Polymer Bulletin 16, 249–256 (1986)

Polymer Bulletin

Cationic grafting from carbon black

V. Grafting of polyesters from carbon black by ring-opening copolymerization of tetrahydrofuran and cyclic acid anhydride initiated by acylium perchlorate group on carbon black

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SUMMARY

The cationic ring-opening copolymerization of tetrahydrofuran (THF) with a cyclic acid anhydride such as phthalic anhydride (PAn) and maleic anhydride was initiated by acylium perchlorate groups on carbon black to give alternating copolymer, i.e., polyester. Epichlorohydrin was found to act as effective promoter in the copolymerization. The polyester formed was effectively grafted from carbon black depending upon the propagation of the polymer from the surface: the grafting ratio of polyester from THF and PAn was increased up to about 65% with an increase in conversion. The polyester-grafted carbon black gave a stable colloidal dispersion in chloroform.

INTRODUCTION

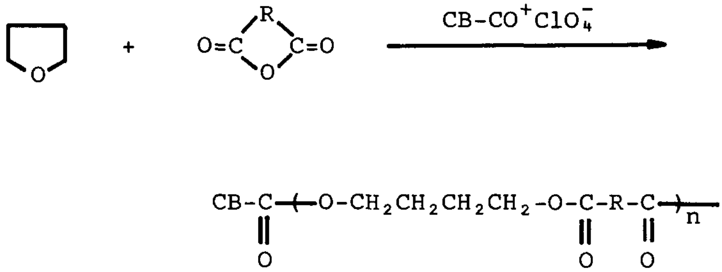
In a series of our papers, anionic grafting of polyesters from carbon black using alkali metal carboxylate groups (COOM: M=Li, Na, K, Rb, and Cs) on the surface has been reported (1-3). For instance, the anionic ring-opening polymerization of β-propiolactone (PL) was initiated by COOM groups on carbon black and poly-PL-grafted carbon black was formed in the polymerization (1). Furthermore, COOM groups were found capable of initiating the anionic ring-opening copolymerization of epoxides or alkylene carbonate with cyclic acid anhydrides to give alternating copolymer, i.e., polyester (2,3). In such polymerization system, the polyester was propagated from COOM groups and effectively grafted from carbon black.

On the other hand, Hilt and his coworkers reported that the ring-opening copolymerization of tetrahydrofuran (THF) with a cyclic acid anhydride is initiated by cationic catalysts such as $AlCl_3$ and $SnCl_4$ to give polyester (4).

As previously reported, we demonstrated that acylium perchlorate groups on carbon black, which is introduced by the reaction of acyl chloride groups with $AgClO_4$, have an ability to initiate the cationic polymerization of styrene (5), and the cationic ring-opening polymerization of lactones (6), cyclic ethers (7), and cyclic formals (8).

In the present paper, the surface grafting of polyesters by the cationic ring-opening copolymerization of THF with a cyclic acid anhydride initiated by acylium perchlorate groups on carbon black was described.

$$\text{CB-COOH} \xrightarrow{\text{SOCl}_2} \text{CB-COCl} \xrightarrow{\text{AgClO}_4} \text{CB-CO}^+\text{ClO}_4^-$$



$$\text{CB-}\underset{\displaystyle \text{O}}{\underset{\|}{\text{C}}}\text{-}\left(\text{O-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-O-}\underset{\displaystyle \text{O}}{\underset{\|}{\text{C}}}\text{-R-}\underset{\displaystyle \text{O}}{\underset{\|}{\text{C}}}\right)_n$$

EXPERIMENTAL

Materials

The carbon black samples used were color channel black Neospectra II (Columbian Carbon Co.; BET specific surface area, 906 m^2/g) and Philblack O (Philips Petroleum Co., 79.6 m^2/g). These carbon blacks were dried in vacuo at 110°C before use. The content of carboxyl groups on Neospectra II and Philblack O was 0.40 and 0 meq/g, respectively.

Tetrahydrofuran (THF) and epichlorohydrin (ECH) were refluxed over CaH_2 and distilled twice before use. Phthalic anhydride (PAn), maleic anhydride (MAn), and succinic anhydride (SAn) were recrystallized and then sublimed under reduced pressure. Methylhexahydrophthalic anhydride (MHHPA) and methyltetrahydrophthalic anhydride (MTHPA) were distilled twice under reduced pressure.

Guaranteed-reagent-grade $AgClO_4$ (Kojima Chemical Co. Ltd., Japan) was dried *in vacuo* at 130°C before use.

All other reagents and solvents were also used after ordinary purification.

