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Responsiveness of electric resistance of polymer-grafted carbon black/alumina gel composite against solvent vapor and solute in solution

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Summary

The carbon black/alumina gel composites were prepared by sol-gel reaction of aluminum isopropoxide in the presence of polymer-grafted carbon black. The electric resistance of the alumina gel composite from polymer-grafted carbon black was very sensitive to vapor of good solvent for grafted polymer on carbon black: the electric resistance of the alumina gel composite suddenly decreased in solvent vapor and returned to initial resistance when it was transferred into dry air. The effect of surface area and particle size of carbon black on the responsiveness was also investigated. In addition, the electric resistance of the alumina gel composite was found to respond to water and methanol in *n*-hexane and diethyl ether.

Introduction

It has been reported that organic polymers whose repeating units possess an *N*-alkyl or *N*,*N*-dialkyl substituted amide group were most suitable for the preparation of organic/inorganic hybrid materials by the sol-gel process because the polymer molecule was dispersed in the three-dimensional network of metal oxide such as silica gel by the formation of hydrogen bond between the amide carbonyl group of polymer and the silanol group of silica (1,2).

In the previous paper, we have reported the preparation and properties of a novel carbon black/silica gel composite (3) and carbon black/alumina gel composite (4) by sol-gel reaction of tetraethoxysilane and aluminum isopropoxide, respectively, in the presence of poly(2-methyl-2-oxazoline) (poly(MeOZO))-grafted and poly(*N*-vinyl-2-pyrrolidone) (poly(NVPD))-grafted carbon black. It became apparent that the polymer-grafted carbon blacks were uniformly incorporated in the silica gel and alumina gel matrix and hydrogen bond was formed between carbonyl groups in grafted polymer chains on carbon black surface and residual hydroxyl groups in silica gel and alumina gel network (3,4). It is expected that the polymer-grafted carbon black/metal oxide gel can be applied to an electroconductive thin film, a plane heater, and a light-shielding film.

In addition, we pointed out that the electric resistance of the polymer-grafted carbon black/alumina gel composite was very sensitive to the vapor of good solvents of the grafted polymer chains on carbon black surface. For instance, the electric resistance of the alumina gel composite from poly(MeOZO)-grafted carbon black suddenly decreased in water and alcohol vapor, but not in *n*-hexane vapor, and returned to initial resistance when it was transferred into dry air (4).

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Table 1 Properties of carbon blacks used

Carbon black	Specific surface area m^2/g	Particle size nm	-OH mmol/g	-COOH mmol/g	-CO mmol/g
FW 200 [a)]	460	13	0.10	0.61	1.42
Philblack I [b)]	116.8	28.6	0.05	~0	0.23
Porousblack [b)]	447	41	0.03	~0	—

a) Channel black b) Furnace black

In the present paper, we wish to report the responsiveness of electric resistance of alumina gel composite from poly(MeOZO)-grafted, poly(NVPD)-grafted, poly(acrylamide) (poly(AAm))-grafted, and poly(*N*,*N*-diethylacrylamide) (poly(DEAAm))-grafted carbon black against various solvent vapor was investigated. In addition, the effect of surface and particle size of carbon black on the responsiveness against water vapor was discussed. The responsiveness of electric resistance of the composite from poly(DEAAm)-grafted carbon black against solute in hexane was also investigated and the possibility of the carbon black/alumina gel composite for the application to a novel gas sensor and a solute sensor in *n*-hexane and diethyl ether were discussed.

Experimental

Carbon black and reagents

Carbon blacks used were furnace black Philblack I (Phillips Petroleum Co.), furnace black Porousblack (Asahi Carbon Co.), and channel black FW 200 (Degussa A. G.). The properties of the carbon blacks are shown in Table 1. These carbon blacks were dried in vacuo at 110°C before use.

2-Methyl-2-oxazoline (MeO2O), *N*-vinyl-2-pyrrolidone (NVPD), acrylamide (AAm), and *N*,*N*-diethylacrylamide (DEAAm) were purified by ordinary methods before use. 2,2'-Azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] was obtained from Wako Pure Chemical Ind. Ltd. and used without further purification.

Guaranteed reagent-grade aluminum isopropoxide (AIP) obtained from Tokyo Kasei Kogyo Co., Ltd. was used without further purification. Other reagents and solvents were purified by ordinary methods.

