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## **ANIONIC GRAFTING OF POLYSTYRENE FROM CARBON BLACKS CATALYZED BY OLi GROUPS ON THE CARBON BLACK SURFACE IN THE PRESENCE OF CROWN ETHER**

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### **ABSTRACT**

Carbon black carrying OLi groups, which was prepared by the reaction of the oxygen-containing groups on the surface with *n*-butyllithium (BuLi), was unable to initiate anionic polymerization of styrene. However, anionic polymerization of styrene is initiated by OLi group on carbon black in the presence of a crown ether, such as 12-crown-4 and 18-crown-6. Then polystyrene was effectively grafted from carbon black owing to the propagation of polystyrene from the OLi groups. The grafting ratio increased with increasing amount of BuLi used for pretreatment of the carbon black and was a maximal (170%) in the presence of carbon black pretreated with BuLi in a quantity equivalent to its oxygen-containing groups. When carbon black was pretreated with excess BuLi, i.e., in the presence of free BuLi, the grafting ratio decreased to less than 20% because the formation of ungrafted polystyrene by free BuLi occurs preferentially to the propagation from the OLi groups on carbon black. Furthermore, it was found that the anionic polymerization of  $\alpha$ -methylstyrene was initiated in the presence of crown ether by OLi groups, but OLi groups failed to initiate the polymerization of isoprene, even in the presence of crown ether.

## INTRODUCTION

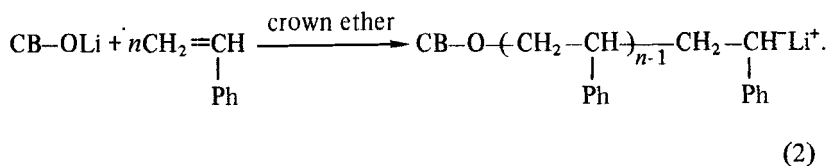
The anionic grafting of vinyl polymers onto carbon black has been widely investigated [1-7]. For instance, Minoura and Katano [1] reported that radical anions, formed by the reaction of carbon black with metallic sodium, initiate the anionic polymerization of styrene and then polystyrene is grafted onto carbon black. They also noted that during the anionic polymerization of styrene initiated by *n*-butyllithium (BuLi) in the presence of carbon black, polystyrene was grafted onto carbon black during the termination, of propagating the polymer anion, with quinonic oxygen groups on the carbon black surface [1].

Furthermore, Donnet and coworkers [3] have reported that metallized carbon black, which was prepared by the reaction of carbon black with BuLi in the presence of tetramethylethylenediamine, initiates the anionic polymerization of styrene and grafting from the carbon black surface. Moreover, the grafting onto carbon black by the reaction of methyl ester and methoxy groups previously introduced on the carbon black and living polymer anion has been investigated [4].

Recently, Ohkita et al. found that a carbon black/BuLi complex, i.e., CB-OLi, which was prepared by treating carbon black with BuLi in toluene, initiates the anionic polymerization of methacrylates and acrylonitrile and that polymers are grafted from the surface: the grafting ratio increased up to 200% [5, 6]. Furthermore, we reported that the hydrogen transfer polymerization of acrylamide is initiated by carbon black carrying OLi groups to give poly- $\beta$ -alanine-grafted carbon black [8]. However, CB-OLi was unable to initiate the polymerization of styrene.

On the other hand, it is known that the addition of crown ethers and cryptates increases the rate of the anionic polymerization significantly and that polymer with a higher molecular weight is formed [9, 10].

In this article we report the anionic polymerization of styrene initiated by an OLi group on carbon black (CB) in the presence of crown ethers and the grafting of polystyrene from the carbon black surface:



## EXPERIMENTAL

### Materials

The carbon black used was a color-channel black Neospectra II (Columbian Carbon Co., 906 m<sup>2</sup>/g). It was stored in a sealed glass container and dried in vacuo at 110°C before use. The content of phenolic hydroxyl, carboxyl, and quinonic oxygen groups on the surface was determined to be 0.24, 0.40, and 0.92 meq/g, respectively.

