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Ring-opening polymerization of 2-oxazolines initiated by chloromethyl groups introduced onto carbon black surface

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SUMMARY

The ring-opening polymerization of 2-oxazolines (OXZs) was found to be initiated by chloromethyl groups introduced onto carbon black surface. The introduction of chloromethyl groups onto the surface was achieved by the reaction of carbon black with 3,3'-bischloromethylbenzoyl peroxide in carbon tetrachloride. During the polymerization, poly-OXZs were grafted from carbon black based on the propagation of the polymers from the surface: percentage of grafting increased with an increase of conversion and reached 40-60%. The polymerization was accelerated by the addition of potassium iodide. Poly-OXZ-grafted carbon black produced stable colloidal dispersions in both hydrophobic and hydrophilic solvents.

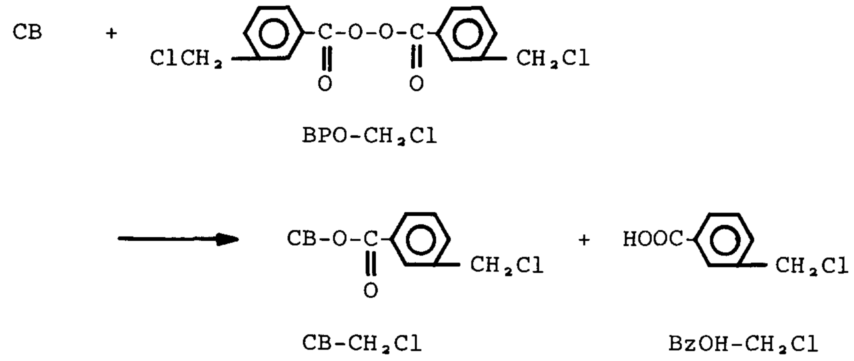
INTRODUCTION

It has been reported that 2-oxazolines (OXZs) are polymerized by methyl iodide (1,2) and benzyl chloride (3). Furthermore, Saegusa et al. reported the graft polymerization of 2-methyl-2-oxazoline onto chloromethylated polystyrene (4).

On the other hand, we demonstrated that the ring-opening polymerization of OXZs is initiated by carboxyl groups on the surface of channel black (5). During the polymerization, poly-OXZs were grafted onto the surface based on the termination reaction of growing polymer chain. Poly-OXZ-grafted carbon black thus obtained produced stable colloidal dispersions in both hydrophobic and hydrophilic solvents. Furnace black, which has no carboxyl groups, however, failed to initiate the polymerization.

As described in the review paper (6), to obtain polymer-grafted carbon black with a higher percentage of grafting, it is necessary to initiate the graft polymerization from initiating groups introduced onto the surface.

In the present paper, to obtain amphiphilic polymer-grafted furnace black with a higher percentage of grafting, the introduction of chloromethyl groups onto the surface (Eq. 1) and the graft polymerization of OXZs initiated by the chloromethyl groups (Eq. 2) were investigated. Furthermore, the stability of dispersion of poly-OXZ-grafted carbon black in various solvents was examined.



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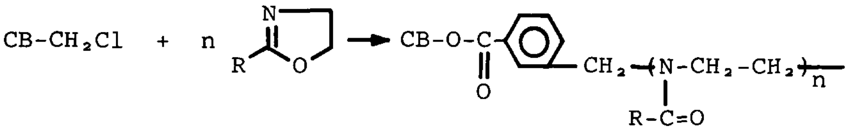

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EXPERIMENTAL

Materials

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 group on the surface was determined to be 0.02, 0, 0.18 mmol/g, respectively.

2-Methyl-2-oxazoline (MeOXZ) and 2-ethyl-2-oxazoline (EtOXZ) obtained from Aldrich Chemical Co. were dried over calcium hydride and fractionally distilled twice before use.

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. (7).

Guaranteed reagent grade potassium iodide was used without further purification.

All other solvent and reagents were used after ordinary purification.

Introduction of Chloromethyl Groups onto Carbon Black Surface

The introduction of chloromethyl groups onto carbon black was achieved by the reaction of carbon black with 3-chloromethylbenzoate radicals formed by the decomposition of BPO-CH_2Cl.

A typical example was as follows. Into a 300 ml flask that contained 3.0 g of carbon black and 50 ml of carbon tetrachloride, 3.0 g of BPO-CH_2Cl was added. The reaction was conducted with stirring under nitrogen at 50°C. After the reaction for 50 h, resulting carbon black was extracted with acetone and dried in vacuo.

