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Grafting of polyesters onto carbon whisker surface

Cationic ring-opening polymerization of lactones 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

Summary

Acylium perchlorate groups were successfully introduced onto the surface of carbon whisker, *i.e.*, vapor grown carbon fiber, by the reaction of surface acyl chloride groups with silver perchlorate in nitrobenzene. It was found that the cationic ring-opening polymerization of lactones, such as ε–caprolactone, δ–valerolactone, and β–propiolactone, is initiated by acylium perchlorate groups introduced onto carbon whisker. During the polymerization, the corresponding polyesters were effectively grafted onto carbon whisker surface based on the propagation of polyester from the surface. The rate of polymerization increased with increasing polymerization temperature, but the percentage of grafting of polyester onto the surface decreased.

Introduction

By the grafting of polymers onto inorganic ultrafine particles, such as carbon black, silica, and titanium oxide, the dispersibility of these particles in solvents and polymer matrices is known to be remarkably improved (1,2). Furthermore, the wettability of these particle surfaces is readily controlled by the surface grafting of polymers (1,2).

In a series of our papers, the grafting of polymers onto carbon black initiated by azo (3), peroxyester (4), potassium carboxylate (5,6), and acyl perchlorate (7–10) groups introduced onto the surface has been reported. During the graft polymerizations, polymer–grafted carbon blacks with higher percentage of grafting were successfully obtained based on the propagation of grafted chains from carbon black surface. For instance, acylium perchlorate groups introduced onto carbon black surface were reported to have an ability to initiate the cationic polymerization of vinyl monomers (7) and the cationic ring–opening polymerization of lactones (8), cyclic ethers (9), and cyclic formals (10) to give the corresponding polymer–grafted carbon blacks.

On the other hand, the grafting of polyesters onto carbon whisker, *i.e.*, vapor grown carbon fiber, was achieved by the anionic ring–opening alternating copolymerization of epoxides with cyclic acid anhydrides initiated by potassium carboxylate groups introduced onto the surface (11). In the previous paper, we reported the introduction of acylium perchlorate groups onto carbon whisker surface and the cationic graft polymerization of vinyl monomers initiated by the initiating groups (12).

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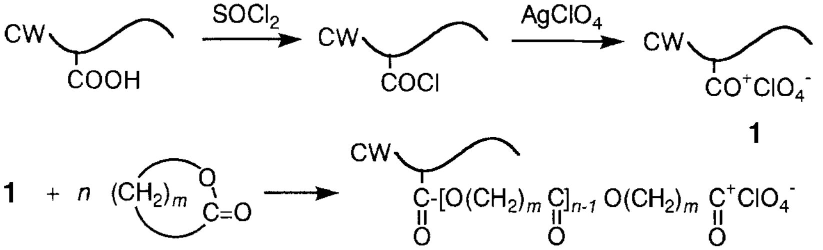
*Corresponding author

By the grafting of polymers onto carbon whisker surface, the physical properties of carbon whisker-filled polymer composite is expected to be improved, because of the modification of wettability between carbon whisker surface with matrix polymer.

In the present paper, to modify the carbon whisker surface by the grafting of polymers, the grafting of polyesters onto carbon whisker surface by the cationic ring-opening polymerization of lactones initiated by acylium perchlorate groups introduced onto the surface was investigated (Eqs.1 and 2).



(1)

(2)

Experimental

Materials and Reagents

Carbon whisker used was obtained from Asahi Chemical Industry Ltd., Japan. The carbon whisker was extracted with chloroform by using a Soxhlet apparatus to remove resinous substances on the surface and dried *in vacuo* at 110°C before use. The properties of carbon whisker are shown in Table 1. The fiber diameter and fiber length were determined by SEM. The determination of the content of phenolic hydroxyl (13), carboxyl (14), and quinonic oxygen groups (15) was carried out by use of 2,2-diphenyl-1-picrylhydrazyl, sodium bicarbonate, and sodium borohydride, respectively.

β-Propiolactone (PL), δ-valerolactone (VL), and ε-caprolactone (CL) were dried over calcium hydride and distilled twice under reduced pressure before use. Nitrobenzene was washed with dilute H_2SO_4, dried over calcium chloride, and distilled under reduced pressure.

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.

TABLE 1 Properties of carbon whisker 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

Introduction of Carboxyl and Acyl Chloride Groups onto Carbon Whisker

To introduce additional carboxyl groups onto carbon whisker, carbon whisker was treated with HNO_3. The procedures were described in detail in the preceding paper (16). The carboxyl group content of HNO_3-treated carbon whisker (CW(M)) was also shown in Table 1.