Introduction of Acylium Perchlorate Groups onto Carbon Black

The introduction of acylium perchlorate groups onto carbon black, i.e., pretreatment, was carried out by the reaction of acyl chloride groups on carbon black with $AgClO_4$ in nitrobenzene according to the method previously reported (5).

Determination of Acylium Perchlorate Groups on Carbon Black

The content of acylium perchlorate groups on carbon black was determined as follows: After the pretreatment of 0.30g of Neospectra II with 0.20g of $AgClO_4$ in 3.0ml of nitrobenzene, nitrobenzene was removed under reduced pressure and 20.0ml of distilled water (chlorine-free) was added. The resulting $HClO_4$ and HCl by the hydrolysis of acylium perchlorate and acyl chloride groups with water were determined by titration with

0.01N-KOH. On the other hand, the content of chloride was titrated with 0.01N-$AgNO_3$ after the neutralization of the solution. From the difference between KOH and $AgNO_3$ titrations, the content of acylium perchlorate groups was estimated to be 0.37meq/g.

Polymerization Procedures

After the pretreatment, 10 mmol of THF, 10 mmol of cyclic acid anhydride , and 0.5-1.0 mmol of ECH as promoter were added to a flask that contained 0.30g of Neospectra II-$CO^{+}ClO_4^{-}$ and the polymerization was conducted with stirring under dry nitrogen. After a definite time, the content of the flask was poured into a large excess of methanol to precipitate the polyester containing carbon black. The conversion was calculated by the following equation:

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

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

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

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

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

On the other hand, the ungrafted polymer was isolated from the extract of the above extraction and purified by reprecipitation (chloroform/methanol). Its intrinsic viscosity ($[\eta]$) was determined with a Ubbelhode viscometer in chloroform solution at 30.0°C.

RESULTS AND DISCUSSION

Initiating Ability of Acylium Perchlorate Group on Carbon Black

It is well known that the cationic polymerization of styrene (9) and the ring-opening polymerization of THF (10) are initiated by benzoyl or acetyl perchlorate which is prepared by the reaction of acid chloride and $AgClO_4$. As mentioned above, we reported the cationic grafting of polystyrene (5), poly-

TABLE I
Copolymerization of THF with PAn under Several Conditions[a]

No.	Carbon black	$AgClO_4$ (g)	$CO^+ClO_4^-$ group (meq/g)	Conversion (%)
1	None	0.20	-	0
2	Neospectra II	-	-	0
3	Neospectra II	0.20	0	0
4	Neospectra II-COCl	-	0	0
5	Neospectra II-COCl	0.20	0.37	9.8
6	$SOCl_2$-Philblack O[b]	0.20	0	0

[a] Pretreatment: carbon black, 0.30g; nitrobenzene, 3.0ml; r.t.;2h. Polymerization: THF=PAn=10 mmol; 70°C; 5d.
[b] Treated with thionyl chloride.

esters (6), polyethers (7), and polyacetals (8) from carbon black by use of carbon black having acylium perchlorate groups as initiator.

Therefore, the ring-opening copolymerization of THF with PAn using $CB\text{-}CO^+ClO_4^-$ as initiator was carried out under several conditions. The results are summarized in Table I.

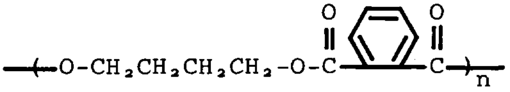
As shown in Table I, the copolymerization of THF with PAn was scarcely initiated by any single component of $AgClO_4$, Neospectra II, and Neospectra II-COCl (Nos. 1, 2, and 4). On the contrary, in the presence of Neospectra II-COCl pretreated with $AgClO_4$ in nitrobenzene, the polymerization was found to proceed (No. 5). No polymerization could be detected at all, even if untreated Neospectra II was pretreated with $AgClO_4$ (No. 3). This indicates that acylium perchlorate groups are unable to introduce onto untreated Neospectra II. In addition, $SOCl_2$-treated Philblack O pretreated with $AgClO_4$ has no ability to initiate the polymerization (No. 6). This may be due to the fact that Philblack O has no carboxyl groups.

To ensure the formation of acylium perchlorate groups on carbon black, the content of the groups was determined by titration. As the result, as shown in Table I, the content of the groups on Neospectra II-COCl treated with $AgClO_4$ was estimated to be 0.37 meq/g. This value corresponds to 92% of carboxyl groups on carbon black. However, acylium perchlorate group on Neospectra II and $SOCl_2$-treated Philblack O treated with $AgClO_4$ were not detected at all.

