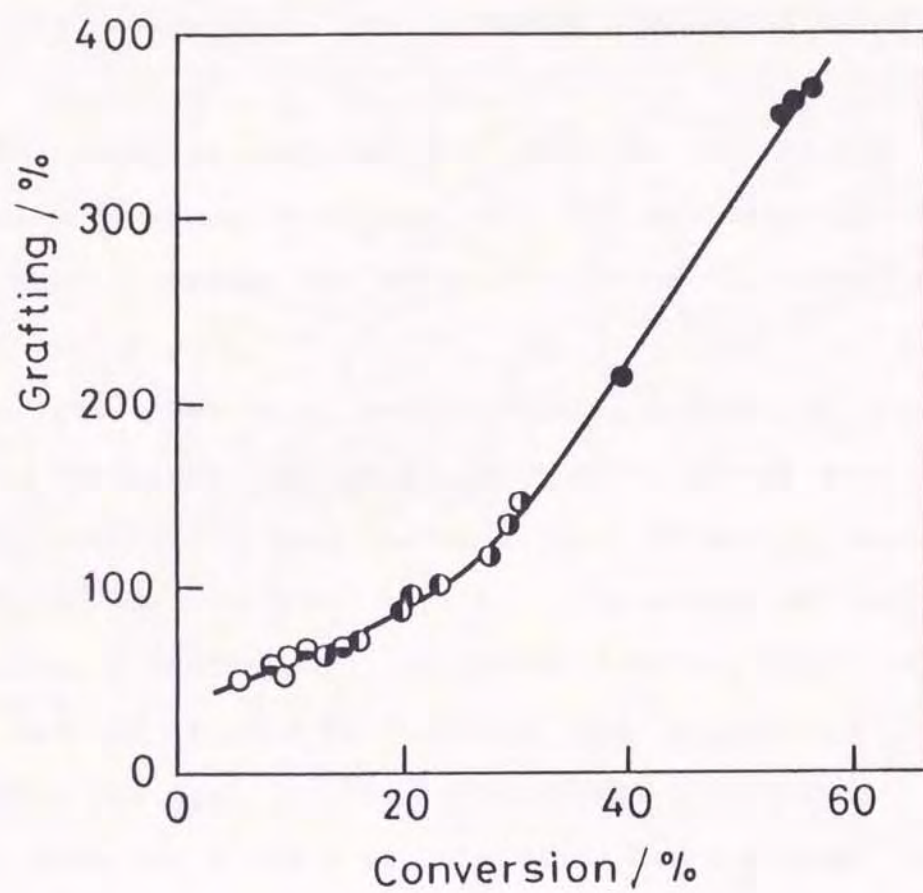


Figure 3-7

Relation between conversion and
percentage of grafting of PAAm

Polymerization conditions and symbol
legends are given in Figure 3-6.

carbon black surface. The percentage of grafting increased up to 350% because the formation of a gel that contained carbon black occurred above 30% conversion. The carbon black obtained below 30% conversions gave a stable colloidal dispersion in water.

The relation between the grafting efficiency and the conversion is shown in Figure 3-8. The grafting efficiency in these redox systems was about 43% before the formation of a gel.

On the other hand, the initiating ability of 2-propanol-adsorbed Philblack O/ceric ion system was almost equal to that of untreated one. This indicates that it is not necessary to take into account the effect of adsorbed alcohol on the initiation. Furthermore, Philblack O having $C(OH)C_2H_6$ groups alone had no ability to initiate the polymerization. Consequently, BPO used for the introduction of alcoholic hydroxyl groups onto the surface is considered to have been completely removed from the surface by the extraction with carbon tetrachloride.

From the above results, it is concluded that PAAm is effectively grafted onto the carbon black surface through the propagation of the polymer from the radicals on the surface produced by the redox reaction of alcoholic hydroxyl groups with ceric ions.

(3) Initiation by Use of Carbon Black Having *N*-(2-Hydroxyethyl)carbamoyl or Imidazoline Groups on the Surface

Carbon black actively reacts with free radicals as mentioned at section 2.3.2 in chapter 2. Therefore, the intro-

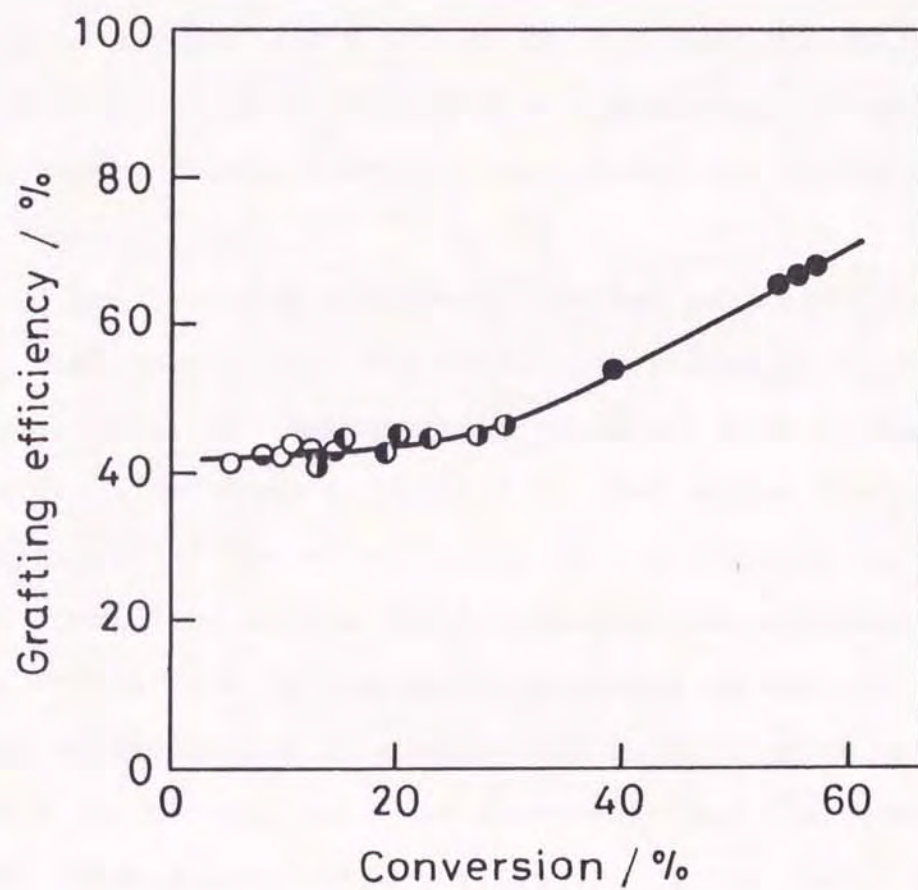


Figure 3-8

Relation between conversion and
grafting efficiency of PAAm

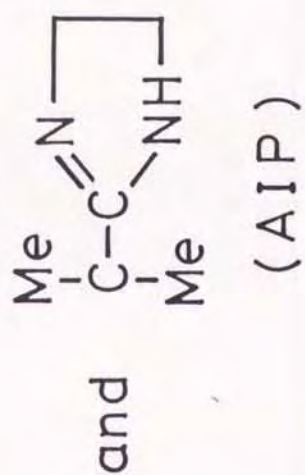
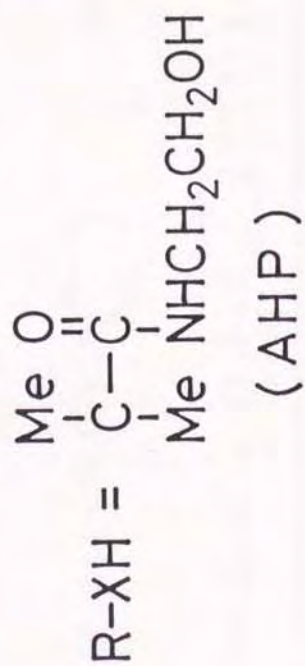
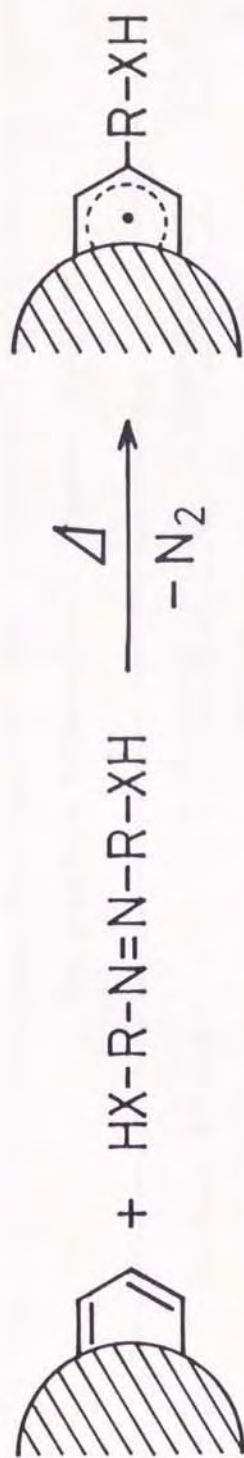
Polymerization conditions and symbol
legends are given in Figure 3-6.

duction of *N*-(2-hydroxyethyl)carbamoyl and imidazoline groups onto the surface by the reaction of carbon black with AHP or AIP was examined (Scheme 3-4). The results are shown in Table 3-2. As a result, *N*-(2-hydroxyethyl)carbamoyl and imidazoline groups were successfully introduced onto the carbon black surface. This indicates that the corresponding radicals formed by the decomposition of AHP or AIP are captured by the carbon black surface.

