

## Carbon Whisker as an Initiator of Cationic Polymerization of *N*-Vinylcarbazole and *N*-Vinyl-2-pyrrolidone

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**ABSTRACT:** The cationic polymerization of vinyl monomers initiated by carbon whisker (vapor grown carbon fiber) was investigated. It was found that the cationic polymerization of *N*-vinylcarbazole (NVC) and *N*-vinyl-2-pyrrolidone (NVPD) is initiated by carbon whisker at 60–80°C. The activation energy of the polymerization of NVC was determined to be 56.5 kJ mol<sup>-1</sup>. During the polymerization, a part of the polymer was successfully grafted onto carbon whisker surface; the percentage of grafting of poly(NVC) in toluene at 60°C reached 89.3%. The percentage of grafting decreased with increase of polymerization temperature and increase of the dielectric constant of solvent. The initiating activity of carbon whisker considerably increased the further introduction of carboxyl groups onto the surface. By the blocking of surface carboxyl groups, carbon whisker lost initiating activity. Based on the above results, it was concluded that carboxyl groups on carbon whisker play an important role in the initiation of cationic polymerization. It was considered that polymerization is initiated by proton addition to monomer and that propagation proceeds with carboxylate anions on the surface as counter anions. The grafting of polymer onto the surface is due to the neutralization of the propagating cation with counter anion.

**KEY WORDS** Carbon Whisker / Cationic Polymerization / Initiator / *N*-Vinylcarbazole / *N*-Vinyl-2-pyrrolidone / Carboxyl Group / Surface Grafting / Termination /

Recently, vapor grown carbon fiber, *i.e.*, carbon whisker, has become applicable to high performance composite material. The properties of fiber reinforced plastics are known to depend not only on the mechanical properties of fiber and polymer matrix, but also the properties of interfacial regions between the fiber surface and matrix. To transmit stress from the matrix to the fiber, surface modification of carbon fiber and glass fiber by the grafting of polymers was widely investigated.<sup>1,2</sup> The surface grafting of polymers onto carbon whisker using its surface functional groups, however, was not reported.

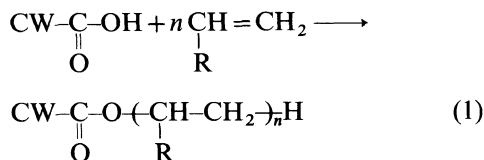
The dissociation constant of the carboxyl groups on carbon materials such as carbon black was considerably larger than that of benzoic acid because of the presence of

phenolic hydroxyl groups as neighboring groups.<sup>3,4</sup> We previously reported that carboxyl groups on carbon black surface are capable of initiating the cationic polymerization of vinyl monomers such as *N*-vinylcarbazole (NVC),<sup>5,6</sup> vinyl ethers,<sup>7</sup> and *N*-vinyl-2-pyrrolidone (NVPD).<sup>8</sup> The carboxyl groups also have ability to initiate the cationic ring-opening polymerization of spiro ortho esters,<sup>9</sup> spiro orthocarbonates,<sup>10</sup> and bicyclo ortho ethers.<sup>11</sup> During the above polymerization initiated by carbon black, a part of the polymer formed was grafted onto the surface based on termination of growing polymer cations by carbon black surface.

Recently, it was found that carboxyl groups on carbon fiber also initiate the cationic polymerization of NVC and NVPD to give

polymer-grafted carbon fiber.<sup>12,13</sup>

In the present study, the cationic polymerization of NVC and NVPD initiated by carboxyl groups on carbon whisker and



the grafting of these polymers onto the surface were investigated (eq 1). The mechanism of initiation and grafting is discussed.

## EXPERIMENTAL

### Carbon Whisker

Carbon whisker used was obtained from Asahi Chemical Ind. Ltd., Japan. The fiber diameter, fiber length, and aspect ratio were 0.1–0.3  $\mu\text{m}$ , 10–30  $\mu\text{m}$ , and 100, respectively. The content of phenolic hydroxyl, carboxyl, and quinonic oxygen groups on the surface was determined to be 0.06, 0.08, and 0.09  $\text{mmol g}^{-1}$ , respectively. The carbon whisker was extracted with chloroform using a Soxhlet apparatus to remove resinous substances on the surface and dried *in vacuo* at 110°C before use.

