Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Tsubokawa, Norio , Maruyama, Hiroshi and Sone, Yasuo(1988) 'Cationic Polymerization of *N*-Vinylcarbazole and *N*-Vinyl-2-Pyrrolidone Initiated by Carboxyl Groups on Carbon Fibers', Journal of Macromolecular Science, Part A, 25: 2, 171 — 182

To link to this Article: DOI: 10.1080/00222338808051961

URL: http://dx.doi.org/10.1080/00222338808051961

J. MACROMOL. SCI.–CHEM., A25(2), pp. 171-182 (1988)

CATIONIC POLYMERIZATION OF *N*-VINYLCARBAZOLE AND *N*-VINYL-2-PYRROLIDONE INITIATED BY CARBOXYL GROUPS ON CARBON FIBERS

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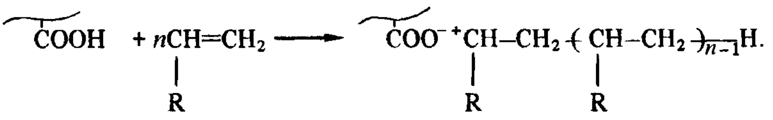
ABSTRACT

The effects of solvent and temperature on the grafting of poly(*N*-vinylcarbazole) (NVC) onto carbon fiber by cationic polymerization initiated by carboxyl groups on the surface were investigated in order to obtain poly-NVC-grafted carbon fiber with a higher percentage of grafting It was found that the rate of the polymerization of NVC increased, depending on the dielectric constant of the solvent, in the following order: toluene < 1,2-dichloroethane < nitrobenzene. However, the percentage of grafting of poly-NVC onto the carbon fiber obtained from polymerization in nitrobenzene was smaller than that in toluene. This may be due to differences in the chain transfer of the growing polymer cation to NVC and these solvents. Furthermore, poly-NVC-grafted carbon fiber with a higher percentage of grafting was formed at a lower polymerization temperature, i.e., 60°C. In addition, it became apparent that carbon fiber is capable of initiating the cationic polymerization of *N*-vinyl-2-pyrrolidone (NVPD), and poly-NVPD was grafted onto carbon fiber, depending on the termination reaction of the growing polymer cation with carboxylate anion on carbon fiber. However, cationic polymerization of isobutyl vinyl ether and α-methylstyrene was scarcely initiated by carbon fiber.

INTRODUCTION

We previously reported that carboxyl groups on carbon black surfaces are capable of initiating the cationic polymerization of vinyl monomers such as *N*-vinylcarbazole (NVC) [1], vinyl ethers [2], *N*-vinyl-2-pyrrolidone (NVPD) [3], and α-methylstyrene [3]. In a preceding paper we demonstrated that cationic polymerization of NVC can be initiated by carbon fiber [4]. The initiating sites of the polymerization were considered to be carboxyl groups on the carbon fiber because of the disappearance of the initiating ability by the blocking of those carboxyl groups [4]. Furthermore, it was found that, during the polymerization, poly-NVC is grafted onto the surface depending on the termination reaction of the growing polymer cation with carboxylate anion on a carbon fiber.

In the present paper the effects of solvent and polymerization temperature on the grafting of poly-NVC onto carbon fibers are reported. Furthermore, the initiating ability of carbon fibers for the cationic polymerization of several vinyl monomers, such as NVPD, isobutyl vinyl ether, and α-methyl styrene, was investigated.



$$\text{COOH} + n\underset{\displaystyle R}{\underset{|}{CH}}{=}CH_2 \longrightarrow \text{COO}^{-}\,{}^{+}\underset{\displaystyle R}{\underset{|}{CH}}-CH_2\left(\underset{\displaystyle R}{\underset{|}{CH}}-CH_2\right)_{n-1}H.$$

EXPERIMENTAL

Materials

Polyacrylonitrile-type carbon fibers obtained from Asahi Nippon Carbon Fiber Co. (CF 1 and CF 2, without sizing treatment) were cut into about 5-mm lengths and extracted with tetrahydrofuran using a Soxhlet apparatus for 24 h. The content of carboxyl and phenolic hydroxyl groups on these carbon fibers are shown in Table 1.

