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GRAFTING OF POLYMERS ONTO A CROSSLINKED POLYMER CARRYING CARBOXYL GROUPS AS A MODEL COMPOUND FOR CARBON BLACK

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ABSTRACT

A cation-exchange resin (a crosslinked polymer carrying carboxyl groups) was used as a model compound for carbon black, and the grafting of several polymers to the resin was investigated. Reaction of acyl chloride groups that had been placed on the ion-exchange resin with polymers having hydroxyl or amino groups, such as polypropylene glycol, polyethylene glycol, polybutadiene glycol, polyvinyl alcohol, silicone diol, silicone diamine, and polyethyleneimine, resulted in grafting to the ion-exchange resin. In further experiments, primary amino groups were placed on the cation-exchange resin by reaction of acyl chloride groups with ethylenediamine. It was found that ring-opening polymerization of γ-methyl *L*-glutamate *N*-carboxyanhydride is initiated by the amino groups on the resin, and polypeptide was grafted from the cation-exchange resin. Therefore, the reactivity of carboxyl groups on the resin was found to be similar to that on carbon black. However, carboxyl groups

on the resin failed to initiate the cationic polymerization of vinyl monomers, in contrast to those on carbon black. This suggested that the acidity of carboxyl groups on carbon black is greater than on the cation-exchange resin.

INTRODUCTION

Crosslinked polymers having functional groups have been widely used as reagents, catalysts, and carriers in organic synthesis [1, 2]. Merrifield successfully introduced the solid-phase technique for polypeptide synthesis [3-5]. Some recent work was reviewed by Patchorinik [6] and by Ford [7].

In a series of papers, we reported the grafting of various kinds of polymers onto carbon black surfaces by use of reactive groups introduced onto the surface [8]. For instance, we reported that polymer-grafted carbon black was obtained by the reaction of acyl azide ($-CON_3$) [9] and acyl chloride ($-COCl$) [10] groups introduced onto the surface of carbon black with polymers having hydroxyl or amino groups. Furthermore, we succeeded in the anionic ring-opening polymerization of α-amino acid *N*-carboxyanhydride (NCA) initiated by amino groups on carbon black surfaces [11].

Carboxyl groups present on the surface were utilized as starting functional groups for the introduction of these reactive groups onto carbon black. On the other hand, we showed that carboxyl groups on carbon black have the ability to initiate the cationic polymerization of vinyl monomers [12, 13].

In analogy with carbon black, a cation-exchange resin, a crosslinked copolymer of acrylic acid and divinylbenzene, carries carboxyl groups, and therefore it is expected that such a cation-exchange resin can be used as a model compound for carbon black.

In this paper the introduction of reactive groups onto a cation-exchange resin (as a model compound for carbon black) and the grafting of several polymers by use of cation-exchange resins having reactive groups are investigated with a view to providing the grafting reaction onto carbon black. Furthermore, the reactivity of carboxyl groups on the resin is compared with that on carbon black.

EXPERIMENTAL

Cation-Exchange Resin

The cation-exchange resin, a copolymer of acrylic acid and divinylbenzene (high-porous type), was obtained from Mitsubishi Chemical Ind., Japan, under designation Diaion WK 20. The particle size and the content of carboxyl group was 297-1190 μm and 8.9 mmol/g, respectively. The cation-exchange resin was dried *in vacuo* at 90°C before use.

Functional Polymers

Diol-type polypropylene glycol (PPG), diol-type polyethylene glycol (PEG), and poly(vinyl alcohol) (PVA), obtained from Wako Pure Chemical Co., Japan, were used without further purification. Diol-type polybutadiene glycol (PBG) was obtained from Nippon Soda Co., Japan. Silicone diol (SDO) and silicone diamine (SDA) were obtained from Shin-etsu Chemical Ind. Co., Japan. Polyethyleneimine (PEI) was obtained from Nippon Shokubai Kagaku Kogyo Co., Japan.

Others

γ-Methyl *L*-glutamate NCA, obtained from Ajinomoto Co., Japan, was recrystallized twice from chloroform-hexane. Isobutyl vinyl ether (IBVE), *N*-vinylcarbazole (NVC), dimethylsulfoxide (DMSO), and dioxane were purified by the usual methods.

