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Cationic Grafting from Carbon Black. 4. Grafting of Poly(Oxytetramethylene) to Carbon Black by Ring-Opening Polymerization of Tetrahydrofuran Initiated by $\text{CO}^+\text{ClO}_4^-$ Groups on Carbon Black

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ABSTRACT

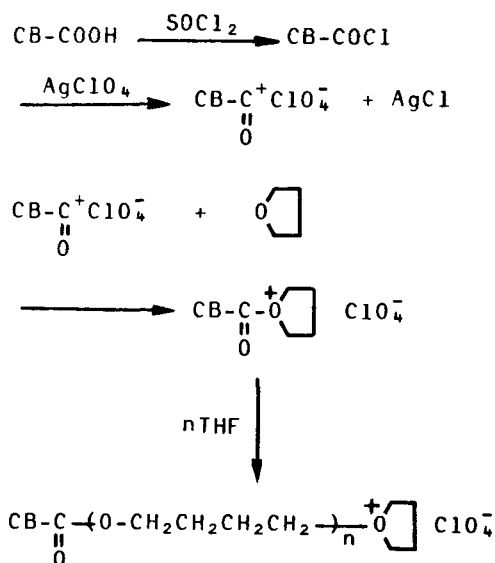
It was found that the cationic ring-opening polymerization of tetrahydrofuran (THF) was initiated by carbon black containing $\text{CO}^+\text{ClO}_4^-$ groups, which had been introduced by the reaction of COCl groups with AgClO_4 , in the presence of promoters such as epichlorohydrin (ECH) and diketene. It was confirmed that formation of poly(oxytetramethylene), i.e., poly-THF, was propagated from $\text{CO}^+\text{ClO}_4^-$ groups on carbon black surfaces and effectively grafted onto it. The grafting ratio with ECH as promoter increased to 66.8% as conversion increased. The activation energy of the polymerization initiated by $\text{CO}^+\text{ClO}_4^-$ groups in the presence of ECH was determined to be 8.1 kcal/mol. Furthermore, poly-ECH, poly(styrene oxide), and poly(propylene oxide) can be grafted onto carbon black surfaces by the ring-opening polymerization of the corresponding alkylene oxides with $\text{CO}^+\text{ClO}_4^-$ groups on the carbon black as initiator. The polyether-grafted carbon black obtained from the above polymerization produced a stable colloidal dispersion in a good solvent for polyether.

INTRODUCTION

In the previous paper we reported the cationic grafting of poly-(oxytetramethylene), i.e., poly(tetrahydrofuran), onto carbon black by the ring-opening polymerization of tetrahydrofuran (THF), using FeCl_3 and carbon black containing COCl groups as catalyst and co-catalyst, respectively [1]. However, the grafting ratio of poly-THF was less than 20%. Moreover, Drappel et al. found that poly-THF can be grafted onto carbon black by the reaction of living poly-THF with carbon black surfaces [2].

On the other hand, we reported the use of carbon black containing $\text{CO}^+\text{ClO}_4^-$ groups, which are introduced by the reaction of COCl groups with AgClO_4 , for the cationic grafting of polystyrene onto carbon black surfaces [3]. Furthermore, it was found that $\text{CO}^+\text{ClO}_4^-$ groups on carbon black have an ability to initiate the cationic ring-opening polymerization of lactones, such as δ -valerolactone, ϵ -caprolactone, and β -propiolactone, to give polyester-grafted carbon black [4]. In these polymerizations, formation of polystyrene or polyesters was confirmed to be propagated from $\text{CO}^+\text{ClO}_4^-$ groups on the surface of carbon black.

In this article we report the cationic grafting of poly-THF by the ring-opening polymerization of THF with $\text{CO}^+\text{ClO}_4^-$ groups as the catalyst. In addition, the ring-opening polymerization of alkylene oxides initiated by $\text{CO}^+\text{ClO}_4^-$ groups and the grafting of polyethers from carbon black are discussed.



