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

Cationic Grafting of Vinyl Polymers onto a Carbon Whisker, Initiated by Acylium Perchlorate Groups Introduced onto the Surface

Norio Tsubokawa[a]; Toshio Yoshihara[a]
[a] Department of Material and Chemical Engineering Faculty of Engineering, Niigata University, Niigata, Japan

To cite this Article Tsubokawa, Norio and Yoshihara, Toshio(1993) 'Cationic Grafting of Vinyl Polymers onto a Carbon Whisker, Initiated by Acylium Perchlorate Groups Introduced onto the Surface', Journal of Macromolecular Science, Part A, 30: 8, 517 — 529

To link to this Article: DOI: 10.1080/10601329308009427

URL: http://dx.doi.org/10.1080/10601329308009427

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.

J.M.S.—PURE APPL. CHEM., A30(8), pp. 517–529 (1993)

CATIONIC GRAFTING OF VINYL POLYMERS ONTO A CARBON WHISKER, INITIATED BY ACYLIUM PERCHLORATE GROUPS INTRODUCED ONTO THE SURFACE

NORIO TSUBOKAWA* and TOSHIO YOSHIHARA

Department of Material and Chemical Engineering
Faculty of Engineering
Niigata University
8050, Ikarashi 2-nocho, Niigata 950-21, Japan

ABSTRACT

The cationic graft polymerization of vinyl monomers onto a carbon whisker, vapor-grown carbon fiber, initiated by acylium perchlorate groups introduced onto the surface, was investigated. The introduction of acylium perchlorate groups onto a carbon whisker was achieved by the treatment of a carbon whisker having acyl chloride groups, which were introduced by the reaction of surface carboxyl groups with thionyl chloride, with silver perchlorate in nitrobenzene. It was found that the cationic polymerization of vinyl monomers, such as styrene, indene, *N*-vinyl-2-pyrrolidone, and *n*-butyl vinyl ether, is initiated by acylium perchlorate groups on a carbon whisker. In the polymerization, the corresponding vinyl polymers were grafted onto a carbon-whisker surface based on the propagation of polymer from the surface: the percentage of grafting of polystyrene and polyindene reached 42.5 and 100.3%, respectively. The percentage of polystyrene grafting decreased with increasing polymerization temperature because of preferential chain transfer reactions at higher temperatures. Polymer-grafted carbon whisker gave a stable colloidal dispersion in a good solvent for grafted polymer.

INTRODUCTION

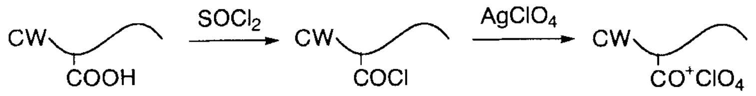
Carbon fibers and carbon whiskers, i.e., vapor-grown carbon fibers, have become applicable for high performance fiber reinforced composite materials. To improve the adhesion of such fibers to a matrix polymer, modifications of surfaces have been widely investigated [1-7].

In preceding papers we reported the grafting of several polymers onto a carbon whisker surface. For instance, the anionic graft polymerization of vinyl monomers onto carbon whiskers was initiated by metallized aromatic rings and/or phenoxy lithium groups introduced onto the surface [6]. Furthermore, the grafting of polyester onto the surface of carbon fibers [3] and carbon whiskers [7] was successfully achieved by the anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides initiated by potassium carboxylate groups introduced onto these surfaces. During the polymerization, the corresponding polymer was effectively grafted onto the surface because of the propagation of grafted chains from the surfaces.

