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CATIONIC GRAFTING FROM CARBON BLACK. IX. CATIONIC RING-OPENING POLYMERIZATION AND COPOLYMERIZATION OF 3,3-BIS-(CHLOROMETHYL)OXETANE INITIATED BY ACYLIUM PERCHLORATE GROUPS ON CARBON BLACK

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ABSTRACT

The cationic ring-opening polymerization of 3,3-bis(chloromethyl)-oxetane (BCMO) was found to initiate by acylium perchlorate groups on carbon black, introduced by the reaction of acyl chloride groups with silver perchlorate. It was confirmed that poly-BCMO propagated from carbon black and effectively grafted from the surface. The percentage of grafting of poly-BCMO increased with increasing conversion and reached about 50%. The grafting efficiency, however, decreased with the extent of polymerization. This suggests that ungrafted polymer formed by chain transfer at higher conversion. The activation energy of the polymerization was estimated to be 28.5 kJ/mol. Furthermore, acylium perchlorate groups on carbon black are able to initiate the copolymerization of BCMO with tetrahydrofuran (THF). Poly-(BCMO-*co*-THF)s of various compositions were grafted from the surface; depending on the propagation of the copolymer, the percentage of grafting was as high as about 40%. The poly-BCMO-grafted and poly(BCMO-*co*-THF)-grafted carbon black gave stable colloidal dispersions in organic solvents.

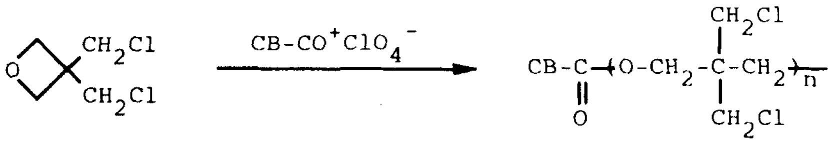
INTRODUCTION

In this series of papers we have reported on the use of carbon blacks containing acylium perchlorate groups, which were introduced by the reaction of acyl chlorides with silver perchlorate, for the cationic graft polymerization of styrene [1], lactones [2], cyclic formals [3], and cyclic ethers [4, 5]. Furthermore, the acylium perchlorate groups were able to initiate the cationic ring-opening copolymerization of tetrahydrofuran (THF) with cyclic acid anhydrides [6] and the cationic ring-opening terpolymerization of THF-chloromethyloxirane-cyclic acid anhydrides [7]. In these systems, polymers were grafted from the carbon black surface.

3,3-Bis(chloromethyl)oxetane (BCMO) undergoes cationic ring-opening polymerization to give polyethers with chloromethyl groups [8-11]. Poly-BCMO is a well-known engineering plastic. The polymer has high resistance to acid and alkali, solvent, and heat.

In the present paper the cationic ring-opening polymerization of BCMO initiated by acylium perchlorate groups on carbon black and the grafting of poly-BCMO from the surface were investigated to improve the miscibility of carbon black (CB) and poly-BCMO. Furthermore, the grafting of BCMO/THF copolymer by the ring-opening copolymerization of BCMO with THF initiated by acylium perchlorate groups was examined to improve the dispersibility of BCMO-grafted carbon black.

$$\text{CB-COOH} \xrightarrow{\text{SOCl}_2} \text{CB-COCl} \xrightarrow{\text{AgClO}_4} \text{CB-CO}^+\text{ClO}_4^- \quad (1)$$



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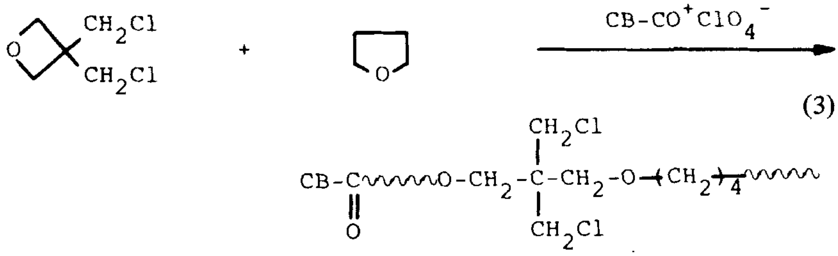

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EXPERIMENTAL

Materials

The carbon blacks used were channel blacks Neospectra II (Columbian Carbon Co.; BET specific surface area, 906 m^2/g) and FW 200 (Degussa A.G.; 460 m^2/g), and furnace black Philblack O (Philips Petroleum Co.; 79.6 m^2/g). The carboxyl contents of Neospectra II, FW 200, and Philblack O, determined by the method of Rivin [12], were 0.40, 0.61, and 0 meq/g, respectively. The carbon blacks were dried *in vacuo* at 110°C before use.

