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CATIONIC GRAFTING FROM CARBON BLACK. X. GRAFT POLYMERIZATION INITIATED BY BENZYLIUM PERCHLORATE GROUPS INTRODUCED ONTO A CARBON BLACK SURFACE

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ABSTRACT

The cationic graft polymerization of various polymers from carbon black initiated by benzylium perchlorate groups introduced onto the surface was investigated. The introduction of benzylium perchlorate groups onto a carbon black surface was achieved by the reaction of silver perchlorate with benzyl chloride groups on the surface. Benzyl chloride groups were introduced by the treatment of carbon black with 3,3′-bischloromethylbenzoyl peroxide in carbon tetrachloride. It was found that the cationic polymerization of styrene is initiated by carbon black having benzylium perchlorate groups, and polystyrene is grafted from the surface based on the propagation of the polymer from the surface. The percentage of grafting increased to 130.1%. The weight-average molecular weight of grafted polystyrene was estimated to be 5.0×10^3. Furthermore, benzylium perchlorate groups on carbon black have an ability to initiate the cationic ring-opening polymerization of cyclic ethers, such as tetrahydrofuran and epichlorohydrin, and lactones, such as ε-caprolactone and δ-valerolactone, to give polyether- and polyester-grafted carbon black, respectively. These polymer-grafted carbon blacks gave a stable colloidal dispersion in good solvents for grafted polymer.

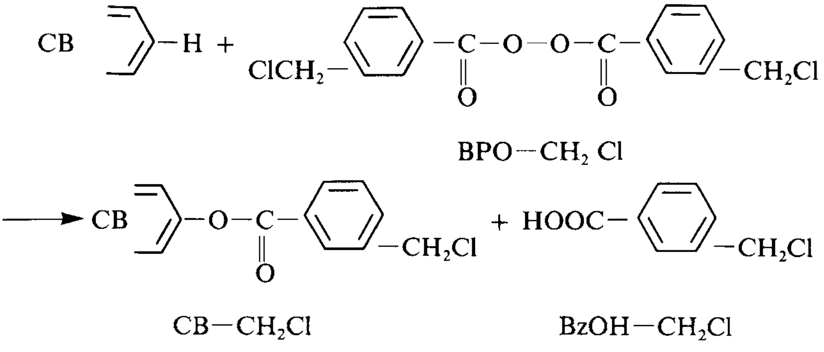
INTRODUCTION

In a previous paper we reported that carboxyl groups on carbon black surface have the ability to initiate the cationic polymerization of vinyl monomers and that a part of the polymer formed was grafted onto the surface based on the termination of a growing polymer cation with a carboxylate anion on the surface [1-3].

Furthermore, the introduction of acylium perchlorate groups onto the carbon black surface was successfully achieved by the reaction of silver perchlorate with acyl chloride groups on the surface, and they were introduced by the treatment of carboxyl groups with thionyl chloride [4-8]. The surface acylium perchlorate groups thus introduced onto carbon black have an ability to initiate the cationic polymerization of vinyl monomers [4] and the cationic ring-opening polymerization of lactones [5], cyclic ethers [6, 7], and cyclic acetals [8] to give polyether-, polyester-, and polyacetal-grafted carbon black, respectively. Polymer-grafted carbon blacks with a higher percentage of grafting were obtained in the polymerization because of the propagation of polymer from the surface acylium perchlorate groups.

However, the cationic grafting of polymers onto carbon black having no carboxyl groups, such as furnace black, was impossible. We have reported the introduction of functional groups, which can be used for grafting sites, onto carbon black having few functional groups. For instance, benzyl chloride groups were introduced onto carbon black, and the grafting of polyoxazolines onto the carbon black surface was successfully achieved by the ring-opening polymerization of 2-oxazolines initiated by benzyl chloride groups on the surface [9].

