

# Novel Gas Sensor from Polymer-Grafted Carbon Black: Vapor Response of Electric Resistance of Conducting Composites Prepared from Poly(ethylene-*block*-ethylene oxide)-Grafted Carbon Black

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**ABSTRACT:** A crystalline block copolymer of poly(ethylene-*block*-ethylene oxide) (PE-*b*-PEO) was successfully grafted onto a carbon black surface by direct condensation of its terminal hydroxyl groups with carboxyl groups on the surface using *N,N'*-dicyclohexylcarbodiimide as a condensing agent. The electric resistance of the composite from PE-*b*-PEO (PEO content is above 50 wt %)-grafted carbon black drastically increased to  $10^4$ – $10^6$  times of the initial resistance in a vapor of dichloromethane, chloroform, tetrahydrofuran, and carbon tetrachloride, which are good solvents for PE-*b*-PEO, and returned immediately to the initial resistance when the composite was transferred in dry air. However, the change of the electric resistance of these composites was less than one-tenth in a poor solvent vapor at the same condition. The response of the electric resistance was reproducible and stable even after exposure to a good solvent vapor and dry air with 30 cycles or exposure to the vapor over 24 h. The effect of PEO content on the vapor response was also investigated. The composite from PE-*b*-PEO-grafted carbon black responded to the low vapor concentration with a linear relationship between the electric resistance and the concentration of the vapor in dry air. This indicates that the composite can be applied as a novel gas sensor. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2437–2447, 2000

**Key words:** carbon black; polymer; poly(ethylene-*block*-ethylene oxide); surface grafting; conducting composite; gas sensor

## INTRODUCTION

The electric resistance of a carbon black (CB)-filled polymer composite often presents a sudden change over several orders of magnitude at the temperature at or near the melting point of the

polymer,<sup>1–5</sup> at the volume fraction of CB at or near a percolation threshold,<sup>6–10</sup> or due to changing of other factors such as the compression-molding temperature, the compression-molding time,<sup>10</sup> and the composition ratio of the polymer blend in the composite.<sup>11</sup> With these properties, the CB-filled polymer composites have many applications such as in heating material, in positive temperature coefficient (PTC) material, and in an electrode as a sensor element.

We pointed out that the sudden increase of resistivity of crystalline polymer-grafted CB at the melting point of polymers is due mainly to the

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**Table I** Grafting of PE-*b*-PEO onto CB Surface

Polymer	PEO			PE- <i>b</i> -PEO			PE
	$M_n$	PEO content (wt %)	Grafting (%)	$M_n$	PEO content (wt %)	Grafting (%)	$M_n$
	1500	100	9.14	1750	80	5.46	1400
				920	50	4.14	920
				875	20	9.45	875
				575	20	10.53	575
				740	0	9.15	740
						4.2	

change of the crystalline structure in the polymer matrices during the increasing temperature.<sup>4,5,12</sup> Based on this assumption, we suppose that the electric resistance of the composite from crystalline polymer-grafted CB can also be changed by absorption of some vapors, because this kind of absorption can lead to a change of the crystallinity of the polymer matrix. Recently, many experimental results showed good accordance with this hypothesis.<sup>13–16</sup>

The vapor sensor based on a conducting polymer<sup>17</sup> and polymer/CB composite<sup>18–20</sup> was reported by Hatfield et al. and Doleman et al., respectively. In our previous works, the electric resistance of a composite with low-polar crystalline polymer-grafted CB such as polyethylene (PE)-grafted CB dramatically increased with several orders of magnitude when it was exposed in a nonpolar or low-polar solvent vapor like toluene, hexane, or tetrahydrofuran (THF). But the resistance hardly changed in a polar solvent vapor like water or alcohol.<sup>15</sup> On the other hand, the electric resistance of a composite with a polar crystalline polymer-grafted CB such as poly(ethylene oxide) (PEO)-grafted CB increased drastically in a polar solvent vapor, but had hardly any response to non (or low)-polar solvent vapor.<sup>16</sup>

In this work, we studied the electric-resistance changing behaviors of the polymer/CB composite prepared from polymer-grafted CB when it was exposed to various solvent vapors. The grafted polymer and matrix are PE-*b*-PEO, which is a crystalline block copolymer containing a nonpolar block of PE and a polar block of PEO. The effects of the block ratio of PE and PEO in the block copolymer, and the molecular weight and the grafting of the block polymer onto the CB surface on the vapor response, are discussed in detail. The relationship between the vapor concentration and the response was also examined.

## EXPERIMENTAL

### Materials and Reagents

Conductive CB with a commercial name of Porousblack was used as a filler component in the

composite. It is a furnace black made by Asahi Carbon Co. Ltd. (Niigata, Japan). The specific surface area of the CB particles is 447 m<sup>2</sup>/g, and the average particle size is 41 nm. The content of surface carboxyl (COOH) and phenolic hydroxyl (OH) groups is 0 and 0.03 mmol/g, respectively.<sup>21,22</sup> The CB was dried in a vacuum at 110°C for 48 h before use.

