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### “LIVING-LIKE” CATIONIC POLYMERIZATION OF ISOBUTYL VINYL ETHER INITIATED BY CARBOXYL GROUPS ON CARBON BLACK SURFACE/ETHYLALUMINUM DICHLORIDE SYSTEM IN THE PRESENCE OF 1,4-DIOXANE

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# “LIVING-LIKE” CATIONIC POLYMERIZATION OF ISOBUTYL VINYL ETHER INITIATED BY CARBOXYL GROUPS ON CARBON BLACK SURFACE/ETHYLALUMINUM DICHLORIDE SYSTEM IN THE PRESENCE OF 1,4-DIOXANE

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**Key Words:** Carbon Black, Carboxyl Group, Ethylaluminum Dichloride, “Living-Like” Cationic Polymerization, Poly(isobutyl vinyl ether), Surface Grafting of Polymer

## ABSTRACT

The effect of 1,4-dioxane as an added base on the cationic polymerization of isobutyl vinyl ether (IBVE) initiated by carboxyl groups on carbon black surface/ethylaluminum dichloride ( $\text{EtAlCl}_2$ ) system was investigated. Although the cationic polymerization of IBVE by carbon black/ $\text{EtAlCl}_2$  system the absence of 1,4-dioxane instaneously proceeded and the monomer conversion

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achieved 100% within a minute. The molecular weight distribution (MWD) of polyIBVE obtained was very broad. On the contrary, the MWD of polyIBVE obtained was very narrow and narrower than that obtained from the carbon black/ $\text{ZnCl}_2$  initiating system by the addition of 1,4-dioxane. The number-average molecular weight ( $M_n$ ) of polyIBVE obtained was directly proportional to monomer conversion in the cationic polymerization. However, the  $M_n$  of polyIBVE obtained from the polymerization by the initiating system in the presence of 1,4-dioxane was smaller than that of the calculated value, assuming that poly(IBVE) chain forms per unit carboxyl group on carbon black surface. It was concluded that carbon black/ $\text{EtAlCl}_2$  initiating systems in the presence of 1,4-dioxane has an ability to initiate "living-like" cationic polymerization of IBVE based on the above results. PolyIBVE was grafted onto a carbon black surface after quenching the above "living-like" cationic polymerization systems with methanol.

## INTRODUCTION

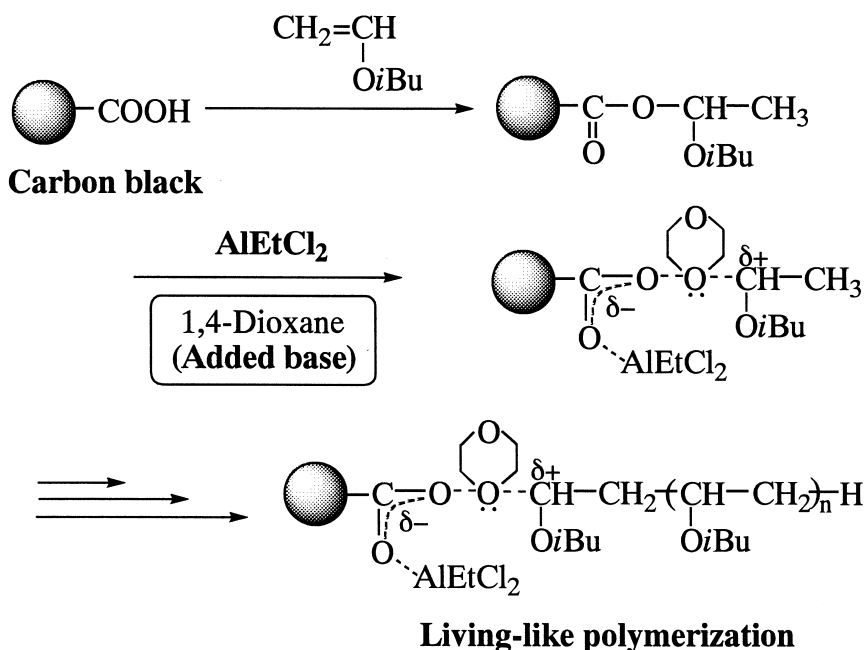
To improve the surface of carbon black, we have achieved the grafting of various polymers onto the surface by the anionic [1, 2], cationic [3, 4], and radical [5, 6] graft polymerizations of various vinyl monomers initiated by potassium carboxylate, acylium or benzylium perchlorate, and peroxyester or azo groups introduced onto carbon black surface, respectively. In the above graft polymerizations, the corresponding polymers are effectively grafted onto the surface due to propagation of the grafted chains from the surface. However, the control of molecular weight of polymer chains grafted onto the surface was hardly achieved, except for the radical polymerization system: in the radical graft polymerization of vinyl monomers initiated by peroxyester groups introduced onto silica surface, the molecular weight of grafted polymer was controlled to a certain extent by the addition of a chain transfer agent [7].

