

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Grafting of Polymers from Carbon Fiber. Anionic Graft Polymerization of Vinyl Monomers Initiated by Metallized Aromatic Rings on Carbon Fiber

Norio Tsubokawa^a; Hiroshi Hamada^a; Yasuo Sone^a

^a Faculty of Engineering, Niigata University, Niigata, Japan

To cite this Article Tsubokawa, Norio , Hamada, Hiroshi and Sone, Yasuo(1990) 'Grafting of Polymers from Carbon Fiber. Anionic Graft Polymerization of Vinyl Monomers Initiated by Metallized Aromatic Rings on Carbon Fiber', *Journal of Macromolecular Science, Part A*, 27: 6, 779 – 789

To link to this Article: DOI: 10.1080/00222339009349657

URL: <http://dx.doi.org/10.1080/00222339009349657>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

GRAFTING OF POLYMERS FROM CARBON FIBER. ANIONIC GRAFT POLYMERIZATION OF VINYL MONOMERS INITIATED BY METALLIZED AROMATIC RINGS ON CARBON FIBER

NORIO TSUBOKAWA, HIROSHI HAMADA, and YASUO SONE

Faculty of Engineering

Niigata University

8050, Ikarashi 2-nocho, Niigata 950-21, Japan

ABSTRACT

The anionic graft polymerization of vinyl monomers onto carbon fiber initiated by metallized carbon fiber was investigated. The metalation of polycondensed aromatic rings of the carbon fiber surface was achieved by the treatment of carbon fiber with *n*-butyllithium (BuLi) in *N,N,N',N'*-tetramethylethylenediamine (TMEDA) or hexamethylphosphorous triamide (HMPT) at 0°C. The anionic polymerization of methyl methacrylate (MMA) and styrene (St) was initiated by the metallized carbon fiber, and these polymers were grafted onto the surface. The conversion and the percentage of grafting increased with increasing amount of BuLi used for the metalation of carbon fiber. When 0.20 g carbon fiber was treated with 0.3 mmol BuLi in TMEDA, the percentage of grafting of PMMA and PSt reached a maximum value (PMMA, 34.5%; PSt, 37.1%). Furthermore, the metalation of aromatic rings of carbon fiber also proceeds by the treatment with BuLi in HMPT. On the contrary, no grafting was observed when carbon fiber was treated with BuLi in tetrahydrofuran (THF) or toluene. This may be

due to the fact that metalation of carbon fiber does not proceed in THF or toluene.

INTRODUCTION

The modification of the surface of vinyl polymers by grafting is one of the important procedures for the improvement of the adhesion of carbon fiber with matrix polymers [1, 2]. For instance, Yosomiya et al. reported the graft polymerization of vinyl monomers initiated by peroxyester groups on carbon fiber [3].

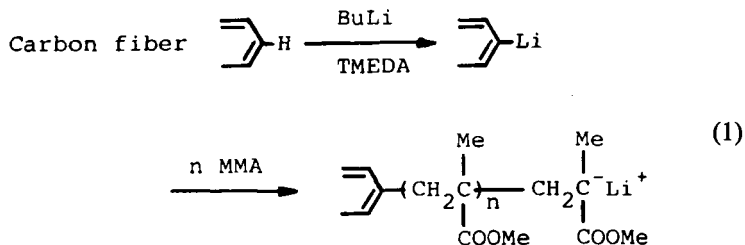
In previous papers we reported that the cationic polymerization of *N*-vinylcarbazole (NVC) and *N*-vinyl-2-pyrrolidone (NVPD) is initiated by carboxyl groups on the surface, and that the polymers formed are grafted onto the surface [4]. Furthermore, we demonstrated that potassium carboxylate (COOK) groups introduced onto a carbon fiber surface have the ability to initiate anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides and that polyester-grafted carbon fiber was formed based on the propagation of the polymer from the surface [5].

Although the percentage of grafting onto carbon fiber reached 20–30% in the above grafting reaction, the mechanical properties of carbon fiber are lowered by the oxidation needed for the introduction of carboxyl groups onto the surface.

Therefore, it is desirable that the graft polymerization be carried out by the use of polycondensed aromatic rings of carbon fiber without severe oxidation of the surface.

Donnet et al. reported anionic grafting onto carbon black initiated by metallized aromatic rings on the surface [6]; the metallized carbon black was prepared by treatment of carbon black with *n*-butyllithium (BuLi) in *N,N,N',N'*-tetramethylethylenediamine (TMEDA).