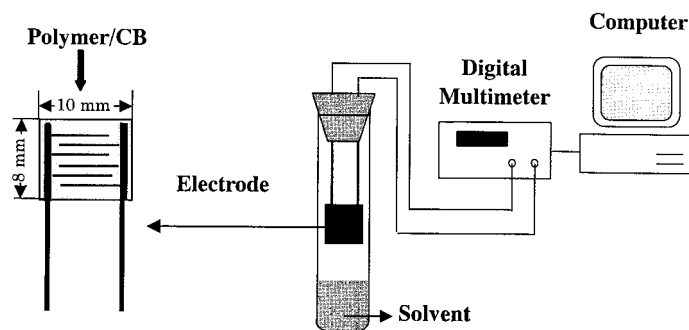
4,4'-Azobis(4-cyanopentanoic acid) (ACPA), used for the introduction of carboxyl groups onto the CB surface, was purchased from Wako Pure Chemical Industries Ltd. (Tokyo, Japan). It was purified by recrystallization from methanol. *N,N'*-Dicyclohexylcarbodiimide (DCC) was also purchased from Wako Pure Chemical Industries. It was dried in a vacuum at room temperature. THF was purified by the ordinary method. Analytical-grade dichloromethane, chloroform, carbon tetrachloride, and other solvents were used without any further purification.

PE-*b*-PEO, PEO, and PE were purchased from Aldrich Japan Co. (Tokyo, Japan) and were used as received. The number-average molecular weight ( $M_n$ ) and the content of PEO of the block copolymer are shown in Table I, together with the data of PEO and PE.

### Introduction of Carboxyl Groups onto CB Surface

To disperse CB particles into the PE-*b*-PEO matrix more uniformly, the block copolymer was grafted onto the surface.<sup>23–25</sup> The conductive CB has almost no active groups, so it is difficult to graft the polymer directly onto the surface. Since CB usually acts as a radical scavenger,<sup>26,27</sup> we designed a method to introduce carboxyl groups by the trapping of the 4-cyanopentanoic acid radicals, formed by thermal decomposing the ACPA, onto the CB.<sup>26</sup>

For a typical process, 6.0 g of CB, 2.0 g of ACPA, and 140 mL of THF were added into a 500-mL flask. The reaction mixture was stirred at 65°C under nitrogen for 48 h. The resulting CB was washed with THF until no more carboxyl groups were detected in the supernatant solution. The amount of 4-cyanopentanoic acid groups trapped by CB was determined by titration<sup>21</sup> and



**Figure 1** Comblike electrode and apparatus for the measurement of electric resistance.

by thermogravimetric analysis (TGA). The latter was conducted under nitrogen at a scan rate of  $10^{\circ}\text{C}/\text{min}$  from 25 to  $500^{\circ}\text{C}$  with the sample of 5–7 mg in an aluminum cell.

#### Grafting of the PE-*b*-PEO onto CB Surface

The grafting of PE-*b*-PEO onto ACPA-treated CB was achieved by the direct condensation of terminal hydroxyl groups of the polymer with carboxyl groups on CB by use of DCC as a condensing agent.<sup>28</sup> ACPA-treated CB, 1.0 g, PE-*b*-PEO, 4.0 g, DCC, 0.2 g, and THF, 80 mL, were mixed in a 200-mL flask, and the reaction mixture was stirred with a magnetic stirrer under nitrogen at  $65^{\circ}\text{C}$  for 48 h. After the reaction, the mixture was centrifuged at  $1.5 \times 10^4$  rpm and the supernatant solution was removed by decantation. The resulting CB was extracted with THF by a Soxhlet apparatus for 48 h to remove ungrafted polymer and dried in vacuum at  $110^{\circ}\text{C}$  for 10 h. The amount of the grafted layer on the CB surface was measured by TGA (under a nitrogen at a scan rate of  $10^{\circ}\text{C}/\text{min}$  from 25 to  $500^{\circ}\text{C}$ ). The grafting of PEO and the PE polymer was also conducted and the grafting was measured by the same method.

#### Preparation of Composite from Polymer and CB

Conducting polymer composites loaded with 20 wt % CB were prepared by dispersing CB into polymer matrix. Into a 100-mL flask, 1.00 g of polymer pellets and 20 mL of THF were charged (when PEO was used, 20 mL of methanol was charged). The mixture was stirred at  $65^{\circ}\text{C}$ . After the polymer dissolved completely, 0.25 g of polymer-grafted or ungrafted CB was added and stirred continually at  $65^{\circ}\text{C}$  for 1 h to disperse CB into polymer solution uniformly. The obtained suspension was coated onto a comblike electrode,

which has an area of  $8 \times 10$  mm, prepared by the screen printing of conductive Ag/Pd paste onto a ceramic substrate. The initial resistance of the comblike electrode before being composite-coated was greater than  $1200 \text{ M}\Omega$ . The film coated on the comblike electrode was dried in air at room temperature for 10 min and then dried in a vacuum at room temperature for 24 h. The coated polymer/CB composite film has an area of  $4 \times 7$  mm. From the weight difference of the comblike electrode before and after the film was coated, the composite film loaded on the electrode is about 0.3 mg and so the thickness is about  $10 \mu\text{m}$ .