On the other hand, it has been reported by Higashimura and Sawamoto that living cationic polymerizations of vinyl ethers and related vinyl monomers were achieved by stabilizing the propagating carbocation either with a counteranion or with an added base [8]. As the former, for example, hydrogen iodide (HI)/iodine [9], HI/zinc halide ( $\text{ZnX}_2$ ; X= Cl, Br, I) [10, 11] and benzoic acid derivatives/zinc chloride ( $\text{ZnCl}_2$ ) [12] initiating systems have been reported. As the latter, 1-(isobutoxy) ethyl acetate ( $\text{CH}_3\text{CH}(\text{OiBu})\text{OCOCH}_3$ ) or acetic acid/

ethylaluminum dichloride ( $\text{EtAlCl}_2$ ) initiating systems in the presence of ether additives (1,4-dioxane, tetrahydrofuran, and diethyl ether) or ester additives (ethyl acetate, methyl chloroacetate, and ethyl benzoate) have been reported [13, 14].

In the preceding paper, we have reported that carboxyl groups on the surfaces of carbon black and crosslinked polystyrene-bead having carboxyl groups as a model compound of carbon black, coupled with  $\text{ZnCl}_2$  as an activator, induced “living-like” cationic polymerization of isobutyl vinyl ether (IBVE) and polyIBVE with controlled molecular weight and narrow molecular weight distribution (MWD) was grafted onto these powder surfaces [15, 16].

In the present paper, cationic polymerizations of IBVE initiated by carboxyl groups on carbon black surface/ $\text{EtAlCl}_2$  system in the presence of 1,4-dioxane as an added base was investigated (Scheme 1). And then, the effect of surface carboxyl group density of carbon black on the living-like cationic polymerization system was discussed. Furthermore, the grafting reaction of polyIBVE with controlled molecular weight and narrow MWD onto carbon



Scheme 1.

TABLE 1. Properties of Carbon Blacks Used

Carbon black	Specific surface area (m <sup>2</sup> /g)	COOH group (mmol/g)	OH group (mmol/g)	>C=O group (mmol/g)
Neospectra II <sup>a)</sup>	906	0.40	0.24	0.92
FW200 <sup>b)</sup>	460	0.61	0.10	1.42
CB#2650 <sup>c)</sup>	390	0.07	0.27	1.95
Oxidized CB <sup>c)</sup>	124	0.19	0.32	1.58

a) Columbian Carbon Co. b) Degussa A.G. c) Mitsubishi Chemical Ind.

black surface after quenching of these polymerization systems with methanol was also investigated.

## EXPERIMENTAL

### Materials and Reagents

The carbon blacks used were color channel black Neospectra II (Columbian Carbon Co., U.S.A.) and FW 200 (Degussa A.G.). Furnace black CB#2650 and oxidized carbon black obtained from Mitsubishi Chemical Ind., Japan were also used. These carbon blacks were dried *in vacuo* at 110°C before use. The properties of these carbon blacks used are shown in Table 1. The content of phenolic hydroxyl, carboxyl, and quinonic oxygen groups existing on the carbon black surface was determined by use of 2,2-diphenyl-1-picrylhydrazyl [17], sodium bicarbonate [18] and sodium borohydride [19], respectively.

Isobutyl vinyl ether (IBVE) (Tokyo Kasei Kogyo Co., Ltd.) was washed with 5% sodium hydroxide aqueous solution, then pure water, dried overnight over potassium hydroxide, refluxed over sodium, and distilled twice just before use. Toluene (Kanto Chemical Co., Inc.) was washed with conc. sulfuric acid, pure water, 5% sodium hydroxide aqueous solution, and pure water, dried overnight over calcium chloride, refluxed over sodium, and distilled twice just before use. Ethylaluminum dichloride (EtAlCl<sub>2</sub>) as an activator was commercially supplied as a solution (Kanto Chemical Co., Inc., about 1.0 mol/L solution in n-hexane), which was diluted with purified toluene to 0.20 mol/L. 1,4-

Dioxane (Kanto Chemical Co., Inc.) was refluxed over sodium, and distilled twice just before use.

### Polymerization Procedures

Polymerization was carried out at 0-40°C under dry nitrogen in backed glass tubes equipped with a three-way stopcock according to the method of Higashimura and Sawamoto [13, 20].

A typical example was as follows. Monomer solution ( $[\text{IBVE}]_0=2.0$  mM in toluene; 8.0 mL) was added into the tube containing vacuum-dried carbon black via a dry syringe and the polymerization was initiated by adding, via a dry syringe, a solution of  $\text{EtAlCl}_2$  ( $[\text{EtAlCl}_2]_0=0.20$  mM in toluene; 1.0 mL). For the polymerization in the presence of 1,4-dioxane (1.0 mL), it was added prior to the initiation of polymerization to the monomer solution via a dry syringe.

Monomer conversion was determined from residual monomer concentration measured by gas chromatography according to the following equation.

$$\text{Conversion (\%)} = [(A-B)/C] \times 100$$

where  $A$  is IBVE charged (g),  $B$  is residual IBVE (g), and  $C$  is IBVE charged (g).