In the present paper, the introduction of benzylium perchlorate groups onto carbon black having few functional groups by the reaction of benzyl chloride groups with silver perchlorate (Eqs. 1 and 2) and the cationic graft polymerization of several monomers initiated by benzylium perchlorate groups were investigated. Furthermore, the stability of a polymer-grafted carbon black dispersion in an organic solvent was examined.



(1)

$$\text{CB—CH}_2\text{Cl} + \text{AgClO}_4 \rightarrow \text{CB—CH}_2^+\text{ClO}_4^- + \text{AgCl} \qquad (2)$$

EXPERIMENTAL

Materials

The carbon black used was furnace black Philblack O (Philips Petroleum Co., BET specific surface area, 79.6 m^2/g). It was extracted with benzene before use to remove the resinous substances on the surface. The content of phenolic hydroxyl, carboxyl, and quinonic oxygen groups on the surface was estimated to be 0.02, 0, and 0.18 mmol/g, respectively.

3,3′-Bischloromethylbenzoyl peroxide (BPO-CH_2Cl) was prepared by the reaction of 3-chloromethylbenzoyl chloride (Aldrich Chemical Co.) with hydrogen peroxide according to the method of Hass et al. [10].

Styrene was washed with aqueous alkali, dried over barium oxide, and distilled twice under reduced pressure. Tetrahydrofuran (THF) and epichlorohydrin (ECH) were refluxed over calcium hydride and distilled twice before use. ϵ-Caprolactone (CL), β-propiolactone (PL), and δ-valerolactone (VL) were dried over calcium hydride and distilled twice under reduced pressure.

Nitrobenzene was washed with dilute sulfuric acid, dried over calcium chloride, and distilled under reduced pressure. Carbon tetrachloride was dried over calcium chloride and distilled.

Guaranteed reagent grade silver perchlorate (Kojima Chemical Co., Japan) was dried *in vacuo* at 120°C before use. All other solvents and reagents were purified by general methods.

Introduction of Benzyl Chloride Groups onto Carbon Black

The introduction of benzyl chloride groups onto a carbon black surface was achieved by the reaction of carbon black with 3-chloromethylbenzoate radicals formed by the decomposition of BPO-CH_2Cl in carbon tetrachloride. The detailed procedures are described in a previous paper [9].

Introduction of Benzylium Perchlorate Groups onto Carbon Black

The introduction of benzylium perchlorate groups onto a carbon black surface, i.e., pretreatment, was carried out by the reaction of benzyl chloride groups with silver perchlorate in nitrobenzene. A typical example is as follows. Into a 100-cm^3 flask, 0.30 g of carbon black having benzyl chloride groups, 0.20 g of silver perchlorate, and 5.0 cm^3 of nitrobenzene were charged, and the reaction mixture was stirred with a magnetic stirrer under dry nitrogen at room temperature for 48 hours.

Graft Polymerization

After the above pretreatment, 10.0 cm^3 of monomer (styrene, CL, PL, or VL) was added to the mixture, and the polymerization was conducted with stirring at 30°C. After the reaction, the content of the flask was poured into an excess of methanol to precipitate ungrafted polymer and polymer-grafted carbon black.

When THF and ECH were used as monomer, the polymerization was carried out in bulk without pretreatment. A typical example is as follows. Into a 100-cm^3 flask, 0.30 g of carbon black and 0.20 g of silver perchlorate were charged. The polymerization was initiated by the addition of 10.0 cm^3 of monomer. After a given polymerization time, the polymerization was stopped by the addition of methanol, and the unreacted monomer was pumped off, yielding ungrafted polyether and polyether-grafted carbon black.