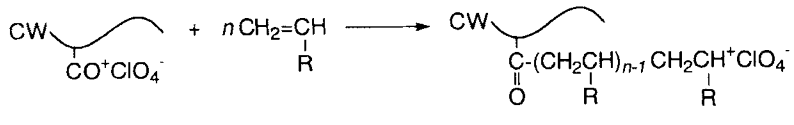
On the other hand, we demonstrated that carboxyl groups present on carbon materials, such as carbon fibers [4], carbon whiskers [5], and carbon black [8], have an ability to initiate the cationic polymerization of *N*-vinylcarbazole and *N*-vinyl-2-pyrrolidone. In the polymerization, a part of the polymer was grafted onto these surfaces based on the termination reaction of the growing polymer cation with the carboxylate anion on the surface. The surface carboxyl groups, however, were unable to initiate the cationic polymerization of other vinyl monomers and the ring-opening polymerization of cyclic ethers and lactones.

On the other hand, we reported the cationic grafting of polystyrene [9], polyesters [10], polyethers [11], and polyacetals [12] onto carbon black by the use of acylium perchlorate groups introduced onto the surface.

In the present paper, the introduction of acylium perchlorate groups onto carbon whiskers (Eq. 1) and the cationic graft polymerization of several vinyl monomers onto carbon whiskers initiated by the acylium perchlorate groups (Eq. 2) are reported. Furthermore, the stability of polymer-grafted carbon whisker dispersion in organic solvents is examined.



(1)



(2)

EXPERIMENTAL

Carbon Whisker

The carbon whiskers used were obtained from Asahi Chemical Industry Ltd., Japan. The carbon whiskers were extracted with chloroform by using a Soxhlet apparatus to remove resinous substances on the surface and dried in vacuo at 110°C

TABLE 1. Properties of Carbon Whiskers Used

Code	Carbon whisker	Diameter, μm	Length, μm	Functional group, mmol/g COOH	OH	C=O
CW	Untreated	0.1-0.3	10-30	0.08	0.02	0.09
CW(M)	HNO_3-treated	0.1-0.3	10-30	0.12	0.03	0.11

before use. The properties of carbon whiskers are shown in Table 1. The fiber diameters and lengths were determined by SEM. The determination of the content of phenolic hydroxyl [13], carboxyl [14], and quinonic oxygen groups [15] was carried out by the use of 2,2-diphenyl-1-picrylhydrazyl, sodium bicarbonate, and sodium borohydride, respectively.

Reagents

Styrene was washed with aqueous alkali, dried over barium oxide, and distilled twice under reduced pressure. *n*-Butyl vinyl ether was washed with aqueous alkali, refluxed over sodium hydride, and fractionally distilled before use. *N*-Vinyl-2-pyrrolidone was distilled under reduced pressure. Indene was stirred overnight with 6 mol/dm^3 hydrochloric acid, refluxed with 40% sodium hydroxide for 2 hours, dried over calcium hydride, and distilled under nitrogen.

Nitrobenzene was washed with dilute H_2SO_4, dried over calcium chloride, and distilled under reduced pressure. Carbon tetrachloride was washed with aqueous alkali and dilute H_2SO_4, dried over calcium chloride, and distilled.

Guaranteed reagent-grade silver perchlorate (Kojima Chemical Co. Ltd., Japan) was dried in vacuo at 120°C before use. Thionyl chloride was used without further purification. All other solvents and reagents were purified by general methods.

Introduction of Carboxyl Groups onto Carbon Whiskers

To introduce additional carboxyl groups onto carbon whiskers, they were treated with HNO_3. The procedures were described in detail in earlier papers [5, 16]. The carboxyl group content of the carbon whisker (CW(M)) thus treated is also shown in Table 1.

Introduction of Acyl Chloride Groups onto Carbon Whiskers

The introduction of acyl chloride groups onto a carbon-whisker surface was achieved by the treatment of surface carboxyl groups with thionyl chloride. A typical example is as follows. Into a flask equipped with a reflux condenser, 1.0 g carbon whiskers, 5.0 cm^3 benzene, and 15.0 cm^3 thionyl chloride were charged. The mixture was refluxed under stirring with a magnetic stirrer for 50 hours. After treatment, benzene and unreacted thionyl chloride were removed under reduced pressure. The resulting carbon whiskers were dried in vacuo at 90°C and stored in vacuo at room temperature.

