

Notes

Preparation of New Novolac-Silica Gel Polymer Hybrids from Phenyltrimethoxysilane with Phenol Novolac Derivatives

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Introduction

Preparation of organic/inorganic polymer hybrids from organic polymer and alkoxyxilanes using the sol-gel technique has been extensively investigated.^{2,3} These materials showed considerable properties such as high thermal stability and good mechanical property due to the nano-ordered combination. They are also expected to reveal several attractive functions derived from each starting material. In the synthetic viewpoint, the advantage of the sol-gel technique for the silicone-containing materials³ is the low temperature synthetic process. Especially, the preparation of a polymer hybrid by utilizing hydrogen bonding interactions between the polymer and the silica matrix is one of the most convenient methods.² Using the hydrogen bond interaction, a large number of polymer-silica hybrids were prepared from polar polymers such as poly(2-methyl-2-oxazoline) and poly(*N*-vinylpyrrolidone).² However, this methodology is inapplicable to hydrophobic or rigid-rod like polymers. The example of a polymer hybrid from these polymers using physical interactions is a limited case. For example, Chujo, *et al.* previously reported a preparation of the polystyrene-silica gel polymer hybrid from an arylalkoxyxilane utilizing the aromatic π - π interaction.⁴ This method is a strong tool for the

formation of nano-ordered hydrophobic hybrid materials from aromatic polymer. It is very important to extend this scope toward other aromatic polymers such as engineering plastics or thermosetting resins. We very recently reported the preparation of a polymer hybrid from phenol novolac (phenolic resin by using acidic catalyst)⁵ utilizing Chujo's method. Novolac and its composite have been industrially important as heat-resistant material, photoresist, and adhesive, *etc.*⁶ However, novolac has a spherical structure in dilute solution and does not have a film-forming property. Therefore, the transparent hybrid film will reveal novel functions of novolac. In addition, organic/inorganic nano-hybrids^{2,8} and three-dimensional network polymers⁹ have considerable material potentials distinguished from each starting material.

In this paper, the scope and limitation of the preparation of polymer hybrids from several phenol novolac derivatives utilizing the aromatic π - π interaction (Figure 1) are described. This type hybrid is expected as a high heat-resistant polymer composite due to the characteristics of both novolac and silica moieties.

Experimental

Materials. Unless otherwise noted, all materials and solvents were obtained from commercial suppliers and used without purification. Phenyltrimethoxysilane (PhTMOS) (1), tetraethoxysilane (TEOS) (2), and tetrahydrofuran (THF) were distilled prior to use. Phenol novolac (3), *o*-*tert*-butylphenol novolac (4), and *o*-nitrophenol novolac (5) were prepared by the hydrochloric acid-catalyzed addition-condensation of phenol derivatives with formaldehyde. These novolacs were dried *in vacuo* prior to use.

Measurements. ¹H-NMR spectra were recorded on a 270 MHz JEOL JNM-EX270 spectrometer. FTIR spectra were obtained on a JASCO FT/IR-460 Plus spectrometer. Gel permeation chromatography (GPC) analyses were carried out on a Tosoh TSKgel G3000HXL column by using

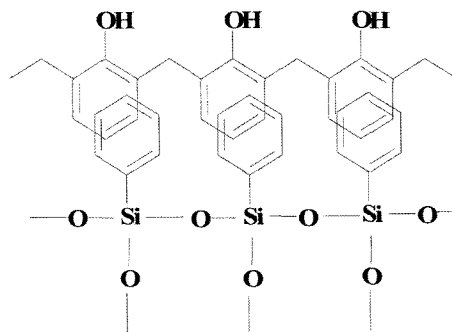


Figure 1. Aromatic π - π interaction between the polymer and the silica matrix.

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THF as an eluent. Thermogravimetric analysis (TGA) was performed on a SII TG/TDA6200 with a heating rate of 10 °C/min in nitrogen or air. Scanning electron microscope (SEM) images were recorded with a JEOL JSM-5310/LV.

