Thermally Reversible IPN Organic−Inorganic Polymer Hybrids Utilizing the Diels−Alder Reaction

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ABSTRACT: Formation of an IPN (interpenetrating polymer network) of organic polymer and silica gel in the form of polymer hybrids was accomplished by utilizing the Diels−Alder reaction between maleimide and furan. Maleimide and furan groups were introduced in the side chain of poly(2-methyl-2-oxazoline), respectively. Polymer hybrids were prepared by acid-catalyzed sol−gel reaction of tetramethoxysilane (TMOS) in the presence of these polymers. The progress of the Diels−Alder reaction between maleimide and furan was confirmed by UV and FT-IR spectroscopy. The solvent resistance of the polymer hybrids was improved by the formation of the IPN structure. Retro-Diels−Alder reaction takes place at an elevated temperature, and these reactions can be cycled.

Introduction

Preparation of nanocomposites of organic polymers and silica gel has been achieved by the sol−gel reaction of alkoxysilanes in the presence of organic polymers.[1−4] The sol−gel reaction involves the hydrolysis of Si−OR groups to Si−OH (silanol) groups and the condensation of the Si−OH groups into −Si−O−Si− linkages.[5] Generally, the nano-dispersion of organic components in a silica matrix can be accomplished either (i) by the formation of covalent bond between organic components and silica or (ii) through weak interactions (hydrogen bonding, aromatic interaction, ionic interaction, and so on) between them. Organic polymers such as poly(2-methyl-2-oxazoline) and poly(*N*-vinylpyrrolidone) were incorporated into a silica network, utilizing the hydrogen bonding interaction between the silanol groups and the amide groups of the organic polymers.[6,7] Organic polymers are dispersed on the scale of a few nanometers in these hybrid materials.

In the polymer hybrids, a linear polymer is embedded in the three-dimensionally cross-linked silica network. This kind of structure is called a "semi-interpenetrating polymer network (semi-IPN)". On the contrary, if both organic and inorganic phases are cross-linked independently and they are interpenetrated each other, it is a complete IPN.[8] Organic-inorganic IPN nanocomposites were prepared by Novak et al. via the synchronous formation of both the inorganic and organic components.[9,10] This was accomplished by the sol−gel reaction of tetraalkoxysilanes possessing polymerizable alkoxides. The hydrolysis and condensation of the alkoxysilanes to form an inorganic silica network liberate unsaturated alcohols which are polymerized in-situ using free-radical or metathesis techniques. A small amount of divinyl monomers was added to the reaction mixture prior to polymerization in order to cross-link the organic polymer. IPN nanocomposites thus prepared showed greater moduli than semi-IPN ones. We proposed two methodologies to prepare the IPN polymer hybrids. One is called the "in-situ polymerization method", where the radical copolymerization of mono- and difunctional vinyl monomers and the sol−gel reaction of alkoxysilanes are carried out simultaneously in situ.[11−13] The other is the preparation of polymer hybrids from preformed organic polymers having pendant cross-linkable functional groups. The hybrid prepared from the cross-linkable prepolymer is semi-IPN, while it is converted to IPN by the cross-link reaction of the polymers. Especially, it is quite interesting when a reversible bond-forming reaction is employed to cross-link organic polymers. Conversion between semi-IPN and IPN can be done by choosing the condition to promote either the bond-forming and bond-cleaving reactions. It is expected that the properties of the hybrids, e.g., mechanical property or solvent resistance, are modified by the formation of IPN. Reversible photodimerization of coumarin groups has been utilized to perform photochemically reversible formation of IPN in the polymer hybrids, and the modification of solvent resistance by light was achieved.[14]

This article describes the thermoresponsive formation of IPN polymer hybrids by utilizing Diels−Alder (DA) reaction of maleimide and furan. Reversible formation of hydrogel of poly(2-methyl-2-oxazoline) by means of DA reaction has been reported previously (Scheme 1).[15] The DA reaction between maleimide group and furan group proceeds at ambient temperature, and the retro-DA reaction takes place on heating.[16] The preparation of the polymer hybrids and the efficiency of the DA and retro-DA reactions in the polymer hybrids, as well as their change in solvent resistance, were investigated.

Experimental Section

General Procedure. ^{1}H NMR spectra were recorded using a 270 MHz JEOL-JNM-GX270 NMR spectrometer. IR spectra were obtained using a Perkin-Elmer 1600 infrared spectrometer. UV absorption spectra were obtained using a JASCO V-530 spectrophotometer.

