

# Grafting of Poly- $\beta$ -Alanine onto Carbon Black: The Hydrogen Transfer Polymerization of Acrylamide Catalyzed by *n*-Butyllithium in the Presence of Carbon Black

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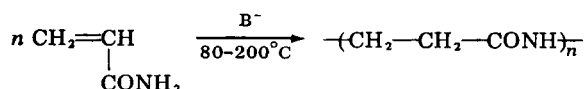
## Synopsis

The hydrogen transfer polymerization of acrylamide (AAM) catalyzed by *n*-butyllithium in the presence of carbon black was carried out at 80–100°C and the grafting of poly- $\beta$ -alanine (nylon 3) was investigated. It was suggested that the growing polymer anion was captured by the quinonic oxygen group on the surface of carbon black. Furthermore, the growing polymer anion reacted with the phenolic hydroxyl group on the surface to give ungrafted polymer and the lithium phenolate ( $-\text{O}^-\text{Li}^+$ ) group (chain transfer to phenolic hydroxyl group). The  $-\text{O}^-\text{Li}^+$  group formed was considered to be capable of initiating the hydrogen transfer polymerization of AAM. Accordingly, during the hydrogen transfer polymerization in the presence of carbon black, poly- $\beta$ -alanine was effectively grafted by the termination of growing polymer anion and the propagation of the polymer from the  $-\text{O}^-\text{Li}^+$  group on the surface. The grafting ratio was determined to be 60–80%. The carbon black obtained from the polymerization gave a stable colloidal dispersion in water, *N,N*-dimethylformamide, and formic acid. Furthermore, it was found that the ratio of hydrogen transfer polymerization to normal vinyl polymerization (*T* ratio) increased with an increase in polymerization temperature.

## INTRODUCTION

In order to obtain a carbon black which can be incorporated easily into a matrix of polymer, the grafting of vinyl polymers onto carbon black has been investigated. In general, this grafting procedure has been carried out during the polymerization in the presence of carbon black using radical,<sup>1,2</sup> anionic,<sup>3,4</sup> and cationic initiators.<sup>5,6</sup> For instance, Ohkita and his co-workers have investigated the polymerization of styrene and methyl methacrylate (MMA) catalyzed by *n*-butyllithium (BuLi) in the presence of carbon black.<sup>3,4</sup> Furthermore, Minoura and Katano obtained polystyrene-grafted carbon black by using the reaction of living anionic polystyrene with carbon black surface.<sup>7</sup> However, the grafting of polymers onto carbon black has been confined to vinyl polymers, and so far the surface grafting of polyamide has not been reported.

On the other hand, it has been reported that acrylamide (AAM) was polymerized into poly- $\beta$ -alanine (nylon 3) of a high degree of polymerization in the presence of anionic initiators such as alkali metal alkoxide, BuLi, or Grignard reagent at relatively high temperature as follows<sup>8–12</sup>:



The polymerization was considered to proceed through the transfer of an amide

hydrogen to a carbanion. Accordingly, such polymerization was designated as hydrogen transfer polymerization.

Therefore, it is expected that in the course of the hydrogen transfer polymerization of AAm in the presence of carbon black, growing polymer anion reacts with carbon black surface to give poly- $\beta$ -alanine-grafted carbon black. In the present paper, the hydrogen transfer polymerization of AAm in the presence of carbon black was carried out using BuLi as a catalyst, and the grafting of poly- $\beta$ -alanine onto carbon black surface was investigated.

## EXPERIMENTAL

**Materials.** The carbon black used was 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, quinonic oxygen, and carboxyl group was determined to be 0.24, 0.92, and 0.40 meq/g, respectively.

Guaranteed-reagent-grade AAm was recrystallized from absolute benzene and then sublimed under reduced pressure.

The catalyst used was *n*-hexane solution of BuLi (about 15%) from Wako Pure Chemical Industries, Ltd. The concentration of BuLi was determined by titration according to the method of the literature<sup>13,14</sup> before use.

Dioxane used as solvent was refluxed over sodium and fractionally distilled.

*N*-phenyl- $\beta$ -naphthylamine was of special grade and used without further purification.