Preparation of Novolac Derivatives. Novolac derivatives (3-5) were prepared by the hydrochloric acid-catalyzed addition-condensation of an equimolar amount of phenol with formaldehyde in good yield. The structure of the polymers was confirmed by FTIR, ¹H-NMR spectra and GPC analysis. These polymers were well-soluble in common organic solvents such as THF, acetone, and DMF, but insoluble in hexane and water. The spectral data of 3-5 are as follows.

Phenol Novolac (3). ¹H-NMR(δ) 3.81 (Ar-CH₂-Ar), 5.01 (Ar-OH), 6.61-6.89 (Ar) ppm; FTIR (KBr) 1500, 1600 (Ar_{C=C}), 2960(Ar-CH₂-Ar), 3400(-OH) cm⁻¹; GPC (THF, PSt standard) $M_n = 2,900$, $M_w/M_n = 1.55$.

***o*-tert-Butylphenol Novolac (4).** ¹H-NMR(δ) 1.34 (*t*-Bu), 3.81 (Ar-CH₂-Ar), 5.00 (Ar-OH), 6.49-6.73 (Ar) ppm; FTIR (KBr) 1375, 1385 (C-(CH₃)₃), 1500, 1600 (Ar_{C=C}), 2960 (Ar-CH₂-Ar), 3400 (-OH) cm⁻¹; GPC (eluent: THF, PSt standard) $M_n = 4,100$, $M_w/M_n = 1.54$.

***o*-Nitrophenol Novolac (5).** ¹H-NMR(δ) 3.82 (Ar-CH₂-Ar), 6.87-7.28 (Ar) ppm; FTIR(KBr) 1340, 1540 (NO₂), 1500, 1600 (Ar_{C=C}), 2960 (Ar-CH₂-Ar), 3270 (-OH) cm⁻¹; GPC (eluent: THF, PSt standard) $M_n = 1,360$, $M_w/M_n = 1.03$.

Preparation of Organic-Inorganic Polymer Hybrid from Novolac. PhTMOS (1) (500 mg) and phenol novolac (3) (500 mg) were dissolved into THF (15 mL), and aqueous HCl (1 mL, 0.1 mol/L) was added at room temperature. The mixture was stirred for 30 min in a beaker. The resulting mixture was then placed in a clear polypropylene (PP) container covered with a paper towel, and left in the drying apparatus. The temperature was raised to 80 °C at the rate of 10 °C/10 min (reaction rate: "Fast condition") and then kept at the same temperature for four days. After the drying solvents were completely removed *in vacuo*, a transparent PhTMOS film containing phenol novolac was then obtained, which is a pale red glassy material. The results of GPC, TGA and SEM measurements are shown in the text.

FTIR(KBr) 1135 (Ph-O-C), 1430 (Si-Ph), 1500, 1600 (Ar_{C=C}), 3300 (-OH) cm⁻¹.

Results and Discussion

The precursors of polymer hybrids are listed in Figure 2. Phenol novolac ($M_n = 2,900$, $M_w/M_n = 1.55$) (3), *o*-tert-butylphenol novolac ($M_n = 4,100$, $M_w/M_n = 1.54$) (4), and *o*-nitrophenol novolac ($M_n = 1,360$, $M_w/M_n = 1.03$) (5) were prepared by the hydrochloric acid-catalyzed addition-condensation of phenol derivatives with formaldehyde.

The organic/inorganic polymer hybrid was prepared by the hydrochloric acid (HCl)-catalyzed sol-gel reaction of PhTMOS in the presence of novolac derivatives (Scheme I).