### Determination of Grafting and Grafting Efficiency

The carbon black obtained from the above polymerization system was dispersed in toluene and the dispersion was allowed to centrifugation at  $1.5 \times 10^4$  rpm until the carbon black precipitated completely. The supernatant solution containing ungrafted polyIBVE was removed and the carbon black precipitated was dispersed again in toluene and centrifuged. The procedure was repeated until no more polyIBVE could be detected in the supernatant solution. The percentage of grafting and  $R$  (i.e. grafting efficiency) were determined by the following equations:

$$\begin{aligned} \text{Grafting (\%)} &= (D/E) \times 100 \\ R \text{ (grafting efficiency) (\%)} &= (D/F) \times 100 \end{aligned}$$

where  $D$  is polyIBVE grafted (g),  $E$  is carbon black used (g), and  $F$  is total polymer formed (g). The amount of polyIBVE grafted ( $D$ ) onto the carbon black surface was determined by weight loss when polyIBVE-grafted carbon black was heated at 500°C by the use of a thermal analyzer.

### Treatment of PolyIBVE-Grafted Carbon Black with Alkali

Into a 50 mL Erlenmeyer flask containing 0.05 g of polyIBVE-grafted carbon black, 20.0 mL of 1.0% methanol solution of NaOH was added. The reaction mixture was stirred with a magnetic stirrer at room temperature for 24 h. After the treatment, the resulting carbon black was isolated by centrifugation and repeatedly washed with methanol until the filtrate was neutral. Furthermore, it was washed with toluene to remove ungrafted polyIBVE. The amount of polyIBVE remaining on the surface, i.e. grafting, was determined by the above method.

### Stability of PolyIBVE-grafted Carbon Black Dispersion

PolyIBVE-grafted carbon black was dispersed in 100 mL of tetrahydrofuran and allowed to stand at room temperature. After a definite time, 5.0 mL of the dispersion liquid was taken out with a pipette and the carbon black dispersed in tetrahydrofuran was determined. The stability of carbon black dispersion was estimated from the content of particle in the dispersion:

$$\text{Carbon black dispersed (\%)} = (G/H) \times 100$$

where  $G$  and  $H$  are carbon black in dispersed phase after standing (g) and before standing (g), respectively.

### Determination of Molecular Weight and Molecular Weight Distribution

The number-average molecular weight ( $M_n$ ) and molecular weight distribution (MWD) of polyIBVE obtained after quenching of the above polymerization systems with methanol were measured by gel permeation chromatography (GPC) using polystyrene standards. For GPC measurement, CCPD instrument (TOSOH) equipped with a polystyrene gel column (TSK-GEL G3000HHR) was used.

## RESULTS AND DISCUSSION

### Effect of 1,4-Dioxane on the Cationic Polymerization of IBVE Initiated by Carbon Black/EtAlCl<sub>2</sub> System

It has been reported by Higashimura and Sawamoto that living cationic polymerization of vinyl ethers was achieved by stabilizing the propagating car-

TABLE 2. Effect of 1,4-Dioxane on the Cationic Polymerization of IBVE Initiated by a Carbon Black/EtAlCl<sub>2</sub> System

1,4-Dioxane (mL)	Time (min)	Conversion (%)	$M_n \times 10^{-4}$	$M_w / M_n$
-	1	100	1.1	2.33
1.0	90	100	2.0	1.19

Neospectra II, 0.10 g; IBVE, 2.0 mmol; EtAlCl<sub>2</sub>, 0.20 mmol; solvent, toluene; 0°C.

bocation with ether additives (1,4-dioxane, tetrahydrofuran, and diethyl ether) in 1-(isobutoxy) ethyl acetate (CH<sub>3</sub>CH(OiBu)OCOCH<sub>3</sub>)/EtAlCl<sub>2</sub> initiating system [8, 13]. Therefore, the effect of 1,4-dioxane as an added base on the cationic polymerization of IBVE initiated by carboxyl groups on carbon black surface/EtAlCl<sub>2</sub> system was investigated. The results are shown in Table 2.

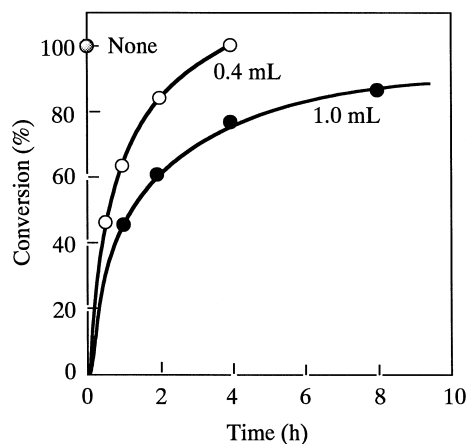
In the absence of 1,4-dioxane, the cationic polymerization of IBVE initiated by the carbon black/EtAlCl<sub>2</sub> system was instantaneously proceeded and the monomer conversion achieved 100% within a minute. But the molecular weight distribution (MWD) of polyIBVE obtained after quenching of the polymerization system with methanol was very broad:  $M_w/M_n$  was determined to be 2.33.

On the contrary, the rate of polymerization extremely decreased by the addition of 1,4-dioxane into a carbon black/EtAlCl<sub>2</sub> initiating system, but the monomer conversion achieved 100% after about 90 minutes. In addition, the MWD of polyIBVE obtained from the polymerization system was narrow ( $M_w/M_n = 1.19$ ) and narrower than that obtained from carboxyl group on a carbon black/ZnCl<sub>2</sub> initiating system previously reported [15].