The introduction of acyl chloride groups onto carbon whisker was achieved by the treatment of surface carboxyl groups with thionyl chloride as described in detail in the preceding paper (12).

Introduction of Acylium Perchlorate Groups onto Carbon Whisker

The introduction of acylium perchlorate groups onto carbon whisker, *i.e.*, pretreatment, was achieved by the reaction of acyl chloride groups with silver perchlorate in nitrobenzene at room temperature. The polymerization was initiated by the addition of monomers without isolation of the pretreated carbon whisker. The detailed procedures were described in the previous paper (12). The amount of acylium perchlorate groups introduced onto CW and CW(M) was determined to be 0.02 and 0.05 mmol/g.

Graft Polymerization

After the above pretreatment, 5.0 cm^3 of lactone was added to the mixture under dry nitrogen and the polymerization was conducted under stirring with a magnetic stirrer. After a definite time, the content of the flask was poured into a large excess of methanol, yielding polymer–grafted carbon whisker and ungrafted polymer. The precipitate was filtered, washed with methanol, and dried *in vacuo* at 45°C . The conversion was calculated by the following equation.

$$\text{Conversion (\%)} = \frac{\text{Precipitate obtained (g)} - \text{Carbon whisker charged (g)}}{\text{Monomer charged (g)}} \times 100$$

Percentage of Grafting and Grafting Efficiency

To separate the polymer–grafted carbon whisker from the reaction mixture containing ungrafted polymer, the product was extracted with chloroform using a Soxhlet apparatus until no more polymer was eluted in the refluxing solvent. Unreacted silver perchlorate and trace amount of silver chloride formed by the reaction of silver perchlorate with surface acyl chloride groups were able to be removed by the extraction. The percentage of grafting and grafting efficiency were calculated by the following equations.

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

$$\text{Grafting efficiency (\%)} = \frac{\text{Polyester grafted (g)}}{\text{Total polyester formed (g)}} \times 100$$

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

Results and Discussion

Evidence of Initiation by Acylium Perchlorate Groups on Carbon Whisker

It is well known that benzoyl or acetyl perchlorate which is prepared by the reaction of acid chlorides with silver perchlorate has an ability to initiate the cationic polymerization of styrene and the ring-opening polymerization of cyclic monomers (17,18). We have reported that acylium perchlorate groups introduced onto carbon black surface are capable of initiating the cationic graft polymerization of vinyl monomers (7) and cationic ring-opening polymerization of cyclic monomers (8–10) to give the corresponding polymer-grafted carbon black. In the preceding paper, it was reported that the graft polymerization of vinyl monomers is initiated by acylium perchlorate groups introduced onto carbon whisker surface (12).

Therefore, the ring-opening polymerization of CL was carried out under several conditions using carbon whisker having acyl chloride groups (CW-COCl) and silver perchlorate. The results are summarized in Table 2. As shown in Table 2, CL was not polymerized by a single component of silver perchlorate, untreated carbon whisker, or CW-COCl (Run nos. 1,2, and 4). In addition, the polymerization could not be detected even if untreated carbon whisker was pretreated with silver perchlorate (Run no. 3).

On the contrary, the polymerization of CL was initiated by CW-COCl pretreated with silver perchlorate (Run no. 5) to give polyCL-grafted carbon whisker. In addition, the conversion and percentage of grafting in the presence of CW(M)-COCl (thionyl chloride-treated carbon whisker after the treatment with HNO_3) pretreated with silver perchlorate were larger than that of CW-COCl (Run no. 6). This may be due to the higher content of acylium perchlorate group of CW(M)-COCl pretreated with silver perchlorate.

Figure 1 shows the infrared spectra of untreated and polyCL-grafted carbon whisker. Infrared spectra of polyCL-grafted carbon whisker exhibited absorptions at 1734, 1205, and 1068 cm^{-1} which are characteristic of polyCL.

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 ring-opening polymerization of CL and grafted polymer chains propagate from carbon whisker surface.

TABLE 2 Polymerization of CL under several conditions

Run No.	CW	$AgClO_4$ (g)	Conversion (%)	Grafting (%)
1	None	0.20	0	-
2	Untreated	-	0	0
3	Untreated	0.20	0	0
4	CW-COCl	-	0	0
5	CW-COCl	0.20	40.0	57.6
6	CW(M)-COCl	0.20	56.2	71.1

Pretreatment: CW, 0.50 g; $C_6H_5NO_2$, 5.0 cm^3; r.t.; 48 h.
Polymerization: CL, 5.0 cm^3; 40°C; 24 h.