BCMO was prepared by ring-closure of trichlorohydrin of pentaerythritol with potassium hydroxide according to Kambara and Hatano [9], purified by refluxing over calcium hydride, and distilled under reduced pressure. THF was refluxed over calcium hydride and distilled before use. Guaranteed-reagent-grade silver perchlorate (Kojima Chemical Co. Ltd., Japan) was dried *in vacuo* at 130°C before use. All other reagents and solvents were used after ordinary purification.

Introduction of Acylium Perchlorate Groups onto Carbon Black

The introduction of acylium perchlorate groups onto carbon black, i.e., the pretreatment, was carried out by the reaction of acyl chloride on carbon black with silver perchlorate in nitrobenzene according to the previously reported method [1]. The content of acylium perchlorate groups introduced onto Neospectra II and FW 200 was determined to be 0.37 and 0.41 meq/g, respectively [6].

Polymerization Procedure

After the pretreatment, without isolation of the carbon black with the acylium perchlorate groups, 10 mmol of BCMO was added to a flask that contained the pretreated carbon black, and the polymerization was conducted with stirring under nitrogen. After the reaction the product was poured into a large excess of methanol to precipitate the polymer-containing carbon black. The conversion was calculated by

$$\text{conversion (\%)} = \frac{\text{precipitate (g)} - \text{carbon black (g)}}{\text{monomer used (g)}} \times 100. \tag{4}$$

Percentage of Grafting and Grafting Efficiency

To separate polymer-grafted carbon black from the reaction product, it was Soxhlet extracted with cyclohexanone. The extracting solvent for the copolymer of BCMO and THF was chloroform. The percentage of grafting and grafting efficiency were determined by

$$\text{percentage of grafting} = \frac{\text{polymer grafted (g)}}{\text{carbon black used (g)}} \times 100 \tag{5}$$

$$\text{grafting efficiency (\%)} = \frac{\text{polymer grafted (g)}}{\text{total polymer formed (g)}} \times 100. \tag{6}$$

Stability of Dispersion of Polymer-Grafted Carbon Black

Polymer-grafted carbon black (0.30 g) was dispersed in 100 mL cyclohexanone or chloroform with a magnetic stirrer, and the dispersion was allowed to stand at room temperature. After a given time, 5.0 mL dispersion liquid was removed with a pipet, and the content of dispersed carbon black was determined. The stability of dispersion was determined by

$$\text{stability of dispersion (\%)} = \frac{\text{carbon black dispersed after standing (g)}}{\text{carbon black dispersed before standing (g)}} \times 100. \tag{7}$$

RESULTS AND DISCUSSION

Evidence of Initiation by Acylium Perchlorate Groups

The cationic ring-opening polymerization of BCMO is initiated by cationic catalyst to give polyether [8-11]. We have found that acylium perchlorate groups on carbon black are able to initiate the cationic ring-opening polymerization of three-, five-, and seven-membered cyclic ethers [4-7]. Therefore, the ring-opening polymerization of BCMO was carried out with carbon-black carrying acyl chloride groups and silver perchlorate under various conditions. The data in Table 1 show that acylium perchlorate groups introduced onto carbon black initiate the polymerization of BCMO.

TABLE 1. Ring-Opening Polymerization of BCMO Initiated by Acylium Perchlorate Groups on Carbon Black[a]

Carbon black	$AgClO_4$, g	Conversion, %
None	0.20	0
Untreated Neospectra II	–	0
Untreated Neospectra II	0.20	0
Neospectra II-COCl	–	0
Neospectra II-COCl	0.20	21.3

[a] Pretreatment: Neospectra II, 0.30 g; nitrobenzene, 3.0 mL; room temperature; 2 h. Polymerization: BCMO, 10 mmol; 90°C; 3 d.