Figure 1 shows the effect of 1,4-dioxane addition on the rate of cationic polymerization of IBVE initiated by the carbon black/EtAlCl<sub>2</sub> system. It was found that the rate of polymerization decreased with an increasing amount of added 1,4-dioxane into the polymerization system. Therefore, these results suggest that added 1,4-dioxane acted as an effective base in the cationic polymerization of IBVE initiated by the carbon black/EtAlCl<sub>2</sub> system.

In the preceding paper, we have pointed out that the rate of cationic polymerization of IBVE initiated by carboxyl group on polystyrene beads (PS-COOH)/ZnCl<sub>2</sub> and carboxyl type cation-exchange resin (PAA-COOH)/ZnCl<sub>2</sub>





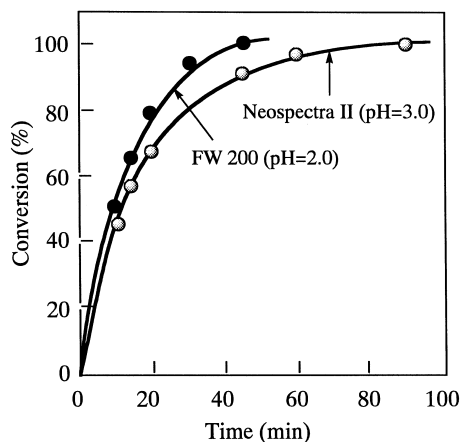
**Figure 1.** Effect of the amount of added 1,4-dioxane on the rate of cationic polymerization of IBVE initiated by a carbon black/ $\text{EtAlCl}_2$  system. Neospectra II, 0.10 g; IBVE, 2.0 mmol;  $\text{EtAlCl}_2$ , 0.12 mmol; solvent, toluene;  $0^\circ\text{C}$ .

systems was smaller than that in the carbon black/ $\text{ZnCl}_2$  initiating system [16]. This is due to the fact that the acidities of carboxyl groups on PS-COOH and PAA-COOH surfaces are smaller than those of carbon black surface. Therefore, the effect of acidity of surface carboxyl groups on the rate of cationic polymerization of IBVE initiated by several carbon blacks/ $\text{EtAlCl}_2$  systems in the presence of 1,4-dioxane was also investigated. The results are shown in Figure 2.

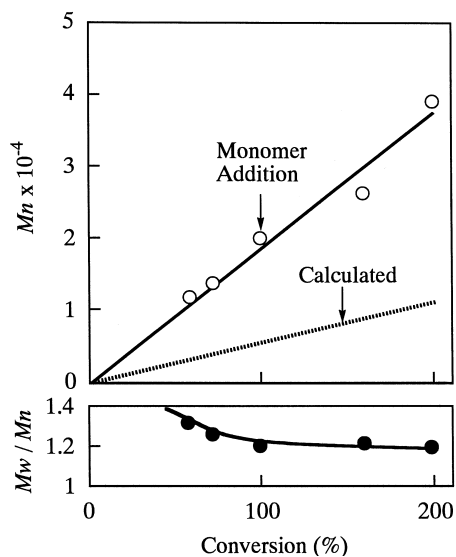
It was found that the rate of polymerization in the presence of FW 200 (pH = 2)/ $\text{EtAlCl}_2$  system was larger than that of Neospectra II (pH = 3)/ $\text{EtAlCl}_2$  system. Therefore, it was considered that the cationic polymerization of IBVE initiated by carboxyl groups on carbon black surface/ $\text{EtAlCl}_2$  systems in the presence of 1,4-dioxane was also influenced by the acidities of carboxyl groups on the surface.

Figure 3 shows the relationship between the  $M_n$  of polyIBVE obtained and monomer conversion in the cationic polymerization of IBVE initiated by a carbon black/ $\text{EtAlCl}_2$  system in the presence of 1,4-dioxane. The  $M_n$  of polyIBVE obtained from the polymerization system was found to be directly proportional to monomer conversion. The result suggests that the propagating carbocation was stabilized by suitably added base, i.e. 1,4-dioxane, as shown in Scheme 1.

And then, the so-called “monomer-addition” experiment, i.e., a fresh feed monomer was added to the reaction mixture when the initial supply of



**Figure 2.** Effect of acidity of surface carboxyl groups on the cationic polymerization of IBVE initiated by a carbon black/ $\text{EtAlCl}_2$  system in the presence of 1,4-dioxane. FW 200, 0.07 g (Neospectra II, 0.10 g); IBVE, 2.0 mmol;  $\text{EtAlCl}_2$ , 0.20 mmol; solvent, toluene;  $0^\circ\text{C}$ .



**Figure 3.** Relation between conversion and molecular weight or  $M_n/M_w$  in the cationic polymerization of IBVE initiated by a carbon black/ $\text{EtAlCl}_2$  system. Neospectra II, 0.10 g; IBVE, 2.0 mmol;  $\text{EtAlCl}_2$ , 0.20 mmol; 1,4-dioxane, 1.0 mL; solvent, toluene;  $0^\circ\text{C}$ .

monomer was completely depleted was also carried out in the above polymerization system. After the "monomer-addition", as shown in Figure 3, the added monomer feed was smoothly polymerized and the  $M_n$  of polyIBVE obtained from the polymerization system further increased in direct proportion to monomer conversion. The result also indicates that long-lived propagating carbocation was formed in the cationic polymerization of IBVE initiated by carbon black/EtAlCl<sub>2</sub> system in the presence of 1,4-dioxane.