Introduction of Acylium Perchlorate Groups onto Carbon Whiskers

The introduction of acylium perchlorate groups onto a carbon-whisker surface, i.e., pretreatment, was achieved by the reaction of acyl chloride groups with silver perchlorate in nitrobenzene. The pretreatment was required for the introduction of acylium perchlorate groups, because silver perchlorate is hardly soluble in nitrobenzene [9, 10]. A typical example is as follows. Into a 100-cm^3 flask, 0.10 g carbon whiskers having acyl chloride groups, 0.20 g silver perchlorate, and 5.0 cm^3 nitrobenzene were charged, and the reaction mixture was stirred with a magnetic stirrer under dry nitrogen at room temperature for 48 hours. The polymerization was carried out without isolation of the pretreated carbon whiskers.

The amount of acyl perchlorate groups introduced onto a carbon-whisker surface was determined by titration as previously reported [17].

Graft Polymerization

After the above pretreatment, 5.0 cm^3 vinyl monomer was added to the mixture and the polymerization was conducted with stirring at 60°C. After a prescribed polymerization time, the content of the flask was poured into an excess of methanol to precipitate ungrafted polymer and polymer-grafted carbon whiskers.

When *N*-vinyl-2-pyrrolidone was used as the monomer, the unreacted monomer and solvent were pumped off under reduced pressure after the polymerization, yielding ungrafted polymer and polymer-grafted carbon whiskers.

The conversion was calculated by the following equation:

$$\text{conversion (\%)} = \frac{A}{B} \times 100$$

where A = precipitate obtained (g) − carbon whiskers charged (g)
B = monomer charged (g)

Percentage of Grafting

To separate the polymer-grafted carbon whiskers from the reaction mixture containing ungrafted polymer, the product was dispersed in a good solvent for an ungrafted polymer and the dispersion was centrifuged at 1.0×10^4 rpm until the carbon whiskers precipitated completely and the supernatant solution containing a large part of the ungrafted polymer was removed. Then the precipitated whiskers were extracted with the solvent for ungrafted polymer with a Soxhlet apparatus until no more polymer could be detected in the refluxing solvent. The extracting solvent for polystyrene, poly(*n*-butyl vinyl ether), and polyindene was tetrahydrofuran, and for poly(*N*-vinyl-2-pyrrolidone) was distilled water.

The percentages of grafting and grafting efficiency were calculated by the following equations:

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

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

RESULTS AND DISCUSSION

Evidence of Initiation by Acylium Perchlorate Groups Introduced onto Carbon Whiskers

It is well known that the cationic polymerization of styrene and the ring-opening polymerization of THF are initiated by benzoyl or acetyl perchlorate which is prepared by the reaction of acid chloride with silver perchlorate [18, 19]. We have reported the introduction of acylium perchlorate groups onto carbon black and the cationic grafting of polystyrene [9], polyesters [10], polyethers [11], and polyacetals [12] from carbon black by the use of acylium perchlorate groups on the surface as the initiator.

Therefore, the polymerization of styrene was carried out under several conditions using carbon whiskers having acyl chloride groups (CW-COCl) and silver perchlorate. The results are summarized in Table 2. As shown, styrene was not polymerized by silver perchlorate, untreated carbon whiskers, or CW-COCl alone (Runs 1, 2, and 4). In addition, polymerization could not be detected even if untreated carbon whiskers were pretreated with silver perchlorate (Run 3).

On the contrary, the polymerization of styrene was initiated by CW-COCl pretreated with silver perchlorate (Run no. 5) to give polystyrene-grafted carbon whiskers. In addition, the conversion and percentage of grafting in the presence of CW(M)-COCl (thionyl chloride-treated carbon whiskers after treatment with HNO_3) pretreated with silver perchlorate was larger than that of CW-COCl (Run

TABLE 2. Polymerization of Styrene under Several Conditions[a]

Run	Carbon whiskers	$AgClO_4$, g	Conversion, %	Grafting, %
1	None	0.20	0	–
2	Untreated	–	0	–
3	Untreated	0.20	0	–
4	CW–COCl	–	0	–
5	CW–COCl	0.20	12.0	42.5
6	CW(M)–COCl	0.20	15.9	55.7

[a] Pretreatment: Carbon whiskers, 0.10 g; nitrobenzene, 5.0 cm^3; RT; 48 hours. Polymerization: Styrene, 5.0 cm^3; 60°C; 48 hours.

