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Cationic ring-opening polymerization of 2-substituted-2-oxazolines initiated by carbon black surface

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SUMMARY

Carbon blacks were found capable of initiating the ring-opening polymerization of 2-substituted-2-oxazolines at relativery high temperatures. The activation energy of the polymerization of 2-methyl-2-oxazoline was estimated to be 13.4 kcal/mol. Carbon black lost the initiating activity of the polymerization upon the blocking of carboxyl groups on the surface by the treatment with potassium hydroxide or diazomethane. Therefore, it was concluded that carboxyl groups on carbon black play an important role in the initiation of the polymerization. Furthermore, it was found that during the polymerization, poly(N-acylethyleneimine) was grafted onto carbon black by the termination of growing polymer chain with the surface.

INTRODUCTION

In a series of our papers, we have reported that the cationic polymerization of vinyl monomers such as N-vinylcarbazole (1), vinyl ethers (2), N-vinyl-2-pyrrolidone (3), and α-methylstyrene (3) are initiated by carboxyl groups on the surface of carbon black. Furthermore, carbon blacks were found to be capable of initiating the ring-opening transfer polymerization of spiro ortho esters, bicyclo ortho esters, and bicyclo ortho carbonates (4,5).

During the above polymerizations of these monomers, polymers formed were grafted onto carbon black by termination of growing polymer chains on the surface.

On the other hand, it is well known that the ring-opening polymerization of cyclic imino ethers such as 2-oxazolines are initiated by cationic catalyst (6), methyl p-toluenesulfonate (7), and iodomethane (8). Nisikubo and his coworkers reported the addition reaction of pendant cyclic imino ethers in polymer chain with carboxylic acids (9).

In the present paper, the cationic ring-opening polymerization of 2-substituted-2-oxazolines initiated by carboxyl groups on carbon black and the grafting of poly(N-acylethyleneimine)s onto the surface were investigated. Furthermore, the mechanisms of initiation by carboxyl groups and grafting onto carbon black were discussed.

ungrafted polymer and dried in vacuo at 110°C. The percentage of grafting of polymer onto carbon black was calculated by the following equation:

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

RESULTS AND DISCUSSION

Polymerization of 2-Oxazolines by Carbon Black

It is well known that 2-oxazolines are polymerized with ring-opening isomerization at relatively high temperature by cationic catalyst such as tin(IV) chloride and p-toluenesulfonic acid (6,7). Therefore, the initiating ability of carboxyl groups on the surface of carbon black for the ring-opening polymerization of 2-oxazolines was examined.

Using channel black FW 200, the polymerizations of 2-methyl-2-oxazoline and 2-ethyl-2-oxazoline were carried out at 110°C. The results are shown in Figure 1.

Even if these 2-oxazolines were heated in the absence of carbon black at 110°C, no polymerization occurred at all. In the presence of FW 200, however, the polymerization proceeded as shown in Figure 1, in which the effect of carbon black as an initiator is clearly shown.

The polymers obtained from the polymerization of 2-methyl- and 2-ethyl-2-oxazoline was identified by IR and NMR spectra as the expected poly(N-acetylethyleneimine) and poly(N-propionylethyleneimine), respectively.

Effect of Temperature on the Polymerization

Figure 2 shows the effect of temperature on the polymerization of 2-methyl-2-oxazoline initiated by carbon black. It was found that the rate of the polymerization increases with a rise in polymerization temperature. The Arrhenius plots for

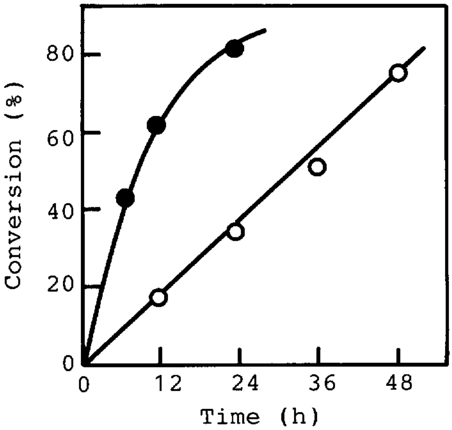


Figure 1. Ring-opening polymerization of 2-oxazolines initiated by carbon black

FW 200, 0.10g; 2-oxazoline, 0.02mol; 110°C
(○); 2-Methyl-2-oxazoline
(●); 2-Ethyl-2-oxazoline

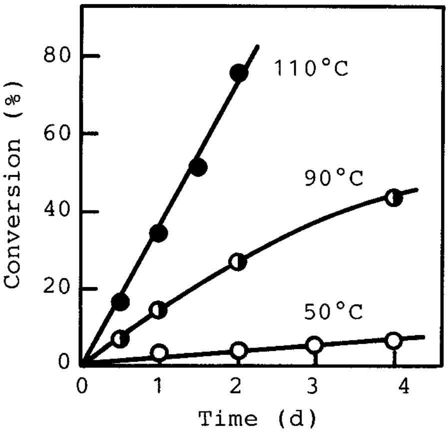


Figure 2. Effect of temperature on the polymerization of 2-methyl-2-oxazoline initiated by carbon black

Polymerization conditions are given in Figure 1.