Preparation of polymer-grafted carbon black

The grafting of poly(MeOZO) and poly(NVPD) onto carbon black surface was achieved by cationic polymerization of the corresponding monomer initiated by surface carboxyl groups on the surface (5,6). Poly(AAm) and poly(DEAAm) were grafted onto carbon black surface by radical graft polymerization initiated by the system consisting of ceric ion and alcoholic hydroxyl groups introduced onto the surface (7). The percentage of grafting was determined by the following equation:

$$\text{Grafting (\%)} = (A/B) \times 100$$

where A (g) is polymer grafted onto carbon black and B (g) is carbon black charged. The amount of polymer grafted onto carbon black surface was determined by weight loss when polymer-grafted carbon black was heated at 500°C by the use of a thermal analyzer.

Preparation of carbon black/alumina gel composite by sol-gel reaction of AIP

The preparation of carbon black/alumina gel composite was achieved by sol-gel reaction of AIP in the presence of polymer-grafted carbon black. The detailed procedures were described in the preceding paper (4).

Electric resistance of polymer-grafted carbon black/alumina gel composite

The measurement of electric resistance of carbon black/alumina gel composite resistor was carried out as follows. The composite paste prepared by the above method was coated onto a comb-like electrode, which was prepared by the screen printing of conductive Ag/Pd paste onto a ceramic plate (10 mm x 8 mm). The comb-like electrode used in this study is shown in Figure 1.

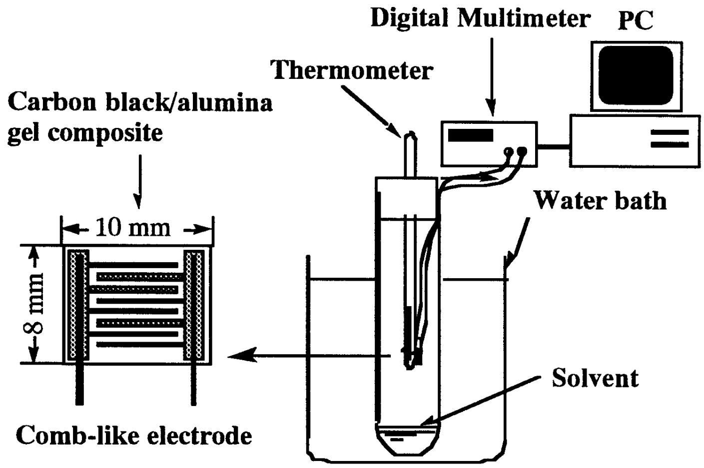

Figure 1 Comb-like electrode and apparatus for the measurement of electric resistance

The electric resistance in solvent vapor and in solution was measured by hanging the composite resistor in a glass container containing water or organic solvent at the bottom as shown in Figure 1 or by dipping the composite resistor in a glass container containing solution. The DC electric resistance was measured by an ohmmeter (a digital multimeter made by Advantest Co. Ltd., Japan: type R6871E-DC), and the resistance was read by a personal computer.

Results and discussion

Grafting of polymers onto carbon black surface

The grafting of poly(MeOZO) and poly(NVPD) onto carbon black surface was achieved by cationic ring-opening polymerization of MeOZO (5) and cationic polymerization of NVPD (6) initiated by surface carboxyl groups on carbon black. In the polymerization, these polymers were considered to be grafted onto carbon black surface based on the termination of growing polymer cation with carboxylate groups on carbon black surface.

On the other hand, poly(AAm) and poly(DEAAm) were grafted onto carbon black surface by radical graft polymerization initiated by the system consisting of ceric ion and alcoholic hydroxyl groups introduced onto the surface (7). The introduction of alcoholic hydroxyl groups onto the surface was achieved by the trapping of 2-methyl-*N*-(2-hydroxyethyl)propionamide radicals formed by the thermal decomposition of 2,2'-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide].

The percentage of polymer grafting (percentage of grafted polymer to carbon black) of poly(MeOZO), poly(NVPD), poly(AAm), and poly(DEAAm) onto channel black FW 200 and that of poly(DEAAm) onto several carbon blacks are shown in Table 2.

Preparation of carbon black/alumina gel composite by sol-gel reaction of AIP in the presence of polymer-grafted carbon black

As described in the previous paper, in the presence of untreated carbon black, thin film of the alumina gel composite was hardly obtained even in the presence of ungrafted poly(MeOZO), because aggregated carbon black particles were formed during the sol-gel reaction. On the contrary, in the presence of these polymer-grafted carbon blacks, a deep black thin film of alumina gel composite, in which carbon blacks were uniformly incorporated, was readily obtained, because these polymer-grafted carbon blacks uniformly dispersed in the reaction mixture during the sol-gel reaction.