Initiation by Various Kinds of Carbon Black Carrying Acylium Perchlorate Groups

The relationship between the initiating ability and the acylium perchlorate group content of various kinds of carbon blacks was examined. As shown by the data in Table 2, the initiating ability of these carbon blacks decreased with decreasing content of acylium perchlorate groups. Philblack O, which has no carboxyl groups, failed to initiate even after it was treated with thionyl chloride and silver perchlorate. Evidently, the polymerization of BCMO is initiated by acylium perchlorate groups previously introduced onto carbon black surfaces.

TABLE 2. Ring-Opening Polymerization of BCMO Initiated by Acylium Perchlorate Groups on Various Carbon Blacks[a]

Carbon black	Acylium perchlorate group, meq/g	Conversion, %
FW 200	0.41	25.2
Neospectra II	0.37	21.3
Philblack O	Trace	Trace

[a] Pretreatment: Carbon black-COCl, 0.30 g; $AgClO_4$, 0.20 g; nitrobenzene, 3.0 mL; room temperature; 2 h. Polymerization: BCMO, 10 mmol; 90°C; 3 d.

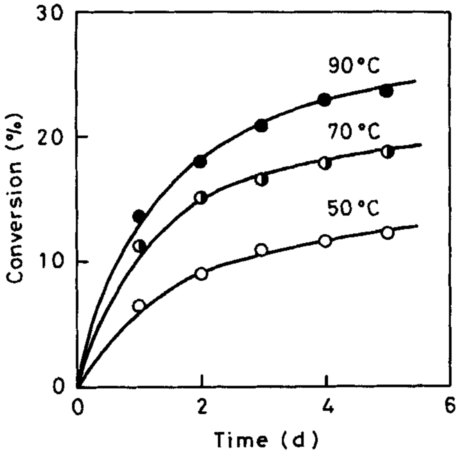


FIG. 1. Ring-opening polymerization of BCMO initiated by acylium perchlorate groups on carbon black. Pretreatment: Neospectra II, 0.30 g; $AgClO_4$, 0.20 g; nitrobenzene, 3.0 mL; room temperature; 2 h. Polymerization: BCMO, 10 mmol.

Effect of Temperature on Polymerization

As shown in Fig. 1, the rate of polymerization was found to increase with rising temperature. The Arrhenius plot for these data gave a straight line, and the apparent activation energy for the polymerization was 28.5 kJ/mol. This value is similar to that of the ring-opening polymerization of THF or oxepane with chloromethyloxirane promoter [4, 5].

Proof of Grafting from Carbon Black

As shown in Fig. 2, the percentage of grafting increased with increasing conversion. The effect of temperature on grafting, however, is negligible in the range from 50 to 90°C. It is apparent from Fig. 2 that to obtain poly-BCMO-grafted carbon black with a higher percentage of grafting, the polymerization should be extended to higher conversion. In contrast, grafting efficiency decreased with increasing conversion, as shown in Fig. 3.

Based on the above results, it is concluded that grafting proceeds from acylium perchlorate groups on the carbon black surfaces (Eq. 8) and that

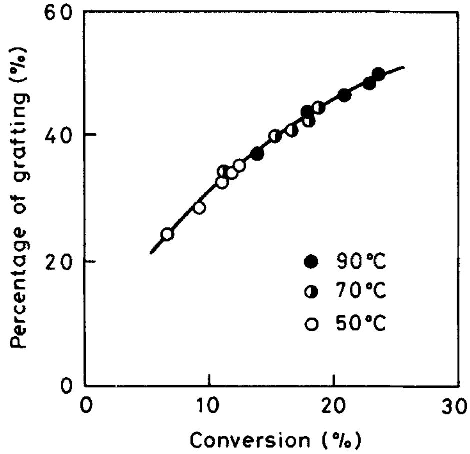


FIG. 2. Relationship between conversion and percentage of grafting of poly-BCMO.

