

Cationic Grafting from Carbon Black VI. Grafting of Polyetheresters from Carbon Black by Cationic Ring-Opening Terpolymerization of Tetrahydrofuran—Cyclic Acid Anhydrides—Epichlorohydrin

Norio TSUBOKAWA, Yu JIAN, and Yasuo SONE

*Department of Applied Chemistry, Faculty of Engineering,
Niigata University,
Ikarashi 2-8050, Niigata 950-21, Japan*

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ABSTRACT: The cationic ring-opening terpolymerization of tetrahydrofuran (THF)—phthalic anhydride (PAn)—epichlorohydrin (ECH) was found to be initiated by carbon black having $\text{CO}^+\text{ClO}_4^-$ groups. The activation energy of the terpolymerization was estimated to be $13.8 \text{ kcal mol}^{-1}$. Evidence for the formation of random terpolymers was obtained by IR, NMR, and GPC analysis. The composition of terpolymer was affected by an initial monomer charge ratio: the content of PAn in terpolymer decreased and that of ECH increased with an increase in the amount of ECH charged. Terpolymer of a 1 : 1 : 1 ratio could be prepared when THF, PAn, and ECH were charged in mole ratios of 1 : 1 : 0.7. In such a polymerization system, terpolymer formed is effectively grafted from carbon black surface depending upon the propagation of polymer chain from $\text{CO}^+\text{ClO}_4^-$ groups. The grafting ratio and molecular weight of ungrafted polymer were found to decrease with a rise in polymerization temperature. Furthermore, the dispersibility of terpolymer-grafted carbon black in chloroform was investigated.

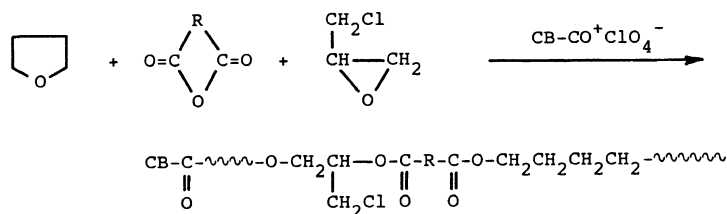
KEY WORDS Ring-Opening Terpolymerization / Random Terpolymer / Polyetherester / Tetrahydrofuran / Phthalic Anhydride / Epichlorohydrin / Grafting / Carbon Black / Acylium Perchlorate Group on Carbon Black / Dispersibility /

In order to prepare carbon black which can be dispersed easily in various polymers, modification of the surface by grafting of polymers onto carbon black has been widely investigated.¹ In a series of our papers, 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 cationic grafting of polystyrene from carbon black.² Furthermore, it was described that $\text{CO}^+\text{ClO}_4^-$ groups on carbon black have ability to initiate cationic ring-opening polymerization of lactones,³ cyclic ethers,⁴ and cyclic formals⁵ to give polyester-, polyether-, and polyacetal-grafted carbon black, respectively.

On the other hand, polyetherester could be grafted onto carbon black during the cationic ring-opening isomerization polymerization of spiro ortho ethers initiated by carboxyl groups or $\text{CO}^+\text{ClO}_4^-$ groups on carbon black.⁶

Hsieh has reported that alternating ring-opening terpolymerization of cyclic ethers with cyclic acid anhydride is initiated by organometallic compounds, particularly trialkyl aluminum and the product has repeating ether—ester—ether linkages along the chain.⁷

In a previous paper, we reported that $\text{CO}^+\text{ClO}_4^-$ groups have ability to initiate the cationic ring-opening copolymerization of tetrahydrofuran (THF) with cyclic acid an-



hydrides to give polyester-grafted carbon black.⁸ Moreover, it became apparent that by the addition of epichlorohydrin (ECH) as a promoter, ECH sequences are included in the copolymer and the grafting ratio onto carbon black increased.

In the present paper, the grafting of polyesteresters by the ring-opening terpolymerization of THF-cyclic acid anhydride-ECH initiated by $\text{CO}^+\text{ClO}_4^-$ groups on carbon black was investigated in order to graft polymers having reactive CH_2Cl groups onto carbon black and to prepare polymer-grafted carbon black with a higher grafting ratio. Furthermore, the dispersibility of the terpolymer-grafted carbon black was compared with that of several polymer-grafted carbon blacks.