Materials. Maleimide- and furan-modified poly(2-methyl-2-oxazoline)s were prepared according to Scheme 2.[15] Poly(2-methyl-2-oxazoline) of $M_n \sim 8500$ (degree of polymerization $\sim$ 100) was used as a main chain polymer. The loading levels of each functional group in the polymer were estimated to be 12.4 and 9.4 mol %, respectively, from ^{1}H NMR data. Tetramethoxysilane (TMOS) was distilled under nitrogen atmosphere. Methanol was dried with magnesium methoxide and distilled under nitrogen atmosphere. Hydrochloric acid (0.1 mol dm^{-3}) and DMF were used as supplied.

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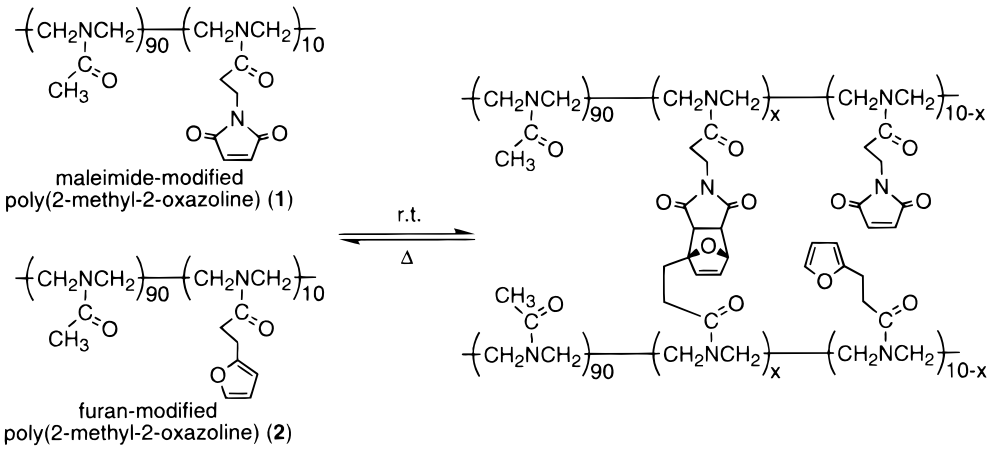
Scheme 1. Hydrogel from Maleimide- and Furan-Modified Poly(2-methyl-2-oxazoline)s[12]



Scheme 2. Preparation of Maleimide- and Furan-Modified Poly(2-methyl-2-oxazoline)s

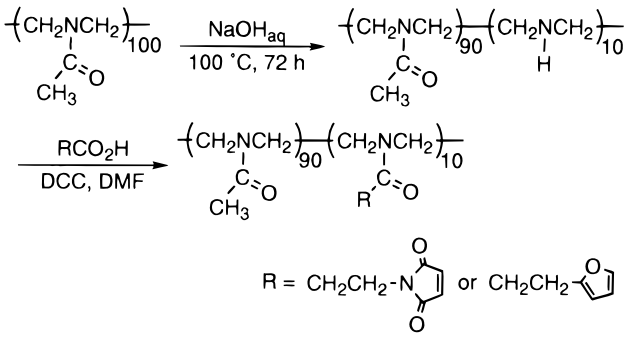
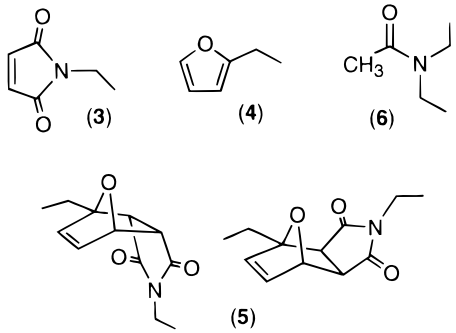


Chart 1. Model Compounds



Preparation of Polymer Hybrids. In a typical experiment, the same quantities of polymers **1** and **2** were dissolved in methanol (10 times to TMOS in volume). To the solution were added TMOS and hydrochloric acid (4 equiv to TMOS). The reaction mixture was sealed and stirred at room temperature for a certain period. Then the mixture was placed in a polypropylene mold covered with a paper towel to allow the evaporation of the solvent. A polymer hybrid was obtained as a glassy solid. Films of the polymer hybrids for absorption measurement were prepared by casting the reaction mixture onto quartz substrates.

Absorption Spectra Analysis. *N*-Ethylmaleimide (**3**) and 2-ethylfuran (**4**) were employed as model compounds. DA adducts (**5**) were prepared from **3** and **4** according to the procedure described previously.[15] Molar absorption coefficients of compounds **3**−**5** and *N*,*N*-diethylacetamide (**6**) (a model for a monomer unit of the main chain) at wavelength of 296 nm were 500, 20, 40 (the same values were observed for exo and endo isomers), and 10 M^{-1} cm^{-1}, respectively. Efficiencies of the DA reaction in the polymer hybrids were estimated from the absorption at 296 nm by utilizing the above values.

Solvent Extraction. The powdered hybrids were suspended in DMF and stirred for 1 week, followed by Soxhlet extraction with methanol to achieve complete removal of DMF. The amount of organic components remaining in the hybrids was evaluated by elemental analysis for nitrogen.