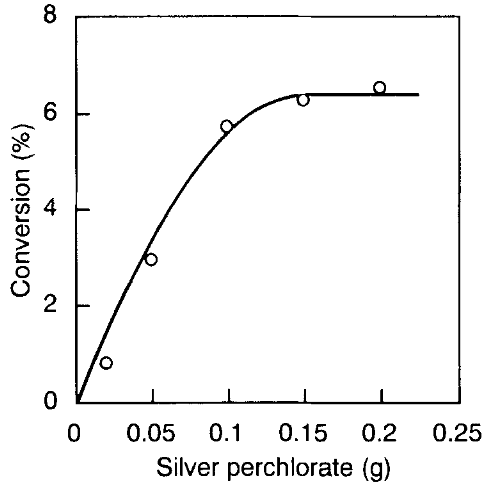


FIG. 1. Effect of the amount of $AgClO_4$ on the pretreatment of carbon whiskers having COCl groups. Pretreatment: CW—COCl, 0.10 g; nitrobenzene, 5.0 cm^3; RT; 48 hours. Polymerization: Styrene, 5.0 cm^3; 24 hours.

6). This may be due to the higher content of the acylium perchlorate group of CW(M)-COCl pretreated with silver perchlorate.

Based on the above results, it is concluded that acylium perchlorate groups formed by the reaction of acyl chloride groups with silver perchlorate initiate the polymerization of styrene, and grafted polymer chains propagate from the carbon-whisker surface.

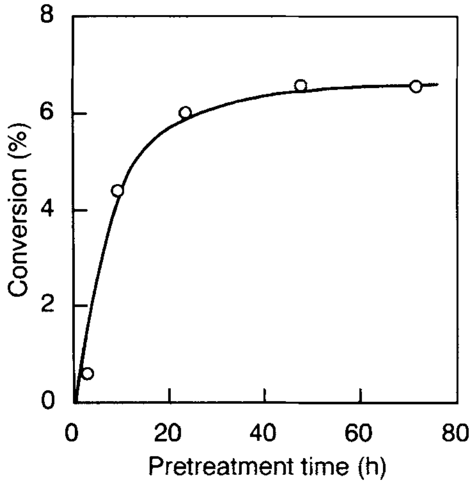


FIG. 2. Effect of pretreatment time on initiation of cationic polymerization of styrene. Pretreatment: CW—COCl, 0.10 g; nitrobenzene, 5.0 cm^3; RT. Polymerization: Styrene, 5.0 cm^3; 60°C; 24 hours.

Effect of Pretreatment Conditions on the Polymerization

To determine the pretreatment conditions for the introduction of acylium perchlorate groups onto carbon whiskers by using 0.10 g CW-COCl pretreated with various amounts of silver perchlorate for 48 hours, the polymerization of styrene was carried out and the initiating activity of carbon whiskers as initiators was examined. The results are shown in Fig. 1.

It was found that the initiating activity of pretreated carbon whiskers increases with an increasing amount of silver perchlorate. The results indicate that more than 0.10 g silver perchlorate is necessary to introduce acylium perchlorate groups onto 0.10 g CW-COCl by the pretreatment.

On the other hand, 0.10 g CW-COCl was pretreated with 0.20 g of silver perchlorate for various time intervals, and the effect of pretreatment time on the initiating activity of the pretreated carbon whiskers was examined. The results are shown in Fig. 2.