#### Measurement of Electric Resistance

The electric resistance of the composite in solvent vapor was measured by hanging the electrode loaded with the composite in a glass tube containing pure solvent at the bottom (Fig. 1).<sup>13–16</sup> The distance between the electrode and solvent surface is 2.0 cm. The dc electric resistance of the composite film was measured as a function of time. Resistance measurements were performed using a simple two-point configuration. The electrode was connected directly to a digital multimeter (made by Advantest Co. Ltd., Japan; type R6871E-DC) via a ribbon cable, and the resistance was read by a personal computer. When the resistance is less than  $10 \text{ M}\Omega$ , the measurement range of  $10 \text{ M}\Omega$  is used, with a constant dc current of  $1 \mu\text{A}$ , while with the measurement range of  $1000 \text{ M}\Omega$  with constant dc a current of  $10 \text{ nA}$  is used when above  $10 \text{ M}\Omega$  of the determined composite in the solvent vapor. The partial pressure of the solvent vapor was controlled at the saturated vapor pressure at  $25^{\circ}\text{C}$ .

To measure the relationship between the vapor concentration and the response, the electrode was hung in a 2000-mL glass vessel. Into the vessel,

the volatile solvent was injected using a microinjection device, and the solvent was volatilized completely in the vessel. The volume concentration of the solvent vapor in the atmosphere was calculated by the thermodynamic equation.

## RESULTS AND DISCUSSION

### Modification of the Surface of CB

It is recognized that the main parameters of CB, which govern their dispersion and conductivity in the polymer matrix, are as follows: (1) the size and distribution of primary particles (or the specific surface area), (2) the size, shape, and distribution of aggregates (generally termed CB "structure"), and (3) the CB surface energy. All these parameters play an important role in the conductivity of the composite through different mechanisms, such as interfacial interaction between the polymer and CB,<sup>29</sup> occlusion of the polymer in the internal voids of the aggregate, and the agglomeration of CB aggregates in the polymer matrix.<sup>30</sup> In this study, considering the former two factors of the CB properties on the dispersion and conductivity, we selected the conductive CB, which has a large surface area of about 447 m<sup>2</sup>/g and a high structure.

The conductive CB is difficult to disperse into the organic polymer or solvent uniformly because of the high surface energy and the small particle size. In general, to increase the ability of CB dispersion in the polymer matrix, the CB surface is usually modified by coating with an organic compound such as an oligomer with a terminal active group. In our laboratory, the modification of the CB surface by a grafting polymer has been studied intensively.<sup>23,24,31–36</sup>

It is difficult to modify the conductive CB surface, because there are almost no active groups on the surface to be used for the grafting reaction. In this study, a two-step modification process was conducted. First, carboxyl groups were introduced onto the CB surface through the trapping of 4-cyanopentanoic acid radicals, which were formed by the thermal decomposition of ACPA. After this treatment, the content of carboxyl groups was determined to be 0.14 and 0.16 mmol/g by titration and the TGA method, respectively. Then, as the second step, PE-*b*-PEO, PEO, and PE were grafted onto the surface by the condensation reaction of terminal hydroxyl groups of

the polymers with surface carboxyl groups in the presence of DCC, as a condensing agent.

Table I shows the results of the percentage of grafting (weight percent of grafting materials on CB) which was determined by TGA. From the results, the surface of the CB particles was grafted by an organic compound at the range of 4–11 wt %.

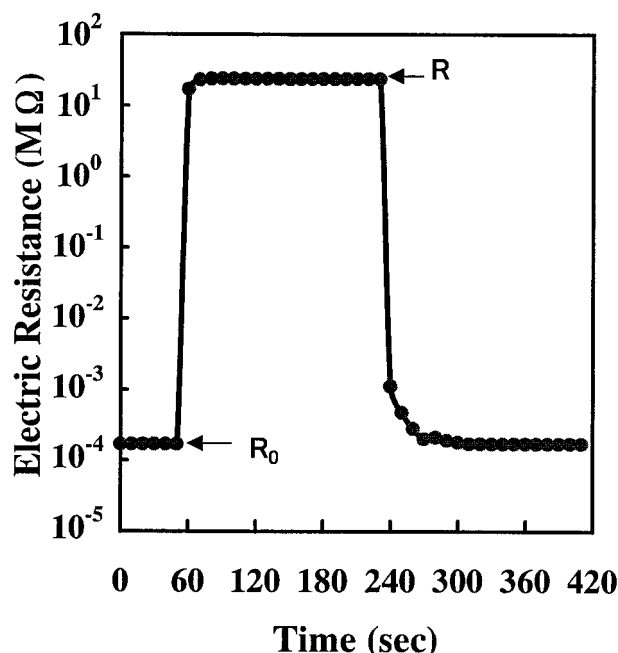
In addition, the percentage of grafting of PE-*b*-PEO with the higher molecular weight was smaller than that with the lower molecular weight. This may be because PE-*b*-PEO with a lower molecular weight has lower steric hindrance and high kinetic viscosity, so it can react with the carboxyl group on the CB surface readily and can obtain a compact polymer layer on the CB surface. On the other hand, PE-*b*-PEO with a high molecular weight has high steric hindrance, slow kinetic velocity, and a lower percentage of the hydroxyl group in the block copolymer, so it is only grafted onto the surface with a relative loose layer and a lower percentage of grafting.