**Polymerization Procedure.** Into a 100-mL teardrop type flask that contained 0.30 g of Neospectra II, 28 mmol of AAm, 0.01 g of *N*-phenyl- $\beta$ -naphthylamine, and 20.0 mL of dioxane, 0.56 mmol of BuLi (hexane solution) was added under nitrogen at 100°C. The reaction mixture was stirred at a constant rate with a magnetic stirrer. After the polymerization, the content of the flask was poured into a large excess of methanol containing a few percent of dilute solution of hydrochloric acid. The precipitate was filtered, washed with methanol, and dried *in vacuo* at 40°C. The conversion was calculated by the following equation:

$$\text{conversion (\%)} = \frac{\text{wt precipitate (g)} - \text{added wt carbon black (g)}}{\text{wt AAm used (g)}} \times 100$$

**Determination of Grafting Ratio, Grafting Efficiency, and Reduced Viscosity of Ungrafted Polymer.** To separate the polymer-grafted carbon black, the reaction product was dispersed in water and centrifuged at 10<sup>4</sup> rpm until carbon black was precipitated completely. The carbon black was then extracted with water by using a Soxhlet apparatus until no more polymer could be detected in the refluxing solvent. Subsequently, it was extracted with *N,N*-dimethylformamide for 50 h. However, no extract was detected in the solvent. The grafting ratio and grafting efficiency were determined by using the following equations:

$$\text{grafting ratio (\%)} = \frac{\text{wt polymer grafted (g)}}{\text{wt carbon black used (g)}} \times 100$$

$$\text{grafting efficiency (\%)} = \frac{\text{wt polymer grafted (g)}}{\text{wt total polymer produced (g)}} \times 100$$

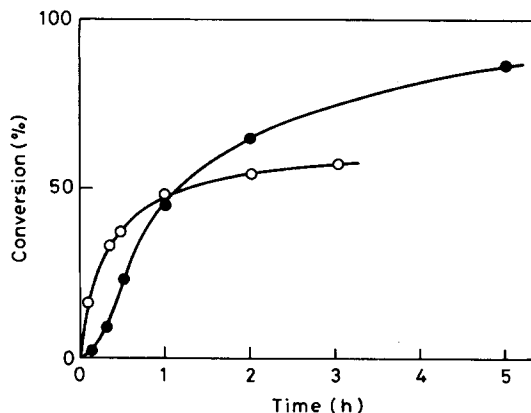


Fig. 1. Hydrogen transfer polymerization of AAm, catalyzed by BuLi, in the presence of carbon black at 80°C: AAm 28 mmol; BuLi 0.56 mmol; *N*-phenyl- $\beta$ -naphthylamine 0.01 g; dioxane 20.0 mL. (O) In the absence of carbon black; (●) in the presence of Neospectra II (0.30 g).

On the other hand, ungrafted polymer was isolated from the supernatant solution by centrifugation, and its reduced viscosity was determined with an Ubbelohde viscometer in water solution (0.9%) at 30.0°C.

**Determination of the Ratio of Hydrogen Transfer Polymerization.** The ratio of hydrogen transfer polymerization (*T* ratio) was determined by the optical density of the IR spectrum of a secondary amide group ( $1535\text{ cm}^{-1}$ ) in the polymer according to the method of Nakayama et al.<sup>15</sup>

**Treatment of Carbon Black with Sodium Tetrahydroborate.** The treatment of carbon black with  $\text{NaBH}_4$  was carried out according to the method of Studebaker.<sup>16</sup> For instance, 2.0 g of carbon black was stirred into 50 mL of an aqueous solution containing 0.2 g of  $\text{NaBH}_4$  and 0.6 g of sodium hydroxide under nitrogen atmosphere.<sup>17</sup> After reacting for 2 h at room temperature, the solution was made acidic with dilute  $\text{H}_2\text{SO}_4$ . The carbon black was subsequently filtered, washed with degassed hot water until filtrate was neutral, and then dried *in vacuo*.