The amount of chloromethyl groups introduced onto the surface was estimated by elemental (chlorine) analysis.

Polymerization Procedures

Into a polymerization tube, 0.30 g of carbon black, 0.20 mol of OXZ, 0.20 mmol of potassium iodide, and a stirrer bar were charged. The tube was cooled in a dry ice/acetone bath, thawed three times under nitrogen, and sealed under vacuum. The polymerization was conducted in a oil bath under stirring with a magnetic stirrer. After the reaction, the polymerization was brought to a stop by cooling of the tube and unreacted monomer was then pumped off at 40°C. The conversion was calculated by the following equation.

$$\text{Conversion (\%)} = \frac{\text{Product (g)} - \text{Carbon black (g)}}{\text{Monomer charged (g)}} \times 100$$

Percentage of Grafting

To isolate the poly-OXZ-grafted carbon black from reaction product, the product was dispersed in methanol and the dispersion was centrifuged at 1.2×10^4 rpm: carbon black dispersed was completely precipitated after 1 h. The carbon black precipitated was extracted with methanol using a Soxhlet apparatus to remove ungrafted polymer on the surface. The percentage of grafting was calculated by the following equation.

$$\text{Percentage of grafting (\%)} = \frac{\text{Polymer grafted (g)}}{\text{Carbon black used (g)}} \times 100$$

Stability of Dispersion of Poly-OXZ-Grafted Carbon Black

Poly-OXZ-grafted carbon black (0.30 g) was dispersed in 100 ml of solvent and the dispersion was allowed to stand at room temperature. After a definite time, 5.0 ml of dispersion liquid was taken out with a pipet and the content of carbon black dispersed was determined. The stability of dispersion was estimated by the content of carbon black in dispersion.

$$\begin{array}{l}\text{Content of carbon black}\\ \text{in dispersion}\end{array} (\%) = \frac{\begin{array}{l}\text{Carbon black dispersed}\\ \text{after standing} \quad \text{(g)}\end{array}}{\begin{array}{l}\text{Carbon black dispersed}\\ \text{before standing} \quad \text{(g)}\end{array}} \times 100$$

RESULTS AND DISCUSSION

Introduction of Chloromethyl Groups onto Carbon Black Surface

It is known that polycyclic aromatic compounds act as a radical scavenger and the reactivity increases with an increase of the number of benzene nucleus (8,9). Therefore, carbon black and graphite, which are consisting of polycondensed aromatic rings, have high reactivity to free radicals.

For instance, Donnet et al. reported that by the reaction of 2,2'-azobisisobutyronitrile (AIBN) with carbon black, 2-cyano-2-propyl radicals are fixed onto the surface (10). Furthermore, it was demonstrated that by the reaction of carbon black with benzoyl peroxide (11) or 2,2'-azobis(2,4-dimethylvaleronitrile) (12), the corresponding radicals are fixed onto benzonoidal rings and oxygen containing groups present on carbon black surface.

Therefore, the introduction of chloromethyl groups onto carbon black surface by the treatment of carbon black with BPO-CH_2Cl was examined.

Carbon black Philblack O was treated with large excess of BPO-CH_2Cl in carbon tetrachloride at 50°C. After the treatment, unreacted BPO-CH_2Cl and by-product (BzOH-CH_2Cl), which formed by hydrogen abstraction from carbon black (11), were removed by extraction with acetone.

Thus treated carbon black gave a positive Beilstein test. The content of chlorine of the treated carbon black determined by elemental analysis was 0.42%. The result indicates that 0.12 mmol of chloromethyl groups is introduced on to the surface. This value is almost equal to that of 2-cyano-2-propyl radicals fixed onto carbon black by the treatment with AIBN (10,12).

Polymerization of OXZ initiated by CB-CH_2Cl

The polymerization of MeOXZ in the presence of untreated carbon black and carbon black treated with BPO-CH_2Cl was carried out at 120°C. The results are shown in Table I.

As shown in Table I, no polymerization was observed in the absence and presence of untreated carbon black. On the contrary, in the presence of carbon black treated with BPO-CH_2Cl, the ring-opening polymerizations of MeOXZ and EtOXZ were initiated to give the corresponding poly-OXZ. These results indicates that chloromethyl groups introduced onto carbon black have an ability to initiate the ring-opening polymerization of MeOXZ and EtOXZ.