The conversion was calculated by the following equation:

$$\text{conversion}\ (\%) = \frac{A}{B} \times 100$$

where A: precipitate obtained (g) − carbon black charged (g)
B: monomer charged (g)

Percentage of Grafting

To separate the polymer-grafted carbon black from the reaction mixture containing 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 percentage of grafting was determined by the following equation:

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

Dispersibility of Polymer-Grafted Carbon Black

The stability of polymer-grafted carbon black dispersion in solvents, dispersibility, was estimated as follows [11]. Polymer-grafted carbon black (0.30 g) was dispersed in 100 cm^3 of THF with a magnetic stirrer, and the dispersion was allowed to stand at room temperature. After a given time, 5.0 cm^3 of dispersion liquid was removed with a pipet, and the content of dispersed carbon black was determined. The stability of dispersion was determined by the following equation:

$$\text{dispersibility}\ (\%) = \frac{A}{B} \times 100$$

where A: carbon black dispersed after standing (g)
B: carbon black dispersed before standing (g)

RESULTS AND DISCUSSION

Introduction of Benzyl Chloride Groups onto Carbon Black Surface

It is well known that polycondensed aromatic rings act as strong radical scavengers and that reactivity increases with increasing benzene nucleus [12, 13]. Therefore, carbon black and graphite have a higher reactivity to free radicals.

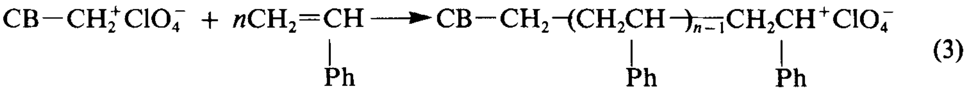
In a previous paper we reported that benzyl chloride groups can be introduced onto a carbon black surface by treatment of carbon black with BPO-CH_2Cl in carbon tetrachloride [9]. In the following experiment, carbon black having a benzyl chloride group content of 0.93 mmol/g was used.

Evidence for Initiation of Polymerization

Dreyfuss and Kennedy reported that the cationic polymerization of THF is initiated by organic halides, such as poly(vinyl chloride) and benzyl chloride, in the presence of silver triflate [14]. Therefore, it is expected that cationic polymerization will be initiated by carbon black having benzyl chloride groups (CB-CH_2Cl) when treated with silver perchlorate.

Therefore, the polymerization of styrene was carried out using CB-CH_2Cl and silver perchlorate under several conditions. The results in Table 1 show that styrene was not polymerized by silver perchlorate, untreated carbon black, or CB-CH_2Cl alone (Runs 1, 2, and 4). In addition, polymerization could not be detected even if untreated carbon black was pretreated with silver perchlorate (Run 3).

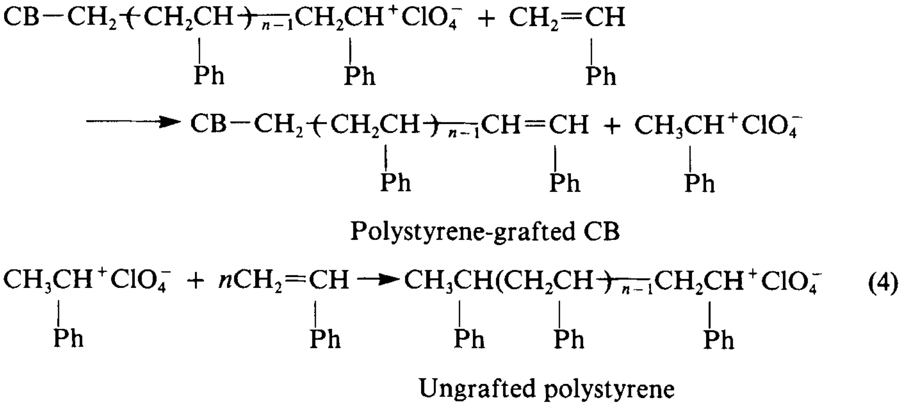
On the other hand, the polymerization of styrene was initiated by CB-CH_2Cl pretreated with silver perchlorate (Run 5) to give polystyrene-grafted carbon black. The results indicate that benzylium perchlorate groups formed by the reaction of CB-CH_2Cl with silver perchlorate (Eq. 2) initiates the polymerization and that grafted polymer chain propagates from the carbon black surface:



$$\mathrm{CB{-}CH_2^+ClO_4^-} + n\mathrm{CH_2{=}\underset{Ph}{CH}} \longrightarrow \mathrm{CB{-}CH_2{-}(CH_2\underset{Ph}{CH})_{\overline{n-1}}CH_2\underset{Ph}{CH}^+ClO_4^-} \qquad (3)$$

