

# Grafting of Polyesters onto Carbon Black.

## III. Polymerization of $\beta$ -Propiolactone Initiated by Quaternary Ammonium Carboxylate Groups on the Surface of Carbon Black

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### Synopsis

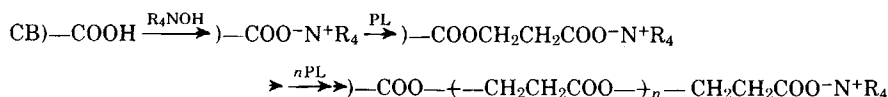
By use of carbon black containing quaternary ammonium carboxylate ( $\text{COO}^-\text{N}^+\text{R}_4$ ) groups as catalyst, the anionic ring opening polymerization of  $\beta$ -propiolactone (PL) was carried out at  $50^\circ\text{C}$ . Although carbon black itself was unable to initiate the polymerization of PL, carbon black containing  $\text{COO}^-\text{N}^+\text{R}_4$  groups, which was prepared by the reaction of carboxyl groups with corresponding quaternary ammonium hydroxide, was found to be able to initiate the polymerization. The carbon black obtained from the polymerization gave a stable colloidal dispersion in an organic solvent, and it was confirmed that the polyester formed was effectively grafted onto the surface. In addition, the effect of quaternary ammonium counteraction on the polymerization was investigated.

### INTRODUCTION

We have reported that the anionic ring opening polymerization of  $\beta$ -propiolactone (PL) was initiated by alkali metal carboxylate groups ( $\text{COO}^-\text{M}^+$ ;  $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{or Cs}$ ) on the surface of carbon black and polyester formed was effectively grafted onto the surface.<sup>1,2</sup> In the polymerization, the rate of polymerization and the grafting ratio of polyester onto the surface of carbon black were remarkably affected by the ionic nature of alkali metal counteraction ( $\text{M}^+$ ); the rate of the polymerization increased, depending on the counteraction, in the following order:  $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ . However, the grafting ratio decreased when the electropositivity of counteraction increased. Furthermore, the effect of temperature and solvent on the polymerization of PL was investigated in the previous paper.<sup>3</sup>

On the other hand, the anionic ring opening polymerization of  $\alpha, \alpha$ -dialkyl- $\beta$ -propiolactone with quaternary ammonium carboxylates such as quaternary ammonium pivalate in organic solvents was reported by Hall.<sup>4</sup> While, it is expected the carboxyl groups present on the surface of carbon black will easily react with quaternary ammonium hydroxide to give quaternary ammonium carboxylate groups ( $\text{COO}^-\text{N}^+\text{R}_4$ )<sup>5</sup> which will have an ability to initiate the anionic ring opening polymerization of PL as well as  $\text{COO}^-\text{M}^+$  groups on the surface.

This article deals with the anionic ring opening polymerization of PL initiated by  $\text{COO}^-\text{N}^+\text{R}_4$  groups on the surface. Moreover, the effect of quaternary ammonium counteraction ( $\text{N}^+\text{R}_4$ ) on the rate of the polymerization and the grafting ratio was investigated:



## EXPERIMENTAL

### Materials

The carbon black used was color channel black FW 200 (Degussa A.G.; BET specific surface area, 460 m<sup>2</sup>/g) and furnace black Philblack O (Philips Petroleum Co.; 79.6 m<sup>2</sup>/g). The content of carboxyl groups on the surface of FW 200 and Philblack O was 0.61 meq/g and 0 meq/g, respectively.

The purification of the carbon black and monomer was as previously described.<sup>1,2</sup>

Tetramethylammonium hydroxide (10% in methanol), phenyltrimethylammonium hydroxide (20–25% in methanol), and cetylbenzyltrimethylammonium hydroxide (10% in methanol) were of special grade and used without further purification.

### Preparation of Carbon Black Containing COO<sup>-</sup>N<sup>+</sup>R<sub>4</sub> Groups

The carbon black containing COO<sup>-</sup>N<sup>+</sup>R<sub>4</sub> groups was prepared by the neutralization of carboxyl groups on the surface with corresponding quaternary ammonium hydroxides in methanol. A typical example was as follows. To 50 mL of methanol solution of quaternary ammonium hydroxide (3 × 10<sup>-2</sup> mol/L), 4.0 g of carbon black was added with stirring at room temperature. After the reaction for 6 h, the carbon black was filtered, washed with absolute methanol until no more ammonium hydroxide could be detected in the filtrate, and then dried *in vacuo* at 40°C over phosphorus pentoxide. The treated carbon black was stored *in vacuo*, and exposure of the treated carbon black to atmospheric moisture was avoided as much as possible.