To evaluate the initiation by adsorbed BzOH-CH_2Cl, which formed during the treatment of carbon black with BPO-CH_2Cl (Eq. 1), the initiating ability of BzOH-CH_2Cl-adsorbed carbon

TABLE I
Ring-Opening Polymerization of OXZs Initiated by Several Treated Carbon Blacks

Carbon black	Monomer	Conversion (%)
None	MeOXZ	0
Untreated	MeOXZ	0
Untreated	EtOXZ	0
BzOH-CH_2Cl adsorbed	MeOXZ	0
BPO-CH_2Cl treated	MeOXZ	18.9
BPO-CH_2Cl treated	EtOXZ	12.6

Carbon black, 0.30 g; OXZ, 0.20 mol; 120°C; 24 h.

black for the polymerization was examined. BzOH-CH_2Cl-adsorbed carbon black was prepared by the mixing of carbon black (1.0 g) with BzOH-CH_2Cl (1,0 g) in carbon tetrachloride (50 ml) at 50°C. After 50 h, the carbon black was extracted with acetone using a Soxhlet apparatus and dried in vacuo. Thus treated carbon black failed to initiate the polymerization. This indicates that the participation of adsorbed BzOH-CH_2Cl on the surface in the initiation is negligible.

Figure 1 shows the relationship between conversion and reaction time for the polymerization of MeOXZ initiated by CB-CH_2Cl at 85 and 120°C. The rate of the polymerization was found to increase with increasing temperature.

Figure 2 shows the relationship between conversion and percentage of grafting of poly-MeOXZ onto carbon black obtained from the polymerization shown in Figure 1 (at 120°C). It is apparent that during the polymerization, poly-MeOXZ is grafted

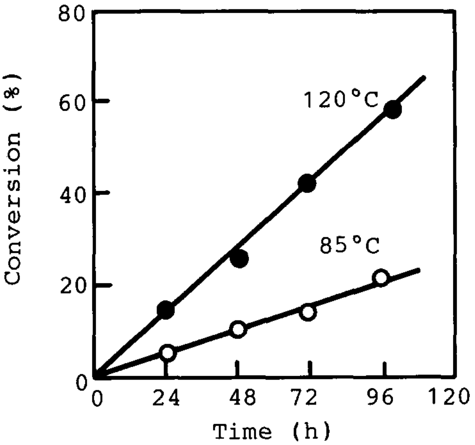


Figure. 1 Ring-opening polymerization of MeOXZ initiated by chloromethyl groups introduced onto carbon black surface.

CB-CH_2Cl, 0.30 g; MeOXZ, 0.20 mol.

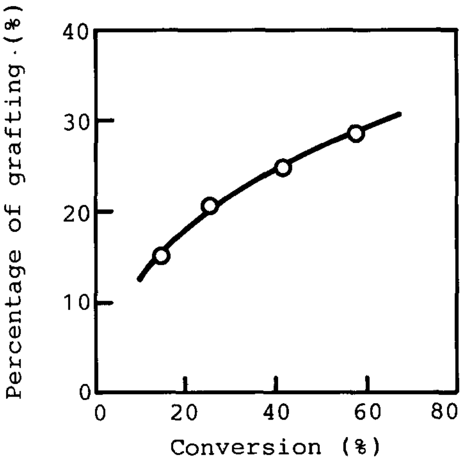
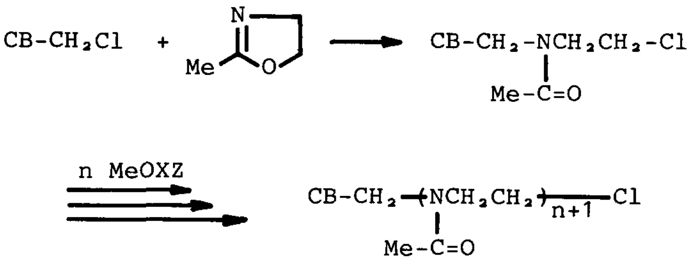


Figure 2. Relationship between percentage of grafting of poly-MeOXZ and conversion at 120°C.

Polymerization conditions are given in Figure 1.

onto carbon black surface and the percentage of grafting increased with an increase in conversion.