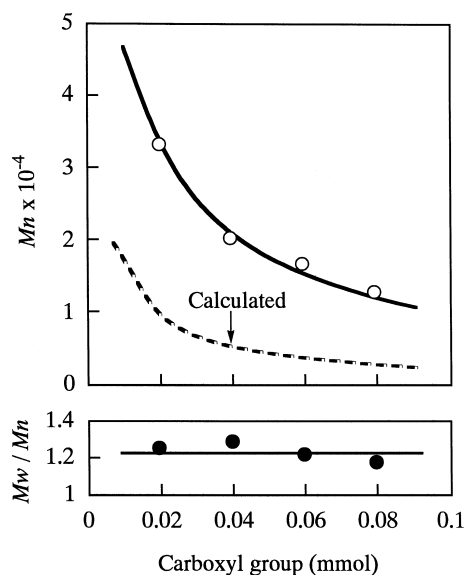
In the first stage of the polymerization initiated by carbon black/EtAlCl<sub>2</sub> system in the presence of 1,4-dioxane. Furthermore, the MWD of polyIBVE obtained was broad to some extent, as shown in Figure 3. But, it was gradually narrower with the progress of polymerization. The same tendency was observed in the living cationic polymerization of IBVE initiated by CH<sub>3</sub>CH(OiBu)OCOCH<sub>3</sub>/EtAlCl<sub>2</sub> system in the presence of 1,4-dioxane [13].

In addition, the MWD of polyIBVE, at near 200% monomer conversion, was considerably narrower than that obtained from the carbon black/ZnCl<sub>2</sub> initiating system previously reported [15].

It is well known that in the living cationic polymerization of vinyl monomers, the  $M_n$  of living polymer obtained is inversely proportional to initiator concentration. Therefore, the effect of carboxyl group concentration of carbon black surface on the  $M_n$  of polyIBVE obtained from carbon black/EtAlCl<sub>2</sub> initiating system in the presence of 1,4-dioxane was investigated. The result is shown in Figure 4.

The  $M_n$  of polyIBVE obtained from the above polymerization system was found to be inversely proportional to carboxyl group concentration of carbon black surface. Based on the above results, it was concluded that the cationic polymerization of IBVE initiated by carbon black/EtAlCl<sub>2</sub> system in the presence of 1,4-dioxane showed the behavior of living polymerization.

Broken lines in Figures 3 and 4 shows calculated  $M_n$  assuming the polyIBVE chain forms per unit carboxyl group on the surface. It became apparent that the  $M_n$  of polyIBVE obtained from carbon black/EtAlCl<sub>2</sub> initiating system in the presence of 1,4-dioxane was not in agreement with the calculated value. Namely, the  $M_n$  of polyIBVE obtained was considerably larger than that of calculated value. From the results, it was concluded that only about one-fourth of carboxyl groups existing on the surface participated in the initiation of cationic polymerization of IBVE. The results differed from that in carboxyl groups on carbon black surface/ZnCl<sub>2</sub> initiating system previously reported: in the carbon black/ZnCl<sub>2</sub> initiating system,  $M_n$  of polyIBVE was in agreement with calculated value [15].



**Figure 4.** Effect of carboxyl group concentration on the molecular weight of polyIBVE in the cationic polymerization of IBVE initiated by a carbon black/ $\text{EtAlCl}_2$  system. IBVE, 2.0 mmol;  $\text{EtAlCl}_2$ ,  $5\chi$  mol ( $\chi$  = carboxyl group concentration); 1,4-dioxane, 1.0 mL; solvent, toluene; 2 hours;  $0^\circ\text{C}$ .

#### Effect of Surface Carboxyl Group Density of Carbon Black on the Cationic Polymerization of IBVE Initiated by the Carbon Black/ $\text{EtAlCl}_2$ System in the Presence of 1,4-Dioxane

The cationic polymerization of IBVE initiated by various carbon blacks/ $\text{EtAlCl}_2$  systems in the presence of 1,4-dioxane was carried out and the effects of surface carboxyl group density of carbon black on the cationic polymerization of IBVE were also examined. Carbon blacks used were FW 200, CB#2650, and oxidized carbon black. The surface carboxyl group density ( $D$ ) of FW 200, CB#2650, and oxidized carbon black was 1.33, 0.19, and  $1.54 \mu\text{mol}/\text{m}^2$ , respectively. The amount of carbon black were adjusted so that the content of surface carboxyl groups became equal in each polymerization systems. The results are shown in Table 3.