These results suggests that acylium perchlorate group is introduced by the pretreatment of CB-COCl with $AgClO_4$ which initiates the cationic ring-opening copolymerization of THF with PAn.

Characterization of Polymer

The polymer obtained from the copolymerization of THF with PAn was analyzed as expected polyester by IR and ^1H-NMR. The polyester should have the repeating unit:



IR (KBr); 1720 (vs;C=O), 1602 (m; aromatic ring),and 1120 and 1070cm^{-1} (s;C-O-C). NMR($CDCl_3$); δ=1.47-2.03 (4H;-CH_2-), 3.97-4.73 (4H;-CH_2-O-CO-), and 7.13-7.87ppm (4H;phenylene).

Effect of Promoter on the Copolymerization

It is well known that the rate of the cationic ring-opening polymerization of THF is accelerated by the addition of a small amount of promoter such as ECH and diketene (11). On the other hand, we reported that ECH acts as effective promoter in the cationic ring-opening polymerization of THF initiated by CB-$CO^+ClO_4^-$ (7). Therefore, the effect of ECH on the copolymerization of THF with PAn was investigated. The results are shown in Table II.

As is seen in Table II, the rate of the copolymerization of THF with PAn was very slow in the absence of ECH. In the presence of ECH, however, the copolymerization initiated by acylium perchlorate groups was accelerated. From the NMR analysis, the polyester obtained in the presence of ECH (0.5 mmol) was confirmed to contain about 8mol% of ECH unit. Therefore, when equimolecular amounts of ECH, THF, and PAn were charged, the formation of terpolymer from THF, PAn, and ECH was expected. The ring-opening terpolymerization of THF-PAn-ECH will be reported in a subsequent article.

Effect of Temperature on the Copolymerization

By use of 0.30g of Neospectra II, the ring-opening copolymerization of THF with PAn in the presence of ECH as promoter was carried out at 30, 50, and 70°C. The results are shown in Figure 1.

The rate of the copolymerization was found to increase with the rise of temperature. From the Arrhenius plots for the above results, the apparent activation energy of the copolymerization was estimated to be 13.1 kcal/mol.

TABLE II

Effect of ECH as Promoter in the Copolymerization of THF with PAn Initiated by CB-$CO^+ClO_4^-$

ECH (mmol)	Temperature (°C)	Conversion (%)
0	50	2.8
0.5	50	16.9
0	70	9.8
0.5	70	30.0
1.0	70	42.6

[a] Pretreatment conditions are given in Table I. Polymerization: THF=PAn=10mmol; 5d.

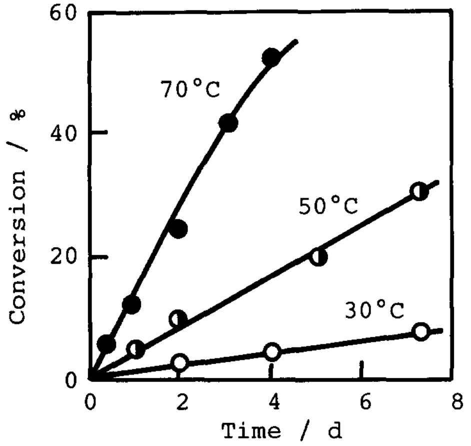


Figure 1. Copolymerization of THF with PAn initiated by acylium chloride group on carbon black. Pretreatment: Neospectra II-COCl, 0.30g;$AgClO_4$, 0.20g;nitrobenzene,3.0ml;r.t.; 2h. Polymerization:THF=PAn=10 mmol; ECH,1.0mmol.

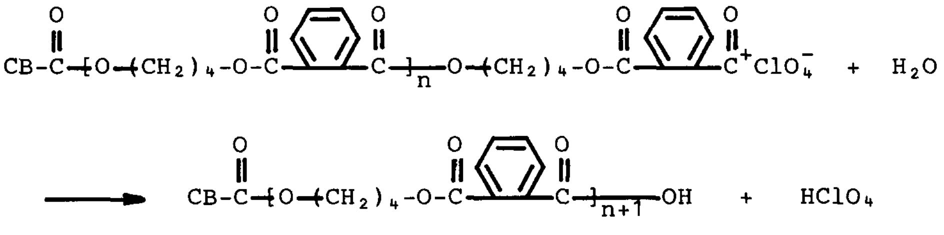
Proof of Grafting of Polyester from Carbon Black

The carbon black obtained from the copolymerization produced a stable colloidal dispersion in a good solvent for polyester. This suggests the formation of polyester-grafted carbon black.