## RESULTS AND DISCUSSION

**Hydrogen Transfer Polymerization of AAm Catalyzed by BuLi in the Presence of Carbon Black.** It has been reported that the polymerization of styrene catalyzed by BuLi was retarded in the presence of carbon black because BuLi was mostly consumed by a reaction with carbon black surface.<sup>3,4</sup> On the other hand, MMA was rapidly polymerized by BuLi even in the presence of carbon black, and the polymer formed was grafted onto carbon black by a reaction of the growing polymer anion with carbon black.<sup>4</sup>

Furthermore, it is well known that the quinonic oxygen and phenolic hydroxyl group present on the carbon black surface react with BuLi to give lithium phenolate ( $\text{—O}^-\text{Li}^+$ ) group on the surface.<sup>18</sup> Ohkita et al. described that the  $\text{—O}^-\text{Li}^+$  group have an ability to initiate the anionic polymerization of vinyl monomers with positive *e* value such as MMA and acrylonitrile.<sup>19,20</sup>

To obtain a polyamide-grafted carbon black, in this paper, the hydrogen transfer polymerization of AAm catalyzed by BuLi in the presence of carbon black was carried out in dioxane at 80°C and 100°C. The results are shown in Figures 1 and 2: an induction period was observed in the presence of carbon black.

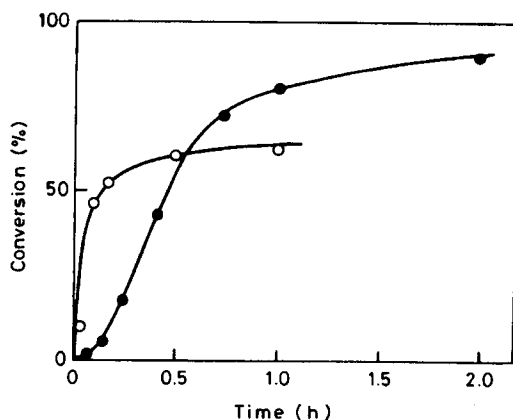
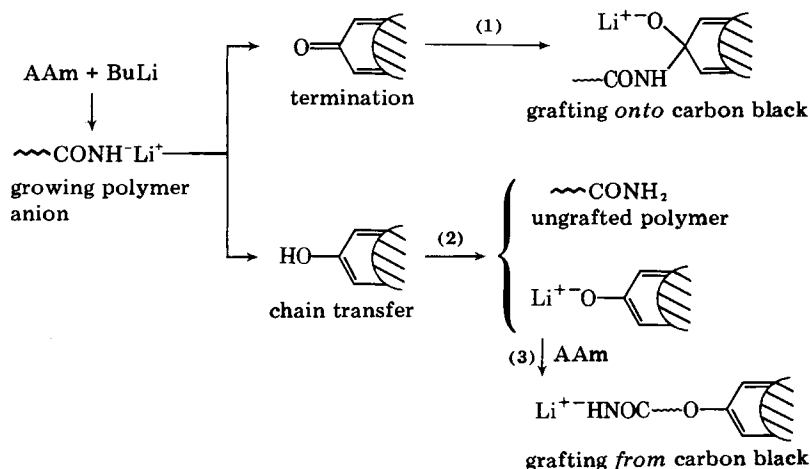


Fig. 2. Hydrogen transfer polymerization of AAm, catalyzed by BuLi, in the presence of carbon black at 100°C: (O) in the absence of carbon black; (●) in the presence of Neospectra II (0.30 g).

The phenomenon was explained as follows. As well as the polymerization of MMA in the presence of carbon black, BuLi will initiate the hydrogen transfer polymerization of AAm with positive  $e$  value rather than react with carbon black surface.

Nakayama et al. reported that, in a nonpolar solvent, the polymerization mainly proceeded by chain reaction with the intramolecular proton transfer of amide group.<sup>21</sup> Therefore, the growing polymer chains in dioxane are considered to be ion pairs such as  $\sim\text{CONH}^-\text{Li}^+$ .