Guaranteed reagent-grade styrene and  $\alpha$ -methylstyrene were washed with aqueous alkali, dried over BaO, and distilled twice under reduced pressure. Isoprene was dried over anhydrous calcium sulfate and distilled twice.

The catalyst used was a *n*-hexane solution of BuLi (about 15%) from Wako Pure Chemical Industries, Japan. The concentration of BuLi was determined by titration according to the literature method before use [11, 12].

Toluene used as solvent was first washed with H<sub>2</sub>SO<sub>4</sub> and then with aqueous alkali, dried over CaCl<sub>2</sub>, and distilled.

12-Crown-4 and 18-crown-6 obtained from Aldrich Chemical Co. were used without further purification.

### Introduction of OLi Group onto Carbon Black (pretreatment) and Polymerization Procedures

Into a 100-mL flask containing 0.30 g vacuum-dried carbon black and 5.0 mL toluene, BuLi (hexane solution) was added under dry nitrogen. The mixture was stirred with a magnetic stirrer at room temperature for 1 h. Subsequently, freshly distilled styrene and crown ether were added to the above mixture, and the graft polymerization was conducted at 0°C with stirring. After the desired time, the content of the flask was poured into a large excess of methanol. The conversion was calculated by

$$\text{conversion (\%)} = \frac{\text{weight of precipitate (g)} - \text{weight of carbon black added (g)}}{\text{weight of monomer used (g)}} \times 100. \quad (3)$$

### Determination of Grafting Ratios

To separate the polystyrene-grafted carbon black from the reaction product also containing the ungrafted polystyrene, the product was dispersed in benzene and the dispersion was centrifuged at  $1.2 \times 10^4$  rpm until the carbon

black was completely precipitated. The precipitated carbon black was extracted with benzene using a Soxhlet apparatus until no more polymer could be detected in the refluxing solvent. The grafting ratio was determined by the equation

$$\text{grafting ratio (\%)} = \frac{\text{weight of polymer grafted (g)}}{\text{weight of carbon black used (g)}} \times 100. \quad (4)$$

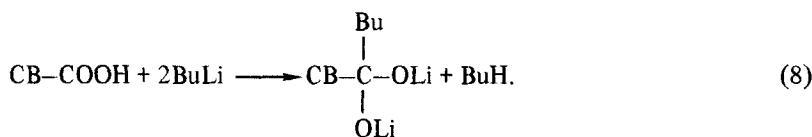
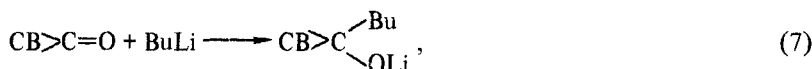
The ungrafted polymer was isolated from the extract of the above extraction and purified by reprecipitation (benzene/methanol). The molecular weight of ungrafted polystyrene was calculated by the following equation from the viscosity measurement in toluene at 30.0°C [13]:

$$[\eta] = 8.81 \times 10^{-5} M^{0.75}. \quad (5)$$

## RESULTS AND DISCUSSION

### Anionic Polymerization of Styrene Catalyzed by CB-OLi in the Presence of Crown Ether

It has been reported that oxygen-containing groups on carbon black, namely quinonic oxygen, phenolic hydroxyl, and carboxyl group, react with BuLi to give OLi groups [14]:



Therefore, the polymerization of styrene containing 3.0 g carbon black pretreated with various amounts of BuLi, in the presence or in the absence of 12-crown-4, at 0°C was studied, and the initiating activity of OLi groups on carbon black was examined.