In addition, it was confirmed by the infrared spectra of the polymer-grafted carbon black/alumina gel composites that carbon black was incorporated into alumina gel matrix by hydrogen bonds between carbonyl groups of the grafted polymer chains on the surface and residual hydroxyl groups in the alumina gel. The schematic representation of the poly(MeOZO)-grafted carbon black/ alumina gel composite is illustrated in Figure 2.

Table 2 Grafting of polymers onto carbon black surface

Carbon black	Polymer grafted	Grafting (%)
FW 200	Poly(NVPD)[a)]	39.6
FW 200	Poly(MeOZO)[b)]	89.4
FW 200	Poly(AAm)[c]	28.5
FW 200	Poly(DEAAm)[c)]	54.8
Philblack I	Poly(DEAAm)[c)]	35.0
Porousblack	Poly(DEAAm)[c)]	40.2

a)FW 200, 0.50 g ; NVPD, 10 mL; 25°C; 8 h.
b)FW 200, 0.10 g ; MeOZO, 1.7 mL; 110°C ; 48 h.
c)Carbon black, 0.30 g; monomer, 3.0 g; Ce(IV) soln., 1.0 mL; total volume (H_2O), 10.0 mL; 30°C; 24 h.

Responsiveness of electric resistance of poly(AAm)-grafted carbon black/alumina gel composite

Figure 3 shows the effect of solvent vapor, such as water, DMF and *n*-hexane, on the electric resistance of poly(AAm)-grafted carbon black/alumina gel composite. The electric resistance of the poly(AAm)-grafted carbon black/alumina gel composite in dry air was very large, over $10^9\Omega$. Under water and *N,N*-dimethylformamide (DMF) vapor, the electric resistance of the composites extremely decreased with the elapse of time and returned to over $10^9\Omega$ when it was transferred in dry air. On the contrary, under the vapor of *n*-hexane the electric resistance was scarcely decreased. The same tendency was also observed in the case of poly(MeOZO)-grafted and poly(NVPD)-grafted carbon black/alumina gel composite as reported in the preceding paper (4).

Responsiveness of electric resistance of various polymer-grated carbon black/alumina gel composite against various solvent vapor

Table 3 shows the responsiveness of electric resistance of the alumina gel composite from several polymer-grafted carbon blacks against various solvent vapor. The alumina gel composites from poly(MeOZO)-grafted and poly(NVPD)-grafted carbon black respond to not only vapor of water, methanol, and DMF, as reported in the preceding paper (4), but also to chloroform and tetrahydrofuran (THF) (in the case of poly(NVPD)), which are good solvent for grafted polymer. In this study, it was found that poly(AAm)-grafted and poly(DEAAm)-grafted carbon black/ alumina gel composite has an ability to respond to vapor of water, methanol, DMF, acetone, dimethyl sulfoxide (DMSO), and chloroform, but not to vapor of *n*-hexane and diethyl ether, which are poor solvent of grafted polymer.

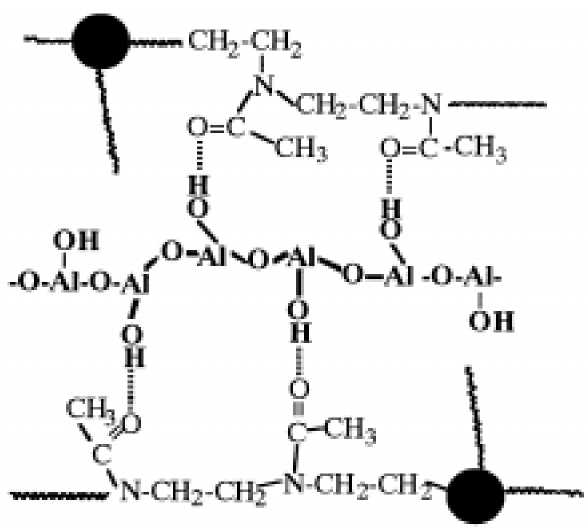

Figure 2 Formation of hydrogen bond between poly(MeOZO)-grafted CB and alumina gel

Effect of surface area and particle size of carbon black on the responsiveness to solvent vapor