Introduction of Acyl Chloride Groups to the Cation-Exchange Resin

A typical example follows: Into a flask equipped with a reflux condenser, 10 g cation-exchange resin, 40 mL thionyl chloride, and 100 mL dioxane were charged. The mixture was refluxed for 50 h. Then unreacted thionyl chloride and dioxane were distilled out under reduced pressure, and the resulting cation-exchange resin was dried *in vacuo.*

Introduction of Amino Groups to the Cation-Exchange Resin

Into a flask equipped with a reflux condenser, 10 g cation-exchange resin having acyl chloride groups, 50 mL ethylenediamine, and 50 mL DMSO were charged. The mixture was stirred at 90°C for 20 h; the reaction mixture was filtered, washed with water, and extracted with methanol in a Soxhlet apparatus.

Reaction of the Cation-Exchange Resin Having Acyl Chloride Groups with Polymers

Into a 100-mL flask, 0.35 g cation-exchange resin with acyl chloride groups, 2.5 mmol polymer (for PVA, 0.015 mmol), 0.40 g triethylamine, and 7.0 mL

DMSO were charged. The mixture was stirred under dry nitrogen at 80-130°C for 20 h. After the reaction, ungrafted polymer was removed by decantation. Then the resulting resin was extracted with a solvent for the polymer in a Soxhlet apparatus to remove unreacted polymer. The percentage of grafting of the polymer to the cation-exchange resin was calculated by

$$\text{Percentage of grafting (\%)} = \frac{\text{polymer grafted (g)}}{\text{cation-exchange resin used (g)}} \times 100.$$

Polymerization of γ-Methyl *L*-Glutamate NCA by the Cation-Exchange Resin Having Amino Groups

Into a 100-mL flask equipped with a calcium chloride tube, 0.30 g of the resin having primary amino groups, 1.0 g NCA, and 20.0 mL dioxane were charged in a dry box. The mixture was stirred under dry nitrogen at 30°C for 4 d. The reaction product was filtered and washed with dioxane.

RESULTS AND DISCUSSION

Introduction of Acyl Chloride Groups onto the Cation-Exchange Resin

The introduction of acyl chloride groups onto the cation-exchange resin was achieved by reaction of its carboxyl groups with thionyl chloride.

Figure 1 shows the IR spectra of the cation-exchange resin before and after the treatment with thionyl chloride in dioxane at 110°C for 50 h.

As shown in Fig. 1, a strong absorption at 1714 cm^{-1} in the untreated cation-exchange resin is characteristic of stretching of the carbonyl bond of a carboxyl group. On the other hand, the IR spectrum of the resin treated with thionyl chloride exhibited absorptions at 1050 and 1804 cm^{-1}, characteristic of an acyl chloride group, besides the one observed in untreated resin. Therefore, it was concluded that acyl chloride groups can be placed on the cation-exchange resin by the reaction of carboxyl groups of the resin with thionyl chloride.

The content of acyl chloride groups on the resin was determined to be 2.5 mmol/g by titration [10]. The result indicates that the amount of acyl chloride groups on the resin was about one-third its carboxyl groups.

Introduction of Amino Groups onto the Cation-Exchange Resin

In a previous paper, we reported that amino groups can be introduced onto carbon black surfaces by the reaction of acyl chloride groups on the sur-

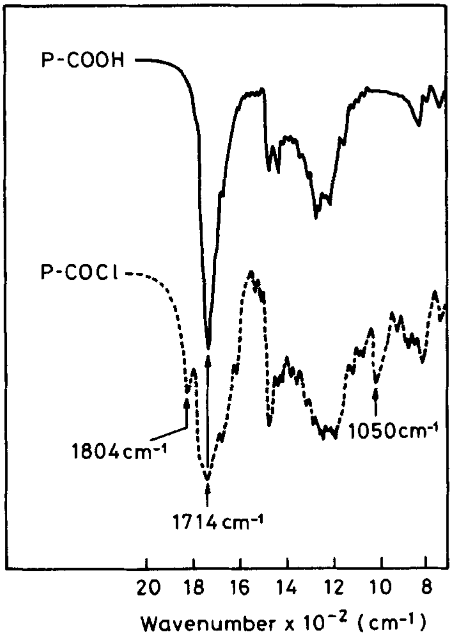


FIG. 1. IR spectra of the cation-exchange resin before and after treatment with thionyl chloride.

face with ethylenediamine [11]. Therefore, the introduction of amino groups onto the cation-exchange resin by the reaction of acyl chloride groups on the cation-exchange resin with ethylenediamine was examined. The treated cation-exchange resin was analyzed by IR spectra. The results are shown in Fig. 2.