### Reagents

Guaranteed reagent grade NVC (Tokyo Kasei Kogyo Co., Japan) was purified by recrystallization from *n*-hexane. NVPD and  $\alpha$ -methylstyrene (Kanto Chemical Co., Japan) were distilled twice under reduced pressure. *n*-Butyl vinyl ether (nBVE), indene, and styrene were also purified by the usual methods. Toluene was washed with concentrated sulfuric acid and water, refluxed over sodium, and distilled. Nitrobenzene was washed with dilute aqueous solution of sulfuric acid, dried over calcium chloride, and distilled under reduced pressure.

Hydroquinone was recrystallized from water. All other reagents and solvents were purified by general methods.

### Preparation of Treated Carbon Whisker

To block the carboxyl group on carbon whisker, carbon whisker was treated with an aqueous solution of potassium hydroxide at 60°C. The reaction procedures were as previously described in detail.<sup>14</sup>

Treatment of carbon whisker with diazomethane was carried out by a method similar to that described by Studebaker *et al.*<sup>15</sup>

Treatment of carbon whisker with nitric acid to introduce carboxyl group on the surface was carried out as follows.<sup>16</sup> Into a 200  $\text{cm}^3$  flask equipped with a reflux condenser, 5.0 g of carbon whisker and 70  $\text{cm}^3$  of 35% nitric acid were added. The mixture was stirred at 110°C for 5 h. After the reaction, the carbon whisker thus obtained was washed with distilled water until the filtrate became neutral.

### Polymerization Procedures

The polymerization of vinyl monomers was carried out as follows. Carbon whisker, monomer, and solvent were introduced into a 100  $\text{cm}^3$  of flask. The mixture was stirred with a magnetic stirrer under dry nitrogen. After a definite period of time, the contents of the flask were poured into a large amount of methanol to precipitate the polymer and carbon whisker. In the case of NVPD, nBVE, and  $\alpha$ -methylstyrene, the polymerization was brought to a stop by introducing a small amount of laurylamine. The unreacted monomer then pumped off at 40–60°C. The conversion was calculated by the following equation:

Conversion (%) =

$$\frac{\text{Precipitate (g)} - \text{Carbon whisker added (g)}}{\text{Monomer charged (g)}} \times 100$$

### Percentage of Grafting and Grafting Efficiency

The isolation of polymer-grafted carbon whisker was achieved by extraction of the ungrafted polymer from the reaction product using a Soxhlet extractor. The procedure for

the extraction was described in detail in the previous paper.<sup>17</sup> The extracting solvent for ungrafted poly(NVC) and poly(nBVE) was tetrahydrofuran and that for poly(NVPD), methanol. The percentage of grafting and grafting efficiency were calculated by the following equations:

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

Grafting efficiency (%) =

$$\frac{\text{Polymer grafted (g)}}{\text{Total polymer formed (g)}} \times 100$$

The amount of polymer grafted was determined from the increment in weight of carbon whisker after the polymerization.

#### Molecular Weight of Ungrafted Poly(NVC)

The molecular weight of ungrafted poly(NVC) was calculated from the intrinsic viscosity measured in benzene at 25°C by the following equation<sup>18</sup>:

$$[\eta] = 3.05 \times 10^{-4} \bar{M}_v^{0.58}$$

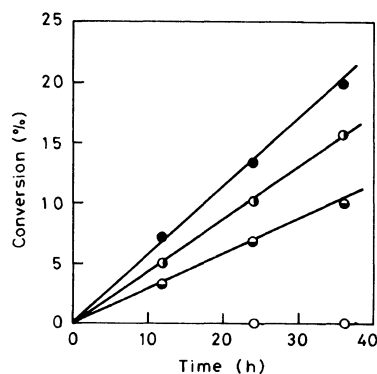
## RESULTS AND DISCUSSION

### Polymerization of NVC by Carbon Whisker

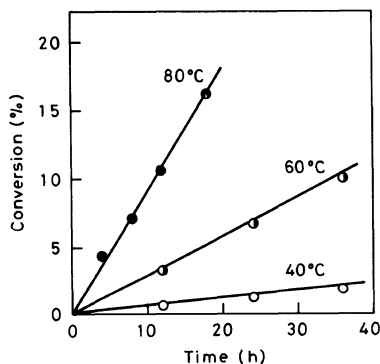
Using various amounts of carbon whisker, the polymerization of NVC was carried out in toluene at 60°C. The results are shown in Figure 1. When the polymerization of NVC was carried out in the absence of carbon whisker, no polymerization was observed at all. In the presence of carbon whisker, the polymerization of NVC was successfully initiated. The rate of polymerization increased with the amount of carbon whisker, on which the effect of carbon whisker as an initiator was clearly shown.