With ACPA treatment, the CB surface is bound with the COOH group. In this respect, the ACPA-treated CB will wet well with the polar polymer of PEO, but is difficult to wet with the nonpolar polymer of PE. Therefore, as shown in Table I, because of the low concentration of PE at the region near the CB surface, the percentage of grafting of PE onto the CB surface is some lower.

### Electric Resistance of Composite from Polymer and Polymer-grafted CB in Various Vapors

The electric resistance of the polymer/CB composite electrode was measured by the digital multimeter at a temperature of 25°C. In a typical measurement process, resistance data on the electrodes were collected for 60 s in dry air to serve as a baseline. This was followed by a 180-s data collection while the electrodes were exposed to the saturated solvent vapor at room temperature and standard pressure. The electrodes were then given 180 s to recover in dry air. The exposure times were varied somewhat, but the steady-state values of the electric resistance change were always reached for any given exposure time.

Figure 2 shows a typical response of the electric resistance of the composite from PE-*b*-PEO ( $M_n = 1750$ )-grafted CB to chloroform. Most of the electrodes displayed an increase in the electric resistance upon exposure to the vapor and returned to their baseline values (initial resistance) after transferred to dry air. The responses



**Figure 2** Typical response of the composite from PE-*b*-PEO ( $M_n = 1750$ )-grafted CB upon exposure to the saturated chloroform vapor at room temperature and standard pressure.

were analyzed by calculating  $(R - R_0)/R_0$ , where  $R$  is the steady-state response value, observed during the exposure to solvent vapor, and  $R_0$  is the baseline value of the resistance, taken as the resistance value just before the exposure began,

and the calculated results were expressed as the response of the composite.

The response of the composite from PE-*b*-PEO with different molecular weight and different PEO contents was determined. As shown in Table II, the response of the composite from PE-*b*-PEO (PEO content over 50 wt %) is very high against dichloromethane, chloroform, carbon tetrachloride, and THF vapor at 25°C under standard atmospheric pressure. On the other hand, the response against water, acetone, and alcohol vapor at the same condition is less than one-tenth. Based on the fact that the former solvents are good solvents for PE-*b*-PEO but the latter are not, it is considered that the former solvents have high affinity for the block copolymer, and so they can be easily absorbed by the block copolymer.

As to the process of the crystalline polymer absorbing the solvent vapor, the crystalline structure of the block copolymer is changed by the absorption of the solvent. With the crystalline region dissolving, the polymer volume swells and the composite viscosity decreases, allowing the polymer chain and the CB particles to move more easily, which may cut the connected CB particles' conducting path, resulting in a drastic increase of the resistance of the composite.

The drastic increase of the electric resistance in solvent vapor is similar to that of PTC material, whose electric resistance increases drastically with increasing temperature at or near the

**Table II** Response of Electric Resistance of Composite from PE-*b*-PEO-grafted CB Against Various Solvent Vapors

Solvent Vapor	Response $(R - R_0)/R_0$						
	PEO Content						
	100 wt %	80 wt %	50 wt %	20 wt %		0%	
	$M_n$						
	1000	1750	1400	920	875	575	740
CH <sub>2</sub> Cl <sub>2</sub>	46	260,000	52,000	68,000	9	1000	25
CHCl <sub>3</sub>	600	140,000	91,000	160,000	24	2300	31
CCl <sub>4</sub>	69	10,300	4100	6400	3	49	5
THF	31	42,000	7900	21,400	5	100	64
Acetone	39	4	1	2	1	1	1
Toluene	20	11	5	7	2	3	5
MeOH	2500	1	1	2	0	0	11
EtOH	2200	1	1	2	0	0	47
Water	2000	20	11	14	1	3	0

melting point of the crystalline polymer matrices. The PTC effect is explained by that the crystalline structure is changed during the temperature increase and it may cut the conducting path.<sup>5,12</sup> Some other workers also explained that the electric resistance of PTC material increased by decreasing the CB concentration, which was caused by the thermal expansion of the polymer matrix during the temperature increase.<sup>1,2,37,38</sup> Since the drastic increase of the electric resistance in solvent vapor is similar to the PTC character, perhaps the similar mechanism can be applied to explain the phenomenon in this study, that is, the crystalline change to cut the conductive path or the polymer expansion led to a change of CB dispersion in the composite.

In general, it is very difficult for CB particles to disperse in the crystalline region. The CB can only be considered dispersing in the amorphous region in the crystalline polymer matrix. Therefore, a conducting network can form easily at a fairly high CB concentration in this amorphous region. Additionally, in the crystalline region, as its dense and ideal structure, it is hardly penetrated by CB particles. As the result, CB particles are densely packing into the crystalline boundary, which makes the conducting particles to more closely form a carbon "chain" that allows current to flow through the composites and leads to a lower electric resistance in the crystalline polymer/CB composite.