Figure 2 shows that the reaction rate of silver perchlorate with acyl chloride groups on carbon whiskers is very small. This may be due to the low solubility of silver perchlorate in the solvent. Based on the results, it was found that a pretreatment time of at least 30 hours is required for the introduction of acylium perchlorate groups onto carbon whiskers.

Based on these results, 0.10 g carbon whiskers was pretreated with 0.20 g of silver perchlorate in nitrobenzene at room temperature for 48 hours in the subsequent experiment. The acylium perchlorate group content of carbon whiskers and HNO_3-treated carbon whiskers (CW(M)) after pretreatment were estimated to be 0.03 and 0.05 mmol/g, respectively. This indicates that about 40% of the carboxyl group on carbon whiskers was converted to acylium perchlorate groups.

Effect of Temperature on the Polymerization of Styrene

Figure 3 shows the effect of temperature on the polymerization of styrene initiated by acylium perchlorate groups introduced onto carbon whiskers. The rate of polymerization was found to increase with a rise in temperature. The Arrhenius plots for the above results were straight lines, and the apparent activation energy of polymerization was estimated to be 36.7 kJ/mol. The value is considerably larger than that of the ordinary cationic polymerization of styrene.

Percentage of Grafting and Grafting Efficiency

Figure 4 shows the relationship between conversion and the percentage of grafting (grafting efficiency) at 60°C in the polymerization of styrene initiated by acylium perchlorate groups on carbon whiskers.

It is apparent that the percentage of polystyrene grafting gradually increased to 42.5% with increasing conversion. On the contrary, the grafting efficiency was very high during the first few percent of conversion, but immediately decreased with increasing conversion.

These results indicate that the grafted polymer is propagated from surface acylium perchlorate groups on carbon whiskers and that ungrafted polymer is grad-

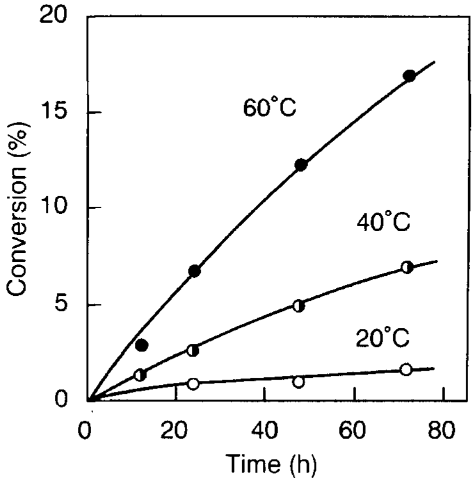
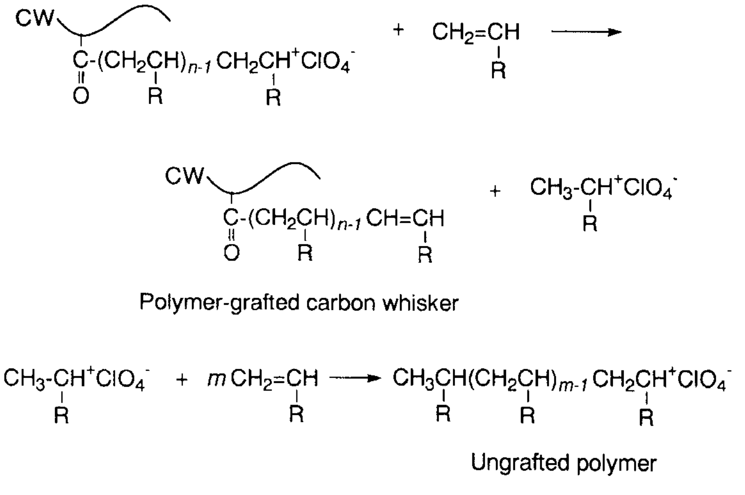


FIG. 3. Effect of temperature on the cationic polymerization of styrene initiated by acylium perchlorate groups introduced onto carbon whiskers. Pretreatment: CW—COCl, 0.10 g; $AgClO_4$, 0.20 g; nitrobenzene, 5.0 cm^3; RT; 48 hours. Polymerization: Styrene, 5.0 cm^3.

ually formed by a chain transfer reaction of growing polymer cation to the monomer (Eq. 3).