In the present paper the anionic graft polymerization of vinyl monomers initiated by metallized carbon fiber is investigated (Eq. 1).



EXPERIMENTAL

Materials

The carbon fibers used were of two types. Polyacrylonitrile-type carbon fiber (CF(A)) was obtained from Asahi Nippon Carbon Fiber Company, Japan (without sizing treatment). Pitch-type carbon fiber (CF(P)) was obtained from Union Carbide Company under the designation THORNEL P-25W4K. These carbon fibers were cut into lengths of about 5 mm and extracted with THF in a Soxhlet apparatus for 24 h. The carboxyl and phenolic hydroxyl groups contents of these carbon fibers are shown in Table 1. The determination of the carboxyl and phenolic hydroxyl groups contents was carried out by use of sodium bicarbonate [7] and 2,2-diphenyl-1-picrylhydrazyl [8], respectively.

Guaranteed reagent-grade methyl methacrylate (MMA) was washed with an aqueous solution of sodium hydrogen sulfite, aqueous alkali, dried over anhydrous sodium sulfate, and distilled twice under reduced pressure. Styrene was also washed with aqueous alkali, dried over BaO, and distilled twice under reduced pressure.

n-Butyllithium (BuLi) (about 15% *n*-hexane solution), obtained from Wako Pure Chemical Industries, Japan, was used without further purification. The concentration of BuLi was determined before use by titration according to the literature method [9, 10].

N,N,N',N'-Tetramethylethylenediamine (TMEDA) and hexamethylphosphorous triamide (HMPT) were refluxed over sodium and distilled twice under reduced pressure.

Metalation of Carbon Fiber

Into a 100-mL flask that contained 0.20 g carbon fiber and 15.0 mL TMEDA (or HMPT), an *n*-hexane solution of BuLi was added by syringe

TABLE 1. Properties of Carbon Fiber

CF	Type	Diameter of filament, μm	COOH $\times 10^5$ mol/g	OH $\times 10^5$ mol/g
CF(A)	PAN	7.0	0.23	0.11
CF(P)	Pitch	10.0	0.20	0.33

under dry nitrogen. The reaction mixture was stirred with a magnetic stirrer at 0°C for 6 h.

Polymerization Procedures

After metalation, without isolation of the metallized carbon fiber, freshly distilled MMA was added to the above reaction mixture, and 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

$$\text{conversion (\%)} = \frac{\text{precipitate (g)} - \text{carbon fiber added (g)}}{\text{monomer charged (g)}} \times 100$$

Percentage of Grafting and Grafting Efficiency

To isolate the polymer-grafted carbon fiber from the reaction product, the product was extracted with chloroform by using a Soxhlet apparatus until no more polymer could be detected in the refluxing solvent. The percentage of grafting and the grafting efficiency were determined by the following equations:

$$\text{percentage of grafting (\%)} = \frac{\text{polymer grafted (g)}}{\text{carbon fiber charged (g)}} \times 100$$

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

The amount of polymer grafted was determined from the increment of carbon fiber after the polymerization.

RESULTS AND DISCUSSION

Anionic Polymerization of MMA in the Presence of Carbon Fiber

The polymerization of MMA catalyzed by BuLi is retarded in the presence of carbon black [11]. Therefore, the polymerization of MMA in the presence of acrylonitrile-type carbon fiber (CF(A)) initiated by BuLi was compared with that initiated by BuLi-treated CF(A) in TMEDA. The results are summarized in Table 2.

It was found that the anionic polymerization of MMA is retarded in

TABLE 2. Anionic Polymerization of MMA Initiated by BuLi in the Presence of Carbon Fiber

Catalyst	CF	Time, h	Conversion, %	Percentage of grafting, %
BuLi	None	1	74.3	—
BuLi ^a	CF(A)	1	15.7	9.5
CF(A)-Li ^b	—	1	30.0	34.5

^aBuLi was added to a mixture of 0.2 g CF(A), 10.0 mL MMA, and 15.0 mL TMEDA at 0°C.

^b0.2 g CF(A) was treated with 0.3 mmol of BuLi in 15.0 mL TMEDA at 0°C for 6 h and then the polymerization was initiated by the addition of 10.0 mL MMA.