As the solvent vapor is absorbed, the crystalline structure may be changed, that is, the crystalline phase may be transformed into an amorphous phase, the volume of the polymer may swell, and the viscosity of the composite may decrease. With those processes, the polymer chain and the CB particles can move more easily, and the CB conducting network can be destroyed, which leads to a large increase of the electric resistance of the composite.

If the CB dispersed in polymer matrix is uniform, the conducting path of the CB network is difficult to form except that the loaded CB in the polymer is very high, and it was reported that there is no abrupt change in the relationship between the electric resistance and CB concentration.<sup>39</sup> Using the same reason, we can conclude that if CB disperses uniformly in the composite there should be no abrupt change when absorbing the solvent. From the experimental result, therefore, we consider that CB was dispersed in the composite nonuniformly even if the composite was prepared from polymer-grafted CB.<sup>1,6,40</sup>

As another possible mechanism, the electric resistance of the composite electrode drastically increases in the solvent vapor due to the swelling of the matrix polymer, which was caused by the absorption of the solvent vapor. But we hardly observed the abrupt resistance change of the composite from amorphous PEI-grafted CB in the vapor of a good solvent of PEI.<sup>14</sup>

In the amorphous polymer, the CB dispersion is more uniform and the CB conducting network is difficult to form until the content of CB is very high. The swelling of the amorphous polymer only leads to a slight decrease of the CB content in the composite, but it is difficult to cut the CB conducting network, which was distributed in the whole composite.

But in the crystalline polymer, the CB conducting network is distributed in the amorphous region and the interface of crystalline regions. As the crystalline structure is changed, the CB network may be cut, leading to a large increase of the resistance. In our experiments, we observed the abrupt change of the electric resistance of the composite from crystalline PEI in the same vapor as described above.<sup>14</sup>

As shown in Table II, the response against chlorocarbon and THF vapor compactly corresponded with the composition of PE and the PEO segment in the block copolymer. It seems that the response is caused only by the PEO segments. But in the case of homopolymer PEO, the response against these solvent vapors is far less than that of the block copolymers. On the other hand, the PEO/CB composite has a high response against water or alcohol vapors. Therefore, the content of PEO units in copolymer affect mainly the response in the chlorocarbon and THF vapor and the PE units play a cooperative role. The response has a relation not only with the two components, but also with their interaction in the block copolymer. In addition, the higher the PEO content, the more easily the chlorocarbon vapor absorbed by the composite is observed in this study. The response highly corresponds with the solvent absorption, indicating that the conductive path is cut by the solvent absorption, and this process leads to a high electric resistance in the solvent vapors.

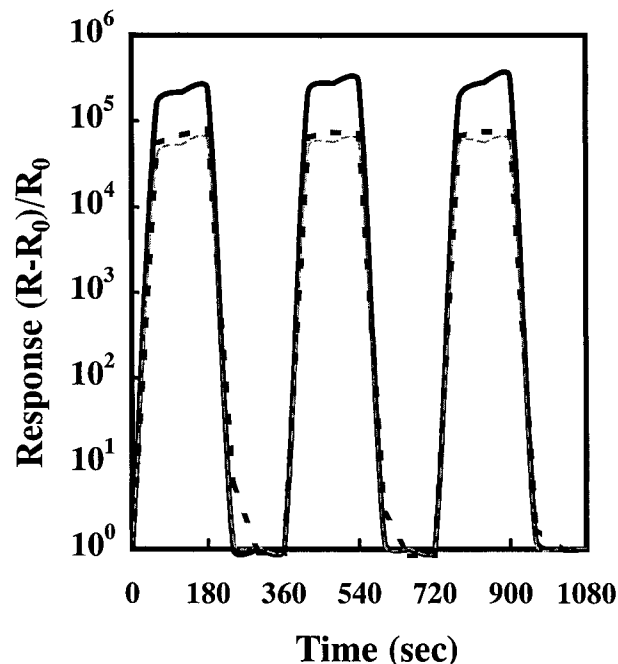
In the case of the same content of PEO in the block copolymer, 50 and 20 wt %, the response of the composite from the low  $M_n$  one is higher than that from high  $M_n$  one. This phenomenon is clearly observed when the PEO content is at 20 wt % and the  $M_n$  is less than 1000. In contrast with

the high  $M_n$ , during the solvent-vapor absorption, with the crystalline structure being destroyed, the low  $M_n$  polymer can move easily and the viscosity is lower, which leads to the CB particles also to move more easily. Therefore, the CB conductive path can be cut more easily by the vapor absorption. As the result, a high electric resistance appeared. One may consider that the lower response of the low  $M_n$  polymer is due to the high grafting percentage as shown in Table I. Generally, the high grafting percentage of the polymer not only decreased the conductivity of the CB particles itself, but it also causes the CB particles to aggregate to form a conductive path in the composite. But, in this study, there are almost no effects of the percentage of grafting on the composite conductivity since the electric resistance is the same order of the magnitude as that from the ungrafted CB.