As shown in Fig. 2, the IR spectra of cation-exchange resin treated with ethylenediamine show that the absorptions at 1050 and 1804 cm^{-1}, which are characteristic of an acyl chloride group, disappeared completely and that new absorptions at 1550 and 1640 cm^{-1}, which are characteristic of an amide and amino group, respectively, appear. Therefore, it was concluded that acyl chloride groups on the cation-exchange resin react with ethylenediamine, and that ethylenediamine is bound to the cation-exchange resin with an amide bond.

The content of amino groups introduced to the resin was determined to be 2.2 mmol/g by titration. The results indicate that about 90% of acyl chloride groups on the resin reacted with ethylenediamine.

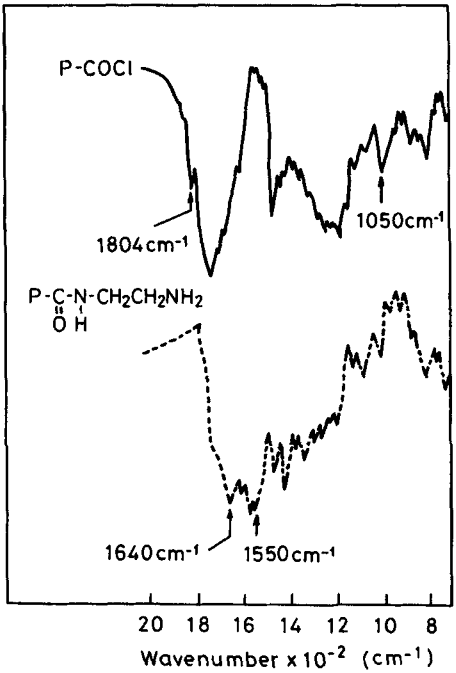


FIG. 2. IR spectra of the cation-exchange resin carrying acyl chloride groups treated with ethylenediamine.

Grafting onto the Cation-Exchange Resin by the Reaction of Acyl Chloride Groups with Functional Polymers

The grafting of PBG, PPG, PEG, PVA, SDO, SDA, and PEI onto the cation-exchange resin by reaction of its acyl chloride groups with hydroxyl or amino groups of these polymers was examined. The results are shown in Table 1.

From the results shown in Table 1, it is apparent that the grafting reaction proceeds by reaction of the acyl chloride groups of the cation-exchange resin with the functional groups of these polymers. In contrast, the polymers merely adsorbed on the cation-exchange resin were found to be removed almost completely by Soxhlet extraction with appropriate solvents.

The grafting of these polymers is also confirmed by the IR spectra. For example, Fig. 3 shows the IR spectra of PEI-grafted cation-exchange resin (35.7% grafting) obtained from the reaction of PEI with the cation-exchange

TABLE 1. Grafting by Reaction of the Cation-Exchange Resin Carrying Acyl Chloride Groups with Functional Polymers

Polymer	$\bar{M}_n \times 10^{-3}$	Temperature, °C	Grafting, %
PBG	1.0	80	24.6[a]
PPG	2.0	130	10.7[a]
PEG	8.2	130	9.3[a]
PVA	22.0	130	3.0[b]
PVA	66.0	130	21.4[b]
SDO	5.6	130	25.0[a]
SDA	3.0	80	43.5[a]
PEI	1.8	80	35.3[a]

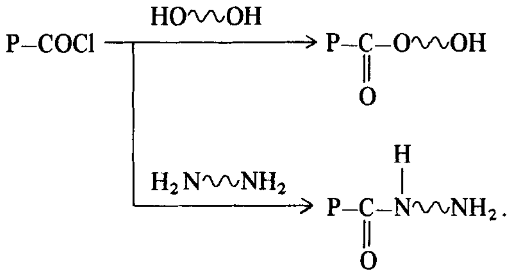
[a] Cation-exchange resin, 0.35 g; polymer, 2.5 mmol; triethylamine, 0.40 g; DMSO, 7.0 mL; 20 h.