As shown in Table 3, the  $M_n$  of polyIBVE obtained from the polymerization systems was also larger than that calculated. And then, the  $M_n$  of

TABLE 3. Effect of Surface Carboxyl Group Density of Carbon Black on the Cationic Polymerization of IBVE Initiated by Carbon Black/EtAlCl<sub>2</sub> System in the Presence of 1,4-Dioxane

Carbon black	In feed (g)	$D^a)$ ( $\mu\text{mol} / \text{m}^2$ )	$Mn \times 10^{-4}$	$\frac{\text{Found}}{\text{Calcd.}}$	$Mw / Mn$
Oxidized CB	0.21	1.54	3.1	6.2	1.30
FW 200	0.07	1.33	3.0	6.0	1.24
Neospectra II	0.10	0.44	2.0	4.0	1.19
#2650	0.54	0.19	1.8	3.6	1.37

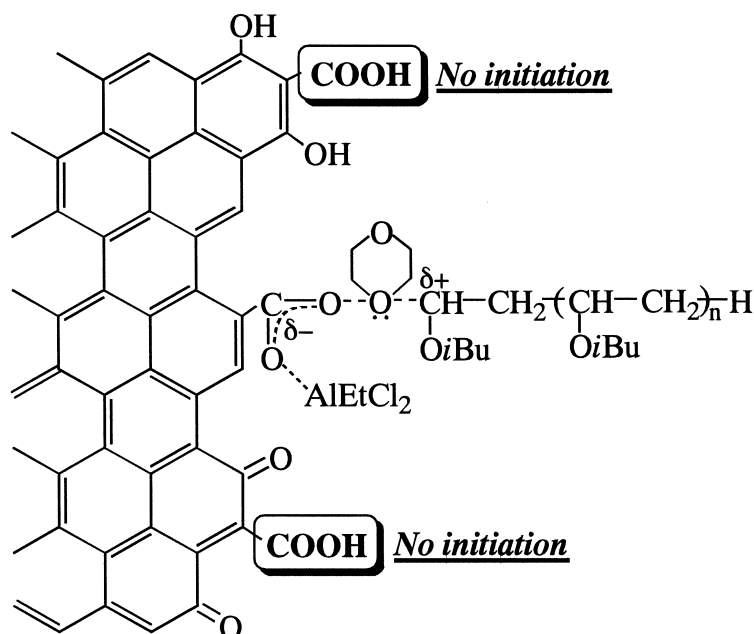
IBVE, 2.0 mmol; EtAlCl<sub>2</sub>, 0.20 mmol; 1,4-dioxane, 1.0 mL; solvent, toluene; 0°C.

a) Surface carboxyl group density of carbon black.

polyIBVE decreased with the decrease of  $D$  value: the  $Mn$  of polyIBVE obtained was 6.2-3.6 times of  $Mn$  calculated from the surface carboxyl group content of carbon blacks. Even in the presence of CB#2650 having very small  $D$  value, however, the  $Mn$  of polyIBVE obtained was about four times larger than that calculated. Therefore, it was considered that the living cationic polymerization of IBVE initiated by carbon black/EtAlCl<sub>2</sub> system in the presence of 1,4-dioxane was influenced not only on  $D$  value but also on other factors.

### Polymerization Mechanism of IBVE in the Carbon Black/EtAlCl<sub>2</sub> Initiating System in the Presence of 1,4-Dioxane

Based on the above results, the mechanism of living polymerization of IBVE initiated by the carbon black/EtAlCl<sub>2</sub> systems in the presence of 1,4-dioxane is considered as follows. As shown in Table 1, it is well known that carbon blacks have not only carboxyl groups but also phenolic hydroxyl and quinonic oxygen groups. Therefore, it seems that the living cationic polymerization of IBVE was initiated only from carboxyl groups being free from neighboring groups. As shown in Scheme 2. In other words, it was expected that carboxyl groups having neighboring groups, such as phenolic hydroxyl and quinonic oxygen groups, has no ability to initiate the living cationic polymerization of IBVE, because of steric hindrance. As a result, the  $Mn$  of polyIBVE became larger than that of calculated value.

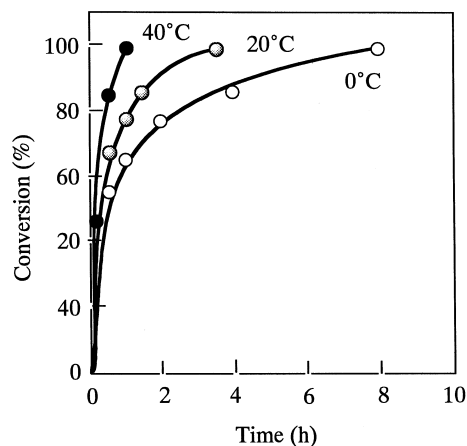


Scheme 2.

### Effect of Polymerization Temperature on the Cationic Polymerization of IBVE Initiated by the Carbon Black/EtAlCl<sub>2</sub> System in the Presence of 1,4-Dioxane

It has been reported that in the presence of added ethers (1,4-dioxane, tetrahydrofuran, and diethyl ether), living cationic polymerization of IBVE initiated by CH<sub>3</sub>CH(OiBu)OCOCH<sub>3</sub>/EtAlCl<sub>2</sub> system was achieved at 0 to 40°C [13]. Therefore, the effect of polymerization temperature on the cationic polymerization of IBVE initiated by carbon black/EtAlCl<sub>2</sub> system in the presence of 1,4-dioxane was investigated. The results are shown in Figure 5 and Table 4.