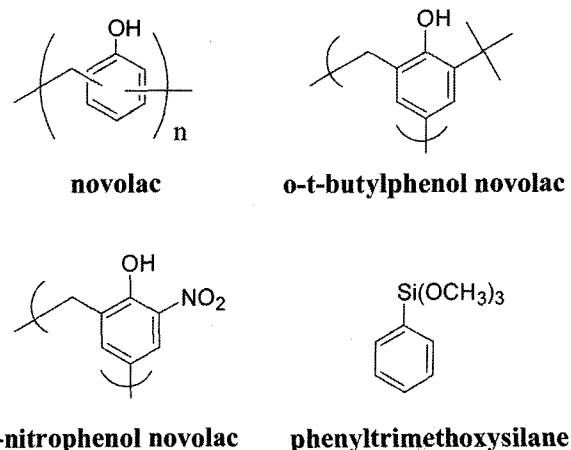
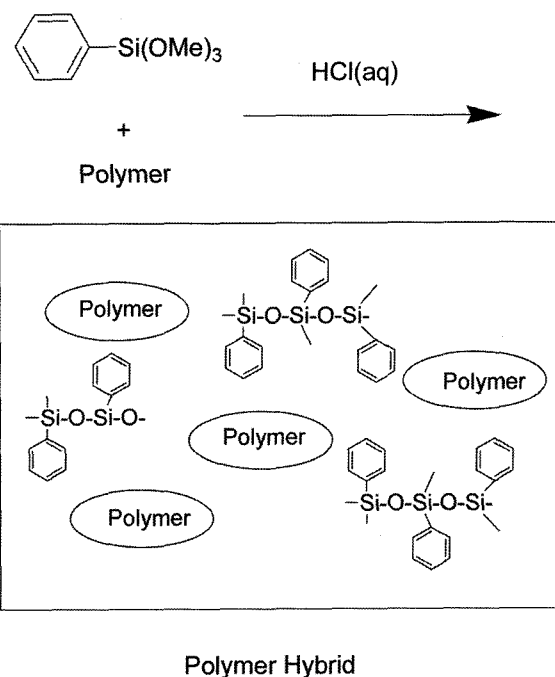


Figure 2. Precursors of organic/inorganic polymer hybrids.



Scheme I. Preparation of novolac-silica hybrids.

The polymer hybrids were found to be transparent and homogeneous in a wide range of novolac/silica ratio. The obtained hybrid is a hard pale red glassy material. The homogeneity of the obtained polymer hybrids was evaluated by optical observations.

In this study, the reaction rate plays a critical role for the transparent film formation. In the case of "Fast condition" (the temperature was raised to 80 °C at the rate of 10 °C/10 min), a transparent and homogeneous hybrid was obtained (Table I: Run 2, 4, 7, 9, 12).

On the other hand, for the "Slow condition" (heating rate of 10 °C/1 h), a phase separation occurred. The transparent polymer hybrid could not be obtained (Table I: Run 1, 3, 5,

Table I. Preparation and Homogeneity of Polymer Hybrids

Run	Polymer	M_n	M_w/M_n	Polymer : PhTMOS ^a	Reaction Rate	Appearance
1	Novolac	2,900	1.55	1 : 10	Fast	Transparent
2					Slow	Turbid
3				1 : 2	Fast	Transparent
4					Slow	Turbid
5					Fast	Transparent
6	<i>o</i> - <i>t</i> -Butylphenol Novolac	4,100	1.54	1 : 10	Fast	Transparent
7					Slow	Turbid
8				1 : 2	Fast	Transparent
9					Slow	Turbid
10					Fast	Transparent
11	<i>o</i> -Nitrophenol Novolac	1,360	1.03	1 : 10	Fast	Turbid
12					Slow	Turbid
13				1 : 5	Fast	Turbid

^aBased on weight.

6, 8, 10, 11, 13). A phase separation in a turbid sample was observed in millimeter (mm) scale. From these experimental results, the most significant factor for the successful synthesis of the polymer hybrid might be the "heating rate." In general, novolac has a spherical structure in dilute solution and it aggregates easily by the intermolecular hydrogen bond. Therefore, it is necessary for obtaining a transparent polymer hybrid to form the silica matrix (sol) before the polymer aggregates.

Similar sol-gel reactions in the presence of *o*-*t*-butylphenol novolac (4) afforded the corresponding polymer hybrids. However, no polymer hybrid was obtained from the *o*-nitrophenol novolac (5) because of its poor solubility and aggregation of itself.

The results are summarized in Table I.

A transparent polymer hybrid was not obtained using tetramethoxysilane (TMOS) and TEOS instead of PhTMOS (Polymer : TEOS = 1 : 10). It was necessary for obtaining a transparent polymer hybrid to use the phenyl ring-including alkoxy silane as a starting material. Therefore, the aromatic π - π interaction between the phenyl ring of the silica matrix and that of novolac might play an important role in the homogeneous integration of the polymer and silica matrix. Direct evidence for the π - π interaction was not supported by the spectroscopic measurements such as NMR, UV, and FTIR, but there is no other effective interaction. The hydrogen bond interaction and covalent bond formation between the phenolic hydroxyl group (Ph-OH) with silanol (Si-OH) made relatively small contributions to hybrid formation.