### Effect of Temperature on the Polymerization

In the presence of carbon whisker, the polymerization of NVC in toluene was carried



**Figure 1.** Effect of the amount of carbon whisker on the polymerization of NVC. NVC, 3.0 g; toluene, 5.0 cm<sup>3</sup>; 60°C. Carbon whisker: (○), 0 g; (◐), 0.05 g; (◑), 0.10 g; (●), 0.15 g.



**Figure 2.** Effect of temperature on the polymerization of NVC initiated by carbon whisker. Carbon whisker, 0.05 g; NVC, 3.0 g; toluene, 5.0 cm<sup>3</sup>.

out at 40, 60, and 80°C and the effect of temperature on the polymerization was examined. The results are shown in Figure 2. The rate of polymerization was found to increase with the temperature of the polymerization. The rate of polymerization at 40°C, however, was small.

Arrhenius plots for the above results gave a straight line and the apparent activation energy of the polymerization was estimated as 56.5 kJ mol<sup>-1</sup>. This value is almost equal to that of the polymerization of NVC initiated by carboxyl groups on carbon black and carbon fiber in toluene.<sup>12,13</sup> This suggests that the initiating mechanism by carbon whisker is

analogous to that of carbon black and carbon fiber.

#### *Proof of Grafting on Carbon Whisker*

The carbon whisker obtained after polymerization produced a stable dispersion in tetrahydrofuran. This suggests that poly(NVC) was grafted onto the carbon whisker.

Figure 3 shows the relationship between conversion and the percentage of grafting. It was found that poly(NVC) is grafted onto carbon whisker and the percentage of grafting is about 90% at 60°C and about 60% at 80°C regardless of the conversion. The percentage of grafting at 60°C is larger than that at 80°C, possibly because a higher temperature facilitates chain transfer of growing polymer chains to monomer.

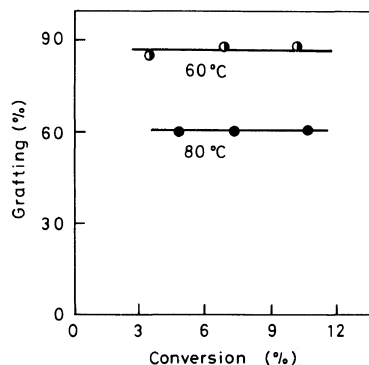
The percentage of grafting of poly(NVC) onto carbon whisker was larger than that onto carbon fiber, because of the higher content of carboxyl groups on carbon whisker.<sup>12,13</sup>

Figure 4 shows the relationship between conversion and the grafting efficiency. As shown in Figure 4, the grafting efficiency decreased with increase in conversion. This indicates that the polymerization is initiated by carbon whisker surface and ungrafted polymer is gradually formed by a chain transfer reaction of growing polymer cations to the monomer.

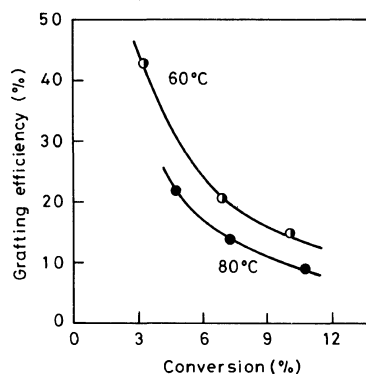
#### *Effect of Solvent on the Polymerization*

The polymerization of NVC was carried out in toluene and nitrobenzene and the effect of the solvent on the polymerization of NVC was studied. The results are shown in Figure 5. The rate of the polymerization in nitrobenzene was found to be much larger than that in toluene. A similar solvent effect was observed in the polymerization of NVC initiated by carbon fiber<sup>12,13</sup> and carbon black.<sup>5,6</sup> This polymerization thus possibly proceeds by cationic mechanism.