### Determination of COO<sup>-</sup>N<sup>+</sup>R<sub>4</sub> Groups on the Surface of Carbon Black

The content of COO<sup>-</sup>N<sup>+</sup>R<sub>4</sub> groups on the surface of carbon black was determined by a semi-micro-Kjeldahl procedure.<sup>6</sup> A typical example was as follows. Into a 100-mL Kjeldahl flask, 0.5 g of carbon black, 3 g of a mixture of K<sub>2</sub>SO<sub>4</sub> and CuSO<sub>4</sub> (10:1), 3 mL of H<sub>2</sub>O<sub>2</sub>, and 20 mL of concentrated H<sub>2</sub>SO<sub>4</sub> were added, and the flask was heated until no more particles of carbon black could be detected. Then the subsequent distillation and titration of ammonia was carried out by a general method.

### Polymerization Procedure, Grafting Ratio, and Intrinsic Viscosity of Ungrafted Polymer

The polymerization procedure was previously described in detail.<sup>2</sup> The grafting ratio (the proportion of grafted polyester to carbon black) was determined as follows. To separate ungrafted polymer from the reaction product, the product was extracted with chloroform by using a Soxhlet apparatus until

TABLE I  
The Content of Quaternary Ammonium Carboxylate Groups on the Surface of Quaternary Ammonium Hydroxide-Treated Carbon Black

Treated carbon black	COOH (meq/g)	COO-N <sup>+</sup> R <sub>4</sub> (meq/g)
Untreated FW 200	0.61	0
[(Me) <sub>4</sub> N] OH-FW 200	—	0.50
[Ph(Me) <sub>3</sub> N] OH-FW 200	—	0.44
[Cet(Me) <sub>2</sub> BzN] OH-FW 200	—	0.42
Untreated Philblack O	0	0
[(Me) <sub>4</sub> N] OH-Philblack O	—	0.02

no more polymer could be detected in refluxing solvent. The grafting ratio was calculated from the amount of polymer irreversibly fixed on the carbon black.<sup>1</sup>

The intrinsic viscosity of ungrafted polymer was determined in chloroform solution at 30.0°C.

## RESULTS AND DISCUSSION

### Polymerization of PL Using FW 200 Containing COO<sup>-</sup>N<sup>+</sup>R<sub>4</sub> Groups as Initiator

It is well known that carboxyl groups present on the carbon black are neutralized by base such as NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH, and NH<sub>4</sub>OH.<sup>5,7</sup>

In order to confirm the formation of COO<sup>-</sup>N<sup>+</sup>R<sub>4</sub> groups by the treatment with quaternary ammonium hydroxides, the content of COO<sup>-</sup>N<sup>+</sup>R<sub>4</sub> groups was determined by a semi-micro-Kjeldahl procedure, and the results are shown in Table I.

Although about 20% of carboxyl groups remained unchanged because N<sup>+</sup>R<sub>4</sub> groups were very bulky, it was apparent that FW 200 treated with quaternary ammonium hydroxides contained COO<sup>-</sup>N<sup>+</sup>R<sub>4</sub> groups. On the other hand, Philblack O, which contains no carboxyl groups, scarcely contained COO<sup>-</sup>N<sup>+</sup>R<sub>4</sub> groups after the treatment.

The ring opening polymerization of PL was carried out by use of FW 200 containing tetramethylammonium carboxylate groups [COO<sup>-</sup>N<sup>+</sup>(Me)<sub>4</sub>] as catalyst. The results are summarized in Table II.

TABLE II  
Polymerization of PL Initiated by Quaternary Ammonium Carboxylate Groups on the Surface of Carbon Black

Carbon black	Conversion (%) <sup>a</sup>
None	0
Untreated FW 200	0
[(Me) <sub>4</sub> N] OH-treated FW 200	41.5
Untreated Philblack O	0
[(Me) <sub>4</sub> N] OH-treated Philblack O	0

<sup>a</sup> Carbon black 0.3 g, PL 5.73 g; 50°C, 9 h.

Hall has reported that the anionic ring opening polymerization of PL was initiated by quaternary ammonium carboxylates, and the rate of the polymerization was faster than that of other anionic ring opening polymerization.<sup>4</sup>

As shown in Table II, not only in the absence of carbon black but also in the presence of untreated FW 200, the polymerization of PL could not be detected. However, the polymerization was found to be initiated at 50°C in the presence of FW 200 containing  $\text{COO}^-\text{N}^+(\text{Me})_4$  groups. In addition, tetramethylammonium hydroxide-treated Philblack O was unable to initiate the polymerization of PL. This is explained by the fact that Philblack O contains no carboxyl groups. The result suggests that it is not necessary to take into account the initiation by tetramethylammonium hydroxide adsorbed on the surface of carbon black.