Guaranteed reagent grade NVC (Tokyo Kasei Kogyo Co., Japan) was purified by recrystallization from *n*-hexane. NVPD and α-methylstyrene (Kanto Chemical Co., Japan) were distilled twice under reduced pressure. Isobutyl vinyl ether (IBVE) (Tokyo Kasei Kogyo Co.) was washed with an aqueous solution of weak alkali and then dried over potassium hydroxide, followed by refluxing over metallic sodium and fractional distillation.

TABLE 1. Polymerization of NVPD Initiated by Various Kinds of Carbon Fiber in the Presence of Hydroquinone

Carbon fiber	COOH, meq/kg	OH, meq/kg	Conversion,[a] %
CF 1	14.4	1.8	7.6
CF 2	2.3	1.1	Trace
$KHCO_3$-CF 1[b]	0	1.8	Trace
CH_2N_2-CF 1[c]	0	0	Trace

[a] Carbon fiber, 0.20 g; NVPD, 15.0 mL; hydroquinone, 0.02 g; 80°C; 48 h.

[b] Treated with potassium bicarbonate.

[c] Treated with diazomethane.

Toluene, 1,2-dichloroethane (EDC), and nitrobenzene used as solvents were purified by the usual methods.

Polymerization Procedures

The polymerization procedures for NVC and α-methylstyrene were described in detail in previous papers [3, 4]. In the case of the polymerization of NVPD and IBVE, the polymerization was brought to a stop by introducing a small amount of base such as laurylamine. Then unreacted monomer was pumped off at 40-60°C.

The conversion was calculated by

$$\text{conversion (\%)} = \frac{\begin{matrix}\text{precipitate} \\ \text{obtained (g)}\end{matrix} - \begin{matrix}\text{carbon fiber} \\ \text{used (g)}\end{matrix}}{\text{monomer charged (g)}} \times 100.$$

Percentage of Grafting

The determination of the percentage of grafting was carried out as described in a previous paper [4]. The extracting solvents for ungrafted poly-NVC and NVPD were tetrahydrofuran and methanol, respectively. The percentage of grafting was calculated by

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

Molecular Weight of Ungrafted Polymer

The molecular weights of ungrafted poly-NVC and poly-NVPD were calculated from the intrinsic viscosity measured in benzene at 25.0°C [5] and in methanol at 30.0°C [6], respectively, by the following equations:

$$\text{poly-NVC:} \qquad [\eta] = 3.05 \times 10^{-4}\, \bar{M}_v^{0.58},$$

$$\text{poly-NVPD:} \qquad [\eta] = 2.30 \times 10^{-4}\, \bar{M}_v^{0.65}.$$

RESULTS AND DISCUSSION

Effect of Solvent on the Polymerization of NVC Initiated by Carbon Fibers

As mentioned above, during the cationic polymerization of NVC initiated by carbon fibers, poly-NVC was grafted onto the surface of carbon fiber based on the termination of growing polymer cation with carboxylate anion on the surface [4].

In order to obtain poly-NVC-grafted carbon fiber with a higher percentage of grafting, the effect of solvent on the polymerization of NVC initiated by carbon fiber in toluene (dielectric constant: 2.24), EDC (10.45), and nitrobenzene (34.6) was studied.

Figure 1 indicates that the rate of the polymerization of NVC increased in the following order: toluene < EDC < nitrobenzene, in agreement with the increasing dielectric constant of these solvents. A similar solvent effect has been reported for the polymerization of NVC initiated by carbon black [7]. The reason may be that this polymerization proceeds by cationic mechanism, as described in a previous paper [4].

Effect of Solvent on the Grafting of Poly-NVC onto Carbon Fiber

Figure 2 shows the effect of solvent on the percentage of grafting of poly-NVC onto carbon fiber. It was found that the percentage of grafting of poly-NVC obtained from the polymerization in nitrobenzene increases with increasing conversion. However, the percentage of grafting in toluene is constant, i.e., about 40%, regardless of the conversion.

These results mean that in toluene, the grafting based on the termination of growing polymer cation with carboxylate anion takes place in the first stage of the polymerization, while in nitrobenzene, the termination (grafting) proceeds gradually with progress of the polymerization.