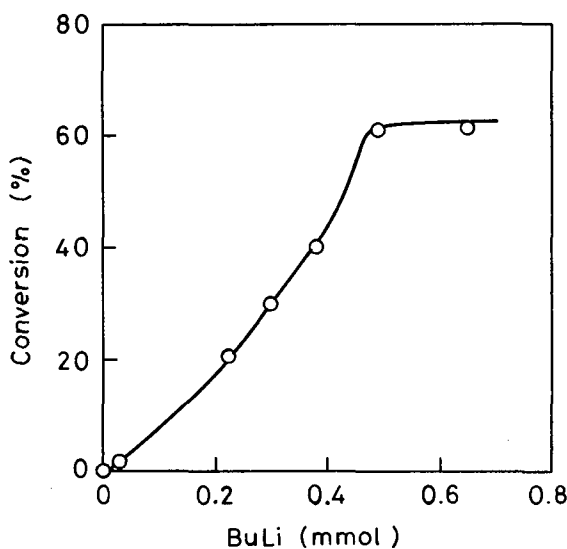


FIG. 1. Relationship between the amount of BuLi used for the pretreatment of CF(A) and conversion in the polymerization of MMA. Pretreatment: CF(A), 0.20 g; TMEDA, 15.0 mL; 0°C; 6 h. Polymerization: MMA, 10.0 mL; 0°C; 1 h.

the presence of carbon fiber. This may be due to the consumption of BuLi by functional groups on the surface or intercalation of BuLi by carbon fiber. The grafting of PMMA onto carbon fiber was scarcely observed in the polymerization system.

On the contrary, when MMA was added after pretreatment of the carbon fiber with BuLi in TMEDA, the PMMA formed was grafted onto the surface. These results suggest that surface aromatic rings of carbon fiber can be metallized and the polymerization is initiated by the metallized carbon fiber.

Effect of the Amount of BuLi for the Metalation on the Anionic Graft Polymerization of MMA

The polymerization of MMA in the presence of carbon fiber (CF(A)) treated with various amounts of BuLi at 0°C was carried out, and the effect of the amount of BuLi for metalation of carbon fiber on polymerization was examined. The results, presented in Fig. 1, show that the

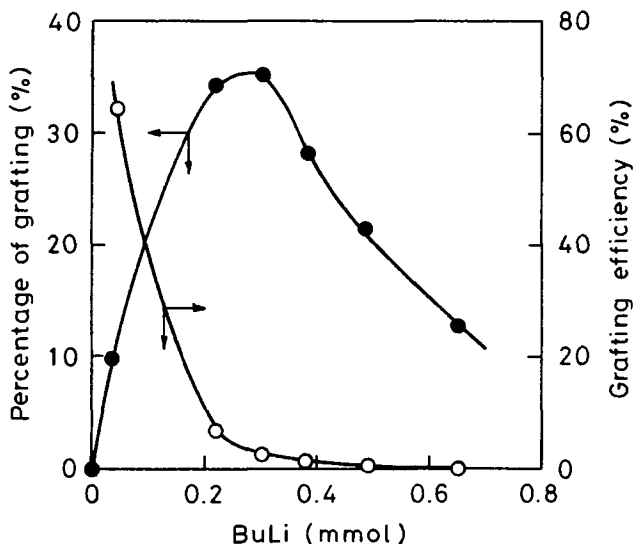


FIG. 2. Relationship between the amount of BuLi used for the pretreatment of CF(A) and percentage of grafting of PMMA onto CF(A) obtained from the polymerization shown in Fig. 1.

conversion of MMA in the polymerization increased gradually with an increasing amount of BuLi used for the metalation. No increase in conversion was observed even if more than 0.5 mmol BuLi was used for metalation.

Figure 2 shows the relationship between the amount of BuLi used for metalation and the percentage of grafting (grafting efficiency) onto carbon fiber (CF(A)) obtained from the polymerization shown in Fig. 1. The percentage of grafting increased with an increase in the amount of BuLi used for metalation and reached a maximum value (34.5%) when the amount of BuLi reached 0.3 mmol. The percentage of grafting decreased gradually, however, when more than 0.3 mmol BuLi was used for metalation of the carbon fiber. These results indicate that the grafting of PMMA onto carbon fiber may be attributed to the propagation of PMMA from metallized carbon fiber. On the other hand, in the presence of excess BuLi, above the maximum point, ungrafted polymer was formed in preference to propagation from the metallized group on the carbon fiber.