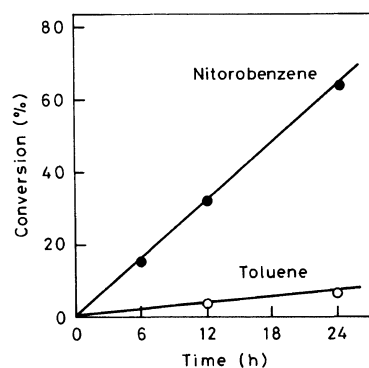
Table I shows the effect of solvent on the percentage of grafting and molecular weight of ungrafted poly(NVC). Contrary to the polym-



**Figure 3.** Relationship between conversion and percentage of grafting of poly(NVC) onto carbon whisker. Polymerization conditions are given in Figure 2.



**Figure 4.** Relationship between conversion and grafting efficiency of poly(NVC) onto carbon whisker. Polymerization conditions are given in Figure 2.



**Figure 5.** Effect of solvent on the polymerization of NVC initiated by carbon whisker. Carbon whisker, 0.05 g; NVC, 3.0 g; solvent, 5.0 cm<sup>3</sup>; 60°C.

**Table I.** Effect of solvent on the polymerization of NVC initiated by carbon whisker<sup>a</sup>

Initiator	Solvent	Conversion	Grafting	$\bar{M}_v \times 10^{-5}$
		%	%	
None	Toluene	0	—	—
None	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	0	—	—
Carbon whisker	Toluene	6.7	89.3	2.7 <sup>b</sup>
Carbon whisker	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	63.2	37.8	1.5 <sup>b</sup>

<sup>a</sup> Carbon whisker, 0.05 g; NVC, 3.0 g; solvent, 5.0 cm<sup>3</sup>; 60°C; 24 h.

<sup>b</sup> Molecular weight of ungrafted polymer determined by viscometry.

erization rate, the percentage of grafting and molecular weight of ungrafted poly(NVC) in nitrobenzene having higher dielectric constant were smaller than those in toluene. The reason for this may be that the chain transfer of growing polymer cation to monomer takes place more easily in nitrobenzene than in toluene having lower dielectric constant.

#### *Functional Group on Carbon Whisker Surface Responsible for the Initiation*

Table II shows the effect of additive on the polymerization of NVC initiated by carbon whisker. As shown in Table II, polymerization was totally inhibited by the addition of water, pyridine, and triethylamine, but not 2,2-diphenyl-1-picrylhydrazyl (DPPH) and hydroquinone. These results indicate the cationic nature of the polymerization.

To clarify the functional group responsible for the initiation, the initiating activity of various treated carbon whiskers was compared with that of an untreated one. The results are shown in Table III.

Carboxyl groups on carbon whisker are easily neutralized by the treatment with potassium hydroxide.<sup>14</sup> It is well known that carboxyl and phenolic hydroxyl groups are blocked by methylation with diazomethane.<sup>15</sup>

On the other hand, by treatment with nitric

**Table II.** Effects of additives on the polymerization of NVC initiated by carbon whisker<sup>a</sup>

Additives	Conversion
	%
None	6.7
DPPH <sup>b</sup>	6.1
Hydroquinone	6.2
Water	0
Pyridine	0
Triethylamine	0

<sup>a</sup> Carbon whisker, 0.05 g; NVC, 3.0 g; toluene, 5.0 cm<sup>3</sup>; additive, 0.5 cm<sup>3</sup> or 0.01 g; 60°C; 24 h.

<sup>b</sup> 2,2-Diphenyl-1-picrylhydrazyl.

**Table III.** Initiating activity of various treated carbon whiskers<sup>a</sup>

Carbon Whisker	Carboxyl group	Conversion
	mmol g <sup>-1</sup>	%
Untreated	0.08	6.7
KOH-treated	0	0
CH <sub>2</sub> N <sub>2</sub> -treated	0	0
HNO <sub>3</sub> -treated	0.12	9.2

<sup>a</sup> Reaction conditions are shown in Table I.

acid, carboxyl groups can be introduced onto carbon whisker.<sup>16</sup> The content of carboxyl group on carbon whisker after treatment with 35% nitric acid (110°C, 5 h) is determined to be 0.12 mmol g<sup>-1</sup> by titration.<sup>19</sup>

The results shown in Table III indicate that carbon whisker lost the ability to initiate the polymerization of NVC by treatment with potassium hydroxide and diazomethane. On the contrary, by treatment of nitric acid, the initiating activity of carbon whisker considerably increased.