Figure 1 shows the relationship between reaction time and conversion and percentage of grafting in the polymerization of styrene initiated by benzylium perchlorate groups on carbon black. As shown in Fig. 1, the conversion of styrene increased with reaction time and reached about 80.7% after 3 hours. The percentage of grafting also increased with increasing conversion and reached 130.1% after 3 hours. In the cationic graft polymerization initiated by acylium perchlorate groups on carbon black, the percentage of polystyrene grafting was 30-40%. Therefore, it was found that polystyrene-grafted carbon black with a very high percentage of grafting can be obtained by the use of benzylium perchlorate groups on a carbon black surface.

On the other hand, the grafting efficiency (the proportion of grafted polystyrene to the total polymer formed) after 3 hours was determined to be 16%. This suggests that the formation of ungrafted polymer preferentially proceeds because of the chain transfer of growing polymer cation to the monomer:



$$\mathrm{CB{-}CH_2{-}(CH_2\underset{Ph}{CH})_{\overline{n-1}}CH_2\underset{Ph}{CH}^+ClO_4^-} + \mathrm{CH_2{=}\underset{Ph}{CH}}$$

$$\longrightarrow \mathrm{CB{-}CH_2{-}(CH_2\underset{Ph}{CH})_{\overline{n-1}}CH{=}\underset{Ph}{CH}} + \mathrm{CH_3\underset{Ph}{CH}^+ClO_4^-}$$

Polystyrene-grafted CB

$$\mathrm{CH_3\underset{Ph}{CH}^+ClO_4^-} + n\mathrm{CH_2{=}\underset{Ph}{CH}} \longrightarrow \mathrm{CH_3\underset{Ph}{CH}(CH_2\underset{Ph}{CH})_{\overline{n-1}}CH_2\underset{Ph}{CH}^+ClO_4^-} \qquad (4)$$

Ungrafted polystyrene

Molecular Weight of Grafted Polystyrene

The grafted polystyrene is bonded to the carbon black surface with an ester bond because benzyl chloride groups are bonded with an ester bond as shown in Eq. (1). Therefore, the grafted polystyrene was isolated from the carbon black surface by hydrolysis of the polystyrene-grafted carbon black.

TABLE 1. Polymerization of Styrene under Several Conditions[a]

Run no.	Carbon black	$AgClO_4$, g	Conversion, %	Grafting, %
1	None	0.20	0	–
2	Untreated	–	0	–
3	Untreated	0.20	0	–
4	CB-CH_2Cl	–	0	–
5	CB-CH_2Cl	0.20	80.7	130.1

[a] Pretreatment: CB, 0.30 g; nitrobenzene, 5.0 cm^3; room temperature; 48 hours. Polymerization: styrene, 10.0 cm^3; 30°C; 3 hours.

Polystyrene-grafted carbon black (the percentage of grafting was 130.1%) was treated with aqueous alkali to isolate the grafted polystyrene. The weight-average molecular weight was estimated to be 5.0×10^3 ($M_w/M_n = 2.31$) by GPC using polystyrene standards. This indicates that 0.26 mmol/g of polystyrene was grafted onto the carbon black surface, and about 30% of the benzylium perchlorate groups on carbon black were used as the grafting sites.

Ring-Opening Graft Polymerization of Cyclic Monomers

Figure 2 shows the results of the cationic ring-opening polymerization of THF initiated by benzylium perchlorate groups on carbon black. In the polymerization, epichlorohydrin (ECH) was used as a promoter because the rate of ring-opening polymerization of THF is very small in the absence of a promoter [15].