The graft polymerization of AAm was examined using ceric ions in combination with the carbon black having *N*-(2-hydroxyethyl)carbamoyl or imidazoline groups on the surface. The results are also shown in Table 3-2. The polymerization of AAm was initiated by these redox systems and PAAm was effectively grafted onto the carbon black surface, particularly, in the case of Philblack O having reducing groups on the surface. In the case of Neospectra II having many more reducing groups than Philblack O, however, both the conversion and the percentage of grafting were lower. As described above, the reason for this may be that the polymerization is inhibited by oxygen containing groups on the surface or phenolic hydroxyl and carboxyl groups also react with ceric ions.

3.4.5 Graft Polymerization of Several Vinyl Monomers

The graft polymerization of several vinyl monomers such as acrylic acid, acrylonitrile, *N*-vinyl-2-pyrrolidone, vinyl acetate, methyl methacrylate, and styrene using Philblack O having imidazoline groups in combination with ceric ions was investigated. The results are shown in Table 3-3, and compared with the results of acrylamide.



Scheme 3-4

Table 3-2 Polymerization of AAm initiated by reducing groups
on carbon black/Ce⁴⁺ redox system

Carbon black	Reducing group mmolg ⁻¹	Conversion %	Grafting %
Philblack O-R-CH ₂ OH	0.20	53.6	173.9
Neospectra II-R-CH ₂ OH	0.99	10.1	17.5
Philblack O-R-C $\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{array}$	0.28	55.2	351.0
Neospectra II-R-C $\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{array}$	1.12	8.4	12.5

Carbon black, 0.30g; AAm, 3.0g; Ce⁴⁺ soln. (0.80 molL⁻¹
1N-HNO₃ aq. soln.), 1.0 mL; total vol. (H₂O), 10 mL; 30°C; 1h.

Table 3-3 Polymerization of vinyl monomers initiated by
 Philblack O-R-C $\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{array}$ /Ce⁴⁺ redox system

Monomer	Time h	Conversion		Grafting	
		%		%	
Acrylamide	1	55.2		351.0	
Acrylic acid	1	43.2		83.9	
Acrylonitrile	6	25.5		20.5	
N-Vinyl-2-pyrrolidone	20	16.5		18.6	
Vinyl acetate	20	3.9		16.8	
Methyl methacrylate	20	trace		—	
Styrene	20	trace		—	

Carbon black, 0.30 g; monomer, 0.042 mol;
 Ce⁴⁺ soln. (0.80 molL⁻¹ 1N-HNO₃ aq. soln.), 1.0 mL;
 total vol. (H₂O), 10 mL; 30°C.

These redox systems had the ability to initiate the graft polymerization of acrylic acid and acrylonitrile, and the corresponding polymer was effectively grafted onto the carbon black surface. In the case of acrylonitrile, the polymerizability was lower than that of acrylamide and acrylic acid. This may be due to the fact that the solubility in water of acrylonitrile is lower than that of acrylamide and acrylic acid.

Though the graft polymerization of *N*-vinyl-2-pyrrolidone and vinyl acetate were retarded, the corresponding polymer was grafted onto the surface. The reason for the retardation seems to be due to the negative e -value of these monomers (See 2.4.3-(3) in chapter 2). But, the polymerization of methyl methacrylate and styrene was not initiated by these redox system. Perhaps these monomers are only sparingly soluble in water.

CHAPTER 4

GRAFT POLYMERIZATION OF VINYL MONOMERS TO GRAFTED POLYMER CHAINS ON CARBON BLACK SURFACE

4.1 ABSTRACT

To prepare the polymer-grafted carbon black with a higher percentage of grafting, radical graft polymerization of vinyl monomers (post-grafting) to unsaturated polyester grafted onto the carbon black surface was investigated. During the polymerization of vinyl monomers with benzoyl peroxide as an initiator in the presence of poly(styrene oxide-alt-maleic anhydride)- or poly(glycidyl methacrylate-alt-phthalic anhydride)-grafted carbon black, the vinyl polymers were grafted to these unsaturated polyester chains on the carbon black surface. The percentage of post-grafting of vinyl polymer onto the carbon black increased with an increase in total conversion; the percentage of grafting of poly(methyl methacrylate), polystyrene, and poly(vinyl acetate) onto poly(styrene oxide-alt-maleic anhydride)-grafted carbon black reached about 500, 110, and 95%, respectively. The effects of the initiator and the structure of unsaturated polyester on the post-grafting of vinyl polymers to unsaturated polyester-grafted carbon black were investigated. The polymer-grafted carbon black with a higher percentage of grafting dispersed easily in various polymers. Furthermore, the tensile strength of polystyrene films compounded of the polystyrene-grafted carbon black with a higher percentage of grafting was compared with that of untreated carbon black.

4.2 INTRODUCTION

A composite material incorporating carbon black particles is practically used as a plane heater or an antistatic material. As described in chapter 1, the surface modification of carbon black is necessary for mixing it homogeneously into a polymer matrix. The dispersibility of carbon black particles influences mechanical and electrical properties of the composite material. High dispersibility of them, therefore, is indispensable in order to keep these properties of the material. The dispersibility of carbon black in a polymer matrix or an organic solvent is remarkably improved by the grafting of polymers onto the surface and increases with an increase in the percentage of grafting.^{16,29)}

Our laboratory reported²⁰⁾ that anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides was initiated by alkali metal carboxylate (COOM ; $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb},$ or Cs) groups introduced onto the carbon black surface to give polyester-grafted carbon black. In this polymerization, various kinds of polyesters were able to graft onto the surface by selecting of epoxides and cyclic acid anhydrides. Unsaturated polyester grafts onto the surface in a combination of an epoxide and a cyclic acid anhydride which contained $\text{C}=\text{C}$ double bond in its structure except for aromatic nucleus.

The discussion in this chapter focuses on the radical graft polymerization of vinyl monomers to unsaturated polyester chains grafted onto the carbon black surface, namely, post-grafting, in order to prepare polymer-grafted carbon black with a higher percentage of grafting. In addition, as one of the

mechanical properties, the tensile strength of films compounded of the polymer-grafted carbon black with a higher percentage of grafting was measured and compared with that of untreated carbon black.

4.3 EXPERIMENTAL

4.3.1 Materials

The used carbon black sample was channel black Neospectra II, dried in vacuo at 110 °C before use. The properties of this carbon black are shown in detail in Table 2-1 at section 2.3.1 in chapter 2.

Styrene oxide (SO) and glycidyl methacrylate (GMA) were dried over calcium hydride and fractionally distilled under reduced pressure. Maleic anhydride (MAn) was recrystallized from chloroform and sublimed under reduced pressure. Phthalic anhydride (PAn) was recrystallized from benzene and also sublimed.

Styrene, methyl methacrylate (MMA), vinyl acetate (VAc), and chloroform were purified according to the methods described at section 2.3.1 in chapter 2.

Benzoyl peroxide (BPO) was dissolved in chloroform and reprecipitated from ethanol. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol.

Dioxane, benzene, ethanol, and methanol were purified by the methods described at section 3.3.1 in chapter 3. Toluene was washed with concentrated sulfuric acid, water, a 5% aqueous solution of sodium hydroxide, and water again. It was dried

over calcium chloride, refluxed over sodium, and then distilled.

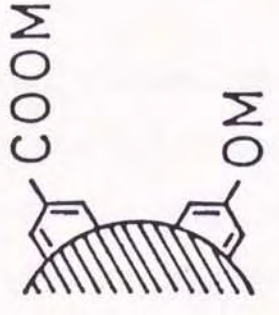
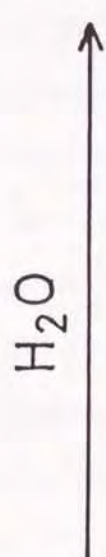
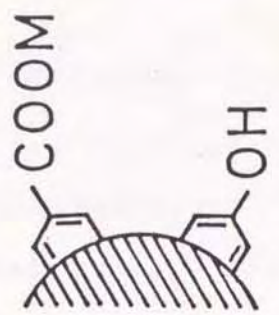
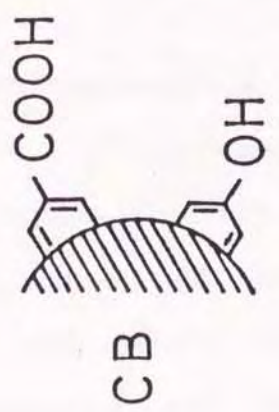
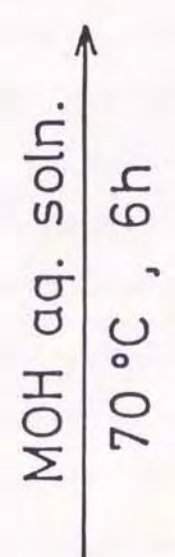
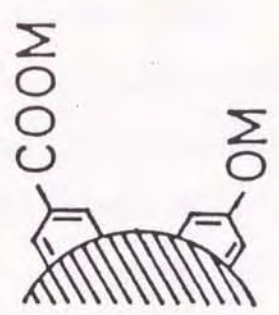
Other solvents and reagents were used without further purification.

4.3.2 Preparation of Unsaturated Polyester-Grafted Carbon Black

(1) Introduction of Potassium Carboxylate (COOK) Groups onto Carbon Black

It is known that carboxyl and phenolic hydroxyl groups on the carbon black surface react quantitatively with alkali metal hydroxides (MOH) to give alkali metal carboxylate (COOM) and alkali metal phenolate (OM) groups, respectively.^{13,56)} However, OM groups are easily hydrolyzed to phenolic hydroxyl groups by treatment with water. Accordingly, it is considered that the carbon black treated with MOH followed by washing with water contains only COOM groups (Scheme 4-1).

Therefore, the introduction of COOK groups onto the carbon black was achieved by the reaction of carboxyl groups on the surface with potassium hydroxide.³⁷⁾ A typical example is as follows: Into a 500 mL flask, 7.0 g of carbon black and 100 mL of an aqueous solution of KOH ($7.0 \times 10^{-2} \text{ molL}^{-1}$) were charged. The mixture was stirred with a magnetic stirrer for 6 h at 70 °C. After the reaction, the resulting carbon black was filtered, washed with water until the filtrate was neutral, and dried in vacuo at 110 °C. The treated carbon black was stored in a desiccator at room temperature.