Subsequently, the growing polymer anion was immediately trapped by quinonic oxygen group according to the reaction (1). Furthermore, the growing polymer anion is considered to be reacting with phenolic hydroxyl group to give the ungrafted polymer and the  $-\text{O}^-\text{Li}^+$  group on the surface, namely, chain transfer reaction to phenolic hydroxyl group [reaction (2)]. Therefore, during the induction period, the growing polymer anion was terminated by the quinonic oxygen group. After the induction period, the polymerization catalyzed by the  $-\text{O}^-\text{Li}^+$  group will predominantly occur [reaction (3)]:



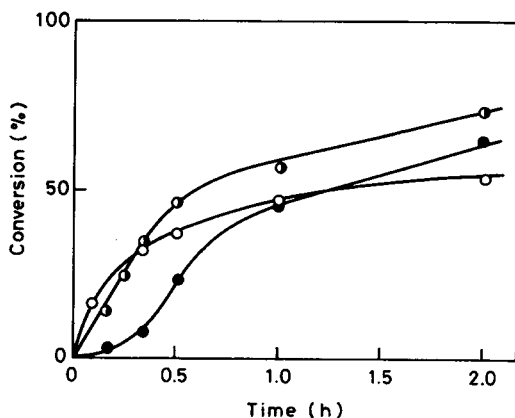


Fig. 3. Hydrogen transfer polymerization of AAm, catalyzed by BuLi, in the presence of  $\text{NaBH}_4$ -treated Neospectra II at  $80^\circ\text{C}$ : (O) in the absence of carbon black; (●) in the presence of untreated Neospectra II (0.30 g); (◐) in the presence of  $\text{NaBH}_4$ -treated Neospectra II (0.30 g).

The conversion in the presence of carbon black was found to be larger than that in the absence of carbon black. This may be due to the difference in the initiating ability of the hydrogen transfer polymerization between BuLi and the  $-\text{O}^-\text{Li}^+$  group.

**Hydrogen Transfer Polymerization of AAm in the Presence of  $\text{NaBH}_4$ -Treated Carbon Black.** To ensure the effect of quinonic oxygen group on the capture of growing polymer anion, the hydrogen transfer polymerization of AAm was carried out at  $80^\circ\text{C}$  in the presence of  $\text{NaBH}_4$ -treated carbon black. The result is shown in Figure 3.

It is well known that the quinonic oxygen group is easily reduced by the treatment with  $\text{NaBH}_4$ .<sup>16</sup>

By reduction of the quinonic oxygen group, the induction period disappeared completely. This phenomenon supports that, in the first stage of the polymer-

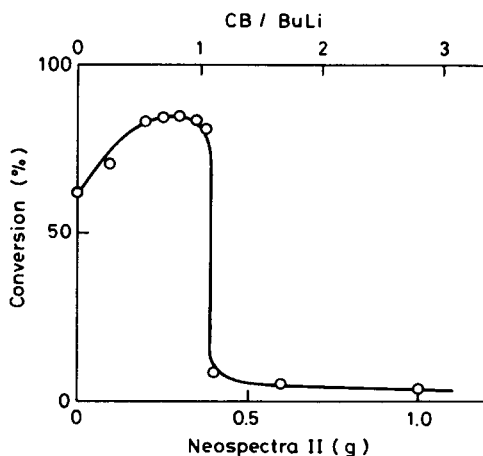


Fig. 4. Effect of the amount of Neospectra II on the hydrogen transfer polymerization of AAm: AAm 28 mmol; BuLi 0.56 mmol; *N*-phenyl- $\beta$ -naphthylamine 0.01 g; dioxane 20.0 mL;  $100^\circ\text{C}$ ; 1 h.

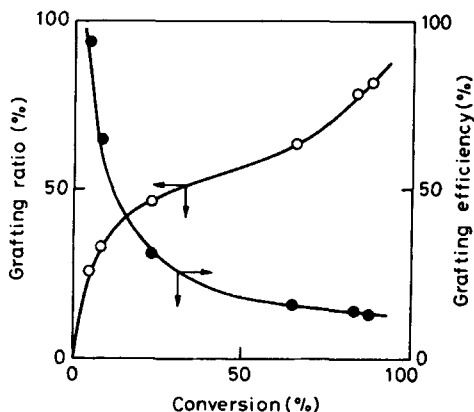


Fig. 5. Relationship between conversion and grafting ratios at 80°C.

ization (during the induction period), the growing polymer anion immediately reacts with the quinonic oxygen group on the carbon black [reaction (1)].

