Polymer Bulletin 10, 404-410 (1983)

Polymer Bulletin

Grafting of Poly-β-Alanine from Carbon Black

Hydrogen Transfer Polymerization of Acrylamide Initiated by Lithium Phenolate Group on the Surface of Carbon Black

Norio Tsubokawa, Yukihiro Nagano and Yasuo Sone

Department of Applied Chemistry, Faculty of Engineering, Niigata University, Ikarashi 2-8050,
Niigata 950-21, Japan

SUMMARY

It was found that the hydrogen transfer polymerization of acrylamide was initiated by lithium phenolate(OLi) group on the carbon black, which was introduced by the reaction of oxygen containing group on the carbon black with n-butyllithium, and that poly-β-alanine(Nylon 3) was effectively grafted onto carbon black surface: the grafting ratio at 80°C increased to 115% with an increase in conversion. The grafted polymer was considered to be propagated from OLi group on the surface. Furthermore, the ratio of hydrogen transfer polymerization to vinyl polymerization (T-ratio) increased with an increase of polymerization temperature.

INTRODUCTION

In a previous paper, we have reported that during the hydrogen transfer polymerization of acrylamide(AAm) catalyzed by n-butyllithium(BuLi) in the presence of carbon black, poly-β-alanine(Nylon 3) was grafted onto carbon black (1). It was considered that the grafting onto carbon black was based on the termination of growing polymer anion with quinonic oxygen group and the propagation of the polymer from lithium phenolate (OLi) group which formed by a chain transfer reaction of the growing polymer anion to phenolic hydroxyl group (1).

On the other hand, Papirer and his coworkers have reported that BuLi reacts with oxygen containing group present on the carbon black surface to give OLi group(carbon black-BuLi complex)(2). In addition, Ohkita et al. have described that OLi group has an ability to catalyze the anionic polymerization of methyl methacrylate and acrylonitrile (3).

In this paper, the hydrogen transfer polymerization of AAm catalyzed by OLi group on the carbon black surface, which was introduced by the reaction of oxygen containing group on the carbon black with BuLi, was carried out and the grafting of poly-β-alanine from carbon black was investigated.

$$\text{CB-OLi} + n\,\underset{\displaystyle \text{CONH}_2}{\text{CH}_2\text{=CH}} \longrightarrow \text{CB-O}\!\left(\text{CH}_2\text{CH}_2\text{CONH}\right)_n\!\!-$$

Poly-β-alanine grafted
carbon black

EXPERIMENTAL

Materials

The carbon black used was color channel black Neospectra II (Columbian Carbon Co., U.S.A., 906 m^2/g) and the contents of phenolic hydroxyl, quinonic oxygen, and carboxyl group were determined to be 0.24, 0.92, and 0.40 mequiv./g, respectively.

The purifications of AAm and dioxane were performed as previously described in detail (1).

n-Butyllithium(about 15% in hexane) obtained from Wako Pure Chemical Ind. Ltd. (Japan) was used without further purification. The content of BuLi was determined by titration (4,5) before use.

Pretreatment (Preparation of Carbon Black Containing OLi Group) and Polymerization Procedures

Into a 100 ml teardrop-type flask that contained 0.30g of vacuum-dried carbon black and 5.0 ml of dioxane, 0.56 mmol of BuLi(hexane solution) was added under dry nitrogen. The mixture was stirred with a magnetic stirrer at 30°C for 1 h.

Subsequently, 15.0 ml of dioxane solution of AAm (1.88 mol/l) and 0.01g of N-phenyl-β-naphthylamine (as an inhibitor of radical polymerization of AAm) were added to the mixture and the hydrogen transfer polymerization was conducted with stirring at 80-120°C. After a definite time, the content of the flask was poured into a large excess of methanol containing a few percent of dilute solution of HCl.

Others

The determinations of conversion, grafting ratio, grafting efficiency, reduced viscosity of ungrafted polymer, and the ratio of hydrogen transfer polymerization to vinyl polymerization (T-ratio) were carried out as previously described in detail (1).

RESULTS AND DISCUSSION

Introduction of OLi Group onto Carbon Black

It has been reported that oxygen containing groups (quinonic oxygen, phenolic hydroxyl, and carboxyl group) on the carbon black surface react with BuLi to give OLi group (2). Ohkita et al. described that OLi group (carbon black-BuLi complex) introduced by the reaction of carbon black with BuLi has an ability to initiate the anionic polymerization of vinyl monomers such as methyl methacrylate and acrylonitrile (3).

In order to find the proper conditions of pretreatment for the introduction of OLi group onto carbon black, by use of 0.30g of Neospectra II pretreated with various amounts of BuLi, the polymerization of AAm was carried out at 80°C and the initiating ability of pretreated Neospectra II was examined.