EXPERIMENTAL

Materials

The carbon blacks used were color channel blacks, Neospectra II (Columbian Carbon Co.; BET specific surface area, 906 m²/g) and FW 200 (Degussa A.G.; 460 m²/g), and furnace black Philblack O (Philips Petroleum Co.; 79.6 m²/g). The content of carboxyl groups on Neospectra II, FW 200, and Philblack O was determined to be 0.40, 0.61, and 0 meq/g, respectively.

Tetrahydrofuran was refluxed over calcium hydride and distilled twice before use. Epichlorohydrin (ECH), styrene oxide (SO), and β -propiolactone (PL) were dried over calcium hydride and distilled twice under reduced pressure. Diketene (DK) and propylene oxide (PO) were also dried over calcium hydride and distilled twice before use.

Guaranteed-reagent-grade AgClO₄ (Kojima Chemical Co. Ltd., Japan) was dried in vacuo at 130°C before use.

Polymerization Procedures

Neospectra II that contained COCl groups (COCl-Neospectra II) was prepared by the reaction of carboxyl groups with SOCl₂ as previously described in detail [3].

The polymerization of THF was carried out as follows: Into a 100-mL teardrop-type flask containing 0.30 g of COCl-Neospectra II and 0.20 g of AgClO₄, freshly distilled THF (10.0 mL) that contained promoter (1.0 mol%) was added under dry nitrogen. The polymerization was continued with stirring with a magnetic stirrer in an atmosphere of dry nitrogen.

After the reaction the product was poured into an excess of ice-cold water to precipitate poly-THF and polymer-grafted carbon black. The precipitate was filtered, washed with ice-cold water, and dried in vacuo. When ECH, PO, and SO were used as monomer, the polymerization was stopped by the addition of methanol or N,N-dimethylformamide, and the unreacted monomer and solvent were pumped off, yielding polyether and polymer-grafted carbon black. The conversion was calculated by

$$\text{conversion (\%)} = \frac{\text{weight of total precipitate (g)} - \text{added weight of carbon black (g)}}{\text{weight of monomer used (g)}} \times 100.$$

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

To separate polyether-grafted carbon black from the reaction product that contained ungrafted polymer, the product was extracted with THF by using a Soxhlet apparatus until no more polymer could be detected in the refluxing solvent. The grafting ratio and grafting efficiency were determined by

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

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

On the other hand, the ungrafted polymer was isolated from the extract of the above extraction and purified by reprecipitation (THF/ice-cold water). Its intrinsic viscosity was determined with an Ubbelohde viscometer in THF solution at 30.0°C.

RESULTS AND DISCUSSION

Evidence of Initiation by CO⁺ClO₄⁻ Groups on Carbon Black

It is well known that the cationic ring-opening polymerization of THF is initiated by cationic catalysts [5]. For instance, oxocarbenium ion (CH₃CO⁺ClO₄⁻), formed by the reaction of HClO₄ with acetic anhydride, can initiate the polymerization of THF [6, 7]. In addition, Franta et al. described that oxocarbenium ion, prepared by the reaction of R-COCl with silver hexafluoroantimonate, initiates the ring-opening polymerization of THF [8]. Also, AgClO₄ with acetyl chloride in THF initiates the polymerization of THF [9].

On the other hand, we found that CO⁺ClO₄⁻ groups are introduced onto carbon black by the reaction of COCl groups with AgClO₄ and have an ability to initiate the cationic polymerization of styrene [3] and the cationic ring-opening polymerization of lactones [4].

Therefore, the ring opening polymerization of THF was carried out with COCl-Neospectra II and AgClO₄ in the presence of ECH as promoter under several conditions.

Table 1 shows that CO⁺ClO₄⁻ groups introduced by the reaction of COCl groups with AgClO₄ have the ability to initiate the polymeriza-

TABLE 1. Ring-Opening Polymerization of THF Initiated by $\text{CO}^+\text{ClO}_4^-$ Groups in the Presence of ECH as Promoter

Carbon black	AgClO_4 , g	Conversion, ^a %
None	0.20	0
Untreated Neospectra II	-	0
Untreated Neospectra II	0.20	0
COCl -Neospectra II	-	0
COCl -Neospectra II	0.20	40.7

^a COCl -Neospectra II, 0.30 g; THF, 10.0 mL; ECH, 1.0 mol%; 40.0°C; 48 h.

tion of THF, because the individual components AgClO_4 , untreated Neospectra II, and COCl -Neospectra II did not initiate the polymerization of THF.

