Cationic Grafting from Carbon Black. III. Grafting of Polyesters from Carbon Black by Ring-Opening Polymerization of Lactones Initiated by $CO^+ClO_4^-$ Groups on Carbon Black

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Synopsis

It was found that the cationic ring-opening polymerization of δ-valerolactone (VL), ε-caprolactone (CL), and β-propiolactone (PL) was initiated by carbon black containing $CO^+ClO_4^-$ groups, which were introduced by the reaction of COCl groups with $AgClO_4$. The polyester was propagated from $CO^+ClO_4^-$ groups and effectively grafted onto carbon black surface. The polymerizability of these lactones by $CO^+ClO_4^-$ groups decreased in the following order: VL > CL > PL. The increasing temperature of the polymerization caused an increase in the rate of the chain transfer reaction of the growing chains and brought about the decrease of grafting ratio of polyester onto carbon black.

INTRODUCTION

It is well known that, during the polymerization of vinyl monomers initiated by various kinds of initiator in the presence of carbon black, a part of growing chains is captured by functional groups on the carbon black to give a polymer-grafted carbon black.[1-3] However, both grafting ratio and grafting efficiency were low because ungrafted polymer was formed in preference to grafting onto carbon black.
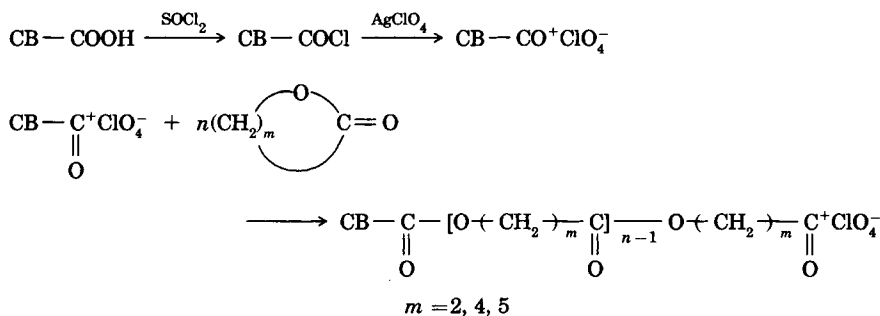
On the contrary, when a polymer is propagated from active sites on the surface of carbon black, a polymer-grafted carbon black with a higher grafting ratio is generally obtained. For instance, the anionic grafting from active sites, such as radical anion,[4] metalized carbon black,[5] and lithium phenolate groups (carbon black/butyllithium complex),[6] has been studied.

Furthermore, we reported that alkali metal carboxylate groups (COOM; M = Li, Na, K, Rb, or Cs) have an ability to initiate the anionic ring-opening polymerization of β-propiolactone (PL) and polyester was propagated from carbon black surface.[7] However, COOM groups failed to initiate the ring-opening polymerization of δ-valerolactone (VL) and ε-caprolactone (CL). In addition, COOM groups were found capable of initiating the ring-opening copolymerization of epoxide or alkylene carbonate with cyclic acid anhydride to give polyester-grafted carbon black.[8,9]

On the other hand, the cationic grafting from carbon black has been scarcely investigated. In the preceding paper, I reported the use of carbon black containing $CO^+ClO_4^-$ groups, which are formed by the reaction of COCl groups with $AgClO_4$, for the initiation of cationic grafting of polysty-

rene from carbon black.[10] In the polymerization, polystyrene was found to be propagated from $CO^+ClO_4^-$ groups on the surface of carbon black.

In this article, I wish to report the cationic grafting of polyesters from carbon black surface by the ring-opening polymerization of lactones, such as VL, CL, and PL, using $CO^+ClO_4^-$ groups on carbon black surface as initiator.

$$CB-COOH \xrightarrow{SOCl_2} CB-COCl \xrightarrow{AgClO_4} CB-CO^+ClO_4^-$$

$$CB-\underset{\underset{O}{\|}}{C}{}^+ClO_4^- + n(CH_2)_m \overset{O}{\underset{}{\diagdown}} C=O$$

$$\longrightarrow CB-\underset{\underset{O}{\|}}{C}-[O{+}CH_2{\rightarrow}_m \underset{\underset{O}{\|}}{C}]_{n-1} O{+}CH_2{\rightarrow}_m \underset{\underset{O}{\|}}{C}{}^+ClO_4^-$$

$$m = 2, 4, 5$$

EXPERIMENTAL

Materials

The carbon blacks used were both furnace black and color channel black. Furnace black Philblack O (Philips Petroleum Co., BET specific surface area, 79.6 m^2/g) was extracted with benzene before use to remove the resinous substances present on the surface. Channel blacks Neospectra II (Columbian Carbon Co.; 906 m^2/g), Carbolac 1 (Cabot Corp.; 839.2 m^2/g), and FW 200 (Degussa A.G.; 460 m^2/g) were used without extraction. The content of carboxyl groups of Philblack O, Neospectra II, Carbolac 1, and FW 200 was determined to be 0, 0.40, 0.54, and 0.61 meq/g, respectively.

