Grafting of Polymers onto a Carbon Black Surface by the Trapping of Polymer Radicals

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The grafting of polymers onto a carbon black surface based on the trapping of polymer radicals by polycondensed aromatic rings of the surface was investigated. It was found that polymer radicals formed by the thermal decomposition of azo-polymer, peroxy-polymer and 2,2,6,6-tetramethylpiperidinyl-1-oxy-terminated polymer are successfully captured by a carbon black surface to give the corresponding polymer-grafted carbon blacks. The grafting of polymers onto carbon black was also achieved by the trapping of polymer radicals formed by the redox reaction of ceric ions with polymers having hydroxyl groups. It was concluded that surface grafting of polymers onto carbon black is effective when there are few functional groups. The electrical resistance of poly(ethylene oxide) (PEO)-grafted carbon black is increased drastically to about $10^5$ times the initial resistance at the melting point of PEO. This may be due to a widening of the gaps between the carbon black particles by melting of PEO. In addition, it was found that the electrical resistance of a crystalline poly(ethylene imine) (PEI)-grafted carbon black drastically increased to $10^3$ times the initial resistance in methanol, ethanol and water vapor, but hardly any change in electrical resistance was observed in n-hexane or toluene vapor. These results suggest the possibility of detecting a slight change in the crystalline structure of PEI upon absorption of solvent vapor as a large increase in the electrical resistance of the polymer-grafted carbon black.

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INTRODUCTION

In a series of papers, we have reported the grafting of polymers onto a carbon black surface by the following methods: (a) grafting from the surface—grafting of polymer chains are initiated from initiating groups introduced onto the surface; (b) grafting onto the surface—propagating polymer radicals are trapped by carbon black surface during the polymerization, initiated by a conventional radical initiator in the presence of carbon black; and (c) polymer reactions with functional groups on the surface—polymers having terminal functional groups are reacted with functional groups on the carbon black surface.

The radical, cationic and anionic polymerization initiated by azo- or peroxyester, acyl perchlorate and potassium carboxylate groups introduced onto a carbon black surface are examples of method (a). An important characteristic of method (c) is the fact that not only the molecular weight and the number of grafted polymers on the carbon black surface are easily controlled, but also a polymer with a well-defined structure can be grafted. Methods (a) and (c), however, cannot be applied to the surface grafting of polymers onto furnace black and acetylene black, because these carbon blacks have few functional groups.

It is well known that the polycondensed aromatic rings of carbon black act as a strong radical-trapping agent. We have reported that during polymerization initiated by the conventional radical initiators in the presence of carbon black, i.e.
method (c), part of the polymer formed is grafted onto the surface, but the percentage of grafting is less than 10%, because carbon black traps more low-molecular-weight initiator fragments than growing polymer radicals.\textsuperscript{11,12} It is expected, therefore, that effective grafting of polymers onto the surface will be achieved if the reaction of carbon black with polymer radicals is conducted in the absence of low-molecular-weight fragment radicals.

In the present work, the grafting of polymers onto a carbon black surface by trapping polymer radicals formed by the thermal decomposition of azo polymers, peroxy polymers and 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO)-terminated polymers was investigated (Schemes 1,2,3, below.) In addition, the reaction of a carbon black surface with polymer radicals formed by the redox reaction of ceric ions with polymers having hydroxyl groups was examined (Scheme 4 below). The electrical properties of polymer-grafted carbon black will be discussed.

### EXPERIMENTAL

#### Carbon blacks and reagents

The carbon blacks used were furnace black Philblack O (BET surface area 79.6 m\(^2\) g\(^{-1}\)) and Philblack I (116.8 m\(^2\) g\(^{-1}\)) obtained from Phillips Petroleum Co. Azo polymers were prepared by the polycondensation of 4,4’-azobis(4-cyanopentanoyl dichloride) with polymers having terminal hydroxyl or amino groups, such as poly(ethylene oxide) (PEO), poly(dimethylsiloxane) (PDS), and poly(ethylene imine) (PEI).\textsuperscript{13,14} Peroxy polymers were prepared by the cationic polymerization of styrene and ring-opening polymerization of tetrahydrofuran (THF) and \(\varepsilon\)-caprolactone (CL) using 3,3’-bis-(chloromethyl)benzoyl peroxide diperchlorate as an initiator.\textsuperscript{15} TEMPO-terminated polystyrene was prepared according to the literature method.\textsuperscript{16,17}

#### Grafting reaction and determination of percentage of grafting

The grafting reaction was conducted in a 100 ml flask under nitrogen and stirred with a magnetic stirrer. The detailed procedures were described previously.\textsuperscript{14,15} The isolation of polymer-grafted carbon black from ungrafted polymer was carried as follows: the reaction product was dispersed in a good solvent of the grafted polymer and the dispersion was centrifuged. The supernatant solution was removed by decantation and the precipitated carbon black was dispersed in solvent. The centrifugation was repeated until no more polymer could be detected in the supernatant solution. The percentage of grafting was determined by the following equation:

\[
\text{Grafting} \% = \left(\frac{A}{B - A}\right) \times 100
\]

where \(A\) is the weight of polymer-grafted carbon black and \(B - A\) is the weight of ungrafted polymer.