EXPERIMENTAL

Materials

The carbon black used was color channel black Neospectra II (Columbian Carbon Co., BET specific surface area, $906\text{ m}^2\text{ g}^{-1}$) and dried *in vacuo* at 110°C before use. The content of carboxyl, phenolic hydroxyl, and quinonic oxygen groups on the surface was 0.40, 0.24, and 0.92 meq g^{-1} , respectively.

Tetrahydrofuran (THF) and epichlorohydrin (ECH) were refluxed over calcium hydride and distilled twice before use. Phthalic anhydride (PAN), succinic anhydride (SAN), and maleic anhydride (MAN) were recrystallized and then sublimed under reduced pressure.

Nitrobenzene used as solvent was washed with dilute H_2SO_4 , dried over CaCl_2 , and distilled under reduced pressure.

Guaranteed-reagent-grade AgClO_4 (Kojima Chemical Co., Ltd., Japan) was dried *in vacuo* at 130°C before use. Boron trifluoride etherate and tin(IV) chloride were used without further purification.

Introduction of $\text{CO}^+\text{ClO}_4^-$ Groups onto Carbon Black

The introduction of $\text{CO}^+\text{ClO}_4^-$ groups onto carbon black, *i.e.*, pretreatment, was carried out by the reaction of COCl groups on carbon black with AgClO_4 in nitrobenzene according to the method previously reported.²

The content of $\text{CO}^+\text{ClO}_4^-$ groups introduced onto the carbon black surface was estimated to be 0.37 meq g^{-1} by the determination of HClO_4 liberated after hydrolysis of $\text{CB-CO}^+\text{ClO}_4^-$.⁸

Polymerization Procedures

After pretreatment, 10.0 mmol of THF, 10 mmol of cyclic acid anhydride, and ECH were added to a flask that contained 0.30 g of $\text{CB-CO}^+\text{ClO}_4^-$ and the polymerization 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*. The conversion was calculated by the following equation:

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

Determination of Grafting Ratio and Intrinsic Viscosity of Ungrafted Polymer

To isolate polymer-grafted carbon black from the reaction product, the product was extracted with chloroform by using a Soxhlet apparatus until no more polymer could be extracted with the refluxing solvent. The grafting ratio was determined by the following equation:

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

On the other hand, the ungrafted polymer was isolated from the extract of the above extraction and purified by reprecipitation (chloroform/methanol). Its intrinsic visco-

sity ($[\eta]$) was determined with a Ubbelohde viscometer in chloroform solution at 30.0°C.

Dispersibility of Polymer-Grafted Carbon Black

The dispersibility of polymer-grafted carbon black was estimated by the fraction of the carbon black dispersed in chloroform after centrifugation. Polyetherester-grafted carbon black (0.50 g) was dispersed in 50.0 ml of chloroform with a magnetic stirrer and centrifuged at 5.0×10^3 rpm. After a definite time, 5.0 ml of the dispersion liquid were taken out with a pipet and the amount of carbon black dispersed in chloroform was determined. The dispersing fraction was determined by the following equation:

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

RESULTS AND DISCUSSION

Copolymerization of THF with PAn in the Presence of ECH Initiated by $\text{CB-CO}^+\text{ClO}_4^-$

Figure 1 shows the results of the copolymerization of THF with PAn initiated by $\text{CB-CO}^+\text{ClO}_4^-$ at 70°C in the presence of various amounts of ECH.

From the results shown in Figure 1, the polymerization of THF was found to be initiated by $\text{CB-CO}^+\text{ClO}_4^-$ in the presence of PAn and ECH. As mentioned in the previous paper, the rate of the polymerization was very small in the absence of ECH. However, by the addition of ECH the rate of polymerization and the conversion increased remarkably. These results clearly show that ECH acts as an effective promoter in the copolymerization of THF with PAn.