(M = Li , Na , K , Rb , Cs ,)

Scheme 4-1

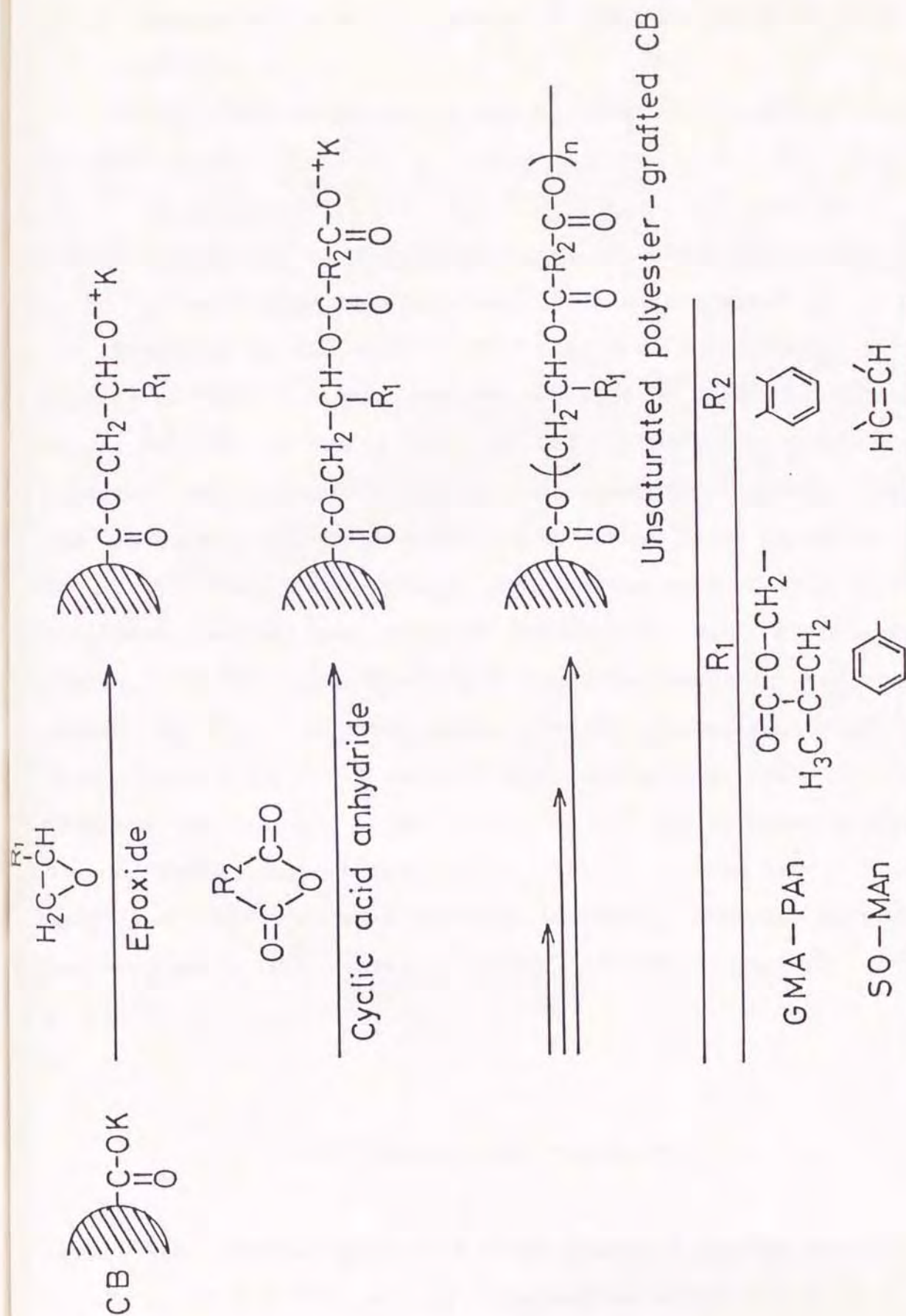
(2) Grafting of Unsaturated Polyester by Copolymerization of Epoxides with Cyclic Acid Anhydrides Using COOK Groups on Carbon Black

Under dry nitrogen, a freshly distilled epoxide (0.17 mol) was added to a 300 mL flask that contained 5.0 g of carbon black, 0.17 mol of a cyclic acid anhydride, and 0.20 g of *N*-phenyl- β -naphthylamine to inhibit the radical cross-linking of the unsaturated polyester formed. The reaction mixture was stirred at 120 °C. After a definite time, the content of the flask was poured into a large excess of methanol to precipitate the polyester containing carbon black (Scheme 4-2).

Then, to separate ungrafted polyester from the reaction product, the product was dispersed in acetone, and the dispersion was centrifuged at 1.2×10^4 rpm until the carbon black precipitated completely. The precipitated carbon black was dispersed again in acetone and centrifuged. The procedure was repeated until no more polymer could be detected in the supernatant solution. The percentage of grafting was calculated by the equation described at section 2.3.10 in chapter 2.

4.3.3 Polymerization (Post-Grafting) Procedures

Into a glass tube, 0.30 g of unsaturated polyester-grafted carbon black, 10 mL of monomer, and 0.30 g of initiator were charged. When MMA and VAc were used as monomer, 7.0 mL of dioxane was added as a solvent. Subsequent procedures of polymerization and the determination of the conversion were performed in the same manner as described at section 2.3.9 in chapter 2.



Scheme 4-2

4.3.4 Determination of Percentage of Grafting and Grafting Efficiency

The procedures were described in detail at section 2.3.10 in chapter 2.

4.3.5 Measurement of Tensile Strength of Polystyrene Films Incorporating Polystyrene-Grafted Carbon Black

Polystyrene ($M_n = 1.7 \times 10^5$) used for compounding polystyrene-grafted carbon black was purified by reprecipitation. Into a 7.0 wt% toluene solution of this polystyrene previously filtered using glass filter, polystyrene-grafted carbon black was added so that the net content of carbon black could be 10 or 20 wt% for the weight of used polystyrene matrix. The resulting polystyrene solution was stirred with a magnetic stirrer for 10 min followed by ultrasonic treatment and then poured on the flat glass plate. It was allowed to stand at room temperature for 1 day and dried in vacuo at 80 °C. The obtained polystyrene film compounded of polystyrene-grafted carbon black was cut into the size of 25 X 50 mm for a test sample of the tensile-strength measurement. Tensile strength was measured with a universal tester, Shimadzu Autograph 100C, at 25 °C.

4.4 RESULTS AND DISCUSSION

4.4.1 Graft Polymerization of Vinyl Monomers (Post-Grafting) to Grafted Unsaturated Polyester on Carbon Black

It has been reported that the graft copolymer is prepared

by the polymerization of a vinyl monomer using initiator such as BPO in the presence of a polymer that contains C=C double bonds.^{85,86)} In this research, post-grafting of various polymers to unsaturated polyester chains grafted onto the carbon black surface by the graft polymerization of vinyl monomers in the presence of unsaturated polyester-grafted carbon black was investigated.

Figure 4-1 shows the results of the graft polymerization of styrene in the presence of poly(SO-alt-MAN) (1)-grafted carbon black using BPO as an initiator. The percentage of grafting of 1 was 60%. As mentioned at section 2.4.3-(1) in chapter 2, the polymerization of styrene, with negative e -value, initiated by BPO is remarkably retarded in the presence of untreated carbon black. This is considered to be due to that the growing polymer radicals are captured by oxygen containing groups or aromatic rings on the surface. As shown in Figure 4-1, though the rate of polymerization of styrene in the presence of 1-grafted carbon black was lower than that in the absence of carbon black, the retardation by carbon black was considerably weakened. The reason for this may be that the oxygen containing groups and aromatic rings on the carbon black surface which are related to the retardation are masked by the grafted polymer chain.⁸⁷⁾

Figure 4-2 shows the relation between the conversion and the percentage of grafting. In Figure 4-2, the left-hand and the right-hand ordinates indicate the percentage of grafting of polystyrene and that of overall polymer (1 + polystyrene), respectively. As shown in Figure 4-2, the percentage of grafting of polystyrene increased with an increase in the

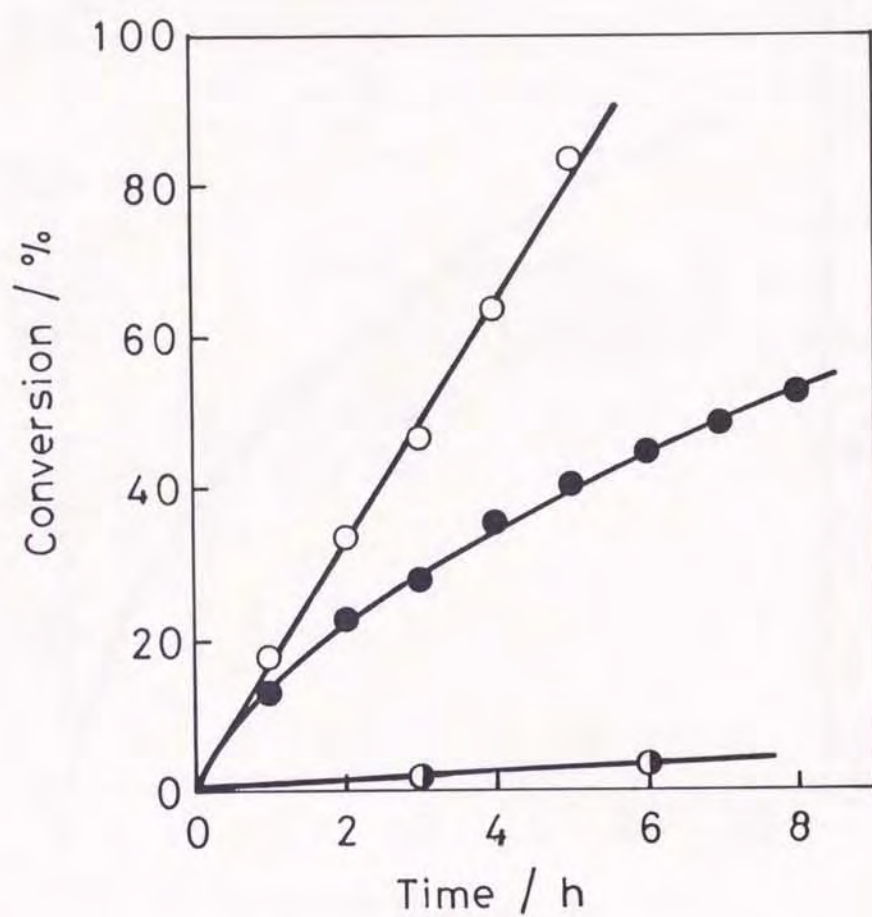


Figure 4-1

Polymerization of styrene initiated by BPO
in the presence of 1-grafted carbon black

Carbon black, 0.30 g; styrene, 10 mL;
BPO, 0.30 g; 70 °C.