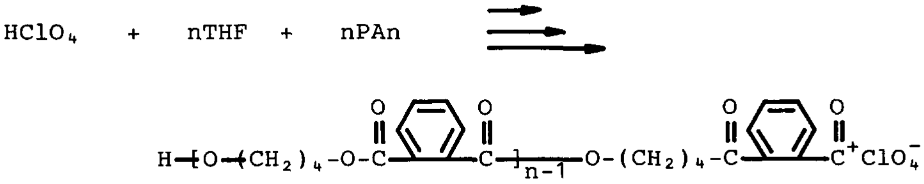
The relationship between conversion and grafting ratio (grafting efficiency) at 70°C is shown in Figure 2. Figure 2 clearly shows that polyester is grafted onto carbon black and the grafting ratio increases with an increase in conversion.

On the other hand, the grafting efficiency is high during the first few percents of conversion. A similar phenomenon was observed in the cationic polymerization of styrene initiated by acylium perchlorate group on carbon black (5).

Formation of Polyester-Grafted Carbon Black



Formation of Ungrafted Polyester



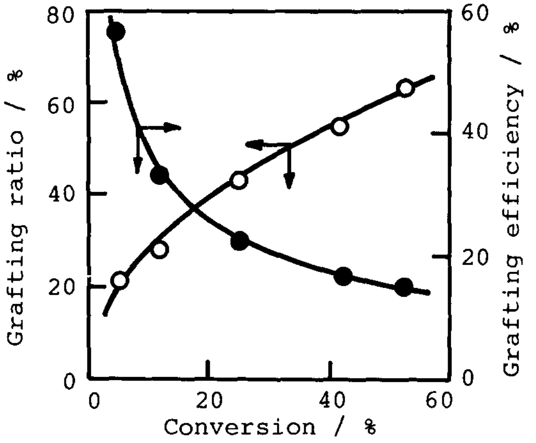


Figure 2. Relationship between conversion and grafting ratio (grafting efficiency). Polymerization conditions are given in Figure 1.

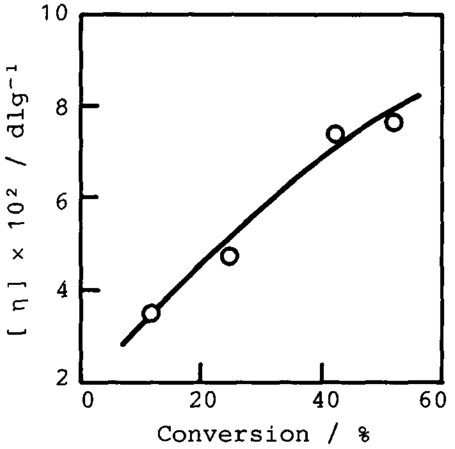


Figure 3. Relationship between intrinsic viscosity and conversion. Polymerization conditions are given in Figure 1.

These results suggest that the grafted polymer is propagated from acylium perchlorate groups on carbon black and that ungrafted polymer is gradually formed by a chain transfer of growing polymer chain with an impurity such as a trace of water as shown in the schemes.

On the other hand, Figure 3 shows the relationship between conversion and intrinsic viscosity of ungrafted polyester in chloroform solution at 30.0°C.

Copolymerization of THF with Several Cyclic Acid Anhydride

The copolymerizations of THF with cyclic acid anhydrides were carried out by using acylium perchlorate groups as initiator and ECH as promoter and the grafting of various kinds of polyesters was evaluated. The results are summarized in Table III.

From the results shown in Table III, it is apparent that acylium perchlorate groups have an ability to initiate the cationic ring-opening copolymerization of THF with cyclic acid anhydrides to give polyester-grafted carbon black. All of the

TABLE III
Grafting of Polyesters from THF and Several Cyclic Acid Anhydrides[a]

Anhydride	Conversion (%)	Grafting ratio(%)	[η][b] (dl/g)
PAn	42.6	55.0	0.08
MAn	52.1	95.3	0.14
SAn	59.1	86.3	0.09
MHHPA	26.0	86.1	0.12
MTHPA	19.3	37.0	0.17

[a] Pretreatment conditions are shown in Table I. Polymerization: THF=anhydride=10 mmol; ECH=1 mmol; 70°C; 3d.

[b] Chloroform solution at 30.0°C.

polymers obtained from the copolymerization shown in Table III were identified as the corresponding alternating polyesters by IR and NMR.

Accordingly, it became feasible to graft various kinds of polyester from carbon black surface by cationic ring-opening copolymerization of THF with cyclic acid anhydrides by use of acylium perchlorate groups on carbon black as initiator.

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Accepted August 14, 1986