It is well known that in the polymerization of THF using ECH as a promoter, the ring-opening of ECH constitutes the initiation reaction, in which the propagating species (oxonium ion) is formed.¹⁰ It is considered

that in the copolymerization of THF with PAn in the presence of ECH, the ring-opening of ECH is also essential for the initiation

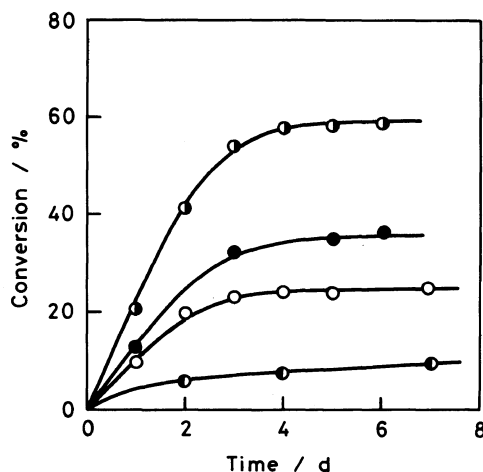


Figure 1. Copolymerization of THF with PAn initiated by $\text{CB-CO}^+\text{ClO}_4^-$ in the presence of ECH at 70°C. Pretreatment: Neospectra II-COCl, 0.30 g; AgClO_4 , 0.20 g; nitrobenzene, 3.0 ml; room temp, 2 h. Polymerization: THF = PAn = 10 mmol, ECH = (●), 10 mmol; (◐), 7 mmol; (○), 0.5 mmol; (●), 0 mmol.

reaction. Therefore, the copolymerization of THF with PAN is accelerated by the addition of ECH.

It has been reported that the cationic ring-opening terpolymerization of THF-ethylene oxide-PAN is initiated by organometallic compounds such as trialkylaluminum to give a polyetherester containing repeating ether-ester-ether linkage along the chain.⁷ On the other hand, Hilt and Hamann described that the copolymerization of THF with cyclic acid anhydrides is initiated by cationic catalyst such as AlCl_3 and SnCl_4 to give polyester.⁹

As mentioned above, we demonstrated that $\text{CO}^+\text{ClO}_4^-$ groups introduced onto carbon black surface have ability to initiate the cationic polymerization of styrene² and the cationic ring-opening polymerization of lactones,³ cyclic ethers,⁴ and cyclic formals.⁵

Based on these results, it is concluded that the cationic ring-opening copolymerization of THF with PAN in the presence of ECH is also initiated by $\text{CO}^+\text{ClO}_4^-$ groups on carbon black. Moreover, the formation of terpolymer from THF, PAN, and ECH was expected when the copolymerization of THF and PAN is carried out in the presence of ECH.

On the other hand, the rate of copolymerization decreased with an increase in the amount of ECH charged when it exceed 0.7 mmol. This may be due to the fact that the rate of propagation of ECH sequence, whose content in the polymer increases with an increase of ECH charged, is smaller than that of THF-PAN sequence.¹¹ The effects of other promoters on the copolymerization of THF with PAN are now under investigation.

Characterization of Ungrafted Polymer

Figure 2 shows IR spectra of ungrafted polymers obtained from the copolymerization of THF with PAN in the absence or in the presence of ECH, respectively.

Infrared spectra of the polymer obtained from the copolymerization of THF with PAN in the presence of ECH (charged in mole ratio,

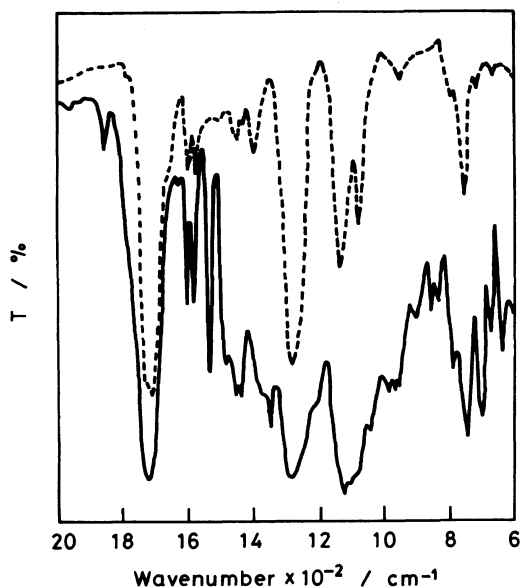
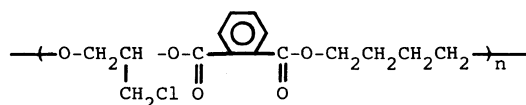


Figure 2. Infrared spectra of polymers obtained from the polymerization shown in Figure 1. Monomer charge ratio: (—), THF: PAN: ECH=1:1:0.7; (---), THF: PAN=1:1.