- (○): in the absence of carbon black
- (●): in the presence of 1-grafted carbon black
- (◐): in the presence of untreated carbon black

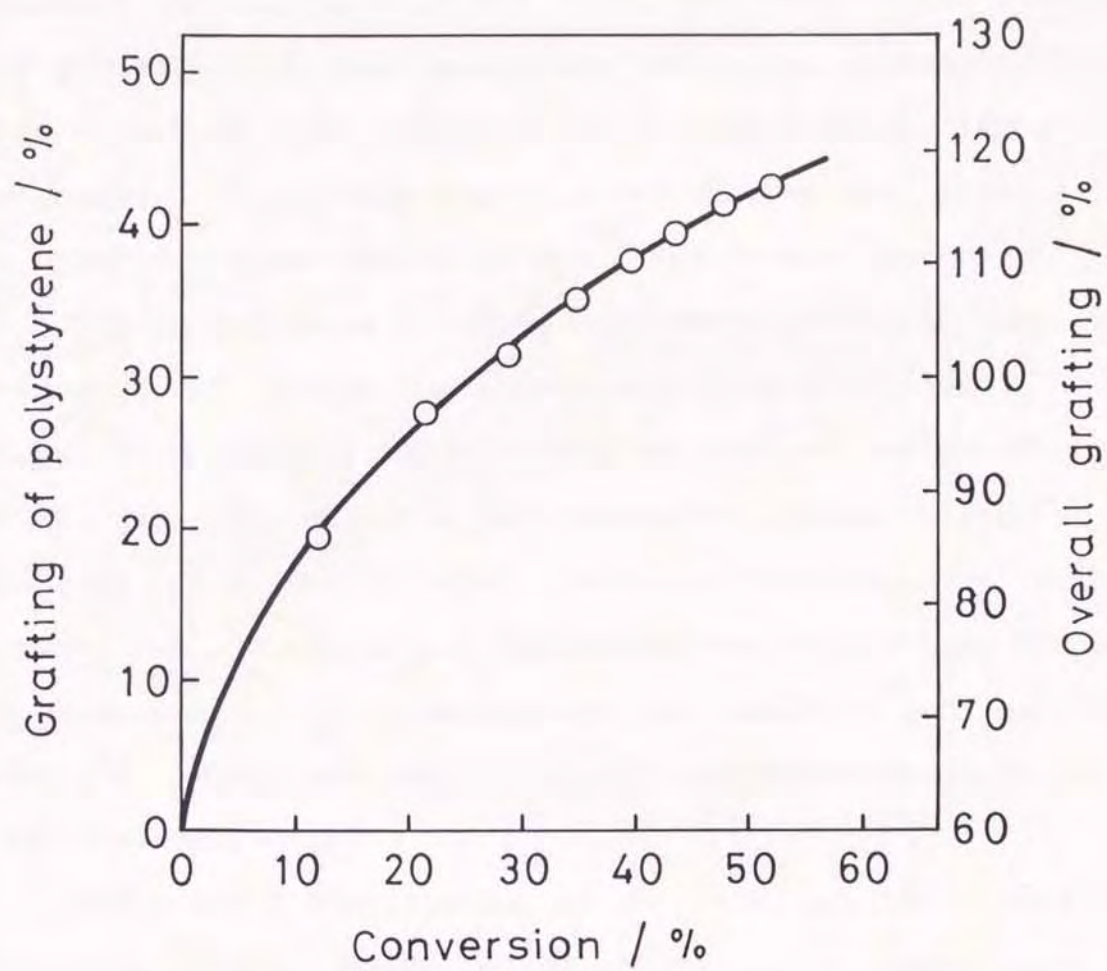


Figure 4-2

Relation between conversion and
percentage of grafting of polystyrene
to 1-grafted carbon black

Polymerization conditions are
given in Figure 4-1.

conversion and to reach more than 40%. The percentage of overall grafting increased to about 120%. As mentioned before, when the polymerization of styrene is carried out in the presence of untreated carbon black using BPO as an initiator, the percentage of grafting is less than 10%. Consequently, it is apparent that the polymer-grafted carbon black with a higher percentage of grafting can be obtained from the post-grafting to grafted polymer chains on the carbon black surface.

Figure 4-3 shows the time-conversion curves of the polymerization of VAc in the presence of γ -grafted carbon black. Though the polymerization in the presence of untreated carbon black was retarded, the retardation by carbon black in the presence of γ -grafted carbon black was relaxed. The relation between the conversion and the percentage of grafting are shown in Figure 4-4. The percentage of grafting of poly(vinyl acetate) (PVAc) and overall polymer increased to about 30 and 100%, respectively.

The graft polymerization of MMA, with positive e -value, to γ -grafted carbon black using BPO as an initiator was also examined. The results are shown in Figure 4-5 and compared with those of the polymerization in the presence or in the absence of untreated carbon black. Compared with the cases of styrene and VAc, the degree of the retardation in the presence of untreated carbon black was lower. This may be due to the fact that the carbon black surface does not react so actively with growing polymer radicals with positive e -value as with ones with negative e -value. The retardation in the presence of γ -grafted carbon black was found to be considerably weakened.

Figure 4-6 shows the conversion-percentage of grafting

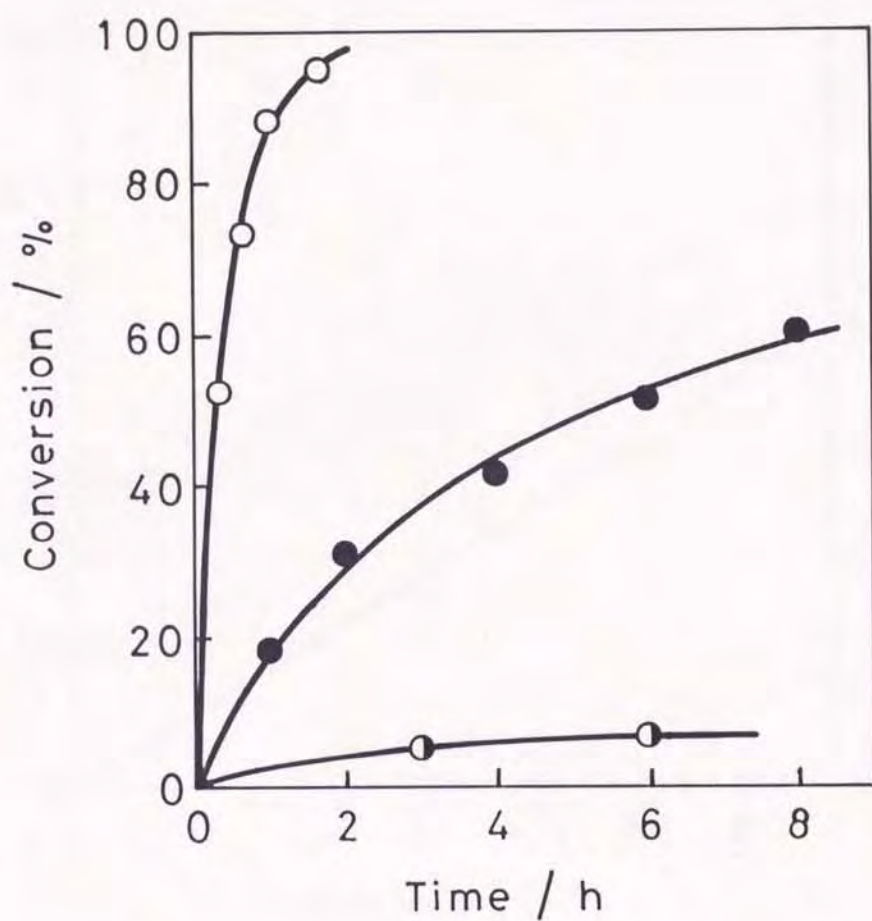


Figure 4-3

Polymerization of VAc initiated by BPO
in the presence of *l*-grafted carbon black

Carbon black, 0.30 g; VAc, 10 mL;
BPO, 0.30 g; dioxane, 7.0 mL; 70 °C.