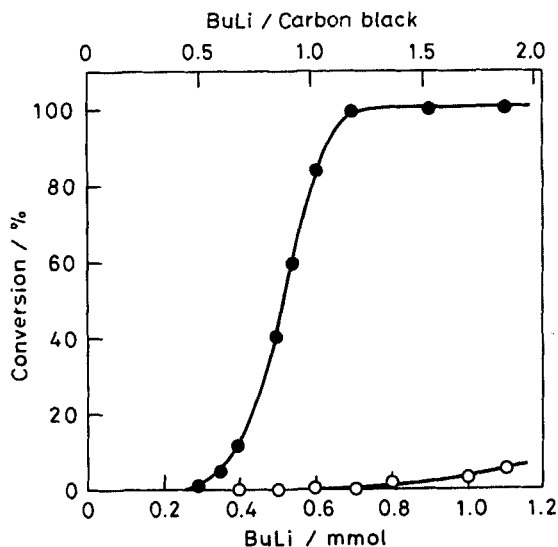


FIG. 1. Effect of the amount of BuLi used for the pretreatment of carbon black on the anionic polymerization of styrene in the presence of 12-crown-4. Pretreatment: carbon black, 0.30 g; toluene, 5.0 mL; room temperature; time, 1 h. Polymerization: styrene, 25 mmol; crown ether, 0.03 g; temperature 0°C; time, 6 h; (●) in the presence of crown ether; (○) in the absence of crown ether. The parameter "BuLi/Carbon black" represents the mol ratio of BuLi to oxygen-containing groups on 0.30 g of carbon black.

The results are shown in Fig. 1. The oxygen-containing groups on 0.30 g carbon black are equivalent to about 0.59 mmol BuLi. Accordingly, it is considered that below this equivalence point, free BuLi is absent because BuLi is consumed completely by the oxygen-containing groups during pretreatment. In contrast, above this equivalence point, free BuLi is present in the reaction system.

Figure 1 shows that, in the absence of 12-crown-4, polymerization was not induced when the amount of BuLi used for the pretreatment was less than 0.59 mmol. This suggests that OLi groups on carbon black do not have the ability to initiate the anionic polymerization of styrene, as reported by Ohkita et al. [5, 6].

On the other hand, in the presence of 12-crown-4, the anionic polymerization of styrene proceeded even below the equivalence point. Furthermore,

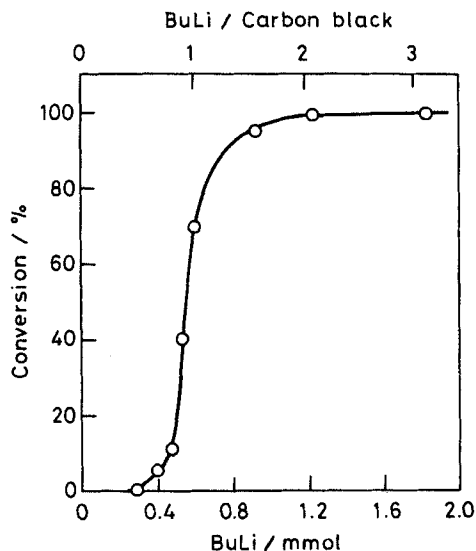


FIG. 2. Effect of the amount of BuLi used for the pretreatment of carbon black on the anionic polymerization of styrene in the presence of 18-crown-6. Polymerization conditions as in Fig. 1.

above the equivalence point, i.e., in the presence of free BuLi, the polymerization of styrene was very slow in the absence of 12-crown-4 but extremely accelerated by the addition of the crown ether.

Figure 2 shows the effect of 18-crown-6 on the anionic polymerization of styrene catalyzed by OLi groups on carbon black. Figure 2 also clearly shows that, in the presence of 18-crown-6, OLi groups on carbon black have the ability to initiate anionic polymerization of styrene.

Crown ethers and cryptates have recently been used in the anionic polymerization of vinyl, diene, and heterocyclic compounds. In their presence the rate of the anionic polymerization was highly accelerated because they lead to the formation of complexed ionic species that are highly reactive [9, 10].

Based on the above results, it was concluded that the activity of OLi groups on carbon black was enhanced by the addition of a crown ether and that CB-OLi was able to initiate the anionic polymerization of styrene.