(3)

This indicates that at the last stage of polymerization, ungrafted polymer is preferentially formed.

The molecular weight of grafted polystyrene on carbon whiskers could not be determined because the isolation of grafted polymer from the carbon-whisker surface was unsuccessful. The molecular weight ($\overline{M}_w$) of ungrafted polystyrene, however, was determined to be 5.0×10^3 by GPC. The molecular weight of polystyrene grafted onto carbon whiskers is considered to be of the same order as that of ungrafted polystyrene.

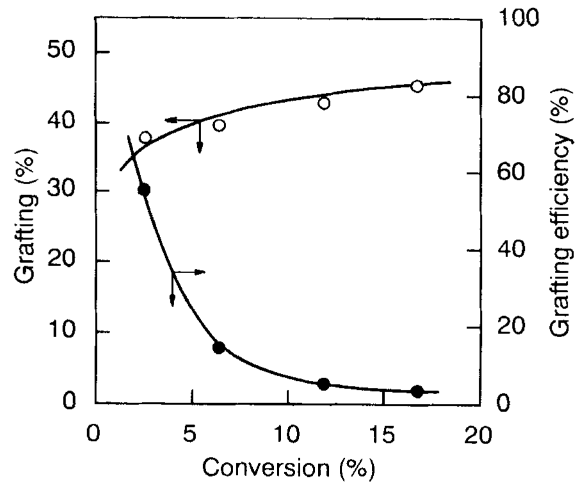


FIG. 4. Relationship between conversion and percentage of grafting (grafting efficiency) of polystyrene at 60°C. Polymerization conditions are given in Fig. 3.

Effect of Temperature on the Percentage of Grafting

Based on the above results, it is believed that the chain transfer reaction of a growing polymer cation lowers the percentage of grafting. Therefore, the effect of temperature on the percentage of grafting of polystyrene was investigated. The results are shown in Fig. 5.

The percentage of grafting was found to decrease with increasing polymerization temperature. The results indicate that the formation of ungrafted polystyrene

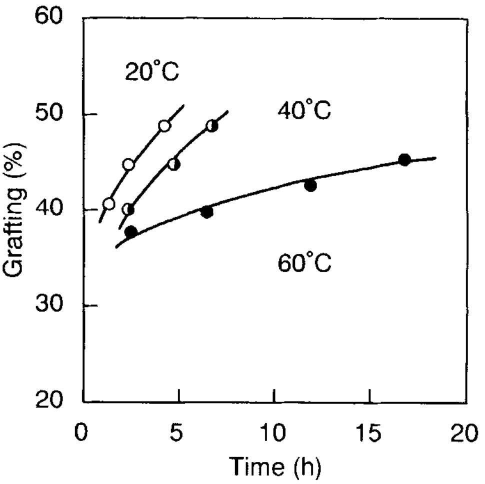


FIG. 5. Effect of temperature on the polystyrene grafting onto carbon whiskers. Polymerization conditions are given in Fig. 3.

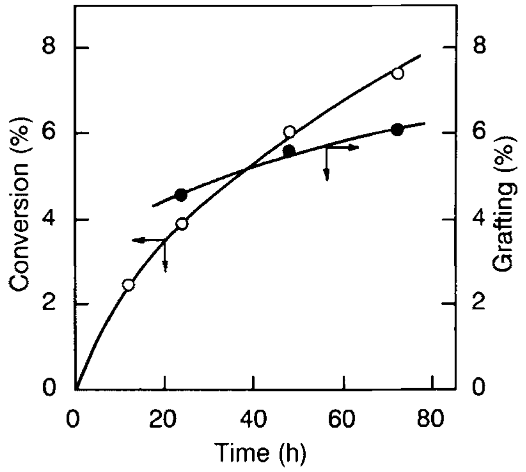


FIG. 6. Cationic graft polymerization of styrene initiated by acylium perchlorate groups introduced onto carbon whiskers in carbon tetrachloride. Pretreatment: CW—COCl, 0.10 g; $AgClO_4$, 0.20 g; CCl_4, 5.0 cm^3; RT; 48 hours. Polymerization: Styrene, 5.0 cm^3; 60°C.

in enhanced by increasing the polymerization temperature because the increasing temperature causes an increase in the rate of the chain transfer reaction of the growing polymer cation.