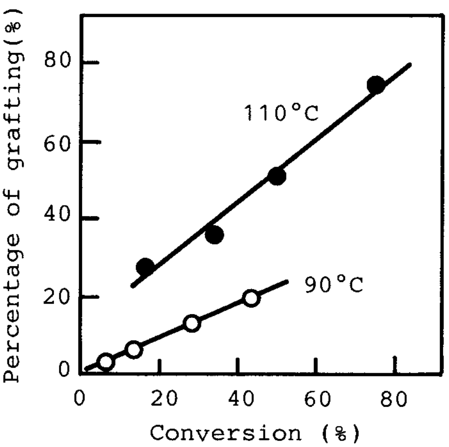


Figure 3. Relationship between conversion and percentage of grafting of poly(N-acetylethyleneimine) onto carbon black obtained from the polymerization shown in Figure 2

the above results gave a straight line and apparent activation energy of the polymerization was estimated to be 10.9 kcal/mol. The value was almost equal to that of cationic polymerization of N-vinylcarbazole initiated by carbon black (1).

Proof of Grafting onto Carbon Black

The carbon black obtained from the polymerization gave a stable colloidal dispersion in organic solvents. This suggests that the poly(N-acylethyleneimine) is grafted onto carbon black surface.

The relationship between percentage of grafting of poly(N-acetylethyleneimine) and conversion at 90°C and 110°C is shown in Figure 3. From the results shown in Figure 3, it is apparent that in the polymerization initiated by carbon black, polymer formed is grafted onto the surface. The percentage of grafting was found to increase with an increase in conversion.

TABLE I
Ring-Opening Polymerization of 2-Methyl-2-oxazoline Initiated by Several Kinds of Carbon Blacks

Carbon black	COOH (meq/g)	OH (meq/g)	Conversion (%)
None	-	-	0
FW 200	0.61	0.10	74.3
Carbolac 1	0,54	0.16	30.5
Neospectra II	0.40	0.24	22.8
Philblack O	0	0.02	trace

Carbon black, 0.10g; 2-methyl-2-oxazoline, 0.02mol; 110°C; 2d.

TABLE II
Ring-Opening Polymerization of 2-Methyl-2-oxazoline Initiated by Modified Carbon Blacks

Carbon black	COOH (meq/g)	OH (meq/g)	Conversion[a] (%)
KOH-FW 200[b]	0	0.10	trace
KOH-Neospectra II[b]	0	0.24	trace
CH_2N_2-FW 200[c]	0	0	0
CH_2N_2-Neospectra II[c]	0	0	0
HNO_3-Philblack O[d]	0.51	0.05	45.7

[a] Polymerization conditions are given in TABLE I.
[b] Carbon black treated with potassium hydroxide.
[c] Carbon black treated with diazomethane.
[d] Carbon black treated with nitric acid.

Functional Groups on Carbon Black Responsible for the Initiation

To clarify the initiating sites, functional groups, on carbon black, the polymerization of 2-methyl-2-oxazoline was carried out with several kinds of carbon blacks was examined. The results are summarized in Table I.

Table I shows that the ring-opening polymerization of 2-methyl-2-oxazoline was initiated by not only channel black FW 200 but also Carbolac 1 and Neospectra II. The initiating ability of channel blacks was found to increase with an increase in carboxyl group content of carbon black. On the other hand, furnace black Philblack O which contains no carboxyl groups failed to initiate the polymerization.

These results suggest that carboxyl groups on carbon black play an important role as initiator in the ring-opening isomerization polymerization of 2-oxazolines.

Polymerization of 2-Methyl-2-oxazoline by Modified Carbon Blacks

To clarify the role of carboxyl groups on carbon black in the initiation, the the results of polymerizations of 2-methyl-2-oxazoline initiated by carbon black samples treated with potassium hydroxide, with diazomethane, and with nitric acid were compared with those initiated by untreated one. The results are shown in Table II.

Carboxyl group on carbon black is easily neutralized by the treatment with aqueous solution of potassium hydroxide (10). By the treatment with diazomethane, carboxyl and phenolic hydroxyl groups are blocked by methylation with diazomethane (12). On the other hand, by the treatment with nitric acid, carboxyl group can be introduced onto furnace black Philblack O.