#### Electrical resistance of polymer-grafted carbon black

The procedure for the measurement of electrical resistance of polymer-grafted carbon black under various conditions was described in detail previously.\textsuperscript{18}

### RESULTS AND DISCUSSION

#### Trapping of polymer radicals formed by decomposition of azo-polymer and peroxy polymer

In general, polymers having azo bonds in the main chain, i.e. azo-polymers, are used for the preparation of block copolymers by radical polymerization of vinyl monomers.\textsuperscript{13} The grafting of polymers by the reaction of carbon black with polymer radicals formed by the thermal decomposition of azo-polymers was therefore investigated. As shown in Table 1, when these azo-polymers reacted with carbon black below 40 °C, the grafting of the polymer onto carbon black scarcely proceeded at

<table>
<thead>
<tr>
<th>Azo polymer</th>
<th>(M_n \times 10^{-3})</th>
<th>Temperature (°C)</th>
<th>Grafting (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDS</td>
<td>4.5</td>
<td>40</td>
<td>9.2</td>
</tr>
<tr>
<td>PDS</td>
<td>4.5</td>
<td>70</td>
<td>42.1</td>
</tr>
<tr>
<td>PDS</td>
<td>9.6</td>
<td>70</td>
<td>30.5</td>
</tr>
<tr>
<td>PEO</td>
<td>4.0</td>
<td>70</td>
<td>35.7</td>
</tr>
<tr>
<td>PEI</td>
<td>4.8</td>
<td>70</td>
<td>20.4</td>
</tr>
</tbody>
</table>

![Table 1](image.png)

\(a\) Carbon black (Philblack I), 0.30 g; polymer, 5.0 g; toluene, 20.0 ml; 24 h.
because the decomposition of the azo-polymer was very slow at that temperature. In contrast, above 70 °C the grafting reaction of these azo-polymers took place and the corresponding polymer-grafted carbon blacks were obtained. In addition, IR spectra of PEI-grafted carbon black, for example, shows new absorptions which are characteristic of PEI. The results indicate that the polymer radicals formed by the thermal decomposition of azo-polymer are effectively captured by the carbon black surface, as shown in Scheme 1.

Table 2 shows the result of the grafting reaction of peroxy-polymers with carbon black. It was found that these peroxy-polymers were readily decomposed in the presence of carbon black, and the polymer radicals formed were successfully trapped by the carbon black surface (Scheme 2). The grafting of polymers onto the carbon black surface was also confirmed by the IR spectra of polymer-grafted carbon black.

It is interesting to note that the grafting reaction proceeds even at 30 °C. This may be due to the fact that peroxide decomposes even at room temperature in the presence of carbon black.19

### Trapping of polymer radicals formed by decomposition of TEMPO-terminated polystyrene

It has been reported that the use of TEMPO-based initiators, or systems containing TEMPO, for the free-radical polymerization of styrene result in a ‘living’ process.16,17 In addition, TEMPO-terminated polystyrene (TEMPO-PolySt) thus obtained has an ability to initiate the radical polymerization of vinyl monomers to give the corresponding block copolymer, because of the formation of polystyryl radicals resulting from the thermal decomposition of C–O–N bonds of TEMPO-PolySt.17

In the present work, the grafting reaction of carbon black with TEMPO-PolySt obtained from the above polymerization was examined. The

### Table 3 Grafting of polymer onto carbon black by the reaction with TEMPO-PolySt

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n \times 10^{-3}$</th>
<th>Temperature (°C)</th>
<th>Grafting (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PolySt</td>
<td>11.4</td>
<td>125</td>
<td>5.0</td>
</tr>
<tr>
<td>TEMPO-PolySt</td>
<td>11.2</td>
<td>125</td>
<td>9.2</td>
</tr>
<tr>
<td>TEMPO-PolySt</td>
<td>3.2</td>
<td>80</td>
<td>4.8</td>
</tr>
<tr>
<td>TEMPO-PolySt</td>
<td>3.2</td>
<td>125</td>
<td>16.0</td>
</tr>
<tr>
<td>TEMPO-PolySt</td>
<td>3.2</td>
<td>135</td>
<td>17.5</td>
</tr>
</tbody>
</table>

a Carbon black (Philblack I), 0.10 g; polymer, 1.0 g; m-xylene, 10.0 ml; 12 h.
No grafting of poly-
styrene was observed when the reaction was
carried out below 80°C, at which temperature
there is scarcely any decomposition of C–O–N
bonds. On the contrary, the grafting of polystyrene
onto carbon black proceeded successfully above
100°C.

Figure 1 shows IR spectra of polystyrene and
polystyrene-grafted carbon black obtained from the
reaction. It became apparent that the IR spectra of
polystyrene-grafted carbon black shows new ab-
sorptions, which are characteristic of polystyrene.
These results indicate that the polystyryl radicals
formed by the decomposition of TEMPO-PolySt
are trapped by the carbon black surface, as shown in
Scheme 3. In the reaction system, the trapping of
TEMPO by the carbon black surface was scarcely
observed, because of the stability and the steric
hindrance of the radical.

