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Carbon Fiber as an Initiator of Cationic Polymerization of N-Vinylcarbazole

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SUMMARY

Carbon fibers were found capable of initiating the cationic polymerization of N-vinylcarbazole (NVC) at 60∿80°C. The activation energy of the polymerization was estimated to be 13.4 kcal/mol. The carbon fiber lost the initiating activity of the polymerization upon the blocking of carboxyl groups on the surface by the treatment with potassium bicarbonate or diazomethane. Therefore, it was concluded that carboxyl groups on carbon fiber play an important role in the initiation of the polymerization. Furthermore, it was found that during the polymerization, poly-NVC was grafted onto the surface; the grafting ratio was determined to be 39.7% (60°C, 24 h).

INTRODUCTION

We have reported that the cationic polymerization of vinyl monomers such as N-vinylcarbazole (NVC) (1), vinyl ethers (2), N-vinyl-2-pyrrolidone (3), α-methylstyrene (3), and indene (3) was initiated by acidic carbon black, namely channel black. The initiating sites of these polymerizations were considered to be carboxyl groups on the surface (3).

Furthermore, the polymerization of NVC was also initiated by furnace black that contains no carboxyl group. Ohkita *et al.* have described that the functional group responsible for the initiation by furnace black was phenolic hydroxyl group on the surface (4). On the other hand, Biswas *et al.* have reported that the initiation mechanism involving electron transfer between unpaired electron on furnace black and lone pair on NVC (5,6).

During the polymerization initiated by carbon black, a part of polymer formed was grafted onto carbon black surface(3).

In this article, the cationic polymerization of NVC initiated by carbon fiber and the grafting of poly-NVC onto the surface were investigated.

EXPERIMENTAL

Materials

Acrylonitrile-type carbon fibers obtained from Asahi Nippon Carbon Fiber Co., Ltd. (CF 1 and CF 2, without sizing-treatment) were cut into about 5mm length and extracted with tetrahydrofuran using a Soxhlet apparatus for 24 h.

Guaranteed reagent grade NVC (Tokyo Kasei Kogyo Co., Ltd., Japan) was recrystallized from absolute *n*-hexane.

Polymerization Procedures

The polymerization was conducted under nitrogen at 40∿80°C and the reaction mixture was stirred at a constant rate with a magnetic stirrer. After the reaction, the product was poured into a large excess of methanol to precipitate the polymer containing carbon fiber. The conversion was calculated by the following equation:

$$\text{Conversion}(\%)=\frac{\begin{matrix}\text{Precipitate}\\ \text{obtained(g)}\end{matrix} - \begin{matrix}\text{Carbon fiber}\\ \text{used (g)}\end{matrix}}{\text{NVC used (g)}}\times 100$$

Determination of Grafting Ratio

The product that contained carbon fiber was extracted with tetrahydrofuran using a Soxhlet apparatus until no more polymer could be detected in the refluxing solvent. The grafting ratio of poly-NVC was determined by using the following equation:

$$\text{Grafting ratio}(\%)=\frac{\text{Polymer grafted(g)}}{\text{Carbon fiber used(g)}}\times 100$$

Treatment of Carbon Fiber

The treatment of carbon fiber by potassium bicarbonate or diazomethane was carried out by a method similar to that of carbon black as previously reported (7,8).

RESULTS AND DISCUSSION

Polymerization of NVC by Carbon Fiber

Using carbon fiber CF 1, the polymerization of NVC in toluene was carried out at 40, 60, and 80°C. The results are shown in Figure 1.

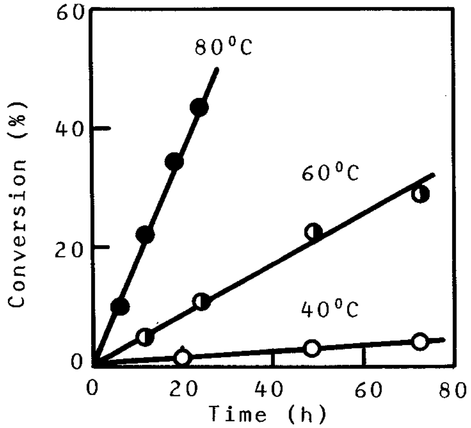


Figure 1. Polymerization of NVC initiated by carbon fiber

Carbon fiber, 0.20g; NVC, 3.0g; toluene, 10.0ml.

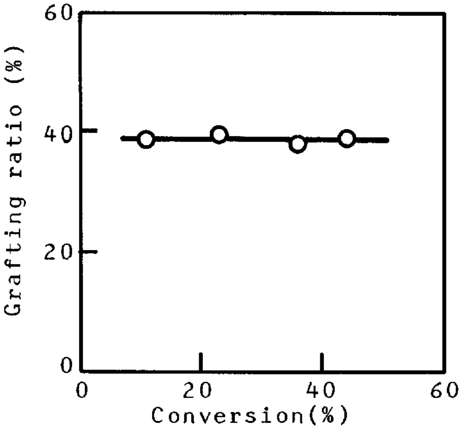


Figure 2. Relationship between the grafting ratio of poly-NVC onto carbon fiber and conversion at 60°C

Polymerization conditions are given in Figure 2.

When the polymerization of NVC was carried out in the absence of carbon fiber, no polymerization occurred at all. In the presence of carbon fiber, however, the polymerization of NVC proceeded as shown in Figure 1, in which the effect of carbon fiber as an initiator is clearly shown.

The Arrhenius plots for the above results gave a straight line and apparent activation energy of the polymerization was estimated to be 13.4 kcal/mol. The value was almost equal to that of the polymerization of NVC initiated by carboxyl group on the surface of carbon black FW 200, *i.e.* 12.8 kcal/mol (9). The result suggests that the initiating mechanism by carbon fiber is analogous to that of carbon black.