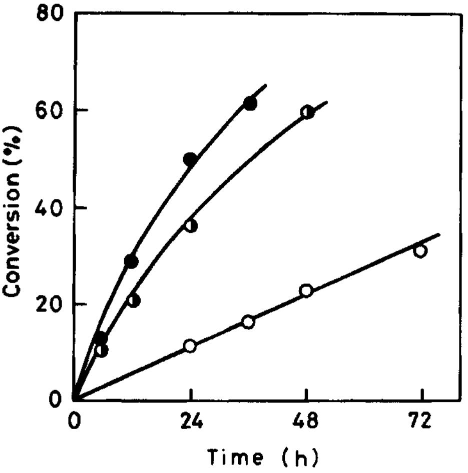


FIG. 1. Effect of solvent on the polymerization of NVC initiated by carbon fiber (CF 1). CF 1, 0.20 g; NVC, 3.0 g; solvent, 10.0 mL; 60°C. (○) Toluene, (◑) EDC, (●) nitrobenzene.

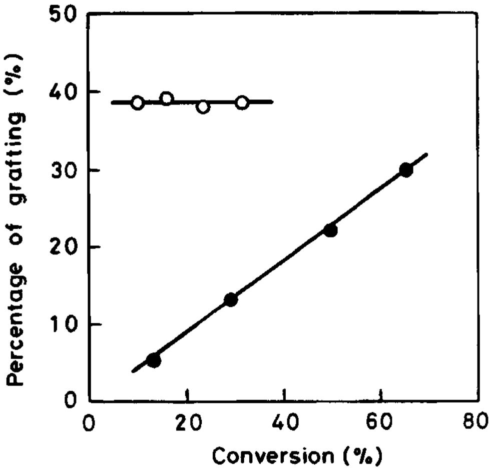


FIG. 2. Effect of solvent on the grafting of poly-NVC onto carbon fiber (CF 1) obtained from the polymerization shown in Fig. 1. (○) Toluene, (●) nitrobenzene.

On the other hand, the grafting efficiency (the proportion of grafted polymer to ungrafted polymer) in the above polymerizations was found to decrease with increasing conversion and to be less than 10%.

Effect of Solvent on the Molecular Weight of Ungrafted Poly-NVC

As shown in Fig. 3, the molecular weight of ungrafted poly-NVC was found to decrease with the progress of the polymerization. Furthermore, the molecular weight of ungrafted poly-NVC formed in toluene was higher than that in nitrobenzene. Therefore, it seems that poly-NVC of lower molecular weight is grafted onto carbon fiber in nitrobenzene than in toluene.

These results suggests that the chain transfer of growing polymer cation to monomer takes place more easily in nitrobenzene than in toluene.

Effects of Temperature on the Grafting and Molecular Weight of Ungrafted Poly-NVC

The effect of temperature on the rate of the polymerization of NVC initiated by carbon fiber was reported in a preceding paper [4]. Since it is ex-

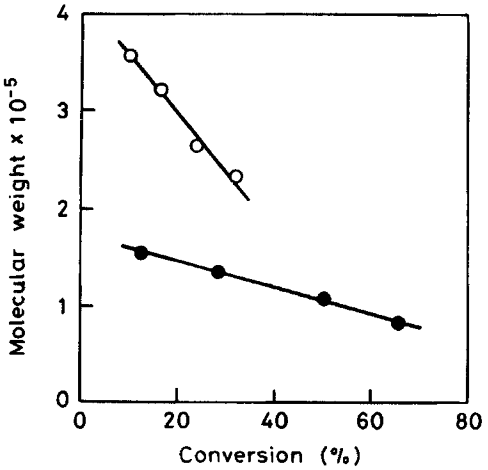


FIG. 3. Effect of solvent on the molecular weight of ungrafted poly-NVC obtained from the polymerization shown in Fig. 1. (○) Toluene, (●) nitrobenzene.

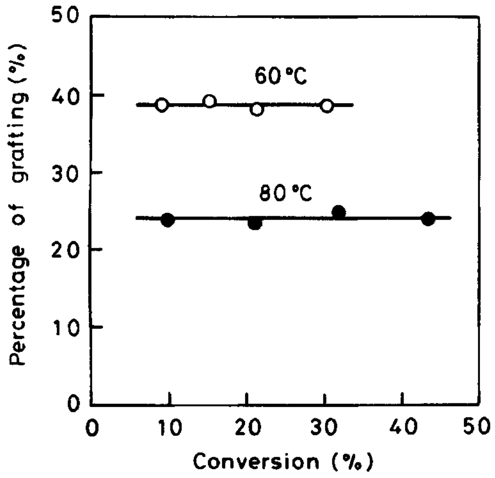


FIG. 4. Effect of temperature on the grafting of poly-NVC onto carbon fiber (CF 1). CF 1, 0.20 g; NVC, 3.0 g; toluene, 10.0 mL.

pected that the grafting of poly-NVC is affected by polymerization temperature, this effect was examined. The results are shown in Fig. 4.