THF: PAN: ECH=1:1:0.7) exhibited a strong absorption at 1118 cm^{-1} besides the one observed in the copolymer of THF and PAN.⁸ This absorption at 1118 cm^{-1} is characteristic of the ether bond, indicating the presence of an ether linkage in the polymer. The NMR spectra of the polymer suggest that the polymer contains ECH sequences: $\delta = 1.47\text{--}2.03$ ($-\text{CH}_2-$), $3.63\text{--}3.97$ ($-\text{CH}_2\text{Cl}$), $3.97\text{--}4.45$ ($-\text{CH}_2\text{O}-$), $4.43\text{--}4.77$ ($-\text{CH}_2\text{O}-\text{CO}-$), and $5.23\text{--}5.63$ ppm ($>\text{CH}-$).

These results indicate that the formation of terpolymer of THF-PAN-ECH, namely a polyetherester, as shown below. It was confirmed by NMR that the terpolymer from THF, PAN, and ECH charged in mole ratios of 1:1:0.7 contains almost equimolar amounts of the three monomers.



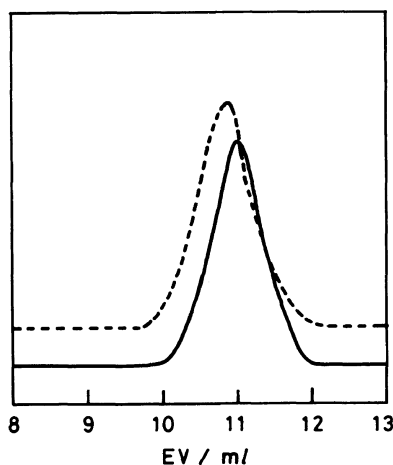


Figure 3. GPC curves of terpolymers obtained from the polymerization shown in Figure 1. Monomer charge ratio: (—), THF:PAAn:ECH=1:1:0.7; (---), THF:PAAn:ECH=1:1:1. Measurement conditions: Column, GELPACK GLS300MDT5; solvent, DMF/THF=1/1; detector, differential refractometer; flow rate, 1 ml/min.

From GPC analysis of the terpolymers (monomer charge ratio; THF:PAAn:ECH=1:1:1 and 1:1:0.7), as shown in Figure 3, it is concluded that these polymers obtained in the presence of ECH are terpolymer from THF, PAAn, and ECH, but not a mixture of polyether and polyester. The molecular weight of these terpolymers was estimated to be $4.0 - 5.0 \times 10^3$ from GPC based on standard polystyrene.

Moreover, the polymer was fractionated into 3 fractions by fractional precipitations (chloroform/methanol). Difference in the composition of terpolymers of these fractions was scarcely observed by NMR and IR.

Based on the above results, it is concluded that when copolymerization of THF with PAAn is conducted in ECH, random terpolymer of THF-PAAn-ECH is produced.

Proof of Grafting from Carbon Black

The carbon black obtained from the polymerization produced a stable colloidal dispersion in organic solvents such as THF and

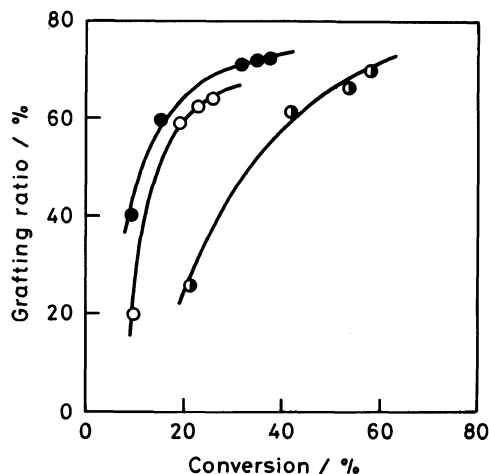


Figure 4. Relationship between conversion and grafting ratio of terpolymers onto carbon black. Polymerization conditions are given in Figure 1. Monomer charge ratio: (●), THF:PAAn:ECH=1:1:1; (○), THF:PAAn:ECH=1:1:0.7; (○), THF:PAAn:ECH=1:1:0.05.

chloroform. This suggests that the terpolymer is grafted from the carbon black surface.