The grafting efficiency rapidly decreased when more than 0.1 mmol

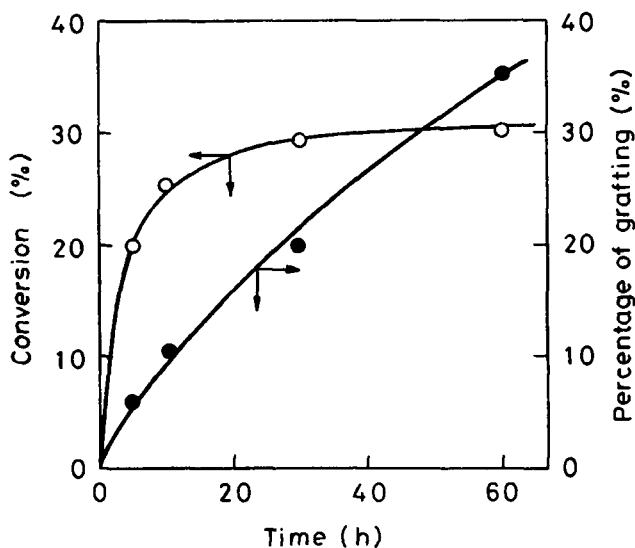


FIG. 3. The anionic graft polymerization of MMA initiated by metallized CF(A). Pretreatment: CF(A), 0.20 g; BuLi, 0.3 mmol; TMEDA, 15.0 mL; 0°C; 6 h. Polymerization: MMA, 10.0 mL.

BuLi was used for metalation. The result also indicates that when an excess of BuLi is used, ungrafted polymer is preferentially formed.

Figure 3 shows the time-conversion and time-percentage of grafting curves for the graft polymerization of MMA initiated by metallized CF(A) (0.3 mmol BuLi was used) at 0°C.

Grafting of PMMA onto Carbon Fiber (CF(P))

The grafting of PMMA onto pitch-type carbon fiber was also examined. Figure 4 shows the effect of the amount of BuLi used for metalation of CF(P) on the percentage of grafting. As well as the grafting of PMMA onto CF(A), shown in Fig. 2, the percentage of grafting increased with an increasing amount of BuLi used for metalation and reached 37.1% when the amount of BuLi used was 0.3 mmol. Furthermore, when an excess of BuLi was used, the percentage of grafting decreased.

It became apparent that PMMA can be also grafted from the surface

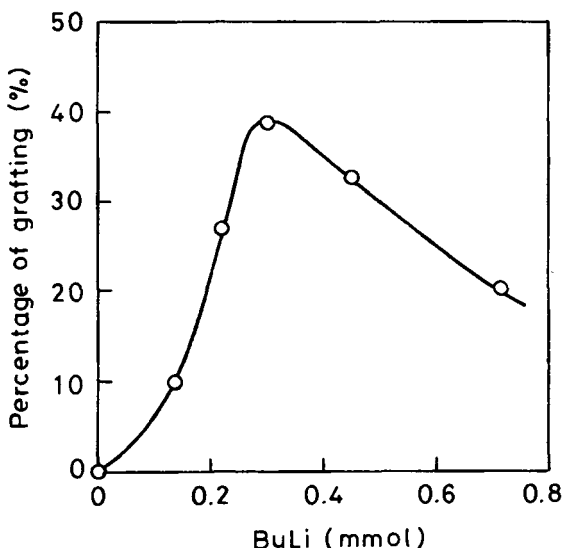


FIG. 4. Relationship between the amount of BuLi used for the pretreatment of CF(P) and percentage of grafting of PMMA onto CF(P) obtained from the polymerization of MMA. Polymerization conditions are shown in Fig. 1.

TABLE 3. Effect of Solvent on the Anionic Polymerization of MMA Initiated by Metallized Carbon Fiber^a

Solvent	Conversion, %	Percentage of grafting, %
Toluene	52.3	0
THF	71.1	0
TMEDA	20.8	35.5
HMPT	6.2	40.9

^aPolymerization conditions are given in Fig. 1.

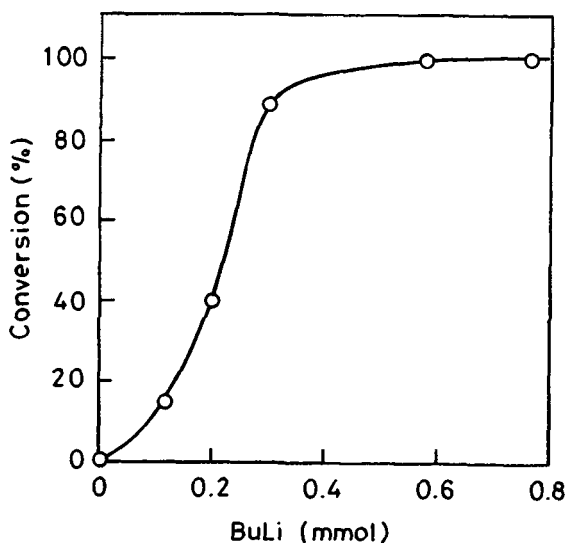


FIG. 5. Relationship between the amount of BuLi used for the pretreatment of CF(A) and conversion in the polymerization of styrene. Pretreatment: CF(A), 0.20 g; TMEDA, 15.0 mL; 0°C; 6 h. Polymerization: Styrene, 10.0 mL; 0°C; 1 h.

of CF(P) by the polymerization of MMA by use of metallized CF(P) as catalyst.