At the content of PEO is 20 wt %, the response is much lower than that when the content is over 50 wt %, and it is somewhat similar to PE with a low  $M_n$ . But the response of the electrode from the CB/PE ( $M_n = 740$ ) composite is different from that of PE-*b*-PEO (PEO content is 20 wt %) as shown in Table II. So, we also can conclude that the interaction of the PE segments and the PEO segments plays an important role in the response to these vapors.

#### Response of Electric Resistance of Composite from PE-*b*-PEO-grafted CB Against Vapor of High-affinity Solvent for the Block Copolymer

The response of the electric resistance of the composite from PE-*b*-PEO-grafted CB against dichloromethane vapor is shown in Figure 3. The  $M_n$  and PEO content of the matrix and grafted PE-*b*-PEO are 1750, 1400, and 920 and 80, 50, and 50 wt %, respectively. As shown in Figure 3, the electric resistance was dramatically increased to  $10^4$ – $10^6$  times that of the initial resistance when the electrode was transferred from dry air to solvent vapor. It also returned quickly to the initial value when the electrode was transferred to dry air. As shown in Figure 3, the response of the electric resistance of the composite has excellent reproducibility and stability, and the same response curve can keep over 30 cycles without a distinct change. In addition, after the initial several minutes, the electric resistance is not changed in the saturate vapor of dichloromethane even for 24 h, which shows an extreme stability of the electrode. There is not any obvious difference



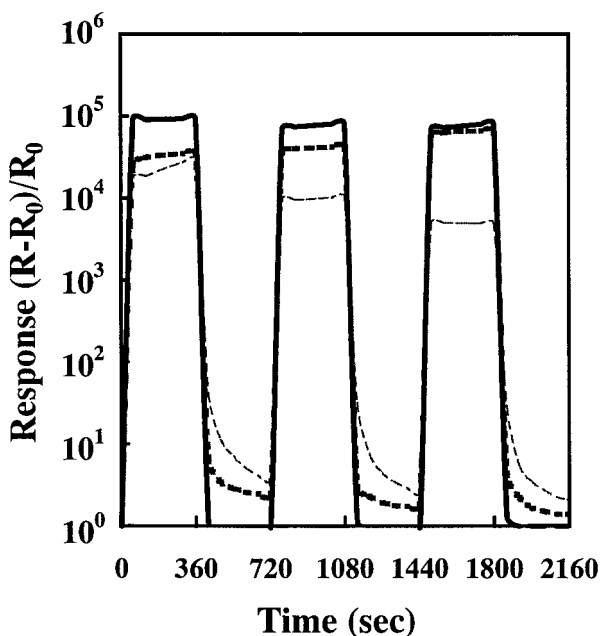
**Figure 3** Effect of molecular weight and composition of PE-*b*-PEO on the electric resistance of PE-*b*-PEO-grafted CB in dichloromethane vapor: (solid line)  $M_n = 1750$ , 80 wt % PEO; (dashed line)  $M_n = 1400$ , 50 wt % PEO; (bold dashed line)  $M_n = 920$ , 50 wt % PEO.

of the response with different  $M_n$  as shown in Figure 3.

As shown in Table II, the response of the electric resistance of the composite from PE-*b*-PEO containing 80 wt % PEO is somewhat larger than that of the others. For the same content of 50 wt % PEO, the response of the composite with a lower molecular weight is a little larger than that with higher molecular weight.

We also detected the reproducibility and stability of the electric resistance of the electrode from the three series of block copolymer against the chloroform solvent vapor at room temperature. The results are very similar to that in dichloromethane as shown in Figure 3, which demonstrate that the response of these composites against chloroform vapor is also sensitive and has good reproducibility.

Based on the results, this kind of composite may be utilized as sensors in an electric nose. Moreover, unlike some general gas sensors made from metallic oxide,<sup>41,42</sup> rapid absorption and desorption kinetics of these composites are observed at ambient temperature, and these properties coincide with the reversible changes in conductivity when it was exposed to some solvent vapor.



**Figure 4** Effect of CB surface characteristics on the response against dichloromethane vapor. The composite was prepared from (bold line) PE-*b*-PEO ( $M_n = 1750$ , PEO content 80 wt %)-grafted CB, (dashed line) ACPA-treated CB, and (bold dashed line) untreated CB.

#### Effect of Grafting of PE-*b*-PEO onto CB Surface on the Response of the Composite

When the polymer/CB composite contains 20 wt % of CB, the dispersion of CB is a main factor in affecting the conductivity of the composite. Generally, either the uniform dispersion or the extreme nonuniform dispersion cannot form an electric conductive path effectively in the composite. In this study, the initial resistance of the composite is low for a conductive material, so the dispersion of CB is considered to be in the middle of the two dispersion states, that is, the CB particles are connected to each other to form a network in an amorphous region of the composite. When the composite absorbs solvent vapor, the polymer molecules can move to alter the dispersion and the network is destroyed. The CB surface characters may have influence on the solvent-absorbing process.

Figure 4 shows the response of the electric resistance of these composites from ACPA-treated CB, PE-*b*-PEO-grafted CB, and untreated CB. Compared to the composite from PE-*b*-PEO-grafted CB, the response of the composite from either ACPA-treated CB or untreated CB is somewhat lower and the response is unreproducible

and unstable. For the composite from untreated CB composite, the response decreased gradually during the cycle detection. Moreover, the electric resistance of the composite from ACPA-treated and untreated CB is hardly returned to the initial resistance in 360 s, while that from the polymer-grafted CB can quickly return to the initial resistance value within 60 s.