(O): in the absence of carbon black

(●): in the presence of *l*-grafted carbon black

(○): in the presence of untreated carbon black

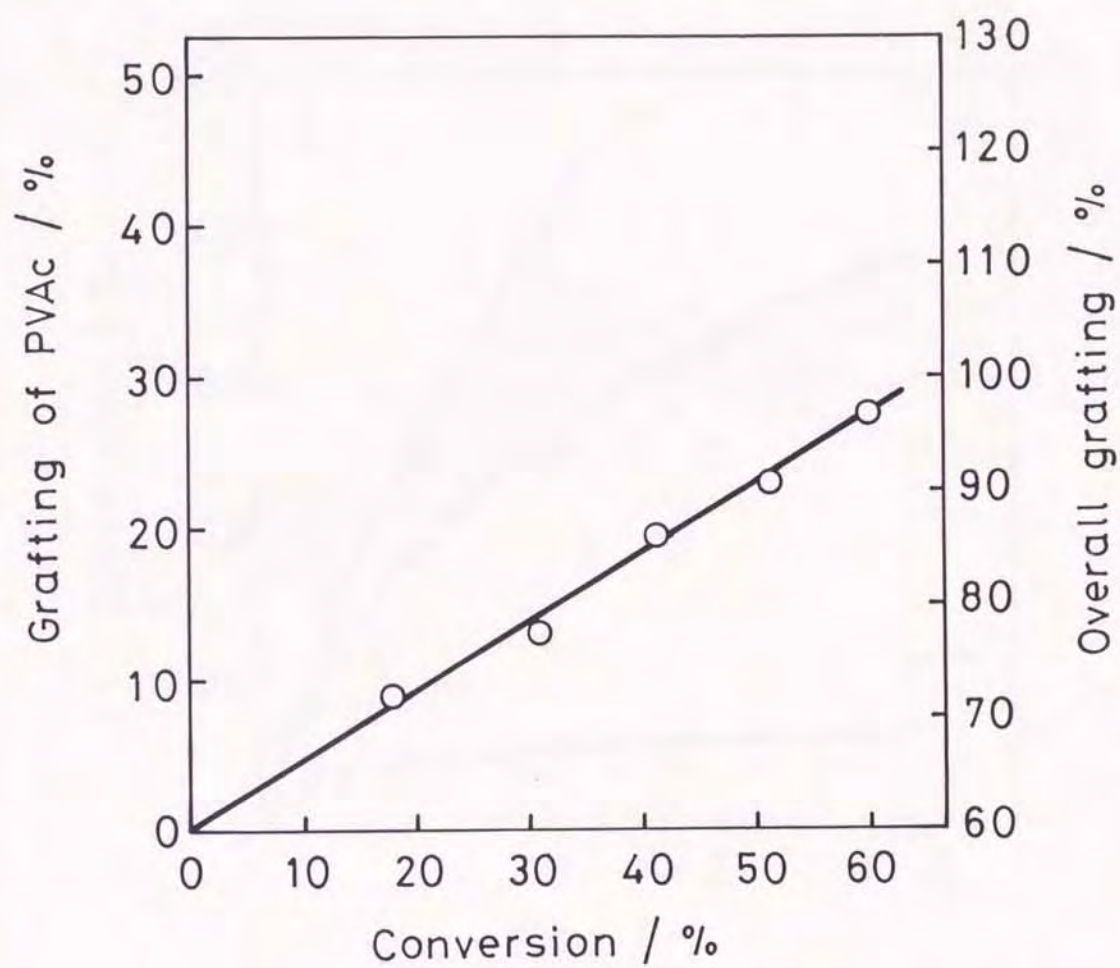


Figure 4-4

Relation between conversion and percentage of grafting of PVAc to 1-grafted carbon black

Polymerization conditions are given in Figure 4-3.

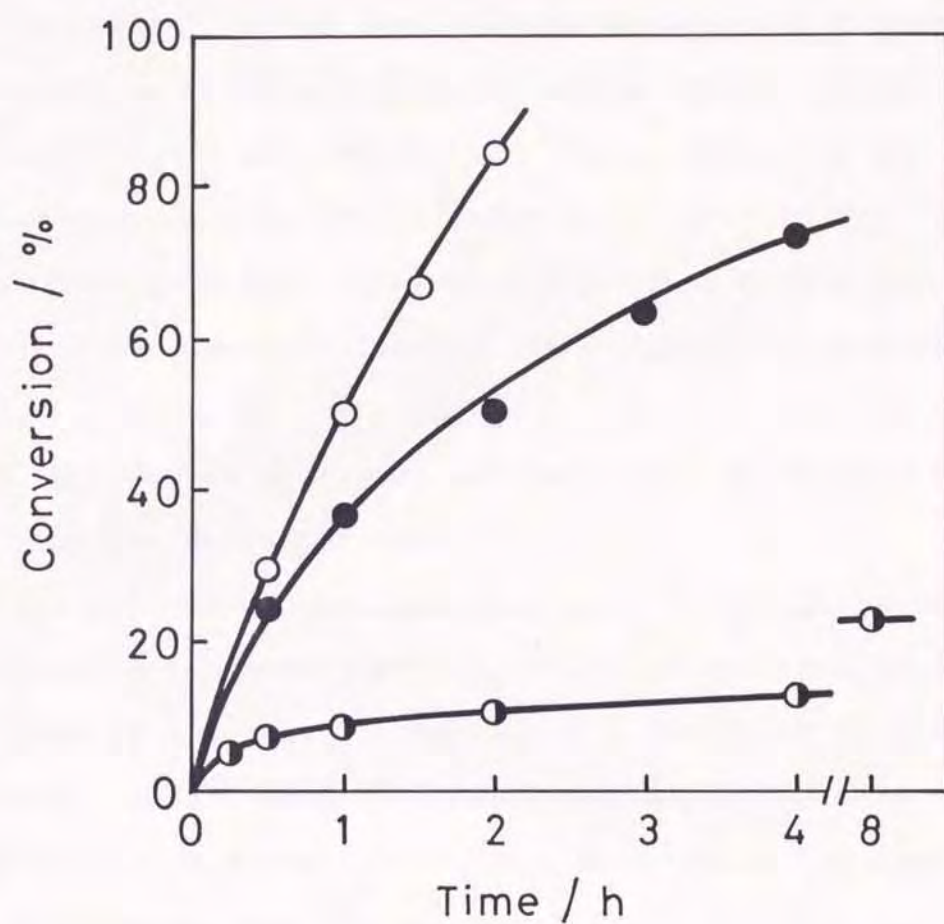


Figure 4-5

Polymerization of MMA initiated by BPO
in the presence of 1-grafted carbon black

Carbon black, 0.30 g; MMA, 10 mL;
BPO, 0.30 g; dioxane, 7.0 mL; 70 °C.

(○): in the absence of carbon black

(●): in the presence of 1-grafted carbon black

(◐): in the presence of untreated carbon black

curve for the graft polymerization of MMA. The percentage of grafting of poly(methyl methacrylate) (PMMA) and overall polymer were found to reach 270 and 500%, respectively, much larger than that of polystyrene or PVAc.

Figure 4-7 shows the relation between the conversion and the grafting efficiency for the above graft polymerizations. The values of the grafting efficiency were very low and decreased gradually as the polymerization proceeded. This indicates that ungrafted polymer initiated by benzoyloxy radicals formed by the decomposition of BPO is produced predominantly.

4.4.2 Effects of Initiator and Structure of Grafted Polyester on the Post-Grafting

The effects of the initiator and the structure of grafted polyester on the post-grafting of polystyrene was investigated. The results are shown in Table 4-1. The types of the grafted polyester chains used in these experiments were the following three: (1) one contained C=C double bonds in the back bone of the main chain, poly(SO-alt-MAn) (1); (2) the other contained C=C double bonds in the pendant groups, poly(GMA-alt-PAn) (2); (3) the rest contained no C=C double bond in its structure, poly(SO-alt-PAn) (3). The initiators used were BPO and AIBN.

As is evident from Table 4-1, the graft polymerization of styrene to 1-grafted carbon black was affected by the initiator, that is, polystyrene was grafted to 1-grafted carbon black using BPO as an initiator but scarcely grafted using AIBN as an initiator. These results are in agreement with those of Brydon et al.,⁸⁶⁾ that is, in the graft polymerization of styrene to polybutadiene, polystyrene was grafted by use of BPO