The result is shown in Figure 1. As shown in Figure 1, the polymerization was not induced when the amount of BuLi used for the pretreatment is less than 0.55 mmol.

The amount of oxygen containing group on 0.30g of Neospec-

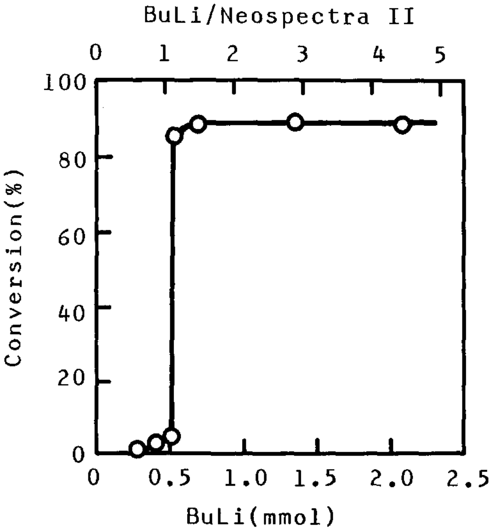

Figure 1. Effect of the amount of BuLi on the pretreatment of carbon black

Pretreatment: Neospectra II, 0.30g; dioxane, 5.0 ml; 30°C; 1 h.

Polymerization: dioxane solution of AAm (1.88 mol/l), 15.0 ml; N-phenyl-β-naphthylamine, 0.01g; 80°C; 5 h.

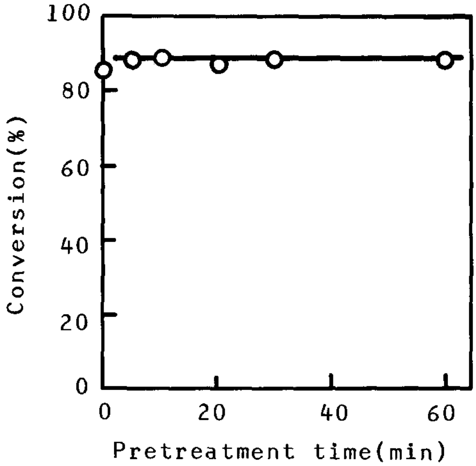

Figure 2. Effect of pretreatment time on the hydrogen transfer polymerization of AAm

Pretreatment: Neospectra II, 0.30g; BuLi;0.56 mmol;dioxane, 5.0 ml; 30°C.

Polymerization: dioxane solution of AAm (1.88 mol/l), 15.0 ml; N-phenyl-β-naphthylamine, 0.01g; 80°C; 5 h.

tra II is almost equivalent to 0.56 mmol of BuLi. Accordingly, it seems that below the equivalent point the anionic polymerization of AAm was almost completely inhibited owing to the acidic nature of the carbon black: pH of Neospectra II being 3.0.

On the other hand, above the equivalent point the polymerization is considered to be initiated both by OLi group formed by the pretreatment and by free BuLi. Therefore, it can be concluded that when 0.30g of Neospectra II was pretreated with 0.56 mmol of BuLi, the hydrogen transfer polymerization is initiated by OLi group only.

Effect of Pretreatment Time on the Polymerization

Figure 2 shows the effect of the pretreatment time of Neospectra II(0.30g) with BuLi(0.56 mmol) on the hydrogen transfer polymerization of AAm. The result indicates that the reaction

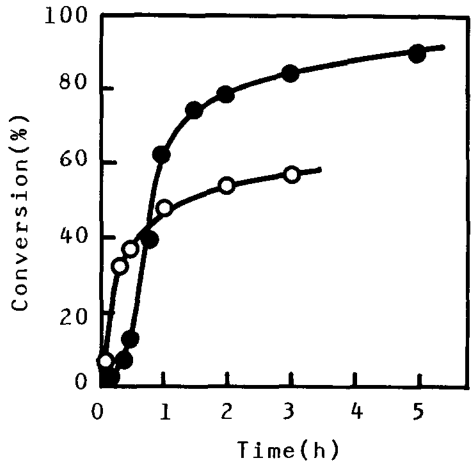

Figure 3. Hydrogen transfer polymerization of AAm initiated by OLi group on the carbon black at 80°C

Pretreatment: Neospectra II, 0.30g; BuLi,0.56 mmol;dioxane, 5.0 ml; 30°C; 1 h.

Polymerization: dioxane solution of AAm (1.88 mol/l), 15.0 ml; N-phenyl-β-naphthylamine, 0.01g.

(●), initiated by OLi group; (○), initiated by BuLi in the absence of carbon black.