On the other hand, the initiating activity of OLi groups in the presence of 12-crown-4, near the equivalence point, is greater than that of 18-crown-6.

### Grafting of Polystyrene from Carbon Black

The carbon black obtained from the above polymerization produced a stable colloidal dispersion in organic solvents such as benzene and tetrahydrofuran. For instance, when such a dispersion in benzene was allowed to stand at room temperature, precipitated carbon black particles were scarcely observed even after 6 months. This phenomenon suggests that polystyrene is grafted from carbon black.

Figures 3 and 4 show the effect of the amount of BuLi used for the pretreatment on the grafting ratio in the presence of 12-crown-4 and 18-crown-6, respectively. As shown in Figs. 3 and 4, the grafting ratio increased with increasing the amount of BuLi used for the pretreatment up to the equivalence point, had its maximal value at that point, and then rapidly decreased beyond the equivalence point.

These results indicate that the grafting of polystyrene onto carbon black may be attributed to the propagation of polystyrene from OLi groups.

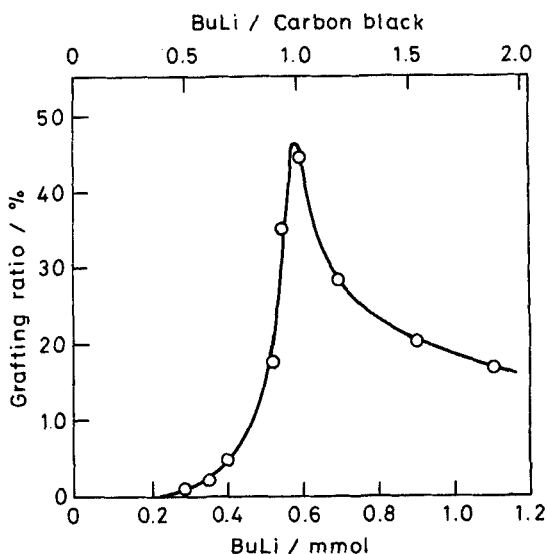


FIG. 3. Effect of the amount of BuLi used for the pretreatment of carbon black on the grafting ratio of polystyrene in the presence of 12-crown-4. Polymerization conditions as in Fig. 1.



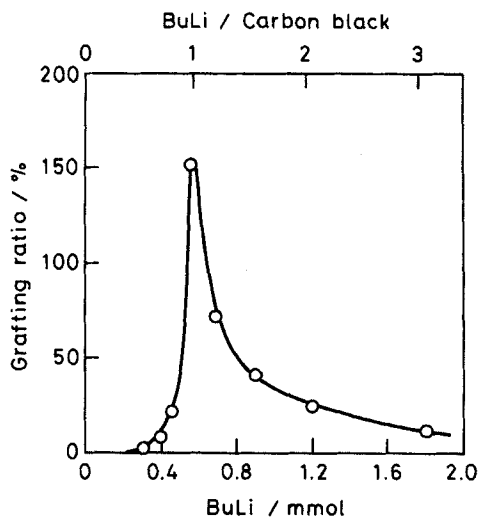
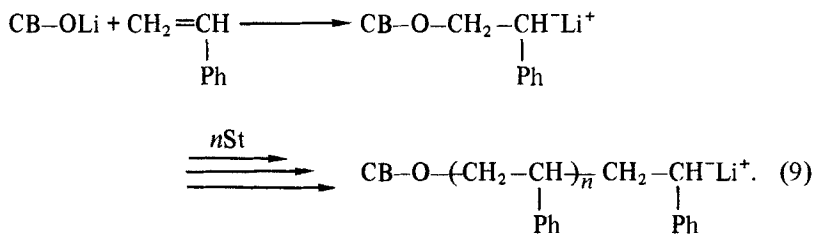


FIG. 4. Effect of the amount of BuLi used for the pretreatment of carbon black on the grafting ratio of polystyrene in the presence of 18-crown-6. Polymerization conditions as in Fig. 1.