Percentage of Grafting and Grafting Efficiency

Figure 2 shows the relationship between conversion and percentage of grafting (grafting efficiency) at 40°C in the ring–opening polymerization of CL initiated by acylium perchlorate groups on carbon whisker.

It is apparent that the percentage of polyCL grafting gradually increased to 71.2% with increasing conversion. On the contrary, the grafting efficiency was relatively high during the low conversion, but immediately decreased with increasing conversion. The same tendency was observed in the cationic graft polymerization initiated by acylium perchlorate groups introduced onto carbon black (7–10) and silica surface (19).

These results indicate that the grafted polyester is propagated from the surface acylium perchlorate groups on carbon whisker and that ungrafted

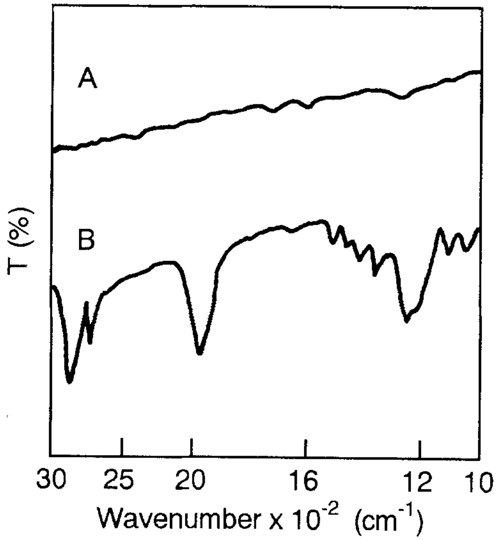


Figure 1. Infrared spectra of (A) untreated and (B) poly–CL–grafted carbon whisker.

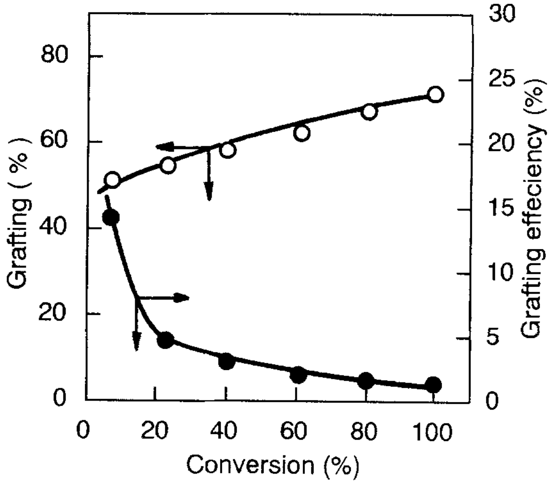
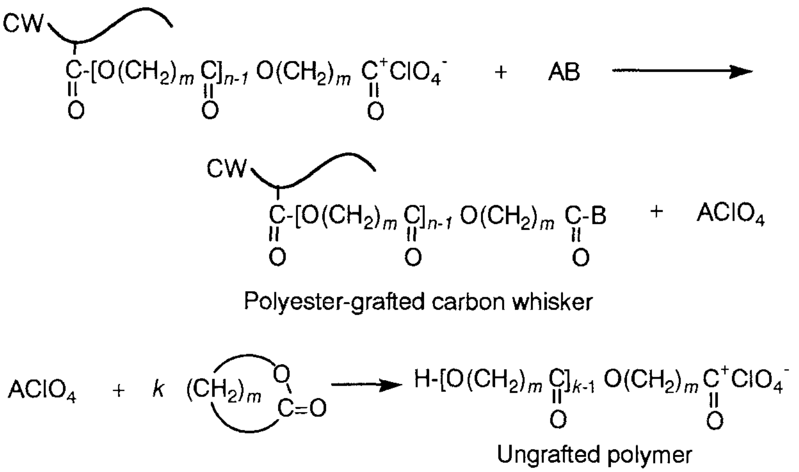


Figure 2. Relationship between conversion and percentage of grafting (grafting efficiency) in the polymerization of CL initiated by acylium perchlorate groups on carbon whisker. Pretreatment: CW–COCl, 0.10 g; $AgClO_4$, 0.20 g; $C_6H_5NO_2$, 5.0 cm^3; r.t.; 48 h. Polymerization: CL, 5.0 cm^3; 40°C.



(3)

polymer is gradually formed by a chain transfer reaction of growing polymer cation with an impurity (AB) such as trace of water and some functional group on carbon whisker (Eq.3). This indicates that at the last stage of the polymerization, ungrafted polymer preferentially formed.