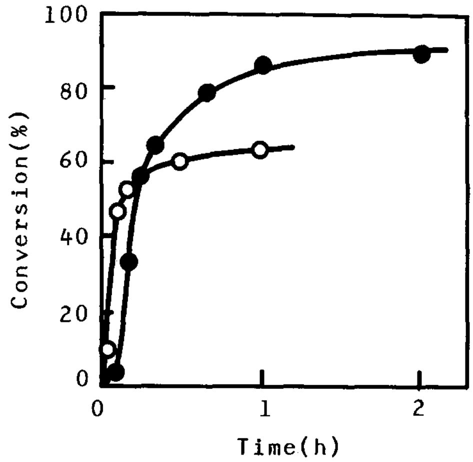

Figure 4. Hydrogen transfer polymerization of AAm initiated by OLi group on the carbon black at 100°C

Polymerization conditions are given in Figure 3.

(●), initiated by OLi group; (○), initiated by BuLi in the absence of carbon black.

of oxygen containing group on the carbon black with BuLi is very rapid. From the result shown in Figure 2, it is concluded that one hour is enough for the introduction of OLi group onto carbon black surface.

Hydrogen Transfer Polymerization of AAm Initiated by OLi Group on the Carbon Black

The hydrogen transfer polymerization of AAm initiated by OLi group introduced by the pretreatment of carbon black with BuLi was carried out at 80 and 100°C. The results are shown in Figures 3 and 4.

Figures 3 and 4 clearly show that OLi group has an ability to initiate the hydrogen transfer polymerization of AAm. The conversion of AAm initiated by OLi group was found to be larger than that catalyzed by BuLi.

Proof of Grafting onto Carbon Black

The carbon black obtained from the hydrogen transfer pol-

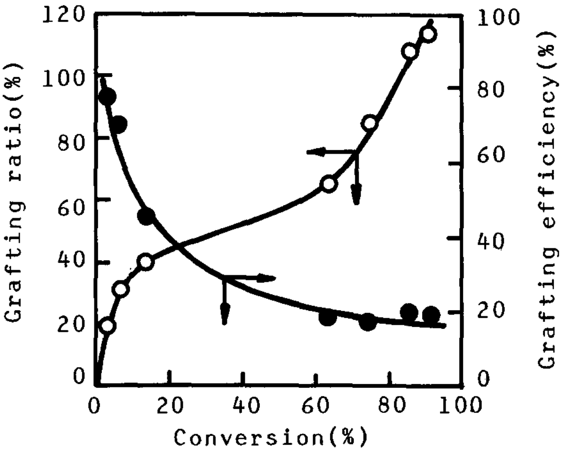

Figure 5. Relationship between conversion and grafting ratio(grafting efficiency) at 80°C

Polymerization conditions are given in Figure 3.

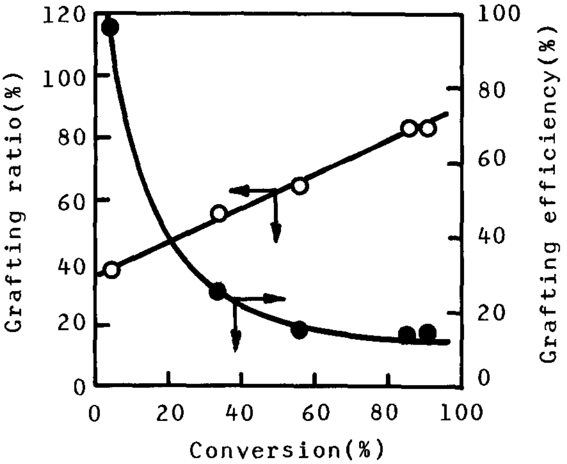

Figure 6. Relationship between conversion and grafting ratio(grafting efficiency) at 100°C

Polymerization conditions are given in Figure 3.

ymerization gave a stable colloidal dispersion in water, N,N-dimethylformamide, and formic acid. The phenomenon suggests that poly-β-alanine is grafted onto carbon black.

To ensure the grafting of polymer onto carbon black, the grafting ratio at 80 and at 100°C was determined. Figures 5 and 6 show the relationship between grafting ratio(grafting efficiency) and conversion.

The grafting ratio at 80°C increased to 115% with an increase in conversion. The values of the grafting ratio at both 80°C and 100°C was higher than those obtained from the hydrogen transfer polymerization of AAm initiated by BuLi in the presence of Neospectra II (1). In addition, the grafting efficiency was very high during the first few percents of conversion but it decreased with an increase in conversion. The result suggests that the grafted polymer is propagated from OLi group on the surface of carbon black and that the ungrafted polymer is gradually formed by a chain transfer reaction of the growing polymer anion to the monomer (6).