On the other hand, in the presence of free BuLi, i.e., above the equivalence point, the ungrafted polymer was formed in preference to the propagation from OLi groups on carbon black.

It is worth noting that the maximal grafting ratio at the equivalence point in the presence of 18-crown-6 is higher than that of 12-crown-4. This indicates that to obtain polystyrene-grafts carbon black with a higher grafting ratio, the use of 18-crown-6 as the activator of the OLi group is desirable.

### Effect of the Amount of Crown Ether on the Polymerization and the Grafting Ratio

The polymerization of styrene with 0.30 g of carbon black pretreated with 0.59 mmol BuLi, i.e., in the absence of free BuLi, was carried out in the presence of various amounts of 18-crown-6, and the effect of the amount of crown ether on the polymerization was examined. The results are shown in Fig. 5.

As mentioned above, no polymerization occurred in the absence of crown ether. In contrast, in the presence of 18-crown-6, the polymerization of styrene proceeded. The rate of polymerization increased with increasing the amount of crown ether from 0.01 to 0.03 g, but no difference occurred when it was raised from 0.03 g to 0.05 g.

Figure 6 shows the effect of the amount of 18-crown-6 on the grafting ratio of polystyrene onto carbon black. It is apparent that the grafting ratio is scarcely affected by the amount of crown ether added, but that it increases with increasing conversion. This suggests that grafted polystyrene is propagated from OLi groups on the carbon black surface.

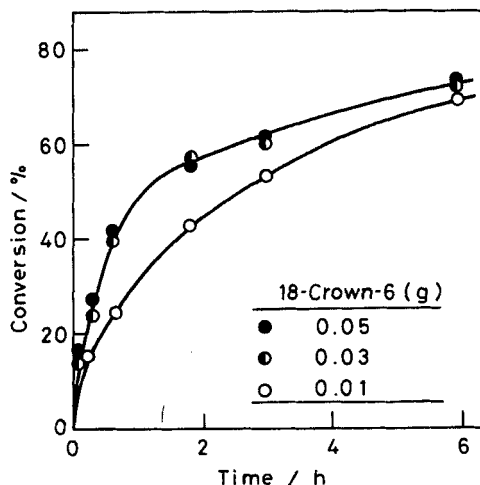


FIG. 5. Effect of the amount of 18-crown-6 on the anionic polymerization of styrene. Pretreatment: carbon black, 0.30 g; BuLi, 0.59 mmol; toluene, 5.0 mL; room temperature; time, 1 h. Polymerization: styrene, 25 mmol; 0°C.

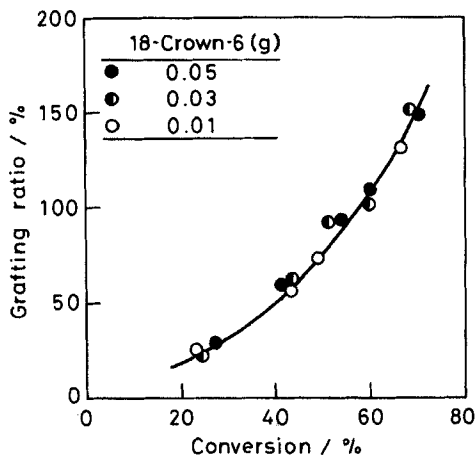


FIG. 6. Effect of the amount of 18-crown-6 on the grafting ratio of polystyrene. Polymerization conditions as in Fig. 5.

#### Molecular Weight of Ungrafted Polystyrene

In the above anionic graft polymerization, ungrafted polymer was formed even in the absence of free BuLi. This may be due to chain transfer from the growing polymer chain to toluene.

Figure 7 shows that the molecular weight of ungrafted polystyrene has its maximal value at the equivalence point, and beyond this it decreased with increasing amount of BuLi used for the pretreatment.