The relationship between the grafting ratio and conversion for each concentration of ECH charged is shown in Figure 4. Figure 4 shows that in such a terpolymerization system, the terpolymer formed is grafted from carbon black and the grafting ratio increases with an increase in conversion.

Accordingly, it became apparent that the terpolymerization of THF-PAAn-ECH can be initiated by $\text{CO}^+\text{ClO}_4^-$ groups on the carbon black surface and terpolymers formed are effectively grafted from carbon black based on the propagation of the polymer from the surface.

Effects of Charge Ratio of Monomers on the Terpolymerization

Using equimolecular amounts (10 mmol) of THF and PAAn and various amounts of ECH, the terpolymerization of THF-PAAn-ECH initiated by $\text{CB-CO}^+\text{ClO}_4^-$ was carried out at 70°C . The results are summarized in Table I.

The rate of the terpolymerization increased

Table I. Terpolymerization of THF-PAn-ECH initiated by $\text{CB-CO}^+\text{ClO}_4^-$ ^a

Monomer charge/mmol			Time	Conversion	Grafting ratio	Mole ratio in polymer		
THF	PAn	ECH	d	%	%	THF	PAn	ECH
10	10	0	7	9.8	—	0.52	0.48	0
10	10	1	6	54.5	70.4	0.42	0.45	0.13
10	10	5	5	68.4	95.2	0.34	0.40	0.26
10	10	7	5	57.3	69.8	0.33	0.34	0.33
10	10	10	5	35.8	65.8	0.34	0.20	0.46
10	10	20	5	12.7	57.6	0.39	0.08	0.53
10	10	50	5	9.9	72.8	0.40	0	0.60

^a Pretreatment: Neospectra II-COCl, 0.30 g; AgClO_4 , 0.20 g; nitrobenzene, 3.0 ml; room temp, 2 h. Polymerization, 70°C.

with an increase in the amount of ECH charged until up to 5 mmol, but decreased when ECH was added more than 5 mmol. On the other hand, the mole ratios of PAn in the terpolymer decreased with an increase in the amount of ECH added. It was found that the terpolymer of a 1:1:1 ratio can be prepared when THF, PAn, and ECH are charged in mole ratios of 1:1:0.7. Then, when the polymerization was carried out in the presence of excess ECH (exceed 10 mmol), the structure of the polymer formed became close to that of the copolymer of THF with ECH.

Accordingly, it became apparent that polyetheresters with various compositions can be effectively grafted onto a carbon black surface by the terpolymerization of THF-PAn-ECH using $\text{CB-CO}^+\text{ClO}_4^-$ as initiator.

Initiation of Terpolymerization by Other Cationic Catalysts

Table II shows the result of the terpolymerization of THF-PAn-ECH initiated by benzoyl perchlorate, boron trifluoride etherate, and tin(IV) chloride at 70°C. As shown in Table II, these catalysts have ability to initiate the terpolymerization of THF-PAn-ECH as well as $\text{CB-CO}^+\text{ClO}_4^-$. Further investigations of the terpolymerization initiated by other cationic catalysts and the detailed characterization of the terpolymer are now in progress.

Table II. Terpolymerization of THF-PAn-ECH initiated by several cationic catalysts^a

Catalyst	mmol	Conversion	Mole ratio in polymer		
		%	THF	PAn	ECH
$\text{Ph-CO}^+\text{ClO}_4^-$	1	35.8	0.30	0.23	0.47
BF_3OEt_2	1	40.5	0.37	0.35	0.28
SnCl_4	2	38.5	0.22	0.33	0.45

^a THF = PAn = ECH = 10 mmol; nitrobenzene, 3.0 ml; 70°C; 5 day.

Effects of Temperature on the Terpolymerization and Grafting Ratio of Terpolymer

Using 10 mmol of THF, 10 mmol of PAn, and 7 mmol of ECH, terpolymerization was carried out at 30, 50 and 70°C and the effects of temperature on the terpolymerization and grafting ratio of terpolymer onto carbon black were examined. The results are shown in Figures 5 and 6.