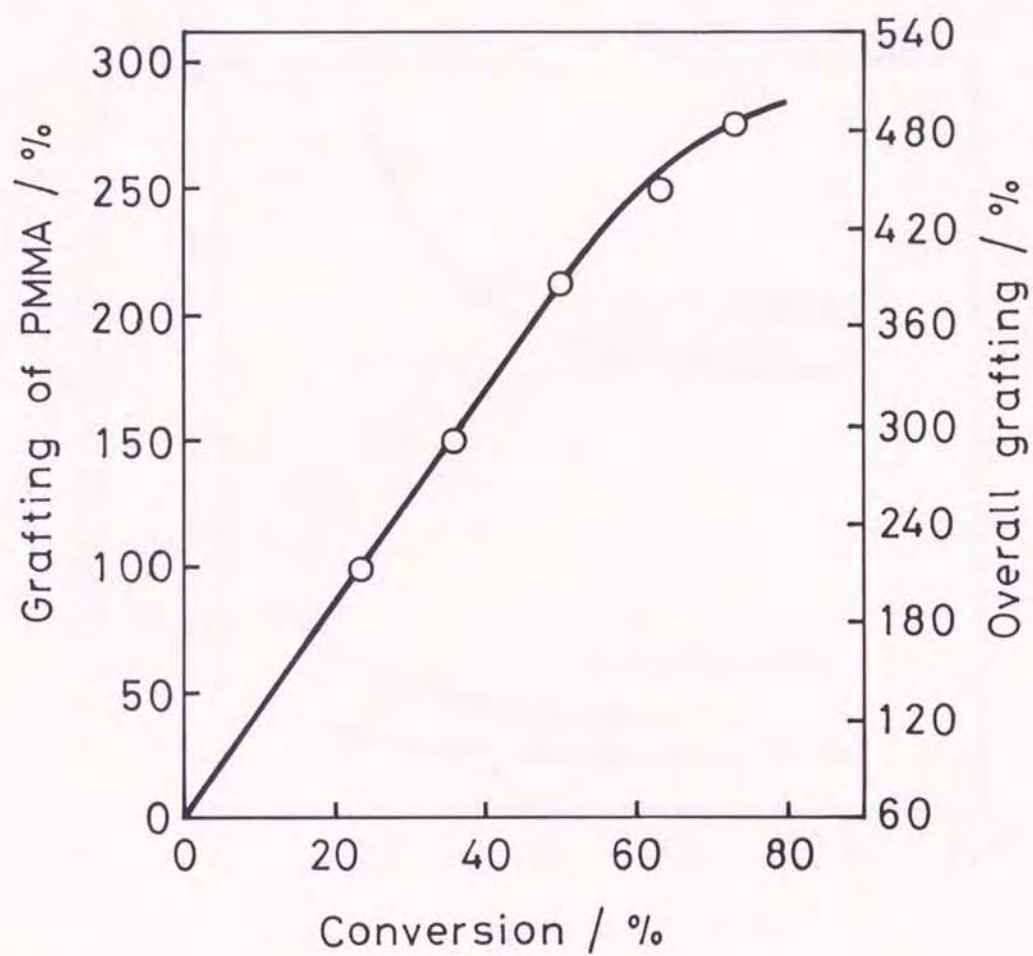


Figure 4-6

Relation between conversion and percentage of grafting of PMMA to 1-grafted carbon black

Polymerization conditions are given in Figure 4-5.

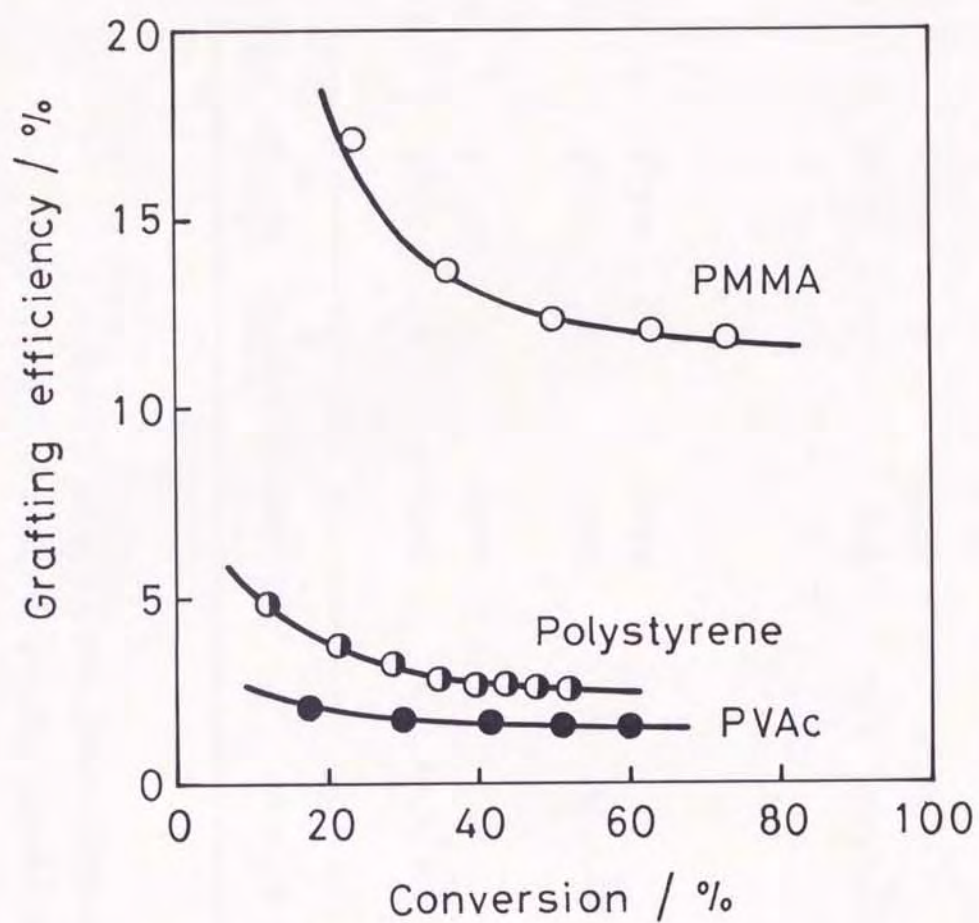
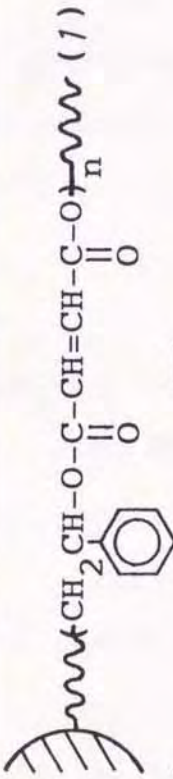
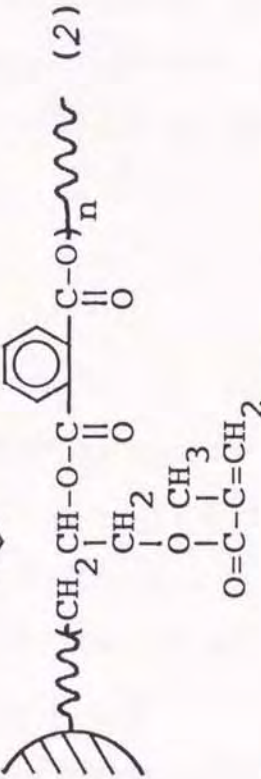
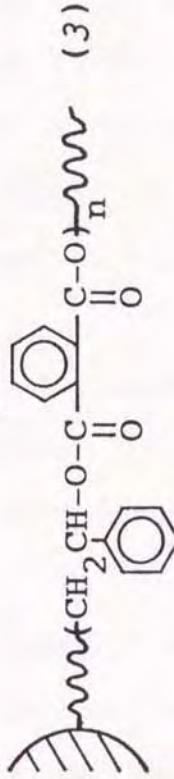


Figure 4-7
Relation between conversion and
grafting efficiency

Table 4-1 Effects of initiator and structure of grafted polyester
on the post-grafting of polystyrene to the
polyester-grafted carbon black

Polyester-grafted carbon black	Initiator	Time h	Conv. %	Grafting %
 <p>(1)</p>	BPO	5	39.5	37.5
	AIBN	3	77.7	0.5
 <p>(2)</p>	BPO	5	65.8	67.9
	AIBN	3	66.1	75.5
 <p>(3)</p>	BPO	5	31.9	10.1
	AIBN	3	65.1	0

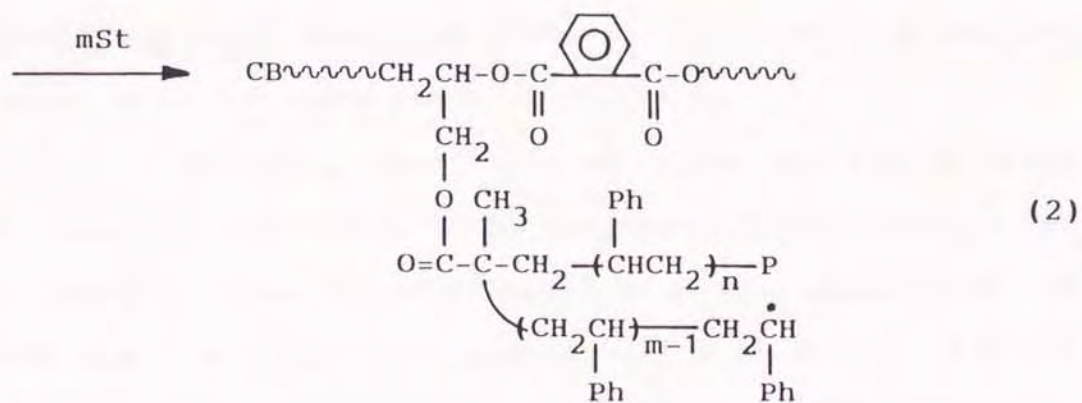
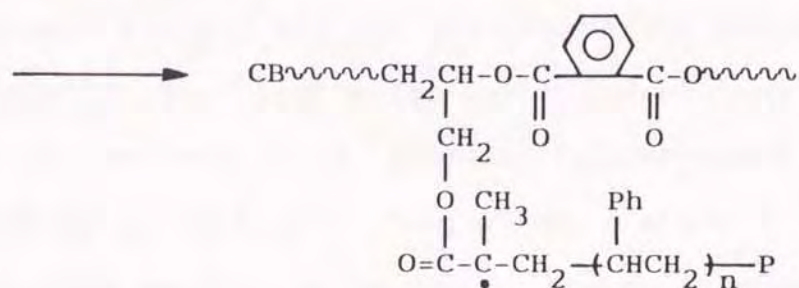
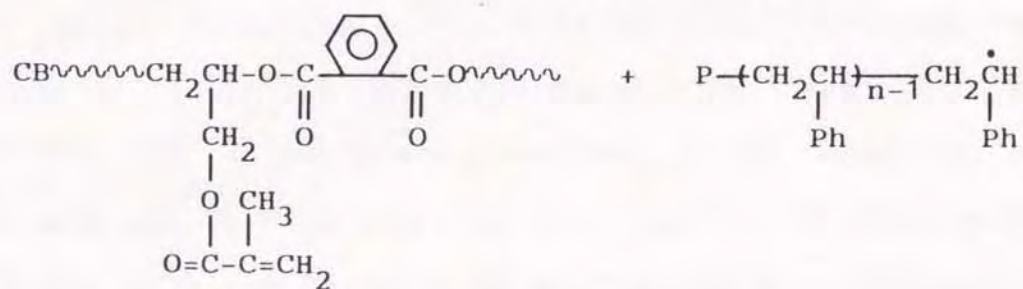
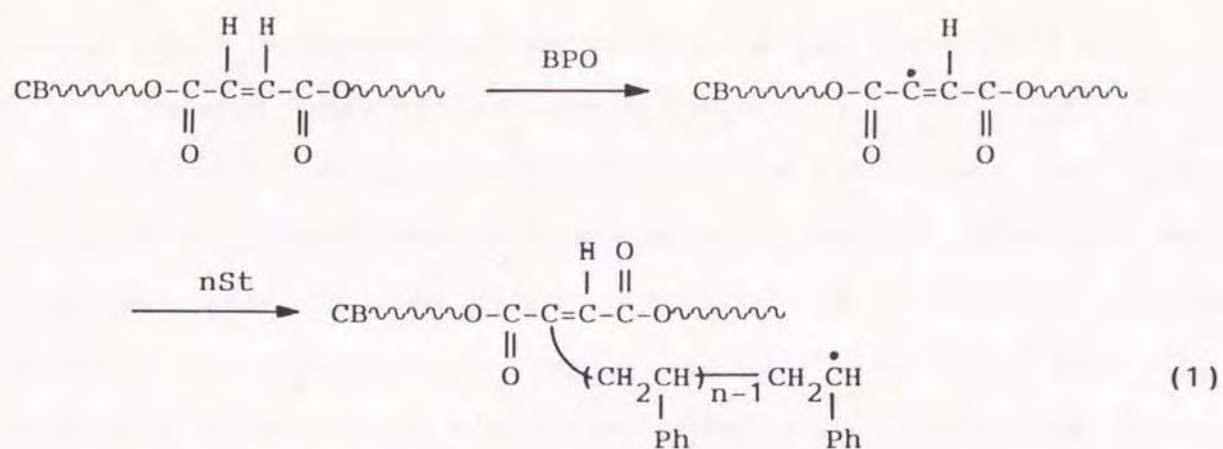
Carbon black, 0.30 g; styrene, 10 mL; initiator, 0.30 g; 70 °C.