Accordingly, it became apparent that the polymerization of PL was initiated by  $\text{COO}^-\text{N}^+(\text{Me})_4$  groups on the surface of carbon black.

### Effect of Quaternary Ammonium Carboxylate Counteraction on the Polymerization

As previously reported, the rate of polymerization of PL was remarkably affected by alkali metal counteraction.<sup>1,2</sup> On the other hand, in the anionic polymerization of acrylonitrile initiated by quaternary ammonium hydroxide, the effect of counteraction on the rate of polymerization and the molecular weight of polymer formed were reported.<sup>8</sup>

Therefore, in order to elucidate the effect of the counteraction, the polymerization of PL initiated by tetramethylammonium carboxylate [ $\text{COO}^-\text{N}^+(\text{Me})_4$ ], phenyltrimethylammonium carboxylate [ $\text{COO}^-\text{N}^+(\text{Me})_3\text{Ph}$ ], and Cetylbenzyltrimethylammonium carboxylate [ $\text{COO}^-\text{N}^+\text{Cet}(\text{Me})_2\text{Bz}$ ] groups on the surface of FW 200 were examined, and the results are shown in Figure 1.

The rate of the polymerization tends to increase, depending on the counteraction, in the following order:  $\text{Cet}(\text{Me})_2\text{BzN}^+ < \text{Ph}(\text{Me})_3\text{N}^+ < (\text{Me})_4\text{N}^+$ .

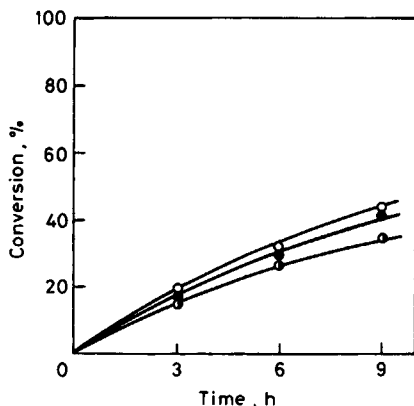


Fig. 1. Bulk polymerization of PL initiated by FW 200 containing  $\text{COO}^-\text{N}^+\text{R}_4$  groups: FW 200- $\text{COO}^-\text{N}^+\text{R}_4$  0.3 g, PL 5.73 g; 50°C. (O)  $[(\text{Me})_4\text{N}]\text{OH-FW 200}$ ; (●)  $[\text{Ph}(\text{Me})_3\text{N}]\text{OH-FW 200}$ ; (◐)  $[\text{Cet}(\text{Me})_2\text{BzN}]\text{OH-FW 200}$ .

However, the effect of the quaternary ammonium counteraction was not appreciable compared with that of alkali metal counteraction.<sup>1,2</sup> This may be due to the fact that these quaternary ammonium counteractions are very bulky so that the approach of the counteraction to the rough surface of carbon black is hindered.

On the basis of foregoing results, it is concluded that  $\text{COO}^- \text{N}^+ \text{R}_4$  groups on the surface of carbon black have an ability to initiate the anionic ring opening polymerization of PL. Furthermore, it is considered that the propagation mechanism in the polymerization is a nucleophilic substitution reaction in which PL ring is opened at the  $\beta$ -carbon-oxygen bond in the same manner as alkali metal carboxylates- and quaternary ammonium carboxylates-initiated polymerization of PL.<sup>4,9,10</sup>

### Proof of Grafting onto Carbon Black

The carbon black obtained from the polymerization of PL gave a stable colloidal dispersion in a good solvent for the polyester. This phenomenon suggests that the polyester is grafted onto the carbon black.

To ensure the grafting of the polyester onto carbon black, the relationship between conversion and the grafting ratio (and also grafting efficiency) was determined. The grafting ratio and grafting efficiency are defined as the proportion of grafted polyester to carbon black and the proportion of grafted polyester compared to the total polymer formed, respectively.<sup>2</sup> The results are shown in Figure 2.

Figure 2 shows that the grafting ratio increased up to 65% with an increase in conversion. The value of the grafting ratio was lower than that obtained from the polymerization of PL initiated by  $\text{COO}^- \text{K}^+$  groups,<sup>2</sup> while the value was considerably high in comparison with that of vinyl polymers obtained from the polymerization using radical,<sup>11</sup> cationic,<sup>12</sup> and anionic<sup>13</sup> initiators in the presence of carbon black.

On the other hand, the grafting efficiency was found to be very low in comparison with that obtained from the polymerization initiated by  $\text{COO}^- \text{K}^+$  groups.