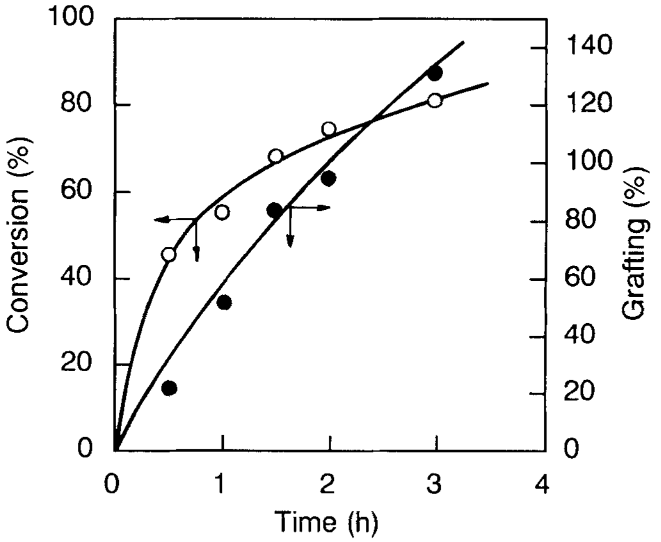


FIG. 1. Graft polymerization of styrene initiated by benzylium perchlorate groups on carbon black surface. Pretreatment: carbon black, 0.30 g; $AgClO_4$, 0.20 g; nitrobenzene, 5.0 cm^3; room temperature; 48 hours. Polymerization: styrene, 10.0 cm^3; 30°C.

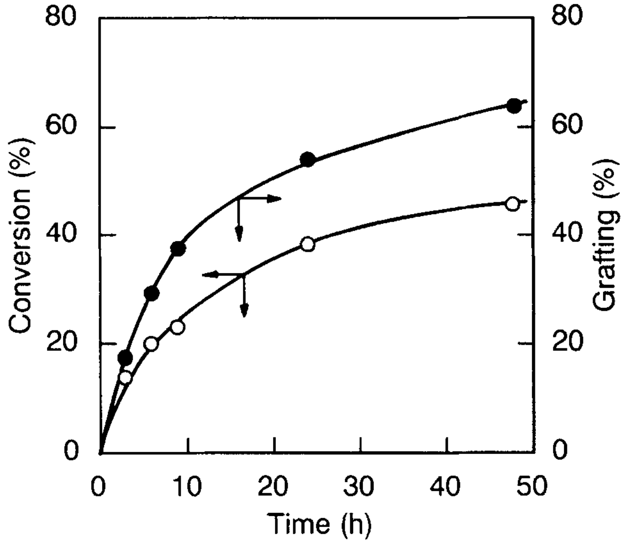


FIG. 2. Graft polymerization of THF initiated by benzylium perchlorate groups on carbon black surface. Carbon black, 0.30 g; $AgClO_4$, 0.20 g; THF, 10.0 cm^3; ECH, 1.0 cm^3; 30°C.

Figure 2 clearly shows that the cationic ring-opening polymerization is initiated by benzylium perchlorate groups on carbon black surface formed by the reaction of $CB\text{-}CH_2Cl$ with silver perchlorate *in situ*, and polyether, i.e., poly(THF), is effectively grafted from the carbon black surface.

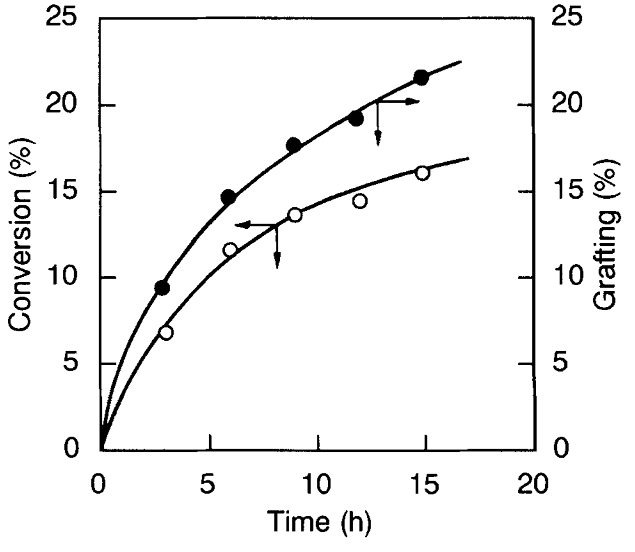


FIG. 3. Graft polymerization of CL initiated by benzylium perchlorate groups on carbon black surface. Polymerization conditions are given in Fig. 1.