As previously reported, for the introduction of $\text{CO}^+\text{ClO}_4^-$ groups onto carbon black, the pretreatment of COCl -Neospectra II with AgClO_4 is required because the rate of the reaction of AgClO_4 with COCl -Neospectra II in nitrobenzene is much slower than that of the polymerization of styrene [3]. In contrast, pretreatment was not required for the ring-opening polymerization of THF, possibly because the rate of the polymerization of THF is very slow compared with that of the reaction of AgClO_4 with COCl -Neospectra II in THF.

Initiating Ability of Various Kinds of Carbon Black Containing $\text{CO}^+\text{ClO}_4^-$ Groups

To ensure the initiation by $\text{CO}^+\text{ClO}_4^-$ groups, by use of AgClO_4 and various kinds of CB- COCl , the relationship between the initiating activity of the polymerization of THF and the content of COCl groups was examined.

The results are shown in Table 2. The content of COCl groups was estimated from that of carboxyl groups, which was determined according to the method of Rivin [10], because SOCl_2 reacts quantitatively with carboxyl groups to give COCl groups [11].

As shown in Table 2, the initiating activity of these carbon blacks was almost proportional to the COCl group content of the channel black. Moreover, the SOCl_2 -treated Philblack O/ AgClO_4 system failed to initiate the ring-opening polymerization of THF. This result may be explained by the fact that SOCl_2 -treated Philblack O has no COCl groups.

TABLE 2. Polymerization of THF Initiated by $\text{CO}^+\text{ClO}_4^-$ 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	40.7
FW 200 ^b	0.61	57.2
Philblack O ^c	0	0

^aCOCl-carbon black, 0.30 g; AgClO₄, 0.20 g; THF, 10.0 mL; ECH, 1.0 mol%; 40°C; 48 h.

^bChannel black.

^cFurnace black.

Accordingly, it is concluded that $\text{CO}^+\text{ClO}_4^-$ groups have the ability to initiate the cationic ring-opening polymerization of THF in the presence of promoter.

Effect of Promoter on the Polymerization of THF

It is well known that the rate of the ring-opening polymerization of THF is accelerated by the addition of a small amount of promoter such as ECH, DK, or PL [12]. Therefore, the effect of ECH, SO, DK, and PL as promoter on the polymerization of THF initiated by $\text{CO}^+\text{ClO}_4^-$ groups was investigated.

As is seen in Table 3, the rate of the polymerization of THF was

TABLE 3. Effect of Promoter on the Polymerization of THF Initiated by $\text{CO}^+\text{ClO}_4^-$ Groups on Carbon Black

Promoter	Conversion, ^a %
None	1.3
ECH	40.7
SO	30.9
DK	37.6
PL	22.8

^aCOCl-Neospectra II, 0.30 g; AgClO₄, 0.20 g; THF, 10.0 mL; promoter, 1.0 mol%; 40.0°C; 48 h.

very slow in the absence of promoter. In the presence of promoter, however, the polymerization of THF initiated by $\text{CO}^+\text{ClO}_4^-$ groups was found to proceed to give poly-THF.

Effect of Temperature on the Polymerization of THF

Figure 1 shows the time-conversion curves of the polymerization of THF initiated by $\text{CO}^+\text{ClO}_4^-$ groups in the presence of ECH as promoter at 0, 10, and 40°C. The rate of polymerization was found to increase with rising temperature. The Arrhenius plot for the above results gave a straight line, and the apparent activation energy (E_a) of the polymerization of THF with ECH as promoter was determined to be 8.1 kcal/mol. On the other hand, E_a of the polymerization with DK as promoter was estimated to be 6.2 kcal/mol. These values are nearly equal to that of the cationic ring-opening polymerization of lactones initiated by $\text{CO}^+\text{ClO}_4^-$ groups on carbon black [4].