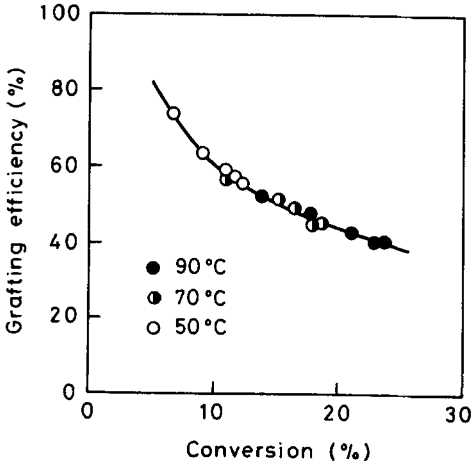
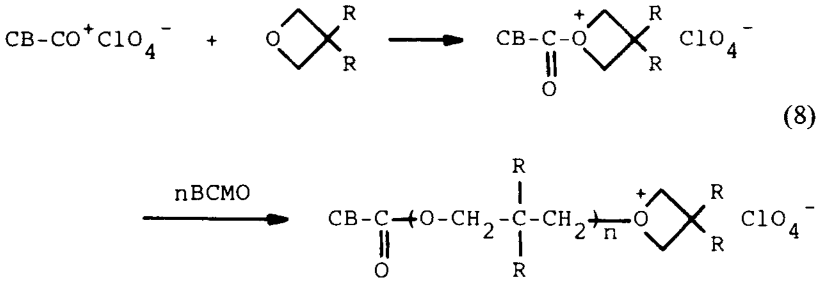


FIG. 3. Relationship between conversion and grafting efficiency.

ungrafted polymer is gradually formed by chain transfer with contaminants, such as traces of water (Eq. 9).



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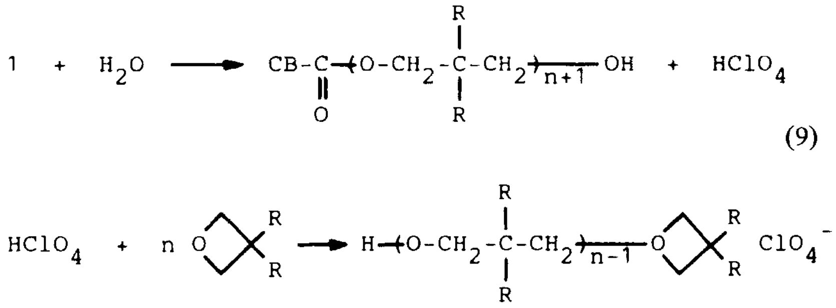

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Copolymerization of BCMO with THF

The cationic ring-opening copolymerization of BCMO with THF is initiated by cationic catalysts such as triethylaluminum and boron trifluoride etherate [13-15]. Therefore, to improve the solubility of poly-BCMO-grafted carbon black, the copolymerization of BCMO with THF initiated by acylium perchlorate groups was carried out, and the grafting of the copolymer onto carbon black was investigated.

Table 3 shows that the copolymerization of BCMO with THF is initiated by acylium perchlorate groups. Ungrafted polymer obtained from the copolymerization was identified by IR and NMR spectra as a copolymer of BCMO and THF. The mole ratio of THF in the copolymer was almost equal to that of the monomer charged (see Table 3). Saegusa et al. reported that the reactivity ratios for copolymerization of BCMO with THF vary with the nature of the catalyst [14]. The reactivity ratios for copolymerization initiated by acylium

TABLE 3. Ring-Opening Copolymerization of BCMO with THF Initiated by Acylium Perchlorate Groups on Carbon Black[a]

Monomer charged		Conversion,	Mole ratio in polymer		Percentage of
BCMO	THF	%	BCMO	THF	grafting, %
0.70	0.30	7.4	0.77	0.23	41.8
0.50	0.50	7.5	0.47	0.53	35.9
0.30	0.70	7.8	0.18	0.82	40.1

[a]Pretreatment conditions as in Table 1. Polymerization: BCMO + THF = 20 mmol; 50°C; 5 d.

perchlorate groups were found to be analogous to those initiated by boron trifluoride etherate. Accordingly, it is concluded that BCMO/THF copolymers of various compositions can be grafted from carbon black surfaces by acylium perchlorate groups.

Stability of Dispersion of Polymer-Grafted Carbon Black

As Fig. 4 shows, BCMO-grafted carbon black gave a stable dispersion in cyclohexanone, but it immediately precipitated from chloroform. This may be due to the fact that chloroform is a poor solvent for poly-BCMO.

Poly-BCMO-grafted carbon black was also found to have good miscibility in cyclohexanone solutions of poly-BCMO.