but not by use of AIBN. This suggests that the graft polymerization to 1-grafted carbon black is initiated by the radicals produced on the C=C double bond at main chains by the hydrogen abstraction of benzoyloxy radicals formed by the decomposition of BPO (See Eq. 1 in Scheme 4-3). On the other hand, no graft polymerization to 1-grafted carbon black using AIBN as an initiator is considered to proceed because 1-cyano-1-methylethyl radicals formed by the decomposition of AIBN have no ability to abstract hydrogen atoms.

In the graft polymerization of styrene to 2-grafted carbon black, polystyrene was effectively grafted in spite of initiator both BPO and AIBN. Hamann et al. reported¹⁶⁾ that the graft polymerization of styrene onto silica particles having methacrylyl groups on the surface proceeded using AIBN as an initiator. Therefore, it is considered that the grafting reaction to 2-grafted carbon black proceeds at first by the addition of the growing polymer radical to the carbon atom of C=C bond at the pendant groups, and the resulting carbon radical also initiates the graft polymerization (Eq. 2 in Scheme 4-3).

In the case of 3-grafted carbon black, no post-grafting of polystyrene was observed using AIBN as an initiator. Using BPO as an initiator, however, polystyrene was slightly grafted to 3-grafted carbon black. This may be due to the fact that benzoyloxy radicals abstract hydrogen atoms from 3, and the resulting radicals on 3 initiate the graft polymerization.

From the above results, it is concluded that the post-grafting to unsaturated polyester-grafted carbon black is affected by both the initiator and the structure of the grafted



Scheme 4-3

unsaturated polyester.

4.4.3 Tensile Strength of Polystyrene Films Compounded of Polystyrene-Grafted Carbon Black

The tensile strength of polystyrene films that was compounded of polystyrene-grafted carbon black was measured and compared with that of films compounded of untreated carbon black. The results are summarized in Table 4-2. When the untreated carbon black was incorporated into polystyrene film, the tensile strength of the film markedly decreased as the content of the carbon black increased. The reason for this may be that the carbon black particles, which disperse heterogeneously and have no compatibility with a polystyrene matrix, interfere with the tangling of each polystyrene molecule.

Though the polystyrene-grafted carbon black with 9.5% of percentage of grafting, which was prepared from the polymerization of styrene in the presence of untreated carbon black using BPO as an initiator, dispersed relatively uniformly into a polystyrene matrix, it failed to prevent the decrease of the tensile strength of the film. This may be due to the fact that the carbon black particles have little affinity with a polymer matrix because of low percentage of grafting.

On the other hand, remarkable decrease of the tensile strength was not observed even in the case of high content of the carbon black when the polystyrene film was compounded of the carbon black with a higher percentage of grafting (105.2%) obtained from the post-grafting of polystyrene to 1-grafted carbon black. This is considered to be that the carbon black particles with a higher percentage of grafting disperse uni-

Table 4-2 Tensile strength of polystyrene films compounded of polystyrene-grafted carbon black

Carbon black	Grafting %	Carbon black content/%	Tensile strength $\text{N}\cdot\text{mm}^{-2}$
None	—	—	26.2
Untreated	—	10	7.2
untreated	—	20	5.3
Polystyrene-grafted ^a	9.5	10	9.3
Polystyrene-grafted ^a	9.5	20	7.4
Polystyrene-post-grafted ^b	105.2	10	22.9
Polystyrene-post-grafted ^b	105.2	20	18.1

^aPrepared by the polymerization of styrene initiated by BPO in the presence of untreated carbon black.

^bPrepared by the polymerization of styrene initiated by BPO in the presence of 1-grafted carbon black.

formly in a polystyrene matrix, and grafted polymer chains have high compatibility with that.

Consequently, it is concluded that the carbon black with a higher percentage of grafting is effective for prevention of the decrease of mechanical strength by its incorporation into a polymer matrix and available as the filler for polymer matrices.

CHAPTER 5

CONCLUDING REMARKS

Surface modification of inorganic powders is now necessary for using them as fillers for composite materials. In this thesis, as one of surface-modification techniques, the grafting of polymers onto inorganic powder surface, particularly the carbon black surface, was discussed. The results may be summarized as follows:

- (1) The radical graft polymerization of vinyl monomers from carbon black was initiated by peroxyester or azo groups introduced onto the surface, and the corresponding polymer was effectively grafted onto the surface.
- (2) In the polymerizabilities of a vinyl monomer initiated by these initiating groups introduced onto the carbon black surface, a clear difference was observed. Carbon black having peroxyester groups had ability to initiate the graft polymerization of vinyl monomers with positive e -value but had no ability to do that with negative e -value. On the other hand, the graft polymerization of vinyl monomers was initiated by carbon black having azo groups regardless of the e -value of monomers.
- (3) The radical graft polymerization of water soluble vinyl monomers, such as acrylamide, acrylic acid and so on, was initiated by a redox system consisting of ceric ions and reducing groups, such as alcoholic hydroxyl and imidazole groups, introduced onto the surface. The polymerization proceeded from the surface, and the corresponding polymer was also effectively grafted onto the surface.
- (4) The radical graft polymerization of vinyl monomers (post-grafting) to unsaturated polyester-grafted carbon black was initiated by benzoyl peroxide or azobisisobutyronitrile to

give polymer-grafted carbon black with a higher percentage of grafting. The graft polymerization was found to be affected by both the initiator and the structure of the unsaturated polyester grafted onto the surface.

- (5) The polymer-grafted carbon black gave a stable colloidal dispersion in a good solvent for the grafted polymer chains. The dispersibility of carbon black was remarkably improved by the grafting of a polymer onto the surface.
- (6) In case the polymer-grafted carbon black was incorporated into a polymer matrix, remarkable decrease of mechanical strength was not observed. The polymer-grafted carbon black with a higher percentage of grafting seems to be useful as the filler for a polymer matrix.

Carbon black has been used for more than 100 years, but only 20 years have passed since the investigation of the reaction, with which the surface of the carbon black was concerned, was made. There are still many points which must be clarified in the grafting of polymers onto the carbon black surface. I will be glad if the results of our investigation is any help to the people concerned.

- 1) J. Biscoe and B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942).
- 2) L. E. Alexander and E. C. Sommer, *J. Phys. Chem.*, **60**, 1646 (1956).
- 3) H. Akamatsu, H. Inokuchi, H. Takahashi, and Y. Matsunaga, *Bull. Chem. Soc. Japan*, **29**, 574 (1956).
- 4) A. E. Austin, *Proc. Third Conference on Carbon*, Pergamon, New York, (1958) p 389.
- 5) C. W. Sweitzer and G. L. Heller, *Rubber World*, **134**, 855 (1956).
- 6) M. L. Studebaker, *Rubber Chem. Technol.*, **30**, 1400 (1957).
- 7) F. A. Heckman, *Rubber Chem. Technol.*, **37**, 1245 (1964).
- 8) F. A. Heckman and D. F. Harling, *Rubber Chem. Technol.*, **39**, 1 (1966).
- 9) W. M. Hess, L. L. Ban, F. J. Eckert, and V. Chirico, *Rubber Chem. Technol.*, **41**, 356 (1968).
- 10) C. W. Sweitzer and W. C. Goodrich, *Rubber Age*, **55**, 469 (1944).
- 11) C. W. Snow, D. R. Wallace, L. L. Lyon, and G. R. Crocker, *Proc. Fourth Conference on Carbon*, Pergamon, New York, (1959) p 79.
- 12) H. P. Boehm, *Advances in Catalysis*, **16**, 198 (1966).
- 13) J. B. Donnet, *Carbon*, **6**, 161 (1968).
- 14) K. Ohkita, *Hyomen*, **2**, 40 (1964).
- 15) T. Tsunoda and M. Koishi, *Kogyo Zairyo*, **28**, (10), 108 (1980); *ibid.*, (12), 105 (1980); *ibid.*, **29**, (1), 124 (1981); *ibid.*, (2), 105 (1981).
- 16) R. Laible and K. Hamann, *Adv. Colloid Interface Sci.*, **13**, 65 (1980).