The effect of surface area and particle size of carbon black on the responsiveness of electric resistance

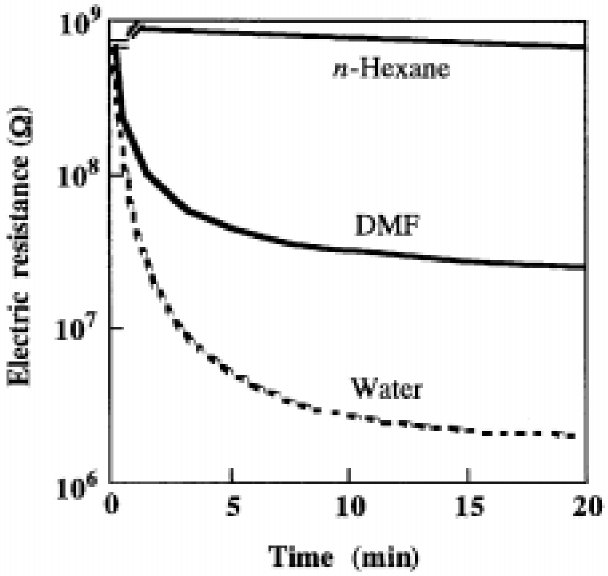

Figure 3 Effect of solvent vapor on the electric resistance of poly(AAm)-grafted CB / alumina gel composite

Table 3 Responsiveness of electric resistance of polymer-grafted CB / alumina gel composite to various solvent vapor

Solvent	Poly(MeOZO)	Poly(NVPD)	Poly(AAm)	Poly(DEAAm)
Water	○	○	○	○
MeOH	○	○	○	○
DMF	○	○	○	○
Acetone	×	×	○	○
THF	×	○	×	○
DMSO	×	×	○	○
Toluene	×	×	×	○
$CHCl_3$	○	○	○	○
n-Hexane	×	×	×	×
Dethyl ether	×	×	×	×

○ : Good response. × : No response.

of poly(DEAAm)-grafted carbon black/alumina gel composite against humidity was investigated. The result is shown in Figure 4. It was found that the rate of response increases in the following order: FW 200 < Philblack I < Porousblack. The rate of response of composite from poly(DEAAm)-grafted Porousblack was very large. This indicates that the rate of response is remarkably improved by use of carbon black with large particle size and large surface area. This may be due to the fact that the adsorption and desorption of solvent vapor favorably proceeds on polymer grafted on carbon black with large particle size and large surface area in the alumina gel matrix.

Responsiveness of electric resistance of poly(DEAAm)-grafted carbon black/alumina gel composite against solute in n-hexane

The electric resistance of poly(DEAAm)-grafted carbon black/alumina gel composite scarcely changed even if it was dipped in pure *n*-hexane and pure diethyl ether.

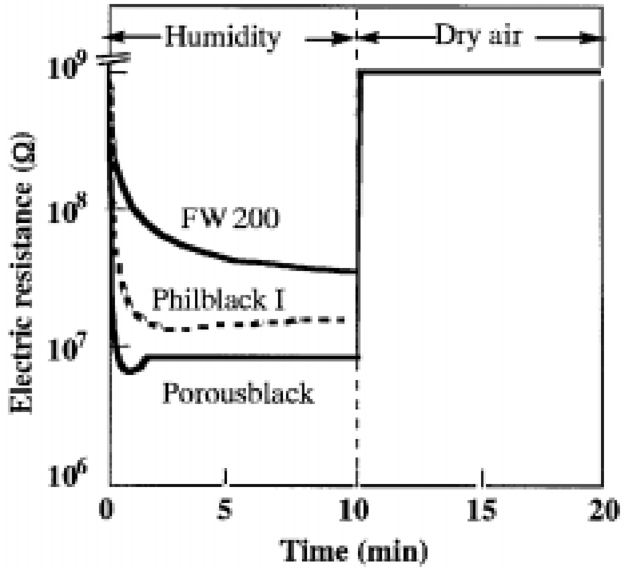

Figure 4 Effect of carbon black on the responsiveness of electric resistance of poly(DEAAm)- grafted carbon black/alumina gel composite to humidity