Effect of Solvent on the Metalation

Carbon fiber was treated with BuLi in TMEDA, HMPT, THF, and toluene, and the effect of solvent on the metalation of carbon fiber was investigated. The results are summarized in Table 3.

The polymerization of MMA was found to be initiated in spite of the solvent used for metalation. It is interesting to note that although PMMA was grafted onto carbon fiber in TMEDA and HMPT, no grafting was observed in THF and toluene. This indicates that the metalation of carbon fiber proceeds in TMEDA and HMPT but not in THF and toluene. Therefore, polymerization was initiated in THF and toluene by free BuLi to give ungrafted PMMA. The rate of metallized carbon fiber was found to be smaller than that of BuLi.

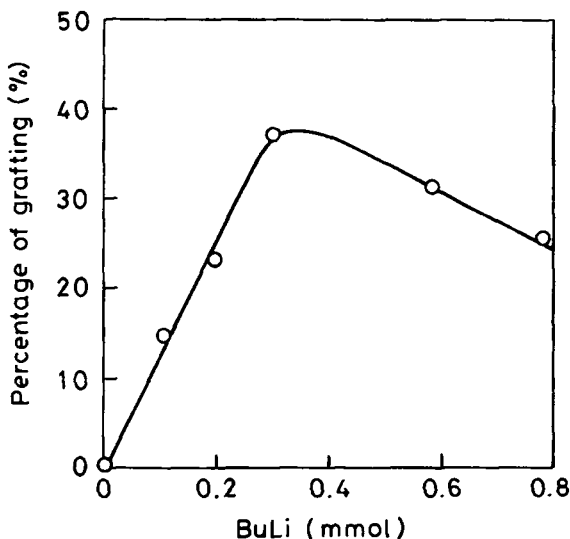


FIG. 6. Relationship between the amount of BuLi used for the pretreatment of CF(A) and percentage of grafting of polystyrene in the polymerization shown in Fig. 5.

Grafting of Polystyrene onto Carbon Fiber

The grafting of polystyrene onto carbon fiber by metallized carbon fiber was also investigated. Figure 5 shows the relationship between the amount of BuLi used for metalation and conversion in the polymerization of styrene: reaction conditions were the same as those in Fig. 1.

Figure 6 shows the effect of the amount of BuLi on the percentage of grafting of polystyrene. It is apparent that anionic polymerization of styrene is initiated by metallized carbon fiber to give polystyrene-grafted carbon fiber.

REFERENCES

- [1] D. W. Mckee and V. J. Mimeault, *Chemistry and Physics of Carbon*, Vol. 8 (P. L. Walker Jr. and P. A. Thrower, eds.), Dekker, New York, 1973, p. 151.
- [2] P. Ehrburger and J. B. Donnet, *High Technology Fibers*, Vol. 3, Part A (M. Lewin and J. Preston, eds.), Dekker, New York, 1985, p. 169.
- [3] R. Yosomiya and T. Fujisawa, *Polym. Bull.*, *13*, 7 (1985).
- [4] N. Tsubokawa, H. Maruyama, and Y. Sone, *Ibid.*, *15*, 209 (1986).
- [5] N. Tsubokawa, H. Hamada, and Y. Sone, *Polym.-Plast. Technol. Eng.*, *28*, 201 (1989).
- [6] J. B. Donnet, G. Riess, and G. Majowski, *Eur. Polym. J.*, *7*, 1069 (1971).
- [7] D. Rivin, *Rubber Chem. Technol.*, *36*, 729 (1963).
- [8] K. Ohkita and N. Tsubokawa, *Carbon*, *10*, 631 (1972).
- [9] H. Gilman and A. Haublin, *J. Am. Chem. Soc.*, *66*, 1515 (1944).
- [10] C. W. Kamienski and D. C. Esmay, *J. Org. Chem.*, *25*, 115 (1960).
- [11] K. Ohkita, N. Nakayama, A. Funaki, and M. Shimomura, *Kobunshi Ronbunshu*, *37*, 595 (1980).

Received August 8, 1989