[b] Cation-exchange resin, 0.25 g; polymer, 0.015 mmol; triethylamine, 0.40 g; DMSO, 7.0 mL; 20 h.

resin. As shown in Fig. 3, the IR spectra exhibited absorptions at 1560 and 1640 cm^{-1}, which are characteristic of an amide and an amino group, respectively. Furthermore, after grafting, the absorptions of the acyl chloride group at 1050 and 1804 cm^{-1} disappeared completely. In addition, these IR spectra showed absorptions characteristic of PEI. These results clearly show that, in analogy with carbon black, PEI could be grafted onto the cation-exchange resin by the reaction of the amino groups with acyl chloride groups of the resin.

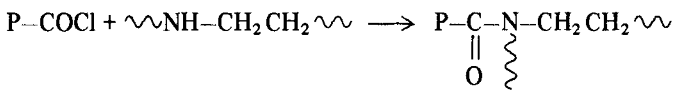
It is believed that polymers having hydroxyl groups, such as PBG, PPG, PEG, PVA, and SDO, are grafted through ester bonds (Eq. 1). On the other hand, polymers having amino group, such as SDA and PEI, are grafted through amide bonds (Eq. 2).

As described in our previous paper, it is considered that, in the grafting of PEI, not only terminal amino group but also imino group in the polymer chain probably react with acyl chloride groups of the cation-exchange resin (Eq. 3).



$$\mathrm{P{-}COCl} \xrightarrow{\mathrm{HO{\sim}OH}} \mathrm{P{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{\sim}OH} \qquad (1)$$

$$\mathrm{P{-}COCl} \xrightarrow{\mathrm{H_2N{\sim}NH_2}} \mathrm{P{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{N}{\sim}NH_2}. \qquad (2)$$



$$\mathrm{P{-}COCl} + \mathrm{{\sim}NH{-}CH_2CH_2{\sim}} \longrightarrow \mathrm{P{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\underset{\wr}{N}{-}CH_2CH_2{\sim}} \qquad (3)$$

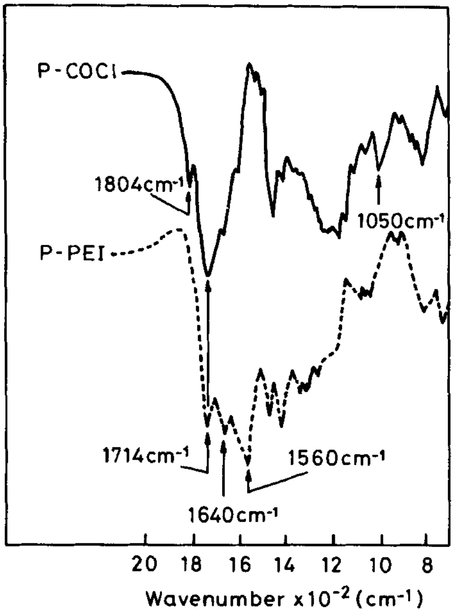


FIG. 3. IR spectra of PEI-grafted cation-exchange resin.

Based on the above results, it is concluded that these polymers can be grafted to the resin as well as to carbon black carrying acyl chloride groups by the reaction of acyl chloride groups of the cation-exchange resin with hydroxyl or amino groups in the polymer.

Graft Polymerization of γ-Methyl *L*-Glutamate NCA Initiated by Amino Groups on the Cation-Exchange Resin

In a previous paper it was reported that carbon black carrying amino groups is capable of initiating the ring-opening polymerization of γ-methyl *L*-glutamate NCA, and polypeptide is grafted from carbon black by propagation of the polymer from the surface [11]. Therefore, the graft polymerization of NCA from a cation-exchange resin with amino groups was examined. The results are shown in Table 2.