Effect of Solvent on the Polystyrene Grafting

By the use of carbon tetrachloride as a solvent for pretreatment and polymerization, the rate of polymerization and percentage of polystyrene grafting were compared with that in nitrobenzene. The results are shown in Fig. 6.

The rate of polymerization and the percentage of polystyrene grafting in carbon tetrachloride were smaller than those in nitrobenzene. This may be due to the fact that silver perchlorate is hardly soluble in carbon tetrachloride and that polar solvents generally accelerate cationic polymerization to give higher molecular weights [20].

Graft Polymerization of Several Polymers onto Carbon Whiskers

The graft polymerization of several vinyl monomers, such as *n*-butyl vinyl ether, *N*-vinyl-2-pyrrolidone, and indene, onto carbon whiskers was carried out by using acylium perchlorate groups introduced onto the surface. The results are summarized in Table 3. It is apparent that acylium perchlorate groups have an ability to initiate the cationic polymerization of *n*-butyl vinyl ether, *N*-vinyl-2-pyrrolidone, and indene to give the corresponding vinyl polymer-grafted carbon whiskers. The percentage of polyindene grafting exceeded 100%.

TABLE 3. Cationic Graft Polymerization of Several Vinyl Monomers Initiated by Acylium Perchlorate Introduced onto a Carbon Whisker Surface[a]

Vinyl monomer	Temperature, °C	Time, h	Conversion, %	Grafting, %
n-Butyl vinyl ether	60	48	82.3	48.1
N-Vinyl-2-pyrrolidone	60	48	100	19.6
Indene	25	24	100	100.3
Styrene	60	48	12.0	42.5

[a] Pretreatment: CW—COCl, 0.10 g; $AgClO_4$, 0.20 g; nitrobenzene, 5.0 cm^3; RT; 48 hours. Polymerization: Monomer, 5.0 cm^3.

Dispersibility of Polymer-Grafted Carbon Whiskers

It was found that polymer-grafted carbon whiskers give a stable colloidal dispersion in good solvents for grafted polymer chains. For instance, when polystyrene-grafted carbon whiskers were dispersed in benzene, the precipitation of the carbon whiskers was scarcely observed even after 10 days, but untreated carbon whiskers precipitated within 1 day. This indicates that a grafted polymer chain on a carbon-whisker surface interferes with the aggregation of carbon whiskers.

Figure 7 shows the schematic results when polystyrene-grafted carbon whiskers and poly(*N*-vinyl-2-pyrrolidone)-grafted carbon whiskers are dispersed in a two-phase mixture of benzene and water. Benzene and water are good solvents for surface-grafted polystyrene and poly(*N*-vinyl-2-pyrrolidone), respectively.

As shown in Fig. 7, polystyrene-grafted carbon whiskers disperse only in the benzene phase and no carbon whiskers are in the water phase. Poly(*N*-vinyl-2-pyrrolidone)-grafted carbon whiskers, however, disperse in the water phase but not in the benzene phase. The results clearly show that the wettability of carbon whiskers can be controlled by the grafting of polymers onto the surface.