Proof of Grafting onto Carbon Fiber

Figure 2 shows the relationship between the grafting ratio of poly-NVC onto carbon fiber and conversion at 60°C. It became apparent that poly-NVC is grafted onto carbon fiber and the grafting ratio is about 40% regardless of the conversion. On the other hand, it was confirmed that poly-NVC adsorbed on the carbon fiber was removed completely by a Soxhlet extraction with tetrahydrofuran.

Functional Group on Carbon Fiber Responsible for the Initiation

To clarify the functional group responsible for the initiation, the initiating activity of various kinds of carbon fiber was examined. The results are summarized in Table I. The content of carboxyl and phenolic hydroxyl group was determined with sodium bicarbonate (10) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) (11), respectively.

As shown in Table I, it was found that the initiating activity of carbon fiber CF 2, which contains minor carboxyl group, was much smaller than that of CF 1.

Carboxyl group on carbon fiber is easily neutralized by the treatment with aqueous solution of potassium bicarbonate. In addition, carboxyl and phenolic hydroxyl group are expected to be blocked by methylation with diazomethane, because these groups on carbon black are easily methylated by this treatment (12).

TABLE I
Polymerization of NVC initiated by Carbon fiber

Carbon fiber	$COOH \times 10^5$ (eq/g)	$OH \times 10^5$ (eq/g)	Conversion (%)
none	-	-	0
CF 1	1.44	0.18	11.2
CF 2	0.23	0.11	1.3

Carbon fiber,0.20g; NVC, 3.0g; toluene, 10.0ml; 60°C; 24 h.

TABLE II
Polymerization of NVC Initiated by Treated Carbon Fiber

Carbon fiber	$COOH \times 10^5$ (eq/g)	$OH \times 10^5$ (eq/g)	Conversion[a] (%)
CF 1	1.44	0.18	44.0
$KHCO_3$-CF 1[b]	0	0.18	trace
CH_2N_2-CF 1[c]	0	0	trace

[a] Carbon fiber,0.20g; NVC,3.0g; toluene,10.0ml; 80°C; 24 h.

[b] Treated with potassium bicarbonate.

[c] Treated with diazomethane.

Therefore, the polymerization of NVC initiated by carbon fiber treated with potassium bicarbonate or diazomethane was compared with that initiated by untreated one. The results are shown in Table II. Carbon fiber CF 1 was found to lose the ability to initiate the polymerization of NVC by the treatment with potassium bicarbonate and diazomethane.

Based on the above results, it is concluded that carboxyl group on carbon fiber plays an important role in the initiation of the polymerization of NVC.

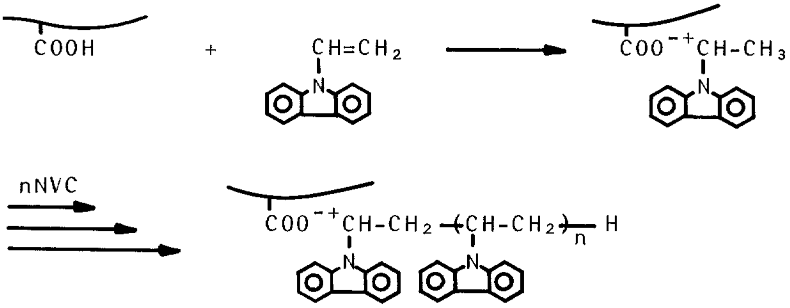
Mechanism of Initiation

It is well known that NVC is readily polymerized either by a free-radical mechanism or by a cationic mechanism. Furthermore, by the addition of organic electron acceptor, the polymerization of NVC are initiated via charge-transfer interaction (13).

The polymerization of NVC initiated by carbon fiber was totally inhibited by triethylamine and pyridine, but DPPH scarcely inhibited the polymerization. The result suggests that the polymerization initiated by carbon fiber proceeded though a cationic mechanism.

Accordingly, the polymerization of NVC is considered to be initiated by proton addition to NVC as shown in the reaction scheme. The propagation will proceed with carboxylate anion on carbon fiber as counter ion. And then grafting of poly-NVC onto carbon fiber is considered to be due to the neutralization of propagating anion. Therefore, poly-NVC was grafted onto carbon fiber with ester bond.

Initiation and Propagation



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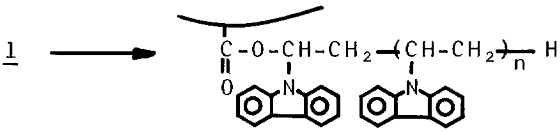
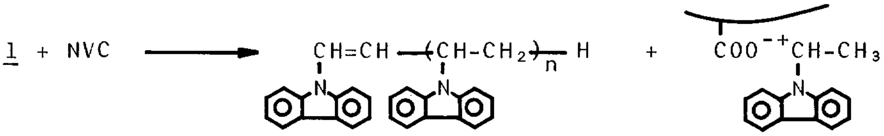
Termination (Grafting)



Formation of Ungrafted Polymer (Chain Transfer)



This grafting mechanism is supported by the fact that poly-NVC grafted onto carbon fiber was removed completely by the hydrolysis of poly-NVC-grafted carbon fiber with an aqueous alkali followed by a Soxhlet extraction with tetrahydrofuran.

On the other hand, ungrafted polymer also formed by chain transfer to the monomer.

In conclusion, the cationic polymerization of NVC can be initiated by carboxyl group on carbon fiber and poly-NVC formed was grafted onto the surface.

The effects of solvent and temperature on the polymerization and the grafting ratio of poly-NVC are now under investigation.

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