The percentage of grafting in the polymerization initiated by CB-CH_2Cl was higher than that obtained from the polymerization initiated by carboxyl groups on channel black surface (5). This may be due to that in the polymerization initiated by CB-CH_2Cl, poly-MeOXZ was propagated from the surface as shown in Eq. 3 (2-4). The formation of ungrafted polymer during the polymerization is probably due to the chain transfer reaction (4,13).



(3)

Based on the above results, it is concluded that the ring-opening polymerization of OXZs is initiated by chloromethyl groups introduced onto carbon black surface and poly-OXZs are effectively grafted from the surface.

Effect of Potassium Iodide on the Polymerization

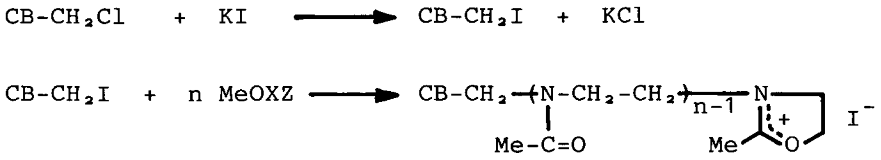
It has been reported that the polymerization of MeOXZ initiated by chloromethylated polystyrene was accelerated by the addition of potassium iodide (4). Therefore, the effect of potassium iodide on the polymerization of MeOXZ initiated by CB-CH_2Cl was investigated. The results are shown in Table II. Table II clearly shows that the rate of the polymerization and percentage of grafting increase by the addition of potassium iodide to the polymerization system. Saegusa et al. has reported that by the addition of potassium iodide, an exchange reaction of chloride with iodide took place between CB-CH_2Cl

TABLE II
Effect of Potassium Iodide on the Polymerization of MeOXZ Initiated by Chloromethyl Groups on Carbon Black Surface

KI (mmol)	Temperature (°C)	Time (h)	Conversion (%)	Percentage of grafting (%)
0	85	48	10.1	15.5
0.20	85	24	42.9	30.6
0.20	85	48	57.0	48.9
0	120	48	25.6	27.1
0.20	120	24	70.0	58.4

CB-CH_2Cl, 0.30 g; MeOXZ, 0.20 mol.

and potassium iodide (Eq. 4) and/or between alkyl chloride propagating end and potassium iodide.



$$\mathrm{CB{-}CH_2Cl} + \mathrm{KI} \longrightarrow \mathrm{CB{-}CH_2I} + \mathrm{KCl}$$

$$\mathrm{CB{-}CH_2I} + n\,\mathrm{MeOXZ} \longrightarrow \mathrm{CB{-}CH_2{-}}\!\left(\underset{\mathrm{Me{-}C{=}O}}{\mathrm{N}}\mathrm{{-}CH_2{-}CH_2}\right)_{n-1}\!\!\mathrm{{-}N^{+}}\!\!\overset{}{\underset{\mathrm{Me}}{\langle}}\!\mathrm{O}\quad \mathrm{I^-} \qquad (4)$$

Dispersibility of Poly-OXZ-Grafted Carbon Black

The stability of dispersion of poly-MeOXZ-grafted carbon black in organic solvents was compared with that of untreated one. The results are shown in Figure 3.

As shown in Figure 3, untreated carbon black completely precipitated after 1 d. On the contrary, poly-OXZ-grafted carbon black was found to produce stable colloidal dispersions in both methanol and benzene. This suggests that poly-MeOXZ chains grafted onto the surface interfere with the aggregation of carbon black in both hydrophobic and hydrophilic solvents. Accordingly, the dispersibility of carbon black in organic solvents were remarkably improved by grafting of poly-OXZ onto the surface.

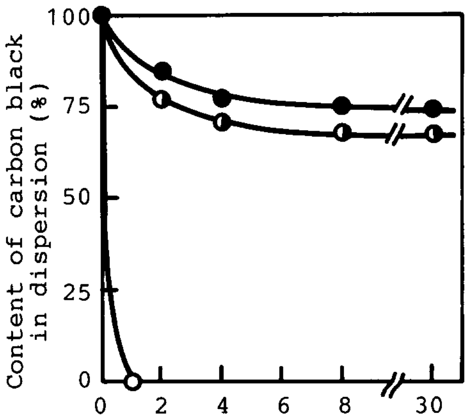


Figure 3. Stability of dispersion of poly-MeOXZ-grafted carbon black (percentage of grafting=58.4%) at room temperature.

○ : Untreated; in benzene.
◐ : Poly-MeOXZ-grafted; in methanol.
● : Poly-MeOXZ-grafted; in benzene

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