β-Propiolactone (Fluka A. G., Chemishe Fabrik), VL (Tokyo Kasei Co. Ltd., Japan), and CL (Tokyo Kasei Co. Ltd., Japan) were dried over calcium hydride and distilled twice under reduced pressure before use.

Guaranteed-reagent-grade AgClO$_4$ (Kojima Chemical Co. Ltd., Japan) was dried *in vacuo* at 130°C before use.

Nitrobenzene was washed with dilute H$_2$SO$_4$, dried over CaCl$_2$, and then distilled under reduced pressure.

Preparation of Carbon Black Containing $CO^+ClO_4^-$ Groups

The introduction of $CO^+ClO_4^-$ groups onto carbon black, i.e., pretreatment, was carried out by the reaction of CB–COCl (carbon black containing COCl groups) with AgClO$_4$ in nitrobenzene according to the method previously reported.[10] CB–COCl was prepared by the reaction of carboxyl groups with SOCl$_2$ as previously described in detail.[11]

Polymerization Procedures

After the pretreatment, 5.0 mL of nitrobenzene solution of lactone (9.0 mol/L) was added to a flask containing CB–CO$^+$ClO$_4^-$, and the polymeriza-

tion was conducted with stirring under dry nitrogen. After the reaction, the product was poured into a large amount of methanol to precipitate the polymer and polymer-grafted carbon black. The precipitate was filtered, washed with methanol, and dried *in vacuo*. Thus the conversion was calculated by the following equation:

conversion (%)

$$= \frac{\text{wt total precipitate (g)} - \text{added wt carbon black (g)}}{\text{wt monomer used (g)}} \times 100$$

Determination of Grafting Ratio, Grafting Efficiency, and Intrinsic Viscosity of Ungrafted Polyester

To separate the polyester-grafted carbon black from the reaction product that contained ungrafted polyester, the product was extracted with chloroform by using a Soxhlet apparatus until no more polymer could not be detected in the refluxing solvent. The grafting ratio and grafting efficiency were determined by the following equations:

$$\text{grafting ratio (\%)} = \frac{\text{wt polymer grafted (g)}}{\text{wt carbon black used (g)}} \times 100$$

$$\text{grafting efficiency (\%)} = \frac{\text{wt polymer grafted (g)}}{\text{wt total polymer obtained (g)}} \times 100$$

On the other hand, the ungrafted polyester was isolated from the extract of the above Soxhlet extraction and purified by reprecipitation (chloroform/methanol). Its intrinsic viscosity was determined with an Ubbelohde viscometer in chloroform solution at 30.0°C.

RESULTS AND DISCUSSION

Evidence of Initiation by $CO^+ClO_4^-$ Groups on Carbon Black

It is well known that the cationic polymerization of styrene[12] and the ring-opening polymerization of tetrahydrofuran[13] are initiated by the compound of the general formula $R-CO^+ClO_4^-$ which is prepared by the reaction of acid chloride (R—COCl) with $AgClO_4$. Furthermore, Cherdron et al. described that the cationic ring-opening polymerization of VL, CL, and PL was initiated by acetyl perchlorate ($CH_3CO^+ClO_4^-$) to give polyester.[14]

In the previous paper, it was reported that $CO^+ClO_4^-$ groups, which were introduced by the reaction of $AgClO_4$ with CB–COCl, have an ability to initiate the cationic polymerization of styrene.[10] Therefore, it is expected that the ring-opening polymerization of lactones is initiated by $CO^+ClO_4^-$ groups on carbon black and that polyester is propagated from carbon black surface.