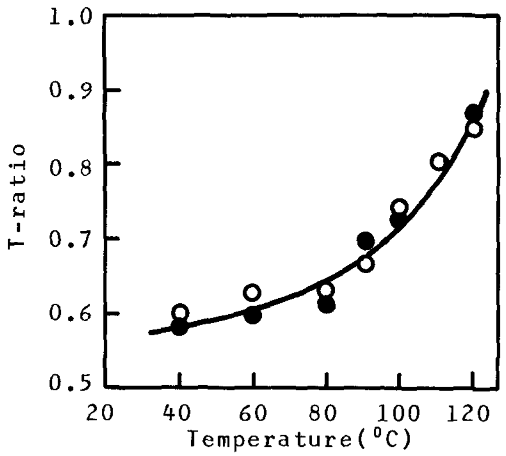

Figure 7. Effect of polymerization temperature on T-ratio of ungrafted polymer

Polymerization conditions are given in Figure 3.

(●), initiated by OLi group; (○), initiated by BuLi in the absence of carbon black.

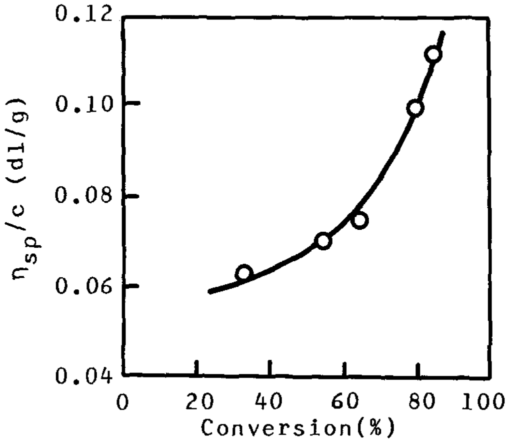

Figure 8. Relationship between conversion and reduced viscosity of ungrafted polymer obtained from the hydrogen transfer polymerization initiated by OLi group at 100°C

Polymerization conditions are given in Figure 3.

η_{sp}/c: 0.9% aqueous solution; 30.0°C.

Furthermore, the grafting ratio at 100°C was lower than that of at 80°C. This may be explained that the increasing temperature increases in the rate of the chain transfer reaction, and then causes a decrease in the grafting ratio.

T-ratio of Ungrafted Polymer

The carbon black obtained from the hydrogen transfer polymerization and ungrafted polymer were hydrolyzed by H_2SO_4. These hydrolysis products show positive ninhydrin test. Therefore, it is concluded that the polymer grafted onto carbon black and ungrafted polymer consist of poly-β-alanine (7,8).

It has been reported that the polymer obtained from the hydrogen transfer polymerization of AAm by a conventional anionic catalyst contains both hydrogen transfer (poly-β-alanine) and vinyl structure (polyacrylamide) in one polymer chain (7).

Therefore, the ratio of hydrogen transfer polymerization, that is T-ratio, was determined by IR spectra according to the method of Nakayama et al. (7).

Figure 7 shows the relationship between T-ratio and polymerization temperature. It is found that T-ratio of the ungrafted polymer increased with an increase in polymerization temperature. Furthermore, no difference in T-ratio of the ungrafted polymer between OLi group- and BuLi-initiated hydrogen transfer polymerizations can be observed.

Reduced Viscosity of Ungrafted Polymer

The reduced viscosity of ungrafted polymer obtained from the polymerization was determined. The result is shown in Figure 8. As shown in Figure 8, the reduced viscosity increased to 0.11 dl/g (H_2O; 30.0°C) with an increase in conversion. The value of the reduced viscosity is somewhat higher than that obtained from the hydrogen transfer polymerization of AAm initiated by BuLi in the presence of carbon black (1).

REFERENCES

1. N.Tsubokawa, Y.Nagano, and Y.Sone, J. Appl. Polym. Sci.,submitted for publication.
2. E.Papirer, V.T.Nguyen, and J.B.Donnet, Carbon,16, 141(1978).
3. K.Ohkita, N.Nakayama, and A.Funaki, Shikizai Kyokaishi, 53, 583(1980).
4. H.Gilman and A.Haublin, J. Am. Chem. Soc., 66, 1515(1944).
5. C.W.Kamienski and D.L.Esmay, J. Org. Chem., 25, 115(1960).
6. H.Nakayama, T.Higashimura, and S.Okamura, Kobunshi Kagaku, 23, 537(1966).
7. H.Nakayama, T.Higashimura, and S.Okamura, Kobunshi Kagaku, 23, 433(1966).
8. N.Ogata, J. Polym. Sci., 46, 271(1960).

Accepted July 26, 1983 *S*