Effect of Temperature on the Grafting of PolyCL

Figure 3 shows the effect of temperature on the ring-opening polymerization of CL initiated by acylium perchlorate groups introduced onto carbon whisker. The rate of the polymerization was found to increase with a rise in temperature. The Arrhenius plots for the above results gave a straight line and apparent activation energy of the polymerization was estimated to be 38.7 kJ/mol. The value is nearly equal to that of styrene initiated by acylium perchlorate groups on carbon whisker (11).

Based on the above results, it is considered that the chain transfer reaction of growing polymer cation lowers the percentage of grafting. Therefore,

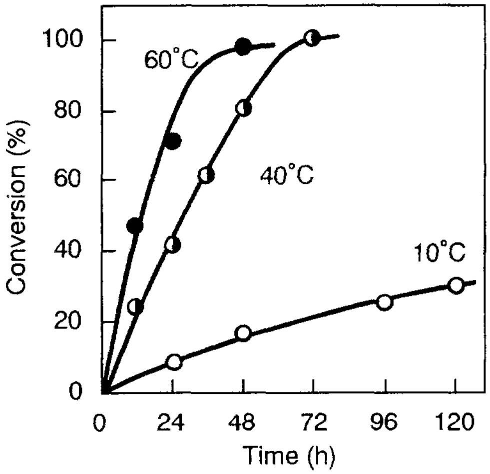


Figure 3. Effect of temperature on the polymerization of CL initiated by acylium perchlorate groups on carbon whisker. Pretreatment: CW–COCl, 0.10 g; $AgClO_4$, 0.20 g; $C_6H_5NO_2$, 5.0 cm^3; r.t.; 48 h. Polymerization: CL, 5.0 cm^3.

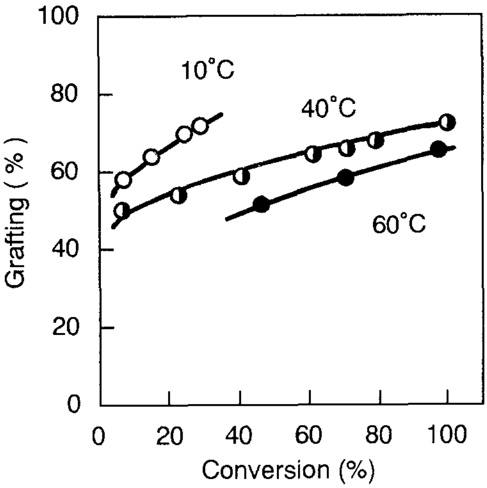


Figure 4. Effect of temperature on the grafting of polyCL onto carbon whisker surface. Polymerization conditions are given in Figure 3.

the effect of temperature on the percentage of grafting of polyCL was investigated. The results are shown in Figure 4.

The percentage of grafting was found to decrease, depending on the polymerization temperature, in the following order: 10°C > 40°C > 60°C. Namely, the result indicates that the formation of ungrafted polyCL is enhanced by increasing polymerization temperature, because the increasing temperature causes an increase in the rate of chain transfer reaction of growing polymer cation.

Graft Polymerization of Several Lactones onto Carbon Whisker

The ring-opening graft polymerization of PL and VL onto carbon whisker was carried out by using acylium perchlorate groups introduced onto the surface. The results are summarized in Table 3.

TABLE 3 Cationic ring-opening polymerization of lactones initiated by acylium perchlorate groups on carbon whisker

Lactone	Temperature (℃)	Time (h)	Conversion (%)	Grafting (%)
PL	10	60	2.5	20.5
PL	60	60	4.5	17.8
VL	10	24	23.4	69.0
VL	60	24	64.2	41.5
CL	10	24	19.4	63.6
CL	60	24	40.0	57.6

Pretreatment: CW, 0.10 g; $AgClO_4$. 0.20 g; $C_6H_5NO_2$, 5.0 cm^3; r.t.; 48 h.
Polymerization: Monomer, 5.0 cm^3.

As shown in Table 3, it is apparent that acylium perchlorate groups have an ability to initiate the cationic ring-opening polymerization of lactones to give the corresponding polyester-grafted carbon whisker.

Conclusions

1. The introduction of acylium perchlorate groups onto carbon whisker surface was successfully achieved by the reaction of silver perchlorate with acyl chloride groups on the surface.
2. The cationic ring-opening polymerization of lactones was initiated by acylium perchlorate groups introduced onto carbon whisker surface.
3. In the polymerization, the corresponding polyester was effectively grafted onto the surface based on the propagation of polymer from the carbon whisker surface.

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