Proof of Grafting of Poly-THF onto Carbon Black

The carbon black obtained from the polymerization produced a stable colloidal dispersion in a good solvent for poly-THF. This sug-

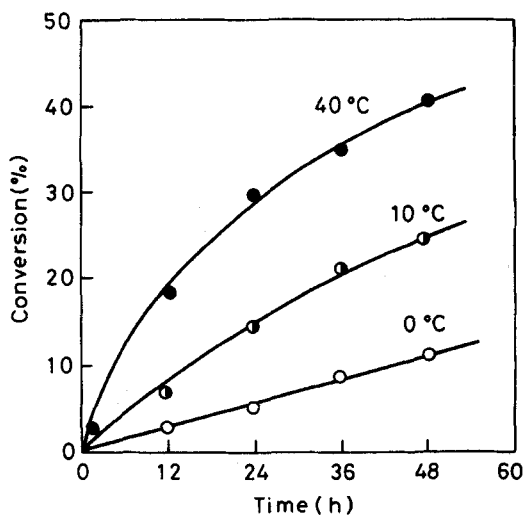


FIG. 1. Ring-opening polymerization of THF initiated by $\text{CO}^+\text{ClO}_4^-$ groups in the presence of ECH as promoter. COCl -Neospectra II, 0.30 g; AgClO_4 , 0.20 g; THF, 10.0 mL; ECH, 1.0 mol%.

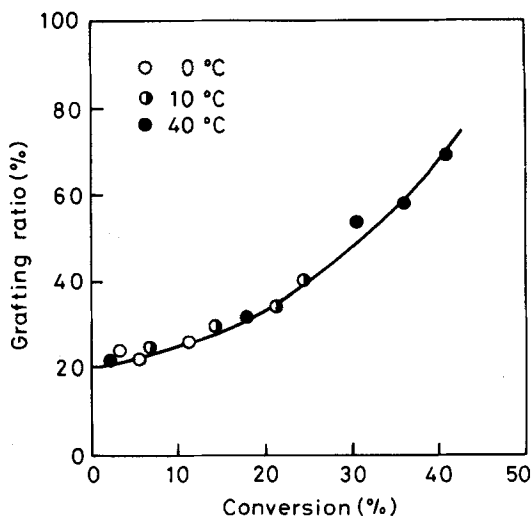


FIG. 2. Relationship between the grafting ratio of poly-THF and conversion. Polymerization conditions are given in Fig. 1.

gests that poly-THF is grafted onto carbon black. To ensure the grafting of poly-THF, the grafting ratio and grafting efficiency were measured.

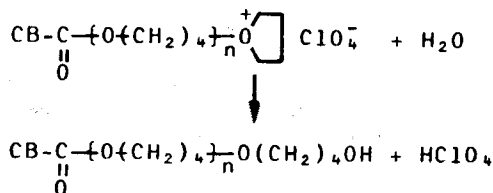
Figure 2 shows that the grafting ratio increased with increasing conversion at each temperature. On the other hand, Fig. 3 shows that the grafting efficiency at 40°C tended to be high during the first few percent of conversion, but decreased with increasing conversion.

A similar phenomenon was observed in the polymerization of styrene [3] and lactones [4] initiated by $\text{CO}^+\text{ClO}_4^-$ groups.

These results suggest that the grafted polymer is propagated from $\text{CO}^+\text{ClO}_4^-$ groups on the carbon black and that ungrafted polymer is gradually formed by a chain transfer reaction of growing polymer chain with an impurity such as a trace of water.

Chain Transfer of Growing Polymer Chain

(1) Formation of poly-THF-grafted carbon black:



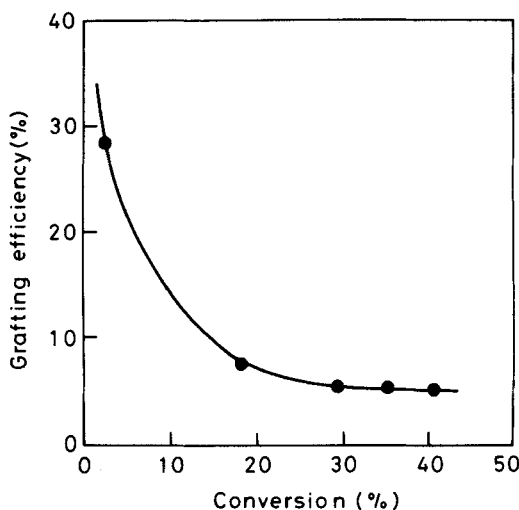
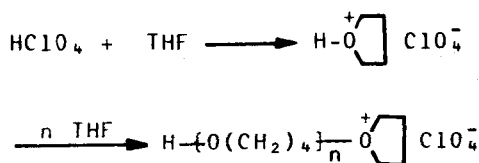