Table I shows the results of the polymerization of VL using COCl–Neospectra II and $AgClO_4$ under several conditions. As shown in Table I, VL

TABLE I
Polymerization of VL Initiated by $CO^+ClO_4^-$ Groups on the Surface of Carbon Black

No.	Carbon black	AgClO$_4$ (g)	Conversion[a] (%)
1	None	0.20	0
2	Untreated Neospectra II	—	0
3	Untreated Neospectra II	0.20	0
4	COCl-Neospectra II	—	0
5	COCl-Neospectra II	0.20	49.5

[a] Pretreatment: carbon black, 0.30 g; nitrobenzene, 5.0 mL; room temp; 48 h. Polymerization: VL (9.0 mol/L nitrobenzene solution), 5.0 mL; temp 40.0°C; 20 h.

was not polymerized by any single component of AgClO$_4$, untreated Neospectra II, or COCl–Neospectra II (nos. 1, 2, 4). In addition, the polymerization could not be detected, even if untreated Neospectra II was pretreated with AgClO$_4$ (no. 3). However, in the presence of COCl–Neospectra II pretreated with AgClO$_4$ in nitrobenzene for 48 h, the ring-opening polymerization of VL was found to proceed to give polyester.

The result suggests that $CO^+ClO_4^-$ groups are introduced by the pretreatment of CB–COCl with AgClO$_4$ and initiate the cationic ring-opening polymerization of VL.

To ensure the formation of $CO^+ClO_4^-$ groups by the pretreatment, by use of various kinds of CB–COCl pretreated with AgClO$_4$, the relationship between the initiating activity of the polymerization of VL and the content of COCl groups was examined. The results are shown in Table II. The content of COCl groups was estimated from that of carboxyl groups, which was determined according to the method of Rivin,[15] because SOCl$_2$ reacts quantitatively with carboxyl groups to give COCl groups.

As shown in Table II, the initiating activity of these carbon blacks as almost proportional to the COCl group content of carbon black. Even if SOCl$_2$-treated Philblack O was pretreated with AgClO$_4$, the system failed to initiate the ring-opening polymerization of VL. The result may be explained by the fact that SOCl$_2$-treated Philblack O has no carboxyl groups.

TABLE II
Ring-Opening Polymerization of VL Initiated by $CO^+ClO_4^-$ Groups on the Surface of Various Kinds of Carbon Black

SOCl$_2$-treated carbon black	COCl group (meq/g)	Conversion[a] (%)
Neospectra II[b]	0.40	49.5
Carbolac 1[b]	0.54	53.3
FW 200[b]	0.61	62.6
Philblack O[c]	0	0

[a] Pretreatment: COCl–carbon black, 0.30 g; AgClO$_4$, 0.20 g; nitrobenzene, 5.0 mL; room temp; 48 h. Polymerization: VL (9.0 mol/L nitrobenzene solution), 5.0 mL; temp 40.0°C; 20 h.
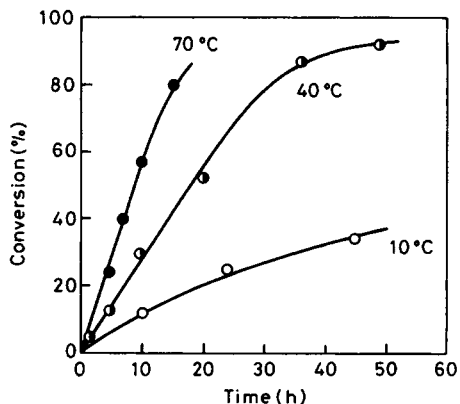[b] Channel black.
[c] Furnace black.

Fig. 1.   Ring-opening polymerization of VL initiated by $CO^+ClO_4^-$ groups on carbon black. Pretreatment: COCl–Neospectra II, 0.30 g; $AgClO_4$, 0.20 g; nitrobenzene, 5.0 mL; room temp; 48 h. Polymerization: VL (9.0 mol/L nitrobenzene solution), 5.0 mL.

Accordingly, it is concluded that $CO^+ClO_4^-$ groups have an ability to initiate the cationic ring-opening polymerization of VL.

Figure 1 shows the time–conversion curves of the polymerization of VL at 10°C, 40°C, and 70°C using $CO^+ClO_4^-$ groups as initiator. The rate of the polymerization was found to increase with a rise in temperature. The Arrhenius plots for the above result gave a straight line and the apparent activation energy (E_a) of the polymerization was determined to be 5.8 kcal/mol. On the other hand, E_a of the polymerization of CL was estimated to be 6.1 kcal/mol. These value are lower than that of cationic polymerization of styrene initiated by $CO^+ClO_4^-$ groups on carbon black.
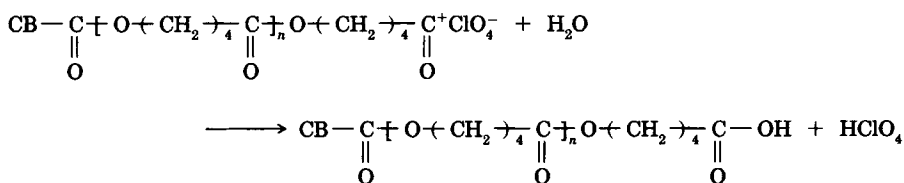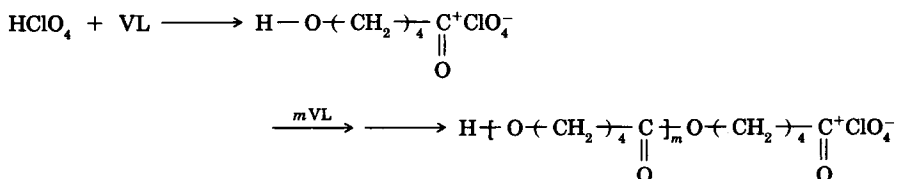
Proof of Grafting of Polyester from Carbon Black Surface