As shown in Figure 5, the rate of polymerization was accelerated with the rise of polymerization temperature. As shown in Table 4, however, the MWD of polyIBVE obtained from the polymerization system became broader with the rise of polymerization temperature: MWD of polyIBVE obtained at 40°C was considerably broad ( $M_w/M_n = 1.58$ ). Furthermore, the  $M_n$  of polyIBVE obtained was decreased with the rise of polymerization temperature. These results differed from that in CH<sub>3</sub>CH(OiBu)OCOCH<sub>3</sub>/EtAlCl<sub>2</sub> initiating system in the presence of 1,4-dioxane [13].



**Figure 5.** Effect of temperature on the cationic polymerization of IBVE initiated by a carbon black/ $\text{EtAlCl}_2$  system in the presence of 1,4-dioxane. Neospectra II, 0.10 g; IBVE, 2.0 mmol;  $\text{EtAlCl}_2$ , 0.12 mmol; 1,4-dioxane, 0.60 mL; solvent, toluene.

This reason is explained as follows. It was reported that the initiating ability of cationic polymerizations of IBVE and N-vinylcarbazole by carboxyl groups on carbon black surface increases with the rise of polymerization temperature [21, 22]. Consequently, it is considered that the cationic polymerization of IBVE by surface carboxyl groups of carbon black has proceeded to some degree before the addition of  $\text{EtAlCl}_2$ .

TABLE 4. Effect of Polymerization Temperature on the Molecular Weight of PolyIBVE Obtained from Carbon

Temperature (°C)	Conversion (%)	$M_n \times 10^{-4}$	$M_w / M_n$
0	100	2.0	1.19
20	98.5	1.8	1.30
40	98.8	1.5	1.58

Neospectra II, 0.10 g; IBVE, 2.0 mmol;  $\text{EtAlCl}_2$ , 0.12 mmol; 1,4-dioxane, 0.60 mL; solvent, toluene.

TABLE 5. Percentage of PolyIBVE Grafting onto Carbon Black Surface and Grafting Efficiency ( $R$ ) in the “Living-Like” Cationic Polymerization

Activator	1,4-Dioxane (mL)	$M_n \times 10^{-4}$	Grafting (%)	$R$ (%)
ZnCl <sub>2</sub>	-	1.0	25.6	6.4
EtAlCl <sub>2</sub>	1.0	3.9	47.6	11.9

Neospectra II, 0.10 g; IBVE, 4.0 mmol; Activator, 0.20 mmol; solvent, toluene; 0°C.

### Grafting Reaction of PolyIBVE onto a Carbon Black Surface

It has been reported that polyIBVE was grafted onto carbon black surface after quenching of a carbon black/ZnCl<sub>2</sub> initiating system with methanol [15]. Therefore, the grafting reaction of polyIBVE onto carbon black surface after quenching of living polymerization of IBVE initiated by a carbon black/EtAlCl<sub>2</sub> system in the presence of 1,4-dioxane with methanol was examined and the results were compared with those of the carbon black/ZnCl<sub>2</sub> initiating system. The results are shown in Table 5.

It was found that in the carbon black/EtAlCl<sub>2</sub> initiating system in the presence of 1,4-dioxane, the percentage of grafting and  $R$  (i.e., grafting efficiency) of polyIBVE were 47.6 and 11.9%, respectively. Therefore, it was concluded that the percentage of grafting and  $R$  in the carbon black/EtAlCl<sub>2</sub> initiating system in the presence of 1,4-dioxane were larger than those in the carbon black/ZnCl<sub>2</sub> initiating system.

Table 6 shows the percentage of grafting and  $R$  of polyIBVE a carbon black surface when various carbon blacks (FW 200, CB#2650, and oxidized carbon black) were used for the above living polymerization. PolyIBVE was also grafted onto these carbon black surfaces after quenching of the polymerization systems with methanol. No correlation between the  $R$  value and the surface carboxyl group density of carbon black ( $D$ ) was observed.

However, the tendency that the  $R$  value correlated with specific surface area of carbon black was observed, as shown in Figure 6: the  $R$  value increased with the increase of specific surface area of carbon black.



TABLE 6. Percentage of PolyIBVE Grafting onto Carbon Black Surface and Grafting Efficiency ( $R$ ) in the "Living-Like" Cationic Polymerization of IBVE

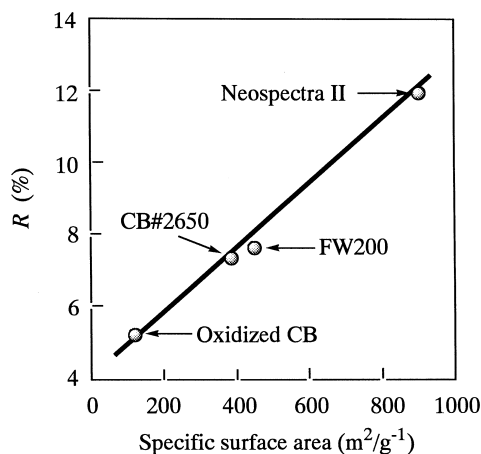
Carbon black	In feed (g)	$D^a$ ( $\mu\text{mol} / \text{m}^2$ )	Grafting (%)	$R$ (%)
Oxidized CB	0.21	1.54	10.0	5.2
FW200	0.07	1.33	46.6	7.6
Neospectra II	0.10	0.44	47.6	11.9
CB#2650	0.54	0.19	5.4	7.3

IBVE, 4.0 mmol;  $\text{EtAlCl}_2$ , 0.20 mmol; 1,4-dioxane, 1.0 mL; solvent, toluene;  $0^\circ\text{C}$ .