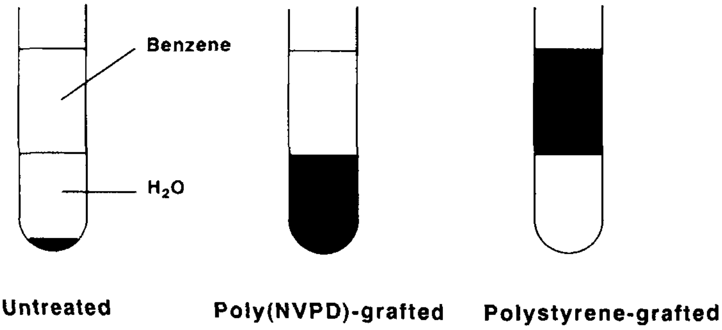


FIG. 7. Dispersibility of polystyrene-grafted and poly(*N*-vinyl-2-pyrrolidone)-grafted carbon whiskers in a two-phase mixture of benzene and water. Poly(NVPD): Poly(*N*-vinyl-2-pyrrolidone).

CONCLUSIONS

1. The introduction of acylium perchlorate groups onto a carbon-whisker surface was successfully achieved by the reaction of silver perchlorate with acyl chloride groups on the surface.
2. The cationic polymerization of vinyl monomers was initiated by acylium perchlorate groups introduced onto a carbon-whisker surface.
3. In the polymerization, the corresponding vinyl polymers were grafted onto the surface based on the propagation of polymer from the carbon-whisker surface.
4. Through the grafting of polymers onto carbon whiskers, the dispersibility in a solvent and the wettability of a surface were remarkably improved.

ACKNOWLEDGMENT

We thank Asahi Chemical Industry Ltd., Japan, for providing us with the carbon whisker.

REFERENCES

[1] A. Tanaka, T. Fujisawa, and R. Yosomiya, *J. Polym. Sci., Polym. Chem. Ed., 18*, 2267 (1980).

[2] K. Hashimoto, T. Fujisawa, M. Kobayashi, and R. Yosomiya, *J. Appl. Polym. Sci., 27*, 4529 (1982).

[3] N. Tsubokawa, H. Hamada, and Y. Sone, *Polym.-Plast. Technol. Eng., 28*, 201 (1989).

[4] N. Tsubokawa, H. Maruyama, and Y. Sone, *J. Macromol. Sci.—Chem., A25*, 171 (1988).

[5] N. Tsubokawa and T. Yoshihara, *Polym. J., 23*, 177 (1991).

[6] N. Tsubokawa, T. Yoshihara, and Y. Sone, *J. Polym. Sci., Part A: Polym. Chem., 30*, 561 (1992).

[7] N. Tsubokawa and T. Yoshihara, *Ibid.*, In Press.

[8] N. Tsubokawa, N. Takeda, and T. Iwasa, *Polym. J., 13*, 1093 (1987).

[9] N. Tsubokawa, *J. Polym. Sci., Polym. Chem. Ed., 22*, 1515 (1984).

[10] N. Tsubokawa, *J. Appl. Polym. Sci., 36*, 2041 (1985).

[11] N. Tsubokawa, H. Nunokawa, and Y. Sone, *J. Macromol. Sci.—Chem., A23*, 105 (1986).

[12] N. Tsubokawa, *J. Polym. Sci., Polym. Chem. Ed., 25*, 1979 (1987).

[13] K. Ohkita and N. Tsubokawa, *Carbon, 10*, 63 (1972).

[14] D. Rivin, *Rubber Chem. Technol., 36*, 729 (1963).

[15] S. Suzuki and K. Miyazaki, *Nippon Kagaku Zasshi, 88*, 299 (1967).

[16] K. Ohkita, N. Tsubokawa, K. Sekine, and T. Yamada, *Nippon Gomu Kyokaishi, 47*, 40 (1974).

[17] N. Tsubokawa, Y. Jian, A. Yamada, and Y. Sone, *Polym. Bull., 16*, 249 (1986).

[18] W. R. Longworth and P. H. Plesch, *Proc. Chem. Soc.*, p. 117 (1958).

[19] P. Dreyfuss and J. P. Kennedy, *J. Polym. Sci., Polym. Lett. Ed., 14*, 139 (1976).
[20] D. C. Pepper, *Trans. Faraday Soc., 45*, 397 (1949).

Received November 26, 1992
Revision received January 21, 1993