- 17) K. Ohkita, N. Tsubokawa, E. Saitoh, M. Noda and N. Takashina, *Carbon*, **13**, 443 (1975).
- 18) K. Ohkita, N. Nakayama, and A. Funaki, *Shikizai Kyokaishi*, **53**, 583 (1980).
- 19) N. Tsubokawa, K. Maruyama, Y. Sone, and M. Shimomura, *Polym. J.*, **21**, 475 (1989).
- 20) N. Tsubokawa, A. Yamada, and Y. Sone, *Polym. Bull.*, **10**, 63 (1983); *Polym. J.*, **16**, 333 (1984).
- 21) N. Tsubokawa, A. Kogure, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 1923 (1990).
- 22) N. Tsubokawa, H. Nunokawa, and Y. Sone, *J. Macromol. Sci.-Chem.*, **A23**, 105 (1986).
- 23) N. Tsubokawa, K. Kobayashi, and Y. Sone, *Polym. Bull.*, **13**, 215 (1985); *ibid.*, **17**, 87 (1987).
- 24) N. Tsubokawa, K. Maruyama, Y. Sone, and M. Shimomura, *Colloid Polym. Sci.*, **267**, 511 (1989).
- 25) N. Tsubokawa, Y. Nagano, and Y. Sone, *Polym. Bull.*, **10**, 404 (1983); *J. Appl. Polym. Sci.*, **29**, 985 (1984).
- 26) N. Tsubokawa, K. Yamamoto, and Y. Sone, *J. Macromol. Sci.-Chem.*, **A25**, 1147 (1988).
- 27) N. Tsubokawa, K. Kobayashi, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 223 (1988); *J. Macromol. Sci.-Chem.*, **A25**, 1475 (1988).
- 28) N. Tsubokawa, A. Kuroda, and Y. Sone, *Polym. J.*, **20**, 721 (1988).
- 29) R. Kroker, M. Schneider, and K. Hamann, *Prog. Org. Coatings*, **1**, 23 (1972).
- 30) R. Laible and K. Hamann, *Angew. Makromol. Chem.*, **48**, 97 (1975).

- 31) K. Bridger and B. Vincent, *Eur. Polym. J.*, **16**, 1017 (1980).
- 32) Y. Minoura and M. Katano, *Kogyo Kagaku Zasshi*, **71**, 1083 (1968).
- 33) J. B. Donnet, G. Henrich, and G. Majoski, *Eur. Polym. J.*, **7**, 1069 (1971).
- 34) N. Tsubokawa and Y. Sone, *Kobunshi Kako*, **33**, 129 (1984).
- 35) N. Tsubokawa, *Nippon Gomu Kyokaishi*, **58**, 306 (1985); *Hyomen*, **28**, 286 (1990).
- 36) K. Ohkita, N. Nakayama, and T. Ohtaki, *Shikizai Kyokaishi*, **54**, 263 (1981); K. Ohkita, A. Funaki, T. Suzuki, and N. Nakayama, *ibid.*, **54**, 599 (1981).
- 37) N. Tsubokawa, A. Funaki, Y. Hada, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 3297 (1982).
- 38) N. Tsubokawa, T. Ohyama, A. Yamada, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 489 (1985).
- 39) J. B. Donnet, G. Riess, and G. Majowski, *Eur. Polym. J.*, **7**, 1069 (1971).
- 40) Y. Minoura and H. Harada, *J. Polym. Sci., Part A-1*, **7**, 3 (1969).
- 41) N. Tsubokawa, Yu Jian, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 2715 (1988); *J. Macromol. Sci.-Chem.*, **A26**, 731 (1989).
- 42) N. Tsubokawa, Yu Jian, A. Yamada, and Y. Sone, *Polym. Bull.*, **16**, 249 (1986).
- 43) N. Tsubokawa, *J. Appl. Polym. Sci.*, **30**, 2041 (1985).
- 44) N. Tsubokawa, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 1979 (1987).
- 45) J. B. Donnet, G. Henrich, and G. Riess, *Rev. Gen. Caoutch. plast.*, **38**, 1803 (1961).

- 46) G. Kraus and R. L. Collins, *Rubber World*, 139, 219 (1958).
- 47) J. W. C. Spackman, *Chem. Ind., London*, (1961) p 1532.
- 48) R. L. Collins, M. D. Bell, and G. Kraus, *J. Appl. Phys.*, 30, 56 (1959); *Rubber Chem. Technol.*, 33, 993 (1960).
- 49) K. Ohkita, N. Nakayama, and T. Tsujita, *Carbon*, 16, 155 (1978).
- 50) K. Ohkita, N. Nakayama, and M. Shimomura, *Carbon*, 18, 277 (1980).
- 51) N. Tsubokawa, *J. Polym. Sci., Polym. Chem. Ed.*, 22, 1515 (1984).
- 52) K. Ohkita, M. Uchiyama, and H. Nishioka, *Carbon*, 16, 195 (1978).
- 53) K. Ohkita, N. Tsubokawa, M. Noda, and M. Uchiyama, *Carbon*, 15, 194 (1977).
- 54) D. Rivin, *Rubber Chem. Technol.*, 36, 729 (1963).
- 55) K. Ohkita and N. Tsubokawa, *Carbon*, 10, 631 (1972).
- 56) M. L. Studebaker, *Proc. Fifth Conference on Carbon*, Pergamon, New York, (1962) Vol. II, p 189.
- 57) S. Suzuki and R. Takakuwa, *Nippon Kagaku Kaishi*, 88, 299 (1967).
- 58) J. B. Donnet and G. Henrich, *Compt. Rend.*, 246, 3230 (1958); J. B. Donnet, G. Henrich, and L. Geldreich, *ibid.*, 249, 97 (1959).
- 59) K. Ohkita, N. Tsubokawa, E. Saitoh, M. Noda, and H. Eguchi, *Nippon Gomu Kyokaishi*, 49, 72 (1976).
- 60) K. Ohkita, N. Tsubokawa, and E. Saito, *Carbon*, 16, 41 (1978).
- 61) K. Ohkita, N. Tsubokawa, E. Saitoh, M. Noda, and H. Eguchi, *Nippon Gomu Kyokaishi*, 49, 900 (1976).

- 62) N. Tsubokawa, K. Kobayashi, and Y. Sone, *Polym. Bull.*, **17**, 87 (1987).
- 63) J. Volhard, *Justus Liebigs Ann. Chem.*, **190**, 40 (1878).
- 64) A. Ueda, Y. Shiozu, Y. Hidaka, and S. Nagai, *Kobunshi Ronbunshu*, **33**, 131 (1976).
- 65) E. Papirer, V. T. Nguyen, and J. B. Donnet, *Carbon*, **16**, 141 (1978).
- 66) R. Yosomiya, T. Fujisawa, and K. Morimoto, *Polym. Bull.*, **12**, 523 (1984).
- 67) R. Yosomiya, K. Morimoto, and T. Suzuki, *J. Appl. Polym. Sci.*, **29**, 671 (1984).
- 68) G. Smets, A. Poot, and G. L. Duncan, *J. Polym. Sci.*, **54**, 65 (1961).
- 69) T. Saegusa, M. Nozaki, and R. Noda, *Kogyo Kagaku Zasshi*, **57**, 249 (1954).
- 70) W. Hahm and A. Fisch, *Macromol. Chem.*, **16**, 36 (1955).
- 71) W. I. Bengough and H. W. Melville, *Proc. R. Soc. London, Ser. A*, **249**, 445 (1959).
- 72) K. Ohkita, N. Tsubokawa, and N. Takashina, *Nippon Gomu Kyokaishi*, **49**, 223 (1976).
- 73) G. Mino, S. Kaizerman, and E. Rasumussen, *J. Polym. Sci.*, **38**, 393 (1959).
- 74) M. D. Fernandez, T. Fernandez, M. J. Fernandez, and G. M. Guzman, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2729 (1984).
- 75) S. V. Subramanian and M. Santappa, *Makromol. Chem.*, **112**, 1 (1968).
- 76) S. V. Subramanian and M. Santappa, *J. Polym. Sci., Part A-1*, **6**, 493 (1968).
- 77) G. Mino and S. Kaizerman, *J. Polym. Sci.*, **31**, 242 (1958).

- 78) N. Tsubokawa, K. Fujiki, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 191 (1986); *J. Macromol. Sci.-Chem.*, **A25**, 1159 (1988).
- 79) M. Sato, T. Kobayashi, and Y. Sima, *J. Catalysis*, **7**, 342 (1976).
- 80) S. Matsuda and S. Okazaki, *Nippon Kagaku Kaishi*, 1287 (1986).
- 81) K. Ohkita and T. Tajima, *Nippon Gomu Kyokaishi*, **43**, 379 (1970).
- 82) M. Imoto, *Kagaku*, **14**, 139 (1944); *Kagaku To Kogyo*, **19**, 84 (1944).
- 83) S. Seto and H. Horiuchi, *Kogyo Kagaku Zasshi*, **60**, 653 (1957).
- 84) F. Gray, A. A. Herod, and A. Jones, *Chem. Rev.*, **71**, 247 (1971).
- 85) P. W. Allen, G. Ayrey, and C. G. Moore, *J. Polym. Sci.*, **36**, 55 (1959).
- 86) A. Brydon, G. M. Burnett, and G. G. Gameron, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 3255 (1973).
- 87) N. Tsubokawa, H. Shirasaka, and Y. Sone, *Nippon Gomu Kyokaishi*, **58**, 26 (1985).

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