The percentage of grafting of poly-NVC at 60°C was larger than that at 80°C (see Fig. 4). However, below 60°C it was very small.

Figure 5 indicates that the molecular weight of ungrafted polymer decreased with increasing polymerization temperature. These results are explained as follows: Higher temperature causes an increase in the rate of chain transfer of growing polymer chains. Accordingly, at higher temperature, poly-NVC-grafted carbon fiber with lower percentage of grafting and ungrafted poly-NVC with lower molecular weight will be formed. On the other hand, the decrease in molecular weight with increasing conversion may be attributed to monomer depletion with a progressing polymerization.

Cationic Polymerization of NVPD Initiated by Carbon Fiber

We previously reported that carboxyl groups on carbon black surfaces also can initiate cationic polymerization of NVPD [3]. Therefore, the polymerizability of NVPD in the presence of carbon fiber (CF 1) was examined. The results are shown in Fig. 6.

As shown in Fig. 6, although thermal polymerization of NVPD occurs at

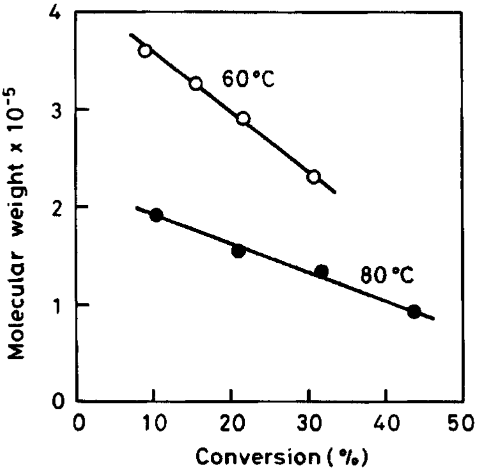


FIG. 5. Effect of temperature on the molecular weight of ungrafted poly-NVC obtained from the polymerization shown in Fig. 4.

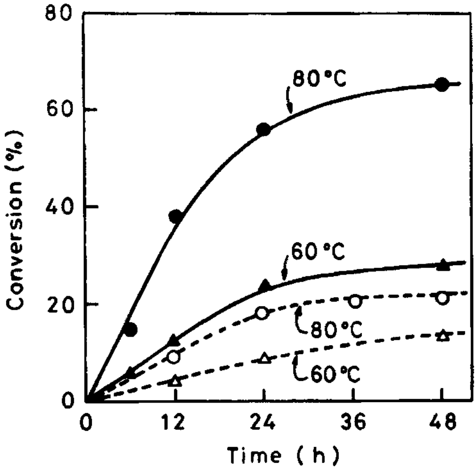


FIG. 6. Polymerization of NVPD in the presence and the absence of carbon fiber (CF 1). CF 1, 0.20 g; NVPD, 15.0 mL. (○, △) In the absence of carbon fibers; (●, ▲) in the presence of carbon fibers.

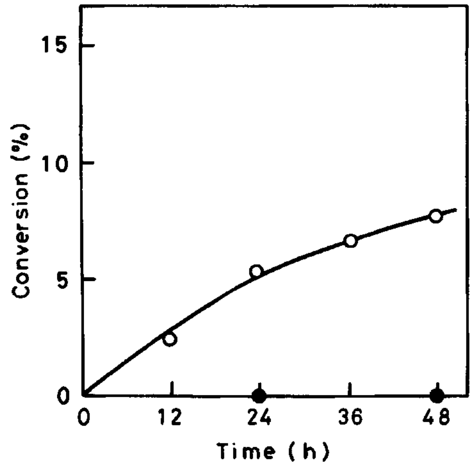


FIG. 7. Polymerization of NVPD initiated by carbon fiber (CF 1) in the presence of hydroquinone. CF 1, 0.20 g; NVPD, 15.0 mL; hydroquinone, 0.02 g; 80°C. (●) In the absence of carbon fiber; (○) in the presence of carbon fiber.

higher temperature, the rate of polymerization in the presence of carbon fiber is greater than that in its absence.