TABLE 2. Ring-Opening Graft Polymerization of Cyclic Monomers Initiated by Benzylium Perchlorate Groups on Carbon Black[a]

Cyclic monomer	Promoter[b]	Temperature, °C	Time, h	Conversion, %	Grafting, %
THF	ECH	30	48	46.1	62.6
ECH	–	50	24	2.4	22.6
CL	–	30	15	15.8	21.3
PL	–	30	12	7.9	64.3
VL	–	30	12	11.1	76.4

[a] Polymerization conditions are given in Table 1.
[b] 1.0 cm^3.

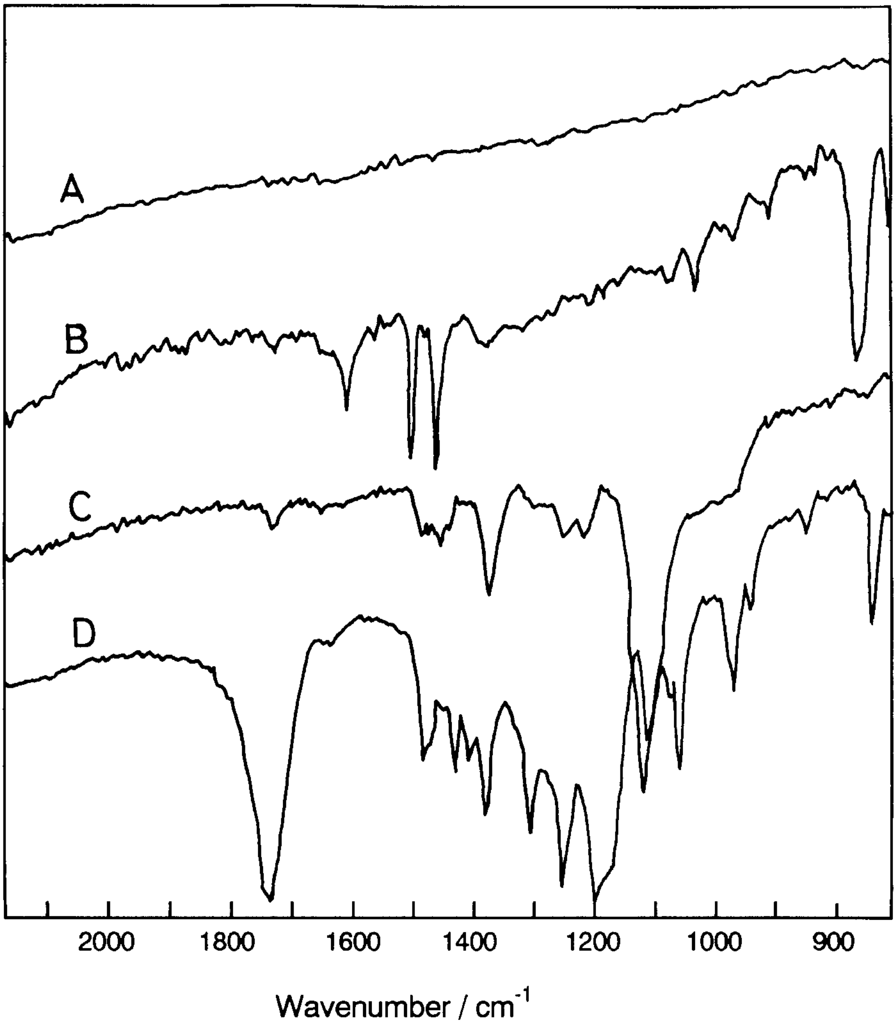


FIG. 4. Infrared spectra of (A) untreated, (B) polystyrene-grafted, (C) poly(THF)-grafted, and (D) poly(CL)-grafted carbon black.