**Effect of the Amount of Carbon Black on the Hydrogen Transfer Polymerization.** By use of 0.56 mmol of BuLi and 28 mmol of AAm, the hydrogen transfer polymerization was carried out in the presence of various amount of carbon black at 100°C for 1 h. The result is shown in Figure 4. Although the monomer conversion after 1 h increased with an increase in the amount of carbon black added, the polymerization was almost inhibited in the presence of more than 0.3 g of carbon black. A similar phenomenon was reported during the polymerization of styrene catalyzed by BuLi in the presence of carbon black.<sup>3,4</sup>

The amount of oxygen containing group (phenolic hydroxyl, carboxyl, and quinonic oxygen group) on 0.3 g of Neospectra II is almost equivalent to 0.56 mmol of BuLi. Therefore, it is considered that, below the equivalent point, the hydrogen transfer polymerization was initiated by BuLi and the  $\text{—O—Li}^+$  group which was formed by chain transfer reaction. On the other hand, above the equivalent point the anionic polymerization was almost inhibited owing to the acidic nature of the carbon black (the pH of Neospectra II is 3.0).

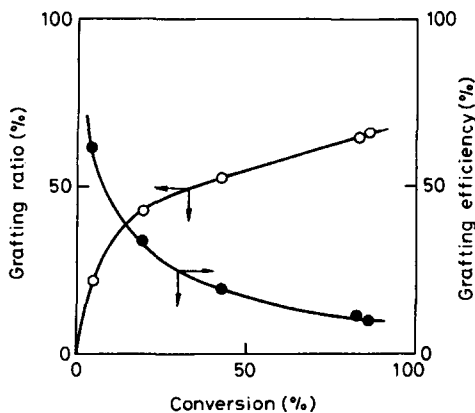


Fig. 6. Relationship between conversion and grafting ratios at 100°C.

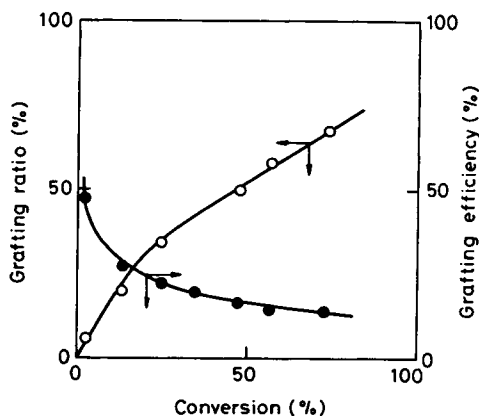


Fig. 7. Relationship between conversion and grafting ratios onto  $\text{NaBH}_4$ -treated Neospectra II at  $80^\circ\text{C}$ .

**Proof of Grafting onto Carbon Black.** The carbon black obtained from the hydrogen transfer polymerization gave a stable colloidal dispersion in water, *N,N*-dimethylformamide, and formic acid. The phenomenon suggests that the polymer (poly- $\beta$ -alanine) is grafted onto carbon black. Therefore, the grafting ratio and grafting efficiency at  $80^\circ\text{C}$  and  $100^\circ\text{C}$  was determined, and the results are shown in Figures 5 and 6, respectively. Furthermore, Figure 7 shows the relationship between conversion and grafting ratio (at  $80^\circ\text{C}$ ) onto  $\text{NaBH}_4$ -treated Neospectra II.

As shown in Figures 5 and 6, during the first few percent conversion both at  $80^\circ\text{C}$  and at  $100^\circ\text{C}$ , the grafting ratio immediately increased, and the grafting efficiency was very high. On the contrary, in the presence of  $\text{NaBH}_4$ -treated Neospectra II, the grafting ratio and grafting efficiency at  $80^\circ\text{C}$  was lower than that of untreated Neospectra II. This may be explained by the fact that, in the presence of untreated Neospectra II, the growing polymer anion was captured

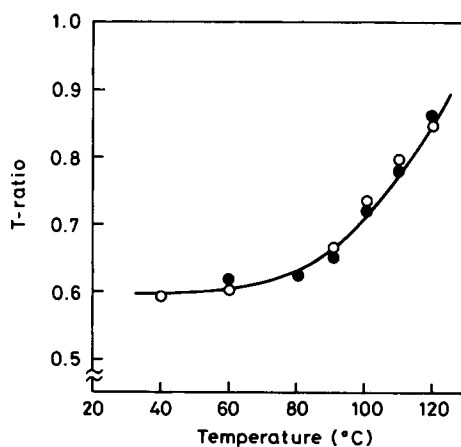


Fig. 8. Effect of polymerization temperature on *T* ratio: AAm 28 mmol; BuLi 0.56 mmol; *N*-phenyl- $\beta$ -naphthylamine 0.01 g; dioxane 20.0 mL; 1 h. (O) in the absence of carbon black; (●) in the presence of Neospectra II (0.30 g).