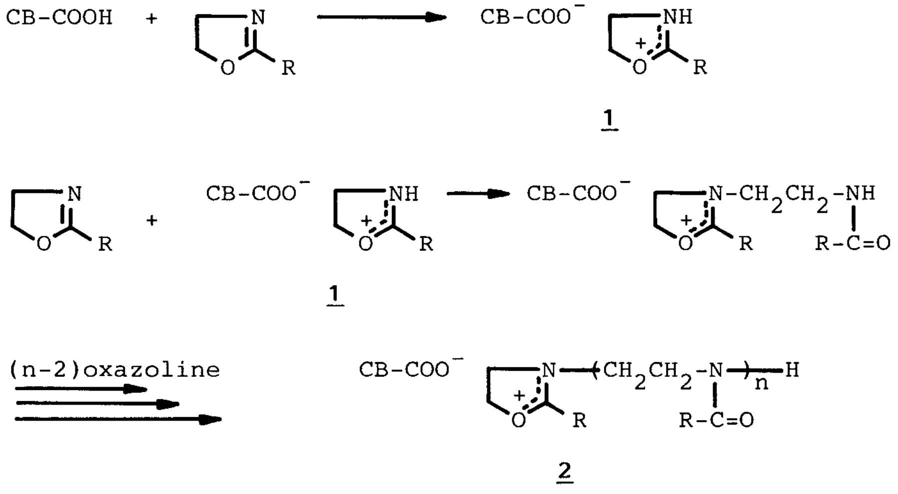
The results shown in Table II indicate that FW 200 and Neospectra II lost the ability to initiate the polymerization by the treatment with potassium hydroxide and diazomethane. Furthermore, it was found that nitric acid-treated Philblack O is able to initiate the polymerization of 2-methyl-2oxazoline. This may be due to carboxyl groups introduced onto the surface by the treatment with nitric acid.

Based on the above results, it is concluded that the functional groups responsible for the initiation of the polymerization are carboxyl groups on the surface of carbon black.

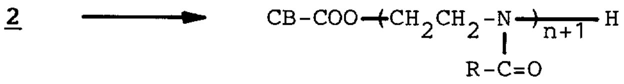
Mechanisms of Initiation and Grafting

It is known that 2-oxazolines are polymerized by two different mechanisms depending upon the nature of initiator (6-8). When Lewis acids, sulfonic acids, and sulfonates were used as catalyst, the species at the propagating end is an oxazolinium ion, which is opened by an S_N2 attack at C-5 atom

Initiation and Propagation



Grafting (Termination)



$$2 \longrightarrow \text{CB-COO}\!\left(\text{CH}_2\text{CH}_2\text{-}\underset{\substack{|\\ \text{R-C=O}}}{\text{N}}\right)_{n+1}\!\text{H}$$

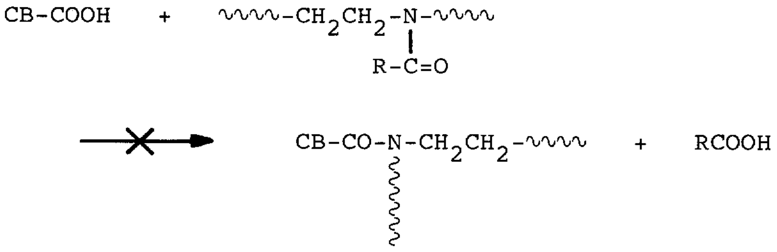
by the monomer (6,7). On the other hand, the polymerization initiated by alkyl iodide proceeds through a species having a terminal structure of β-(N-acylamino)ethyl iodide (8).

As analogous to the initiation by p-toluenesulfonic acid, the initiation by carboxyl groups on carbon black is considered as follows:

The polymerization is initiated by proton addition to nitrogen of 2-oxazoline to give oxazolinium carboxylate (1). The oxazolinium ion is ring-opened (between 1-5 bond) by a S_N2 attack at C-5 atom by the monomer nucleophile. The propagation proceeds with oxazolinium ion as propagating end and carboxylate anion as counter ion.

On the other hand, the grafting of polymer onto carbon black was considered to be due to the neutralization of propagating cation with carboxylate anion. However, there is a possibility of grafting by amide interchange reaction of poly-(N-acylethyleneimine) with carboxyl group on carbon black.

Therefore, carbon black (Neospectra II) was heated with poly(N-acetylethyleneimine) in N-methyl-2-pyrrolidone at 110°C for 48h and the grafting of the polymer by amide interchange reaction was examined. As the result, the amount of the polymer remained on the surface after Soxhlet extraction with methanol was 5.5 wt%. This value is comparable to that of polymers (having no amide group) adsorbed on the surface. The result indicates that it is not necessary to take into account the grafting by amide interchange reaction under the above condition.



$$\text{CB-COOH} + \sim\!\sim\text{-CH}_2\text{CH}_2\text{-}\underset{\substack{|\\ \text{R-C=O}}}{\text{N}}\text{-}\sim\!\sim$$

$$\not\longrightarrow \text{CB-CO-}\underset{\substack{\wr\\ \wr}}{\text{N}}\text{-CH}_2\text{CH}_2\text{-}\sim\!\sim + \text{RCOOH}$$

Accordingly, it is concluded that poly(N-acylethyleneimine) is grafted by the termination of growing polymer chain with carbon black surface.

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