FIG. 3. Relationship between the grafting efficiency at 40°C and conversion. Polymerization conditions are given in Fig. 1.

(2) Formation of ungrafted poly-THF:



On the other hand, Fig. 4 shows the relationships between the intrinsic viscosity of ungrafted poly-THF and the polymerization temperature. The intrinsic viscosity of ungrafted poly-THF obtained at 40°C was lower than that obtained at 0 and 10°C, possibly because the increasing temperature of polymerization causes an increase in the rate of chain transfer of the growing polymer chains.

Ring-Opening Polymerization of SO, ECH, and PO

It is well known that the ring-opening polymerization of alkylene oxides is also initiated by cationic initiators to give polyethers. Thus, the ring-opening polymerization of SO, ECH, and PO initiated by $\text{CO}^+\text{ClO}_4^-$ groups and the grafting of polyethers initiated at the carbon black surface were investigated.

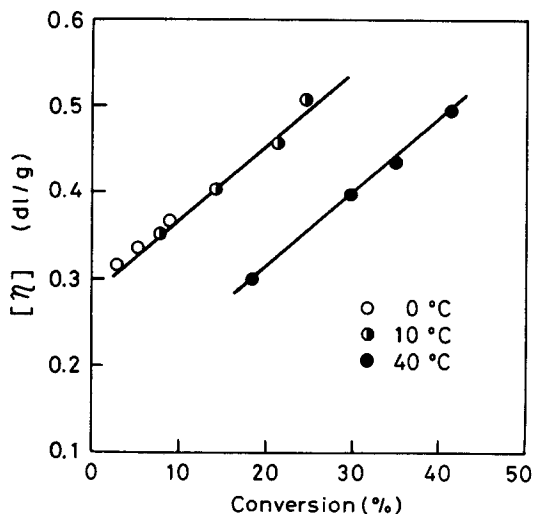


FIG. 4. Relationship between the intrinsic viscosity of ungrafted poly-THF and conversion. Polymerization conditions are given in Fig. 1. $[\eta]$: THF solution, 30.0°C.

TABLE 4. Ring-Opening Polymerization of Alkylene Oxides Initiated by $\text{CO}^+\text{ClO}_4^-$ Groups on Carbon Black

Monomer	Temperature, °C	Time, h	Solvent, mL	Conversion, ^a %	Grafting ratio, %
SO	25	~0 ^b	-	~90	-
SO	0	2	10 ^c	75.5	46.5
SO	-10	2	10 ^c	74.6	57.9
ECH	40	48	-	10.0	42.4
ECH	0	48	-	3.5	-
PO	0	48	-	4.0	40.7
PO	-5	48	-	3.1	31.5

^a COCl -Neospectra II, 0.30 g; AgClO_4 , 0.20 g; monomer: SO, 5.0 mL; ECH, 10.0 mL; PO, 10.0 mL.

^bExplosively polymerized.

^cCarbon tetrachloride.

As shown in Table 4, SO was explosively polymerized in bulk as soon as SO was added to the mixture of COCl -Neospectra II and AgClO_4 . In contrast, in solution polymerization with CCl_4 as solvent, the polymerization proceeded moderately to give poly-SO-grafted carbon black. The intrinsic viscosity of ungrafted poly-SO was 0.04 dL/g (THF solution, 30.0°C).

Furthermore, it became apparent that $\text{CO}^+\text{ClO}_4^-$ groups on the carbon black were capable of initiating the polymerization of ECH and PO. However, the rate of the polymerization of ECH and PO was slow compared with that of SO. The intrinsic viscosity of these polyethers was 0.02-0.04 dL/g (THF solution, 30.0°C).

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