These phenomena may be explained as follows. Below the equivalent point, the growing polymer anion is terminated by acidic sites on the carbon black surface, such as carboxyl and phenolic hydroxyl groups, which remain unreacted after the pretreatment, and this gives rise to polystyrene of low molecular weight. On the other hand, above the equivalence point, the molecular weight of polystyrene will decrease with increasing amount of BuLi owing to the increase of free BuLi [16, 17].

On the other hand, the molecular weight of ungrafted polymer obtained in the presence of excess BuLi was larger than that calculated from the amount of BuLi used. This may be because some BuLi is adsorbed on the carbon black [3], which decreases its concentration.

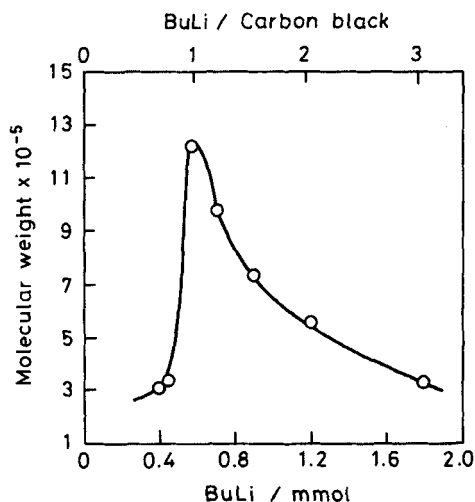


FIG. 7. Effect of the amount of BuLi used for the pretreatment of carbon black on the molecular weight of ungrafted polystyrene. Polymerization conditions as in Fig. 1.

### Graft Polymerization of Other Vinyl Monomers

Graft polymerization of  $\alpha$ -methylstyrene catalyzed by OLi groups on carbon black activated with 12-crown-4 was also examined. The results are shown in Fig. 8.

As with styrene, OLi groups alone failed to initiate the anionic polymerization of  $\alpha$ -methylstyrene. In the presence of 12-crown-4, polymerization was initiated by OLi groups, and poly- $\alpha$ -methylstyrene could be grafted from the carbon black surface.

Moreover, it was found that OLi groups on carbon black are unable to initiate the polymerization of isoprene even in the presence of crown ether.

The anionic grafting of block polymer initiated by CB-OLi in the presence of crown ether is now under investigation.

### Catalytic Activity of Butoxylithium as a Model Compound for OLi Groups on Carbon Black

*n*-Butoxylithium and lithium phenoxide, as model compounds for OLi groups on carbon black, failed to initiate the polymerization of styrene even

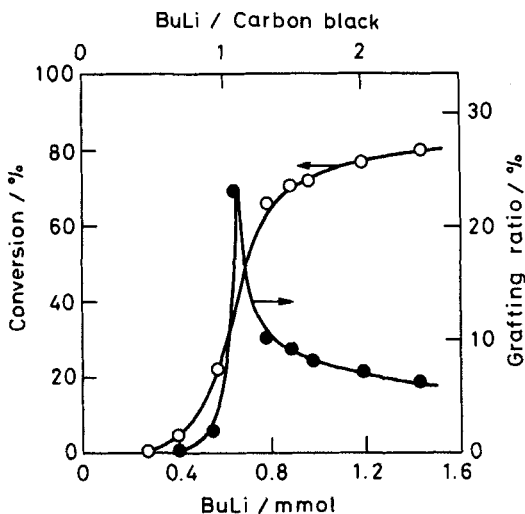


FIG. 8. Effect of the amount of BuLi on the polymerization of  $\alpha$ -methylstyrene and on the grafting ratio in the presence of 12-crown-4. Pretreatment: carbon black, 0.30 g; toluene, 5.0 mL; room temperature; time, 1 h. Polymerization:  $\alpha$ -methylstyrene, 25 mmol; 12-crown-4, 0.03 g; 0°C.

in the presence of 12-crown-4. This may be because the basicity of OLi groups on carbon black is possibly enhanced by the polycondensed aromatic rings of carbon black, and thus they have the ability to initiate the anionic polymerization of styrene in combination with crown ether.

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