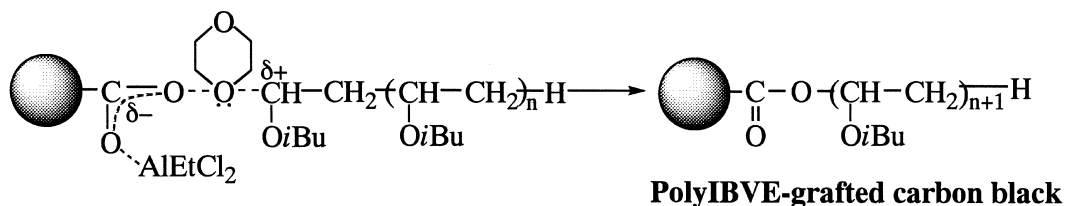
a) Surface carboxyl group density of carbon black.

### Grafting Mechanism of PolyIBVE onto Carbon Black Surface

In the preceding paper, we have pointed out that polyIBVE was grafted onto a carbon black surface with ester bonds based on the termination of living end with carboxylate groups on the surface after the quenching of living polymerization initiated by the carbon black/ $\text{ZnCl}_2$  system [15]. Therefore, it is



**Figure 6.** Relationship between specific surface area of carbon black and  $R$  in the cationic polymerization of IBVE initiated by a carbon black/ $\text{EtAlCl}_2$  system in the presence of 1,4-dioxane. Polymerization conditions are given in Table 6.



**Scheme 3.**

expected that polyIBVE is also grafted onto a carbon black surface in the polymerization initiated by a carbon black/ $\text{EtAlCl}_2$  system in the presence of 1,4-dioxane after the quenching of the polymerization system with methanol as shown in Scheme 3.

It was found that grafted polyIBVE on a carbon black surface was removed from the surface by the treatment with alkali: for example, the percentage of polyIBVE grafting decreased from 17.4% to 9.1% after treatment with 10% aqueous solution. Therefore, it was concluded that polyIBVE was grafted onto the surface with ester bonds.

### Dispersibility of PolyIBVE-Grafted Carbon Black in THF

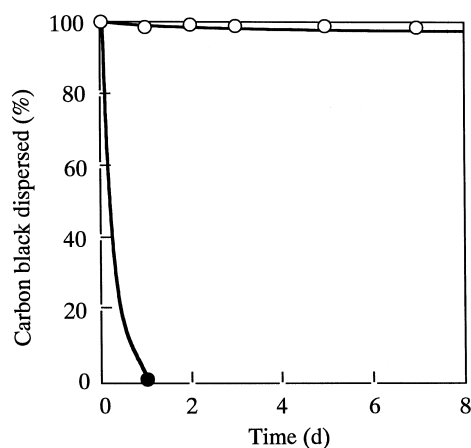
It has been pointed out that the dispersibility of ultrafine powders, such as carbon black and silica, in solvents and polymer matrices is remarkably improved by the grafting of polymers onto these surfaces [23-25]. The dispersibility of polyIBVE-grafted carbon black in THF was compared with that of untreated carbon black. The results are shown in Figure 7.

Although untreated carbon black precipitated immediately, polyIBVE-grafted carbon black gave a stable dispersion in THF, a good solvent of polymer chains. This indicates that the polyIBVE chains grafted on the surface interfere with the reciprocal aggregation of carbon black particles.

## CONCLUSION

The cationic polymerization of IBVE was readily initiated by carboxyl groups on a carbon black/ $\text{EtAlCl}_2$  system in the presence of 1,4-dioxane as an added base and 100% monomer conversion was achieved.

The  $M_n$  of polyIBVE obtained from the above polymerization systems



**Figure 7.** Stability of polyIBVE-grafted carbon black dispersion in THF in room temperature.

was directly proportional to monomer conversion. The  $M_n$  of polyIBVE was inversely proportional to carboxyl group content of carbon black surface.

The  $M_n$  of polyIBVE obtained from the cationic polymerizations of IBVE initiated by carbon black/ $\text{EtAlCl}_2$  systems in the presence of 1,4-dioxane was influenced by surface carboxyl group density of carbon black and neighboring groups of carboxyl groups on carbon black surface, because of steric hindrance.

Based on the above results, it was concluded that in the presence of 1,4-dioxane as an added base, carboxyl groups on carbon black surface, coupled with  $\text{EtAlCl}_2$  as an activator, induced living-like cationic polymerization of IBVE.

PolyIBVE was grafted onto carbon black surface after quenching of the above polymerization systems with methanol.

PolyIBVE-grafted carbon black obtained from the above polymerization system gave a stable dispersion in THF.

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