The homogeneity of silica in the novolac derivatives (Run 10) was evaluated by the SEM measurement (Figure 3). As expected, no nano-scale phase separation was confirmed in

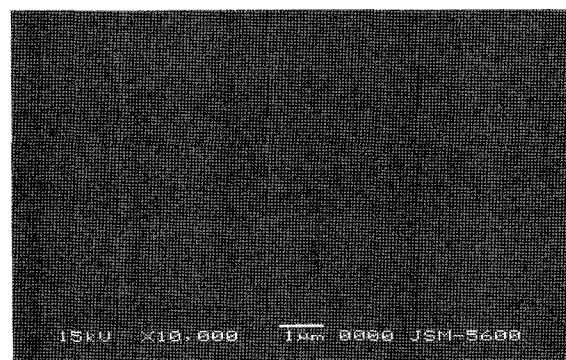


Figure 3. SEM image of polymer hybrid (run 5).

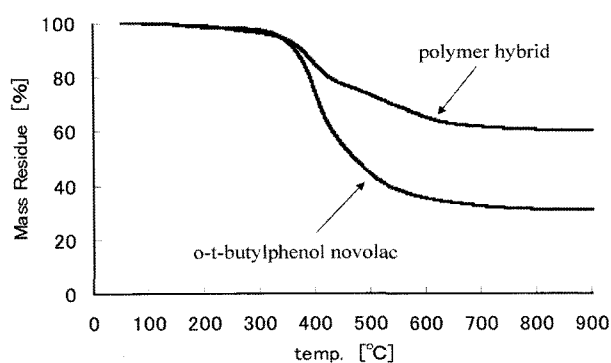


Figure 4. TGA thermograms of PhTMOS/*o*-*t*-butylphenol novolac hybrid (run 10) and polymer under nitrogen.

this sample.

The polymer hybrid showed high heat-resistance. For example, typical data of the TGA is as follows. Figure 4

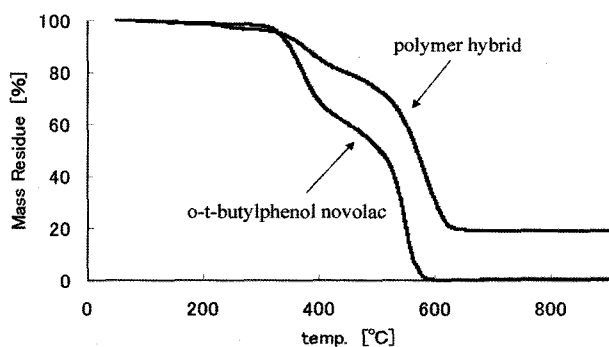


Figure 5. TGA thermograms of PhTMOS/*o*-*t*-butylphenol novolac hybrid (run 10) and polymer under air.

(under nitrogen) and Figure 5 (under air) shows the TGA traces of the polymer hybrid (Run 10) and its *t*-butylphenol novolac (precursor) (4), respectively. In the case of nitrogen atmosphere condition, the 10% weight loss of the polymer hybrid was 350 °C and that of 50% was 450 °C, respectively. The weight loss of polymer hybrid at 900 °C was 65%. The residue might be mainly carbon and silica (Figure 4). On the other hand, in the case of air condition, the 10% weight loss of the polymer hybrid was 350 °C and that of 50% was 590 °C, respectively. The weight loss at 900 °C was 20%. The residue might be mainly silica (SiO₂). These were observed that the hybrid shows higher thermal stability than that of the precursor itself.

Conclusions

Functional novolac-silica gel polymer hybrids were prepared by the sol-gel reaction of phenyltrimethoxysilane (PhTMOS) in the presence of novolacs. The driving force of the dispersion of the two components might be the π - π interaction between the phenyl ring of the silica matrix and that of novolac, and the significant factor for nano-scale homogeneity was the "heating-rate." The obtained polymer hybrid was a high heat-resistant material, which will be applicable for coatings, adhesive, plastic lens, etc.

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