Table 4 Grafting of carbon black with polymer radicals
formed by redox reaction with Ce(IV)*

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mₙ × 10⁻³</th>
<th>Time (h)</th>
<th>Grafting (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>3.0</td>
<td>12</td>
<td>49.7</td>
</tr>
<tr>
<td>PEO</td>
<td>8.0</td>
<td>12</td>
<td>57.5</td>
</tr>
<tr>
<td>PEO</td>
<td>20.0</td>
<td>12</td>
<td>56.5</td>
</tr>
<tr>
<td>PVA</td>
<td>22.0</td>
<td>12</td>
<td>33.5</td>
</tr>
<tr>
<td>Soluble starch</td>
<td>—</td>
<td>6</td>
<td>54.4</td>
</tr>
</tbody>
</table>

* Carbon black (Philblack I), 0.30 g; polymer, 1.0 g; Ce(IV)
soln., 1.0 ml; 25°C.

Trapping of polymer radicals
formed by redox reaction of ceric ions with polymers having hydroxyl groups

It has been reported that the radical polymerization
of vinyl monomers is initiated by radicals formed
by redox reaction of ceric ions with reducing agents
such as alcohols, aldehydes and acids. Particularly,
a system consisting of ceric ions and alcohols
has been applied to the grafting of vinyl monomers
onto poly(vinyl alcohol) (PVA) and cellulose.
It is therefore expected that polymer radicals formed
by the redox reaction of ceric ions with polymers
having hydroxyl groups are trapped by the carbon
black surface to give the corresponding polymer-
grafted carbon black.

For this paper, the grafting of polymers by the
above system was investigated. Table 4 shows the
results of the grafting reaction of diol-type PEO,
PVA and soluble starch in the presence of ceric ion.
In the absence of ceric ions no grafting of
these polymers onto the surface was observed. In
contrast, in the presence of ceric ions the corre-
sponding polymers were effectively grafted onto
the carbon black surface, as shown in Scheme 4. No
gelation of polymers was observed in the reaction
system. This indicates that radicals formed on the
grafted chain on the carbon black surface hardly

Scheme 3 Surface grafting onto carbon black by trapping polymer radicals formed by decomposition of TEMPO-PolySt.
react with other carbon black particles, because the grafted polymer chain is fixed on the surface.

**Grafting mechanism**

When carbon blacks were treated with a conventional radical initiator such as benzoyl peroxide and 2,2'-azobis(isobutyronitrile), the corresponding radicals are bonded onto the surface by addition reaction with polycondensed aromatic rings and quinonic oxygen groups on the surface. The free radicals formed on the carbon black surface by the addition of initiator radicals were considered to be stabilized by polycondensed aromatic rings: the increase in surface radicals after the treatment with the radical initiators has been confirmed by ESR.

Grafted polymer were therefore considered to be bonded to polycondensed aromatic rings by addition of polymer radicals. It seems that quinonic oxygen groups on the surface also act as trapping sites for polymer radicals, especially in the case of the reaction with channel black, which has many quinonic oxygen groups.

**Electrical properties of polymer-grafted carbon black**

It has been reported that vinyl polymer-grafted carbon black, which was crosslinked with a variety of crosslinking agents, shows a positive temperature coefficient of resistance (PTC) near the glass transition temperature of the grafted polymer.

The effect of temperature on the electrical resistance of crystalline polymer-grafted carbon black was investigated. Figure 2 shows the relationship between temperature and electrical resistance of PEO-grafted carbon black prepared by the radical-trapping method. The electrical resistance of the PEO-grafted carbon black increased dramatically to $10^3$–$10^4$ times the initial resistance in methanol, ethanol and water vapor.

In the present paper, the effects of methanol, water and n-hexane vapor on the electrical resistance of PEO-grafted carbon black were investi-
gated. Figure 3 shows the results. It became apparent that the electrical resistance of PEO-grafted carbon black increased to $10^2$–$10^3$ times the initial resistance in methanol and water vapor, which are good solvents for PEO, but a change in electrical resistance of the composite was hardly observed in n-hexane vapor, which is a nonsolvent of PEO.

These results suggest the possibility of detecting a slight change in the crystalline structure of PEO by the absorption of solvent vapor as a large increase in the electrical resistance of the composite.

Figure 4 shows that the electrical resistance of PEI-grafted carbon black returned immediately to the initial resistance value when the composite was transferred to dry air. The responsiveness of the electrical resistance was reproducible even after 30 cycles of exposure to methanol vapor and dry air.

CONCLUSIONS

Polymer radicals, which were formed not only by the thermal decomposition of azo polymer, peroxy polymer and TEMPO-PolySt but also by the redox reaction of ceric ions with polymer having hydroxyl groups, were successfully trapped by a carbon black surface to give the corresponding polymer-grafted carbon black.

The grafting of PEO, PVA and soluble starch onto carbon black was achieved by trapping the polymer radicals formed by redox reaction of ceric ions with these polymers.

The electrical resistance of PEO-grafted and PEI-grafted carbon black was found to respond to temperature and various vapors.

REFERENCES