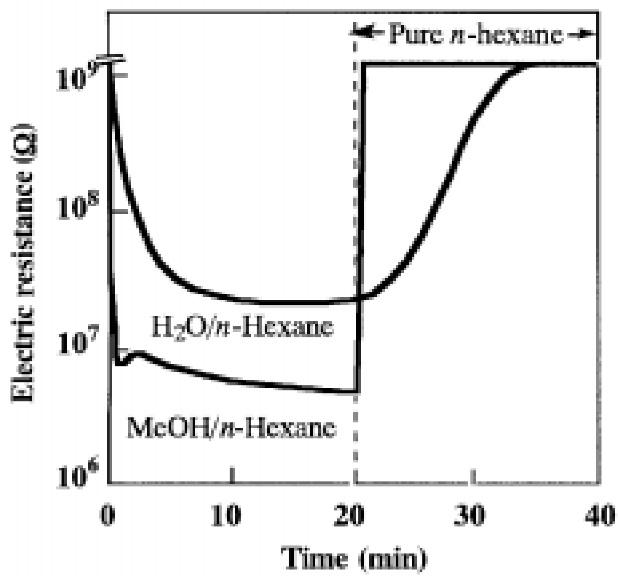

Figure 5 Effect of *n*-hexane solution of water and methanol on the electric resistance of poly(DEAAm)-grafted carbon black/alumina gel composite

Therefore, the responsiveness of the electric resistance of the alumina gel composite against water and methanol in *n*-hexane was examined. Figure 5 shows the effect of water and methanol in *n*-hexane on the electric resistance of poly(DEAAm)-grafted carbon black/alumina gel composite. The concentration of water and methanol is 5.0%.

It is interesting to note that the electric resistance of the poly(DEAAm)-grafted carbon black/alumina gel composite suddenly decreased in *n*-hexane solution of methanol and returned to initial resistance (over $10^9\Omega$) when it was dipped in pure *n*-hexane. On the other hand, the electric resistance of the composite gradually decreased in *n*-hexane solution of water with the elapse of time and returned slowly to over $10^9\Omega$ when it was transferred in pure *n*-hexane. This may be due to the fact that the desorption of water from the composite into *n*-hexane is slower than that of methanol.

In addition, the electric resistance of the alumina gel composite from poly(MeOZO)-grafted, poly(NVPD)-grafted, and poly(AAm)-grafted carbon black also decreased in *n*-hexane solution of water, methanol, DMF, and chloroform, which are good solvent for grafted polymer on the carbon black surface.

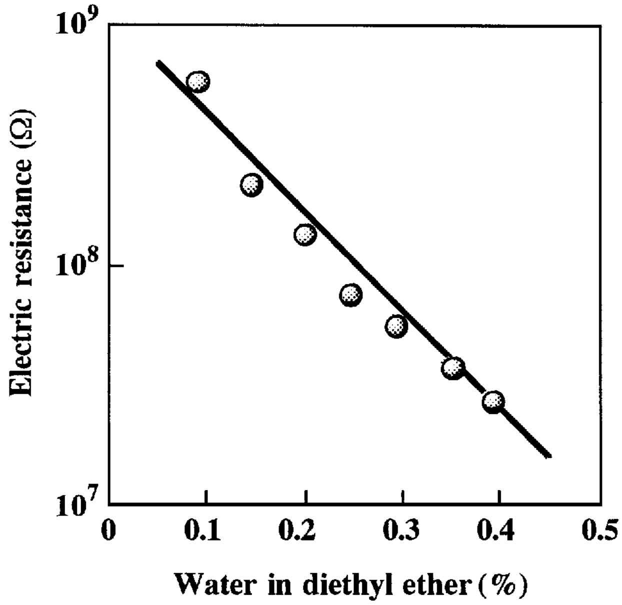

Figure 6 Relationship between electric resistance of poly(DEAAm)-grafted carbon black/alumina gel composite and water concentration in diethyl ether