Since the thermal polymerization of NVPD was found to be completely inhibited by the addition of hydroquinone, the initiating ability of carbon fiber for the cationic polymerization of NVPD was examined in the presence of hydroquinone. The results are shown in Fig. 7, which clearly shows that the cationic polymerization of NVPD is initiated by carbon fiber.

On the other hand, Table 1 shows that carbon fiber CF 2, which contains fewer carboxyl groups, was unable to initiate the polymerization of NVPD. Furthermore, on blocking of the carboxyl groups with diazomethane [8] or potassium bicarbonate [9], carbon fiber CF 1 was found to lose its polymerization initiating ability. Based on the above results, it is concluded that carboxyl groups on carbon fiber are capable of initiating the cationic polymerization of NVPD.

Proof of Grafting of Poly-NVPD onto Carbon Fiber

Figure 8 shows the relationship between conversion and percentage of grafting of poly-NVPD onto carbon fiber obtained from the polymerization

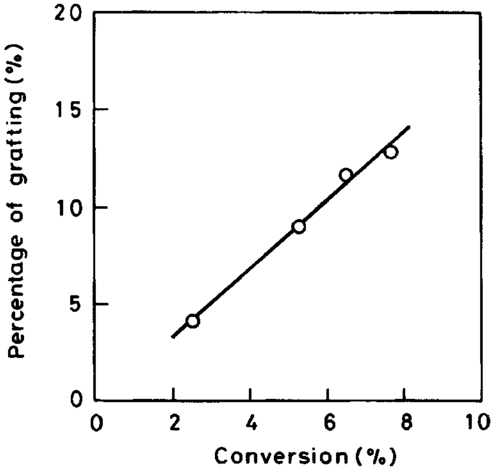


FIG. 8. Relationship between conversion and the percentage of grafting of poly-NVPD onto carbon fiber obtained from the polymerization shown in Fig. 7.

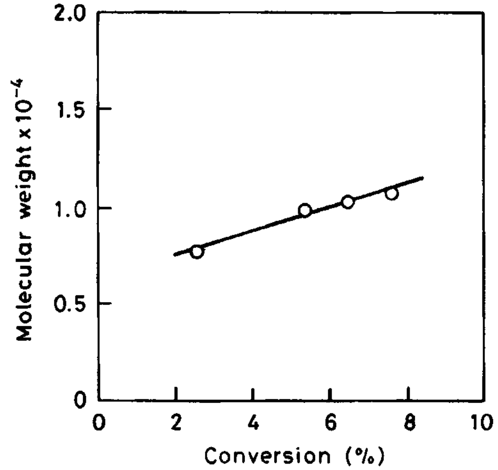


FIG. 9. Relationship between conversion and the molecular weight of ungrafted poly-NVPD obtained from the polymerization shown in Fig. 7.

shown in Fig. 7. It became apparent that during the polymerization of NVPD initiated by carbon fiber, poly-NVPD is grafter onto the surface. Similar to the grafting of poly-NVC, the grafting of poly-NVPD may be due to the termination reaction of growing polymer cation with carboxylate anion [4].

Figure 9 shows that the molecular weight of ungrafted poly-NVPD is about 10 000 and increases with progressing polymerization.

Polymerizability of Other Monomers

The polymerization was carried out at 60°C on 15.0 mL of IBVE and 0.20 g of carbon fiber CF 1. The conversion after 3 days was less than 1.0%. Furthermore, polymerization of α-methylstyrene in the presence of carbon fiber produced hardly any polymer.

CONCLUSIONS

The rate of the polymerization of NVC initiated by carboxyl groups on the surface of carbon fibers, and the grafting of poly-NVC onto the surface was affected by the solvent and the temperature. To obtain poly-NVC-grafted carbon fiber with a higher grafting ratio, the polymerization should be conducted in a solvent with a lower dielectric constant and at a lower temperature. Furthermore, carbon fiber was capable of initiating the cationic polymerization of NVPD, and poly-NVPD was grafted onto the surface.

ACKNOWLEDGMENT

We thank Asahi Chemical Industry Co., Japan, for providing us with the carbon fibers.

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Received May 18, 1987
Revision received July 16, 1987