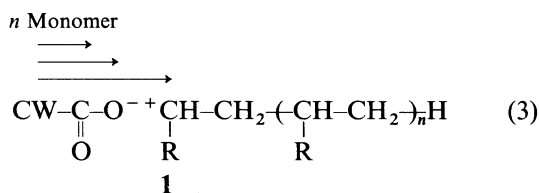
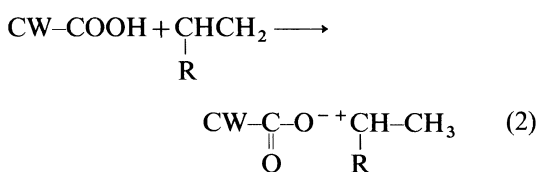
The above results clearly show the role of carboxyl groups on the surface as an initiator in the polymerization of NVC.

#### *Mechanism of Initiation and Grafting*

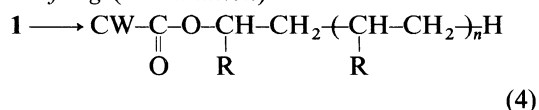
Based on the above results, the polymerization of NVC is considered to be initiated by

proton addition to NVC as shown in the reaction scheme (eq 2, 3, 4, and 5). The propagation will proceed with carboxylate anion on carbon whisker as counter ion. The grafting of polymer onto the surface is thus considered to be due to the neutralization of propagating cation. On the other hand, ungrafted polymer also formed by a chain transfer of propagating cation to monomer.

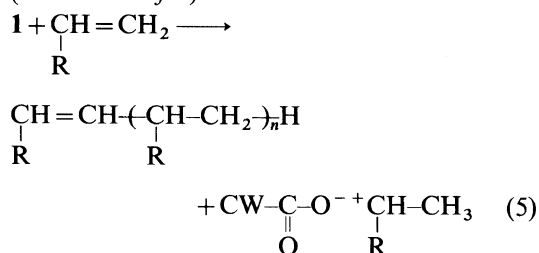
#### Initiation and Propagation



#### Grafting (Termination)



#### Formation of Ungrafted Polymer (Chain Transfer)



This grafting mechanism is supported by the fact that poly(NVC) grafted onto carbon whisker was completely removed by hydrolysis of poly(NVC)-grafted carbon whisker.

As shown in Figures 2 and 3, conversion increased with the progress of polymerization,

**Table IV.** Initiating activity of carbon whisker for the cationic polymerization of several vinyl monomers<sup>a</sup>

Monomer	Time	Conversion	Grafting
	h	%	%
<i>N</i> -Vinylcarbazole	24	6.7	89.3
<i>n</i> -Butyl vinyl ether	48	0.2	trace
<i>N</i> -Vinyl-2-pyrrolidone	72	10.3	14.8
$\alpha$ -Methylstyrene	72	0	—
Indene	24	0	—
Styrene	24	0	—

<sup>a</sup> Reaction conditions are given in Table I.

but the percentage of grafting leveled off at the initial stage of the polymerization. This indicates that after the percentage of grafting reached about 90% at 60°C, ungrafted polymer preferentially formed by the chain transfer reaction and termination by neutralization of growing polymer cation scarcely proceeded. This may be due to the change of acidity of carboxyl group by the influence of neighboring ester groups formed by the grafting of polymers.

#### Initiating Ability of Carboxyl Group on Carbon Whisker

The polymerization of several vinyl monomers initiated by carbon whisker was investigated. The results are shown in Table IV. In the polymerization of NVPD, hydroquinone was added to inhibit the thermal polymerization. As shown in Table IV, carbon whisker has the ability to initiate the cationic polymerization of NVPD and nBVE as well as NVC. The polymerization rate of nBVE, however, was negligibly small. Carbon whisker failed to initiate the polymerization of  $\alpha$ -methylstyrene, indene, and styrene. The same tendency was observed in the cationic polymerization initiated by carboxyl groups on carbon fiber. This may be due to the relatively lower polymerizability of these monomers by cationic catalyst.

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