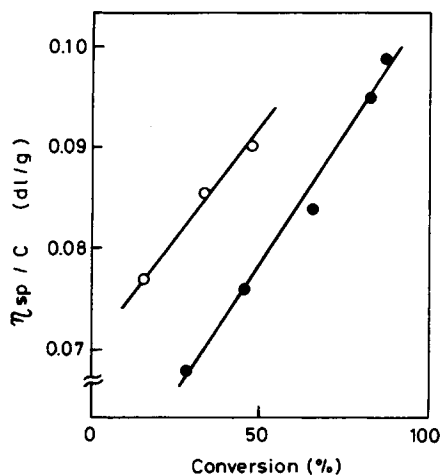


Fig. 9. Relationship between conversion and reduced viscosity of ungrafted polymer obtained at 80°C: (O) in the absence of carbon black; (●) in the presence of Neospectra II (0.30 g).

by the quinonic oxygen group during the initial stage of the polymerization as mentioned above. On the other hand, it is considered that, in the presence of  $\text{NaBH}_4$ -treated Neospectra II, the chain transfer reaction of growing polymer anion predominantly occurs in the initial stage of the polymerization because  $\text{NaBH}_4$ -treated Neospectra II have no quinonic oxygen group. Consequently, the grafting of the polymer gradually proceeds based on the propagation of the polymer from the  $-\text{O}^-\text{Li}^+$  group [reaction (3)], which is introduced by the chain transfer reaction.<sup>19</sup>

**Ratio of Hydrogen Transfer Polymerization (*T* ratio) of the Ungrafted Polymer.** The polymer grafted onto carbon black and the ungrafted polymer were hydrolyzed with  $\text{H}_2\text{SO}_4$ . These hydrolysis products show positive ninhydrin test.<sup>10,15</sup> Therefore, it is concluded that both the grafted and ungrafted polymers consist mostly of poly- $\beta$ -alanine.

It is well known that the polymer obtained from the hydrogen transfer polymerization of AAm by a conventional anionic catalyst contains both hydrogen transfer (poly- $\beta$ -alanine) and vinyl structure (poly-AAm) in one polymer chain.<sup>15</sup>

Therefore, the ratio of hydrogen transfer polymerization, that is, *T* ratio, was determined by IR spectra according to the method of Nakayama et al.<sup>15</sup> The result is shown in Figure 8.

Figure 8 shows that the *T* ratio of ungrafted polymer increased with an increase in polymerization temperature. Furthermore, the *T* ratio was found to be not affected by the presence of carbon black.

**Reduced Viscosity of Ungrafted Polymer.** The reduced viscosity of ungrafted polymer obtained from the polymerization in the presence of carbon black was compared with the one prepared in the absence of carbon black. As shown in Figure 9, it was found that the lower molecular weight polymer formed in the presence of carbon black. This may be due to the fact that the chain transfer reaction [reaction (2)] is occurring in the presence of carbon black.



## CONCLUSIONS

In the course of the hydrogen transfer polymerization of AAm catalyzed by BuLi in the presence of carbon black, poly- $\beta$ -alanine is grafted onto carbon black. The grafting process is possibly based, on the one hand, on the termination of the growing polymer anions with the quinonic oxygen groups and, the other hand, on the propagation of the polymer from the  $-\text{O}^-\text{Li}^+$  surface groups which are formed by chain transfer reaction of the growing polymer anion to phenolic hydroxyl group.

The hydrogen transfer polymerization of AAm catalyzed by the  $-\text{O}^-\text{Li}^+$  groups, previously introduced by pretreatment of phenolic hydroxyl groups with BuLi, is now under investigation.

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