Both in the absence of cation-exchange resin and in the presence of untreated cation-exchange resin, no polymerization of the NCA could be detected. Moreover, ethylenediamine-adsorbed cation-exchange resin, which was extracted with methanol after the adsorption of ethylenediamine, had scarcely any initiating ability for the polymerization. This suggests that it is not necessary to take into account the effect of adsorbed ethylenediamine on the initiation.

In contrast, the polymerization of NCA was initiated by the cation-exchange resin carrying amino groups. Furthermore, it became apparent that polypeptide is grafted from the cation-exchange resin. The grafting of polypeptide to the resin was also confirmed by IR analysis. Figure 4 shows the IR spectra of polypeptide-grafted cation-exchange resin.

TABLE 2. Ring-Opening Polymerization of γ-Methyl *L*-Glutamate NCA Initiated by Amino Groups on Cation-Exchange Resin[a]

Cation-exchange resin	Conversion, %	Grafting, %
None	0	–
Untreated (P–COOH)	0	–
EDA-adsorbed[b]	Trace	–
$P{-}CONHCH_2CH_2NH_2$	7.6	16.0

[a] Cation-exchange resin, 0.50 g; NCA, 1.0 g; dioxane, 10 mL; 40°C; 4 d.

[b] Extracted with methanol after the adsorption of ethylenediamine.

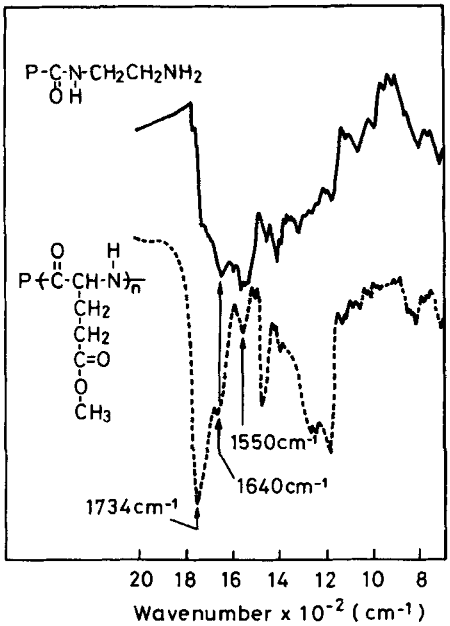


FIG. 4. IR spectra of poly(γ-methyl *L*-glutamate NCA)-grafted cation-exchange resin.

The IR spectra of the polypeptide-grafted cation-exchange resin exhibited a strong absorption at 1734 cm^{-1}, which is characteristic of a stretching vibration of the carbonyl group of an ester bond in the side chain of the polypeptide, and at 1550 cm^{-1}, which is characteristic of an amide bond. Moreover, the IR spectra exhibited other absorptions at 1200-1300 cm^{-1}, characteristic of the polypeptide.

Based on these results, it is concluded that the polymerization of NCA is initiated by cation-exchange resin carrying amino groups, and polypeptide is grafted from the cation-exchange resin as well as from carbon black.

Initiating Ability for Cationic Polymerization

We reported that the cationic polymerization of vinyl monomers, such as vinyl ethers and NVC, is initiated by carboxyl groups on the carbon black surface [12, 13]. Therefore, the initiating ability of carboxyl groups on the

TABLE 3. Initiating Ability of Cation-Exchange Resin for the Polymerization of IBVE and NVC

Monomer	Solvent	Temperature, °C	Conversion, %
IBVE	–	30	0[a]
IBVE	–	50	0[a]
NVC	Toluene	60	0[b]
NVC	Toluene	90	0[b]

[a] Cation-exchange resin, 0.50 g; IBVE, 10.0 mL; 24 h.
[b] Cation-exchange resin, 0.50 g; NVC, 1.0 g; toluene, 5.0 mL; 24 h.

resin for the polymerization of IBVE and NVC was examined. The results are shown in Table 3.

As shown in Table 3, the cation-exchange resin failed to initiate cationic polymerization of IBVE and NVC, perhaps due to the difference in the acidity of the carboxyl groups. As mentioned in a previous paper, the acidity of carboxyl groups on the surface of carbon black is expected to be higher than that of ordinary carboxylic acids because of the effect of neighboring hydroxyl groups [14, 15].

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