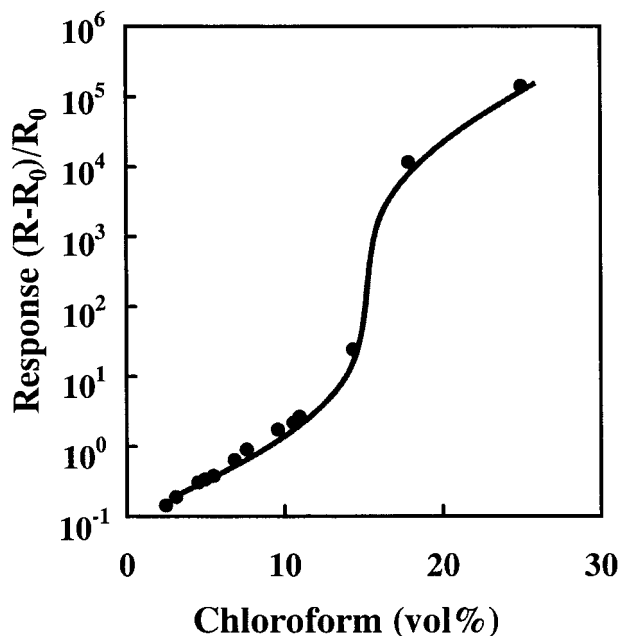
The initial electric resistance (measured in dry air at room temperature) of the composite from untreated CB and the ACPA-treated CB has the same order of magnitude as that from PE-*b*-PEO-grafted CB, indicating that the characteristic of CB in the composite has no distinct effect on the conductivity of the composite in dry air. But in the vapor, there is a remarkably different response.

The drastic increasing of the electric resistance is due to the conductive path being cut by the absorption of the solvent. In dry air, CB dispersed in the composite nonuniformly and formed the conductive network by the aggregation of CB. But during absorbing the solvent by the composite, the crystalline structure will be destroyed, the polymer chain will move, following the Brownian movement, and CB particles will be aggregated as the composite viscosity becomes lower. With this process, the CB network may be cut and the electric resistance will be drastically increased. In the case of the composite from PE-*b*-PEO-grafted CB, CB particles have a better fluidity than that of the ACPA-treated or untreated particles. As even the CB network can be cut during the solvent absorption, the network by the polymer-grafted CB particles can resume completely during the solvent desorption, whereas the network from the ACPA-treated CB, especially from the untreated CB particles in the composite, could not resume completely during the solvent desorption, which led to the electric resistance not returning to the initial value. The ACPA-treated CB and untreated CB particles may aggregate during the solvent absorption because of their high surface energy, leading to a decreasing of the electric resistance in the solvent in every cycle. Compared with ACPA-treated CB and untreated CB, as shown in Figure 4, the response of the composite from the PE-*b*-PEO-grafted CB has excellent reproducibility and stability in some solvent vapors and dry air.

#### Application of the Composite from PE-*b*-PEO-Grafted CB as a Gas Sensor

As discussed above, the composite from PE-*b*-PEO-grafted CB can be expected to be used in a

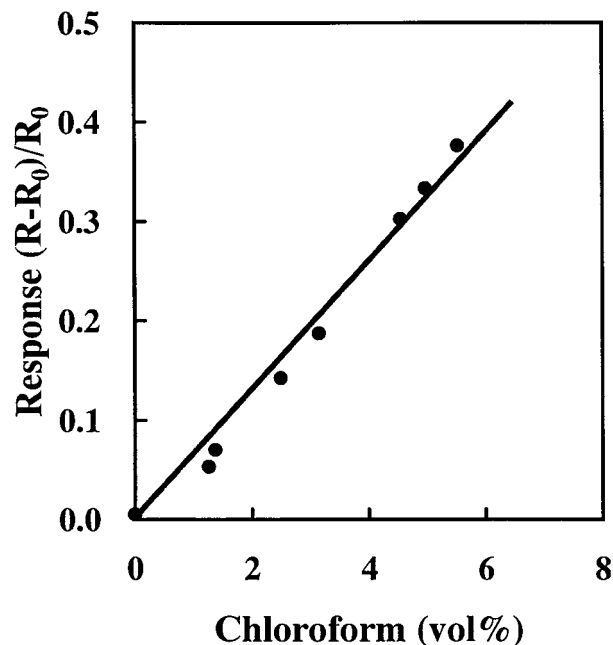




**Figure 5** Response of the electric resistance against chloroform vapor.

gas sensor field. In this section, we studied the relationship between the response of the composite from PE-*b*-PEO ( $M_n = 1750$ , PEO content is 80 wt %)-grafted CB and the concentration of chloroform vapor. The response was estimated by  $(R - R_0)/R_0$ . The results are shown in Figure 5. At a lower concentration of less than 10 vol % of the chloroform in dry air, the response is lower, but when the chloroform concentration was increased over 15 vol %, there was a sudden increase of the response with the increasing concentration. At the concentration of 25.6 vol %, which is the maximum concentration at room temperature and standard pressure, the electric resistance is dramatically increased 140,000 times. This drastic increase of the electric resistance at a high concentration of the solvent vapor may have application in some field.