Figure 5 clearly shows that the rate of the terpolymerization at 30°C does not proceed more than 5% conversion even after 6 days. While at 70°C, the terpolymerization was accelerated and 70% conversion was obtained after 6 days.

The activation energy of the polymerization was estimated to be 13.8 kcal/mol. This value is somewhat larger than that of the ring-opening polymerization of THF initiated by

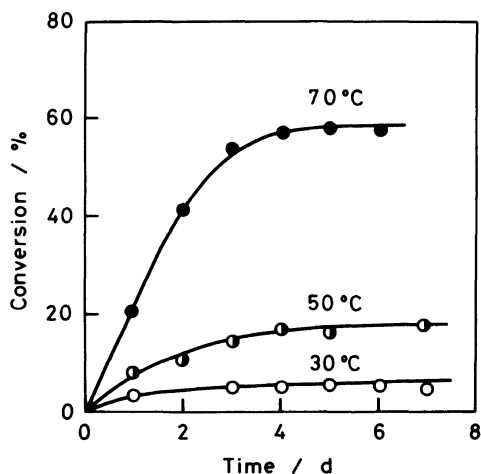


Figure 5. Effects of temperature on the terpolymerization of THF-PAN-ECH. Pretreatment: Neospectra II-COCl, 0.30 g; AgClO₄, 0.20 g; nitrobenzene, 3.0 ml; room temp, 2 h. Polymerization: THF=PAN=10 mmol, ECH=7 mmol.

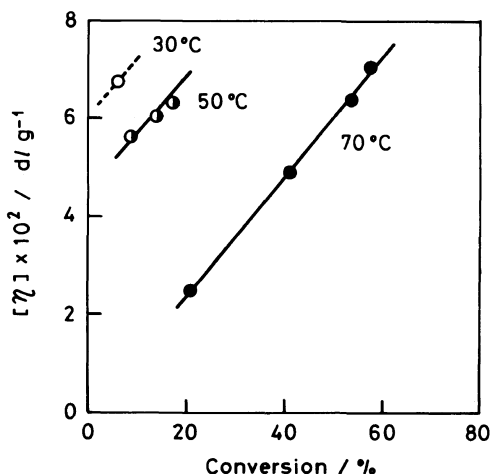


Figure 7. Effects of temperature on the intrinsic viscosity of ungrafted terpolymer from THF, PAN, and ECH. Polymerization conditions are given in Figure 5.

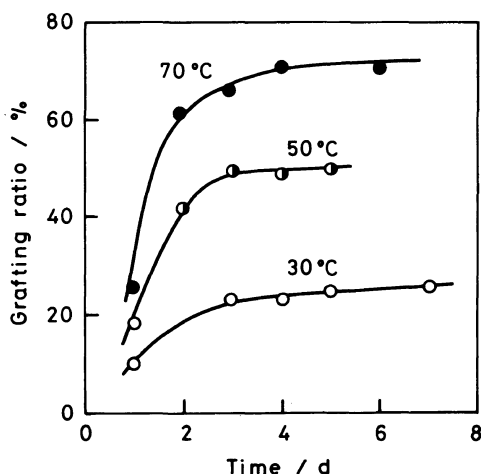


Figure 6. Effects of temperature on the grafting ratio of terpolymer from THF, PAN, and ECH. Polymerization conditions are given in Figure 5.

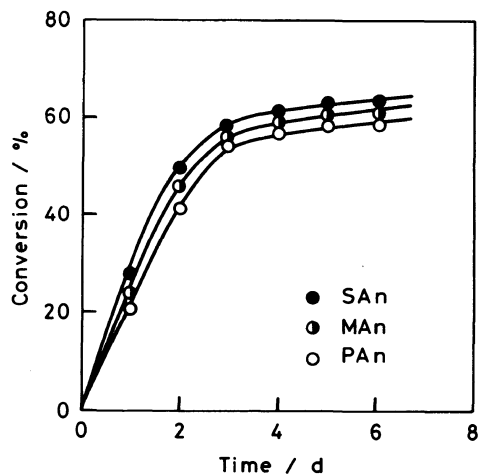


Figure 8. Terpolymerization of THF-cyclic acid anhydride-ECH initiated by CB-CO⁺ClO₄⁻. Pretreatment: Neospectra II, 0.30 g; AgClO₄, 0.20 g; nitrobenzene, 3.0 ml; room temp, 2 h. Polymerization: THF=anhydride=10 mmol, ECH=7 mmol; 70°C.