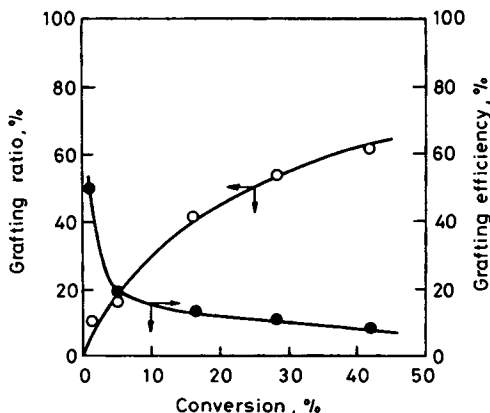


Fig. 2. Relationship between conversion and grafting ratio (grafting efficiency): FW 200- $\text{COO}^- \text{N}^+ (\text{Me})_4$  0.3 g, PL 5.73 g; 50°C.

These results suggest that, although the polymer is propagated from  $\text{COO}^- \text{N}^+ \text{R}_4$  groups on the surface, very soon a chain transfer of the growing polymer anion takes place.<sup>14</sup> As a result, when  $\text{COO}^- \text{N}^+ \text{R}_4$  groups is used as catalyst, polyester-grafted carbon black having lower grafting ratio and lower grafting efficiency will be obtained.

### Effect of Counteraction of the Molecular Weight of Ungrafted Polymer

The effect of the quaternary ammonium counteraction on the molecular weight of polymer was reported by Zilkha et al. in the anionic polymerization of acrylonitrile.<sup>8</sup> They described that the molecular weight of polymer obtained decreased with an increase in size and electropositivity of quaternary ammonium counteraction.<sup>8</sup> Furthermore, we reported in the previous paper that in the polymerization of PL initiated by  $\text{COO}^- \text{K}^+$  groups on the surface, the molecular weight of ungrafted polyester decreased with an increase of the electropositivity of alkali metal counteraction.<sup>1,2</sup>

Figure 3 shows the effect of quaternary ammonium counteraction on the intrinsic viscosity of the ungrafted polymer formed. From the results shown in Figure 3, it was found that the molecular weight of the ungrafted polymer was decreased, depending on the counteraction, in the following order:  $(\text{Me})_4\text{N}^+ > \text{Ph}(\text{Me})_3\text{N}^+ > \text{Cet}(\text{Me})_2\text{BzN}^+$ . This order is in agreement with that of increasing size of the counteraction.

The phenomenon may be explained as follows. The growing chain is ion pair such as  $\text{CB}^{\text{---}} \text{COO}^- \text{N}^+ \text{R}_4$ . Increasing the size of quaternary ammonium counteraction ( $\text{N}^+ \text{R}_4$ ) will cause a corresponding increase in the ionic nature of the ion pairs, leading to a greater attraction of protons by growing anion (chain transfer reaction).<sup>8,14</sup> Accordingly, lower molecular weight ungrafted polymer will be obtained.

Based on the above consideration, it may be noted that, in order to increase the grafting ratio (or grafting efficiency), it is necessary to adopt a small size of

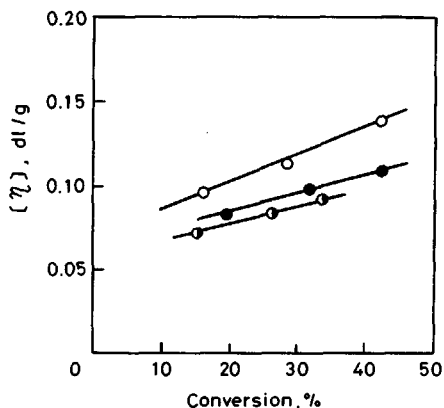


Fig. 3. Effect of quaternary ammonium counteraction on intrinsic viscosity of ungrafted polymer: FW 200- $\text{COO}^- \text{N}^+ \text{R}_4$  0.3 g, PL 5.73 g; 50°C. (○)  $[(\text{Me})_4\text{N}]\text{OH-FW 200}$ ; (●)  $[\text{Ph}(\text{Me})_3\text{N}]\text{OH-FW 200}$ ; (◐)  $[\text{Cet}(\text{Me})_2\text{BzN}]\text{OH-FW 200}$ .

countercation. Therefore, to obtain polyester-grafted carbon black with a large grafting ratio, a small size of alkali metal counteraction is preferred to quaternary ammonium ion as previously reported.<sup>2</sup>

In conclusion, it was found that the anionic ring opening polymerization of PL was easily initiated by  $\text{COO}^- \text{N}^+ \text{R}_4$  groups on the carbon black, and the polyester was grafted on the surface. Further application to the polymerization of other lactones is now under investigation.

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