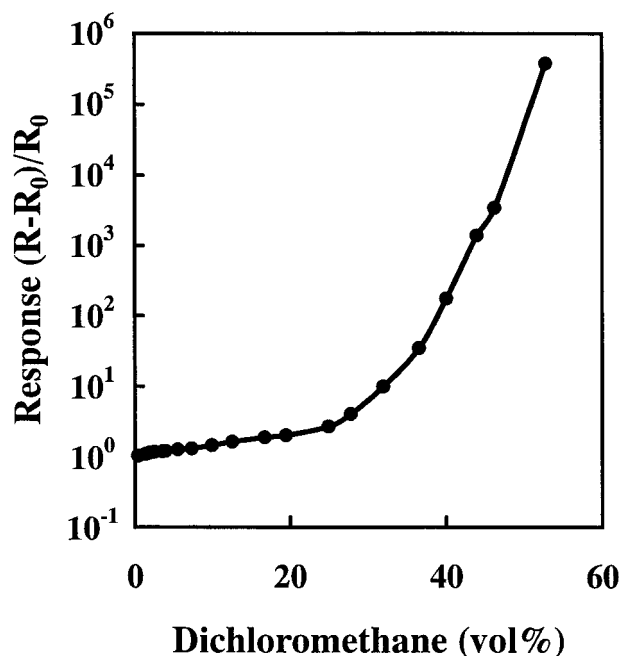
As a gas-sensor material, we are interested in the change of the electric resistance at the range of low vapor concentration in dry air. In this study, the response of the electric resistance of the composite to the lower vapor concentration was examined in detail. As shown in Figure 6, we found that the response of the composite is proportional to the concentration of chloroform vapor in dry air. So, the response can indicate the solvent concentration in the air. This is advantageous, as simple computational methods may be



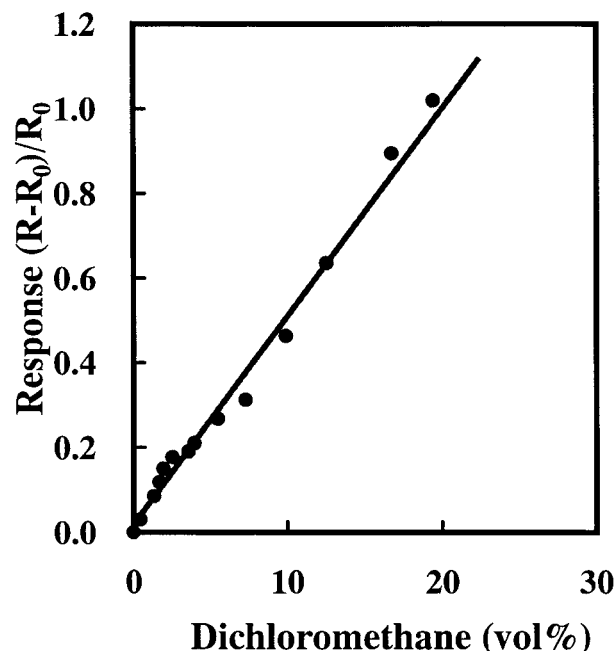
**Figure 6** Response of electric resistance against chloroform vapor.

used for high information processing when the composite is used in gas sensors.

As shown in Figures 7 and 8, we also observed a similar response to dichloromethane vapor and



**Figure 7** Response of electric resistance against dichloromethane vapor.



**Figure 8** Response of electric resistance against dichloromethane vapor.

a linear relationship at the low vapor concentration in dry air. In addition, we detected the response of the composite in the alcohols or water vapor at the lower concentration but hardly observed these phenomena, indicating that the composite as a sensor element does not display high specificity to individual gases, but can be chemically tailored to enhance differences in the response to particular classes of nonpolar or low-polar molecules. If the electrode series with different CB composites is used, it is possible to get a sensor series which can identify and quantify the solvent vapor at the same time.

## CONCLUSIONS

The surface of conductive CB particles was successfully modified by grafting PE-*b*-PEO onto its surface using a two-step method. The electric resistance of the composite from PE-*b*-PEO-grafted CB drastically increased to  $10^4$ – $10^6$  times of the initial resistance in a good solvent vapor such as dichloromethane, chloroform, carbon tetrachloride, and THF and returned immediately to the initial resistance when it was transferred to dry air, whereas in the vapor of a polar solvent such as water or alcohol, the electric resistance only increased several times. The electric resistance of

the composite also increased in a low concentration of vapor in dry air: The resistance change and vapor concentration shows a linear relationship over a wide vapor concentration. In contrast to the untreated CB, the response of the electric resistance of the composite prepared from PE-*b*-PEO-grafted CB has excellent electric reproducibility and stability in a good solvent vapor and dry air, indicating that the composite from polymer-grafted CB can be expected to be a promising material to prepare a solvent or vapor sensor.

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