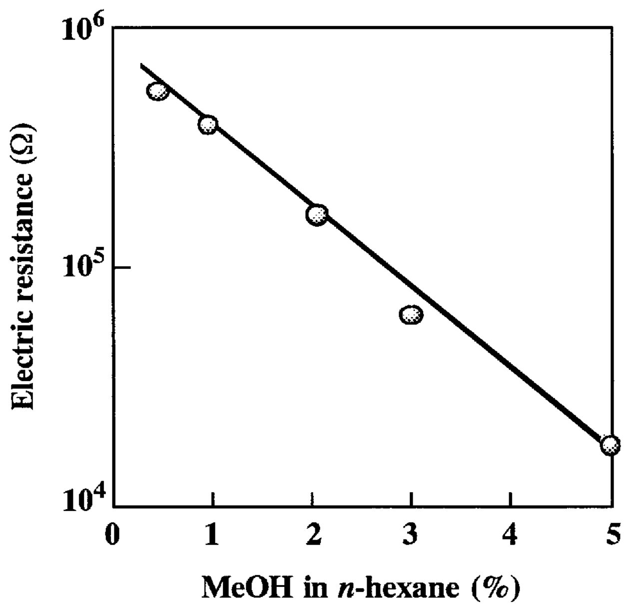

Figure 7 Relationship between electric resistance of poly(DEAAm)-grafted carbon black/alumina gel composite and MeOH concentration in *n*-hexne

Relationship between electric resistance of poly(DEAAm)-grafted carbon black/alumina gel composite and concentration of solute

Figures 6 and 7 show the relationship between the electric resistance of poly(DEAAm)-grafted carbon black/alumina gel composite and concentration of water in diethyl ether and methanol in *n*-hexane, respectively. The electric resistance decreased as water and methanol concentration increased and good correlation between logarithm of electric resistance and the concentration was observed. Therefore, it is considered that poly(DEAAm)-grafted carbon black/alumina gel composite can be applied to a densitometer.

Speculated mechanism of response

It seems that hydrogen bonds formed between carbonyl groups of grafted polymer chains and residual hydroxyl groups in alumina gel matrix play an important role in the decrease of the electric resistance of the composite under solvent vapor and solute in solution. Hydrogen bonds in the composite formed under dry air were destroyed under solvent vapor and in solution based on the absorption of solvent by grafted polymer on carbon black, thus the distance between carbon black particles are shortened, because of relaxation of strain based on the formation of hydrogen bond, so that electric circuit formed. When the composite was transferred in dry air and pure *n*-hexane and diethyl ether, the solvent was desorbed from the composite and the distance between carbon black particles are extended, because of formation of the hydrogen bonds.

It was confirmed by IR spectra that hydrogen bonds between carbonyl groups of grafted poly(MeOZO) and residual hydroxyl groups in alumina gel were cleaved under methanol vapor: the absorption of carbonyl group of poly(MeOZO) sifts from 1614 cm^{-1}, which suggests the formation of hydrogen bond, to 1634 cm^{-1} in methanol vapor.

Conclusions

1. The electric resistance of poly(NVPD)-grafted, poly(MeOZO)-grafted, poly(AAm)-grafted, and poly(DEAAm)-grafted carbon black/alumina gel composite decreased under the vapor of good solvent for grafted polymer on carbon black, such as water, methanol, DMF, and chloroform, and returned to initial resistance when it was transferred to dry air.
2. The rate of response to solvent vapor was affected by kinds of carbon black: the alumina gel composite from carbon black with large particle size and large surface area has high sensitivity against solvent vapor.
3. The electric resistance of the composite also decreased in *n*-hexane solution and diethyl ether solution of methanol and water and returned to initial resistance when it was transferred into pure *n*-hexane and diethyl ether.
4. The logarithm of electric resistance of polymer-grafted carbon black/alumina gel composite linearly decreased in proportion to the concentration of methanol and water in *n*-hexane and diethyl ether.
5. It was pointed out that polymer-grafted carbon black/alumina gel composite can be applied to a gas sensor, a solute sensor, and a densitometer.

Acknowledgments

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References

1. J. E .W. Norll, G. L. Wilkes, D. K. Mohanty, and J. E. McGrace, *J. Appl. Polym. Sci.*, **40**, 1177 (1990).
2. Y. Chujo, E Ihara, H. Ihara, and T. Saegusa, *Macromolecules*, **22**, 2040(1989).
3. K. Fujiki, T. Ogasawara, and N. Tsubokawa, *J. Mater. Sci.*, **33**, 1871 (1998).
4. N. Tsubokawa, T. Ogasawara, J. Inaba, and K. Fujiki, *J. Polym. Sci., Polym. Chem.*, **37**, 3591 (1999).
5. N. Tsubokawa, I. Asano, and Y. Sone, *Polym. Bull.*, **18**, 377 (1987).
6. N. Tsubokawa, N. Takeda, and T. Iwasa, *Polym. J.*, **13**, 1093 (1981).
7. K. Fujiki, N. Tsubokawa, and Y. Sone, *J. Polym. Sci.: Polym. Chem. Ed.*, **24**, 191 (1986).