The carbon black obtained from the polymerization produced a stable colloidal dispersion in chloroform. This phenomenon suggests that polyester is grafted from carbon black. To ensure the grafting of polyester, the relationship between conversion and the grafting ratio (grafting efficiency) of poly-VL at 40°C was determined. The result is shown in Figure 2.

As shown in Figure 2, the grafting ratio increased with an increase in conversion. The value of the grafting ratio was nearly equal to that of polystyrene obtained from the cationic polymerization of styrene using $CO^+ClO_4^-$ groups as initiator.[10]

On the other hand, the grafting efficiency tended to be high during the first few percents of conversion but decreased with an increase in conversion. A similar phenomenon was observed in the anionic polymerization of PL initiated by COOK groups[7] and in the cationic polymerization of styrene initiated by $CO^+ClO_4^-$ groups.[10]

These results suggest that the grafted polymer is propagated from $CO^+ClO_4^-$ groups on the surface of carbon black and that ungrafted polymer is gradually formed by a chain transfer reaction of growing polymer chain $(CB \sim CO + ClO_4^-)$ with an impurity such as trace of water.

Formation of polyester-grafted carbon black:

$$CB-\underset{\underset{O}{\|}}{C}\text{+}O\text{+}CH_2\text{+}_4\underset{\underset{O}{\|}}{C}\text{+}_nO\text{+}CH_2\text{+}_4\underset{\underset{O}{\|}}{C}^+ClO_4^- \ + \ H_2O$$

$$\longrightarrow \ CB-\underset{\underset{O}{\|}}{C}\text{+}O\text{+}CH_2\text{+}_4\underset{\underset{O}{\|}}{C}\text{+}_nO\text{+}CH_2\text{+}_4\underset{\underset{O}{\|}}{C}-OH \ + \ HClO_4$$

Formation of ungrafted polyester:

$$HClO_4 \ + \ VL \longrightarrow H-O\text{+}CH_2\text{+}_4\underset{\underset{O}{\|}}{C}^+ClO_4^-$$

$$\xrightarrow{m\,VL} \longrightarrow H\text{+}O\text{+}CH_2\text{+}_4\underset{\underset{O}{\|}}{C}\text{+}_mO\text{+}CH_2\text{+}_4\underset{\underset{O}{\|}}{C}^+ClO_4^-$$

Effect of Polymerization Temperature on Grafting Ratio and Intrinsic Viscosity of Ungrafted Polyester

In order to obtain polyester-grafted carbon black with a higher grafting ratio, it is necessary to control the chain transfer reaction. Therefore, the effect of polymerization temperature on the grafting ratio of poly-VL was then investigated.

Figure 3 shows the relationship between the grafting ratio and conversion at each temperature. Contrary to the rate of the polymerization, the grafting ratio in the same conversion decreased, depending on the temperature, in the following order: 10°C > 40°C > 70°C. This means that the formation of
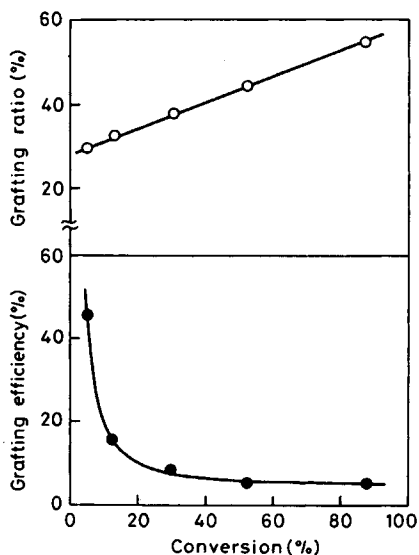