Figure 5 shows the stability of dispersion of poly(BCMO-*co*-THF)-grafted carbon black. Ungrafted carbon black precipitated completely after 10 h. In contrast, poly(BCMO-*co*-THF)-grafted carbon black gave a stable dispersion even in chloroform because poly(BCMO-*co*-THF) is soluble in chloroform. Increasing the THF content of the copolymer was found to increase its stability of dispersion in chloroform. Evidently, the stability of dispersion of carbon black in organic solvents can be improved by grafting polymers onto it.

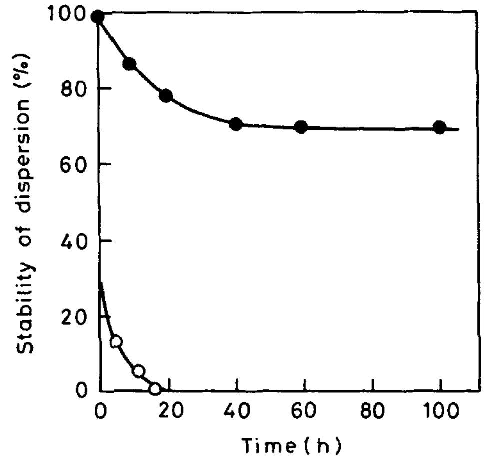

FIG. 4. Effect of solvent on the stability of dispersion of poly-BCMO-grafted carbon black. (○) In chloroform; (●) in cyclohexanone.

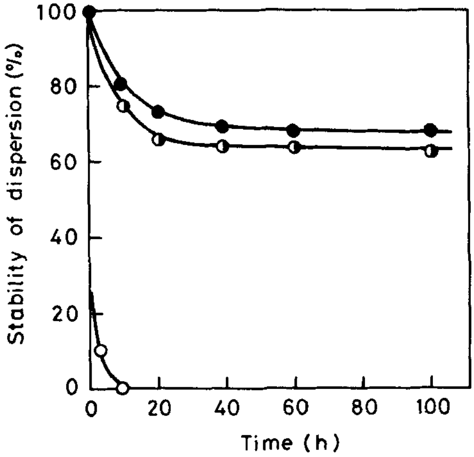

FIG. 5. Stability of dispersion of poly(BCMO-*co*-THF)-grafted carbon black in chloroform. (○) Ungrafted; (●) copolymer (BCMO/THF = 0.18/0.82)-grafted; (◑) copolymer (BCMO/THF = 0.77/0.23)-grafted.

REFERENCES

[1] N. Tsubokawa, *J. Polym. Sci., Polym. Chem. Ed., 22,* 1515 (1984).
[2] N. Tsubokawa, *J. Appl. Polym. Sci., 30,* 2041 (1985).
[3] N. Tsubokawa, *J. Polym. Sci., Polym. Chem. Ed., 25,* 1979 (1987).
[4] N. Tsubokawa, H. Nunokawa, and Y. Sone, *J. Macromol. Sci.–Chem., A23,* 105 (1986).
[5] N. Tsubokawa, Yu Jian, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed., 26,* 2715 (1988).
[6] N. Tsubokawa, Yu Jian, and Y. Sone, *Polym. Bull., 16,* 249 (1986).
[7] N. Tsubokawa, Yu Jian, and Y. Sone, *Polym. J., 19,* 221 (1987).
[8] A. C. Farthing and R. J. W. Reynolds, *J. Polym. Sci., 12,* 503 (1954).
[9] S. Kambara and M. Hatano, *Kogyo Kagaku Zassi, 59,* 77 (1956).
[10] T. Saegusa, H. Imai, S. Hirai, and J. Furukawa, *Makromol. Chem., 53,* 203 (1962).
[11] I. Penczek and S. Penczek, *Ibid., 67,* 203 (1963).
[12] D. Rivin, *Rubber Chem. Technol., 36,* 729 (1963).
[13] T. Saegusa, H. Imai, and J. Furukawa, *Makromol. Chem., 56,* 55 (1962).
[14] T. Saegusa, T. Ueshima, H. Imai, and J. Furukawa, *Ibid., 79,* 221 (1964).
[15] I. Penczek and S. Penczek, *J. Polym. Sci., Part B, 5,* 367 (1961).

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