CB-CO⁺ClO₄⁻.

The grafting ratio of the terpolymer increased with an increase in conversion at each temperature as shown in Figure 6.

The relationship between polymerization temperature and the intrinsic viscosity of ungrafted polymer is shown in Figure 7. The

intrinsic viscosity of ungrafted terpolymer obtained at higher temperature was lower than that at lower temperature, possibly because the increasing temperature of the polymerization causes an increase in the rate of chain transfer of the growing polymer chains.

Table III. Terpolymerization of THF–cyclic acid anhydride–ECH initiated by $\text{CB-CO}^+\text{ClO}_4^-$ ^a

Anhydride	Conversion	Grafting ratio	Mole ratio in polymer		
	%	%	THF	Anhydride	ECH
PAn	57.3	69.3	0.33	0.34	0.33
MAN	58.2	84.1	0.28	0.37	0.34
SAn	59.8	100.3	0.20	0.46	0.34

^a Pretreatment: Neospectra II-COCl, 0.30 g; AgClO_4 , 0.20 g; nitrobenzene, 3.0 ml; room temp, 2 h. Polymerization: THF = anhydride = 10 mmol, ECH = 0.7 mmol; 70°C; 5 day.

Table IV. Dispersibility of several polymer-grafted carbon black in chloroform

Polymer grafted	Grafting ratio	Dispersibility/% ^a		
	%	10 min	1 h	3 h
Ungrafted	—	0	0	0
Polystyrene ¹²	153.7	100	98	91
Poly(β -propiolactone) ¹³	154.8	100	100	96
Polyester(THF–PAn) ⁸	70.4	65	40	9
Polyetherester(THF–PAn–ECH)	69.8	78	63	20
Polyetherester(THF–SAn–ECH)	100.3	97	84	70

^a After centrifugation at 5.0×10^3 rpm at room temperature.

Terpolymerization of THF–Cyclic Acid Anhydrides–ECH Initiated by $\text{CB-CO}^+\text{ClO}_4^-$

The grafting of terpolymers onto carbon black was carried out with SAn or MAN as cyclic acid anhydride in place of PAn at 70°C. The time–conversion curves of the polymerizations are shown in Figure 8.

As shown in Figure 8, the rate of the polymerization increased depending on the cyclic acid anhydride, in the following order: PAn < MAN < SAn. The grafting ratio onto carbon black and the composition of these terpolymers analyzed by NMR are summarized in Table III.

From these results, it was concluded that $\text{CB-CO}^+\text{ClO}_4^-$ has ability to initiate the cationic ring-opening terpolymerization of THF–cyclic acid anhydrides–ECH and that the polyetherester is effectively grafted onto the carbon black surface.

Dispersibility of Terpolymer-Grafted Carbon Black

As mentioned above, terpolymer-grafted carbon black produced a stable colloidal dispersion in chloroform. It is well known that the dispersibility of polymer-grafted carbon black is affected by its grafting ratio and solubility of grafted polymer chains in the dispersion medium. The dispersibility of a polyetherester (terpolymer of THF–PAn–ECH)- or polyester (copolymer of THF–PAn)-grafted carbon black was compared with that of several polymer-grafted carbon blacks. The results are shown in Table IV.

Table IV clearly shows that the dispersibility of carbon black in chloroform is much improved by the grafting of polymers onto carbon black. The dispersibility of polymer-grafted carbon black increases with an increase of its grafting ratio, because there is no difference in the solubility in chloroform between these polymers. Furthermore, it was

found that the dispersibility of copolymer (THF-PAn)-grafted carbon black considerably improved by the introduction of ECH sequences in the grafted chain because of the increase of the grafting ratio. In particular, terpolymer (THF-SAn-ECH)-grafted carbon black with high grafting ratio produced a stable dispersion and its dispersibility was comparable to that of polystyrene- or poly- β -propiolactone-grafted carbon black that obtained from anionic grafting.^{12,13}

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