Fig. 2.   Relationship between conversion and grafting ratio (grafting efficiency) of polyester from VL at 40°C. Polymerization conditions are given in Figure 1.
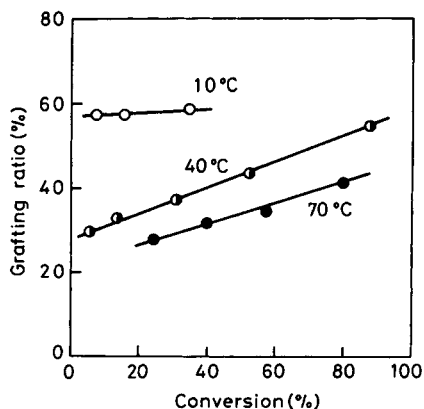
Fig. 3.   Effect of polymerization temperature on the grafting ratio of polyester from VL. Polymerization conditions are given in Figure 1.

ungrafted polyester increase with an increase in polymerization temperature.

On the other hand, Figure 4 shows the effect of temperature on the intrinsic viscosity of ungrafted poly-VL obtained from the above polymerization. It is apparent that the intrinsic viscosity of ungrafted polyester decreased, depending on the temperature, in the following order: 10°C > 40°C > 70°C.

These results are explained as follows. The grafted polyester is propagated from $CO^+ClO_4^-$ groups on the surface of carbon black. Then, the increasing temperature of the polymerization will cause an increase in the rate of chain transfer reaction of growing polymer chains. Accordingly, when the polymerization was carried out at higher temperatures, lower grafting ratio and ungrafted polyester with lower molecular weight will be formed.

Ring-Opening Polymerization of CL and PL Initiated by $CO^+ClO_4^-$ Groups on Carbon Black

The ring-opening polymerization of CL and PL was carried out and the initiating ability of $CO^+ClO_4^-$ groups was compared with that of VL. The results are shown in Table III.

As shown in Table III, $CO^+ClO_4^-$ groups were found to initiate the polymerization of CL as well as VL. In comparison with VL and CL, the rate of the polymerization of PL was very slow. Thus, the polymerizability of these lactones was found to decrease in the following order: VL > CL > PL. This order is in agreement with the general polymerizability of lactones using acetyl perchlorate as catalyst.[14]

Although COOK groups were unable to initiate the anionic ring-opening polymerization of VL and CL, $CO^+ClO_4^-$ gorups were capable of initiating the cationic ring-opening polymerization not only of PL but also of VL and CL. Furthermore, Table III shows that polyester from VL, CL, and PL were grafted from $CO^+ClO_4^-$ groups on the surface of carbon black.

The grafting ratio and the intrinsic viscosity of ungrafted poly-PL obtained from the cationic polymerization were lower than that from the
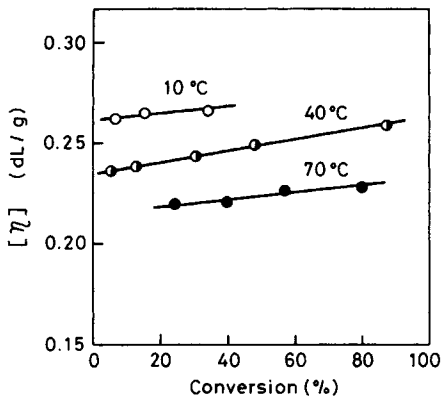
Fig. 4. Effect of polymerization temperature on the intrinsic viscosity of ungrafted polyester from VL. Polymerization conditions are given in Figure 1. [η]: chloroform solution, 30.0°C.

anionic polymerization by COOK groups.[7] This may be due to the fact that the chain transfer reaction of growing polymer occurred more frequently in the cationic polymerization system.

CONCLUSIONS

It became apparent that the cationic ring-opening polymerization using $CO^+ClO_4^-$ groups as catalyst enabled the grafting of polyester from VL, CL, and PL. The increasing temperature of the polymerization caused the decrease of the grafting ratio of polyester onto carbon black because of the increase of the rate of chain transfer reaction.

TABLE III
Ring-Opening Polymerization of Lactones Initiated by $CO^+ClO_4^-$ Groups on the Surface of Carbon Black

Lactone	Temp (°C)	Time (h)	Conversion[a] (%)	Grafting ratio (%)	[η][b] (dL/g)
VL	40	36	87.2	55.0	0.26
VL	70	15	79.9	41.5	0.23
CL	10	48	26.1	58.2	0.25
CL	40	36	52.0	54.3	0.33
CL	70	15	61.5	46.0	0.30
PL	40	114	11.2	30.4	0.05
PL	70	60	18.8	28.0	0.04

[a] Polymerization conditions are given in Table II.
[b] Chloroform solution, 30.0°C.

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