The cationic ring-opening polymerization of CL initiated by benzylium perchlorate groups on carbon black was also examined. The results are shown in Fig. 3. It was found that the ring-opening polymerization of CL is also initiated by benzylium perchlorate groups on the carbon black surface to give poly(CL)-grafted carbon black.

The ring-opening graft polymerization of several cyclic monomers, such as ECH, CL, PL, and VL, are summarized in Table 2. Table 2 shows that benzylium perchlorate groups introduced onto a carbon black surface have the ability to initiate the cationic ring-opening polymerization of various cyclic monomers to give the corresponding polymer-grafted carbon black.

Characterization of Polymer-Grafted Carbon Black

Figure 4 shows the infrared spectra of untreated, polystyrene-grafted, poly(THF)-grafted, and poly(CL)-grafted carbon black. As shown in Fig. 4, the infrared spectra of polystyrene-grafted carbon black exhibits absorptions at 1604, 1498, 1456, and 700 cm^{-1}, which is characteristic of polystyrene. On the other hand, the infrared spectra of poly(THF)-grafted and poly(CL)-grafted carbon black exhibit absorptions characteristic of poly(THF) and poly(CL), respectively. These results indicate that polystyrene, poly(THF), and poly(CL) are grafted onto a carbon black surface by cationic polymerization of the corresponding monomers initiated by benzylium perchlorate groups.

In general, by the grafting of polymers onto a carbon black surface, the dispersibility of carbon black was remarkably improved. The dispersibility of polystyrene-, poly(THF)-, and poly(CL)-grafted carbon black was compared with untreated carbon black. The results are shown in Fig. 5.

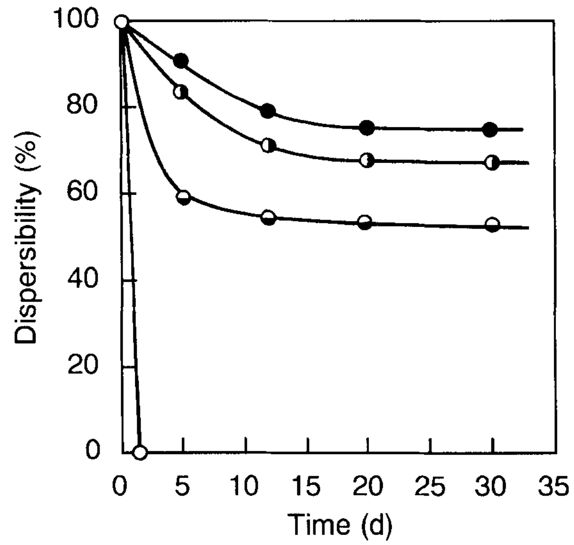


FIG. 5. Stability of dispersion of polymer-grafted carbon black in THF at room temperature: (○) untreated, (◑) polystyrene-grafted, (◒) poly(THF)-grafted, and (●) poly(CL)-grafted.

It was found that although untreated carbon black precipitated immediately, polymer-grafted carbon blacks gave stable colloidal dispersions in organic solvents. This indicates that grafted polymer chains on the surface interfere with the aggregation of carbon black particles.

CONCLUSIONS

1. Benzylium perchlorate groups were successfully introduced onto a carbon black surface by the reaction of benzyl chloride groups on carbon black with silver perchlorate.
2. Benzylium perchlorate groups on carbon black were capable of initiating the cationic polymerization of styrene and the cationic ring-opening polymerization of cyclic ethers and lactones to give the corresponding polymer-grafted carbon black.
3. Polymer-grafted carbon blacks gave stable colloidal dispersions in organic solvents.

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