Table 1. Preparation and Properties of Polymer Hybrids from Polymers 1 and 2

run	polym **1** (mg)	polym **2** (mg)	TMOS (mg)	stirring time (h)	appearance	polymer content (wt %) calcd	polymer content (wt %) obsd
1	100		1000	1	transparent	20.0	14.7
2		100	1000	1	transparent	20.0	14.4
3	50	50	1000	1	turbid		
4	50	50	1000	3	transparent	20.0	14.3
5	50	50	1000	24	transparent	20.0	15.1
6	50	50	250	48	transparent	50.0	45.5
7	100	100	250	48	transparent	66.7	62.8
8	200	200	250	48	transparent	80.0	76.8

[a] Calculated from elemental analysis for nitrogen.

Results and Discussion

To achieve the thermally reversible formation of organic−inorganic IPN polymer hybrids, polymer hybrids were prepared from maleimide- and furan-modified poly(2-methyl-2-oxazoline)s. Maleimide- and furan-modified poly(2-methyl-2-oxazoline)s were successfully prepared by condensation of partially hydrolyzed poly(2-methyl-2-oxazoline) with the corresponding carboxylic acid derivatives as depicted in Scheme 2. These polymers cross-link in a mixed bulk film by DA reaction between maleimide and furan.[15] The resulting hydrogels do not dissolve but rather swell in water. By heating at 80 °C, the retro-DA reaction takes place, and the degraded hydrogels become soluble.

At first, polymer hybrids were prepared from each polymer via the acid-catalyzed sol−gel reaction of TMOS (Table 1, runs 1 and 2). Both gave transparent and homogeneous polymer hybrids. These polymers were then applied to the preparation of IPN polymer hybrids. The same quantities of polymers 1 and 2 were dissolved in methanol. To the solution was added a certain quantity of TMOS and hydrochloric acid (4 equiv to TMOS). The resulting mixtures were stirred in sealed bottles for a certain time before allowing the solvent to evaporate in air. It was found that the length of the stirring time had the significant effect on the homogeneity of the resulting polymer hybrids. Too short a stirring time resulted in phase separation of polymer and silica gel (run 3). Homogeneous polymer hybrids could be prepared with stirring times

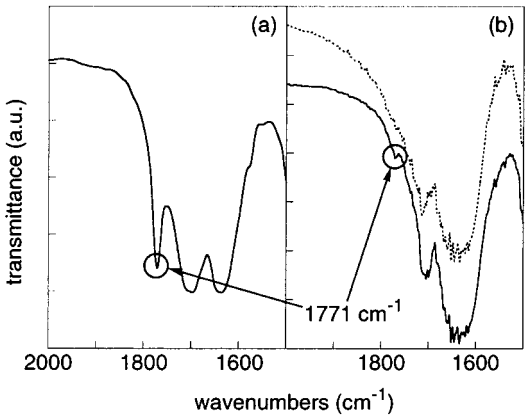


Figure 1. FT-IR spectra of (a) compound **5** and (b) the polymer hybrid (run 8) before (dotted line) and after (solid line) the DA reaction.

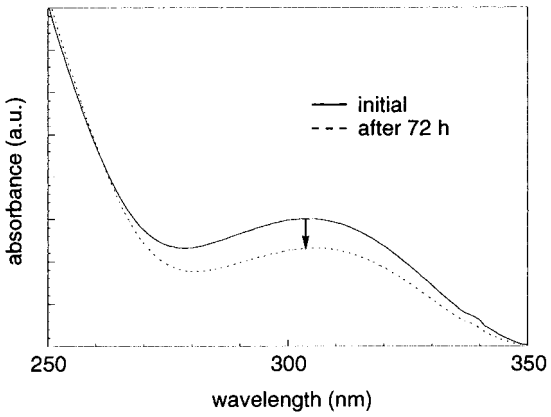


Figure 2. UV absorption spectra of the polymer hybrid (run 7).

longer than 3 h. To attain the quantitative conversion of TMOS to silica gel, stirring time of 48 h was employed for further preparation of polymer hybrids with different weight ratios of polymer to silicate (runs 6−8). The weight ratios could be varied widely without affecting the homogeneity of the polymer hybrids. The organic−inorganic compositions of the polymer hybrids were found to be in agreement with the theoretical values.

DA reaction of maleimide and furan groups in the polymer hybrids was monitored by FT-IR as well as UV absorption spectroscopy. In the FT-IR spectrum of 5, a new peak at 1771 cm^{-1} specific to DA adducts of maleimides was observed (Figure 1a). This peak appeared on the shoulder of the amide carbonyl peak (Figure 1b, solid line) after keeping the polymer hybrid at room temperature for sufficient time, indicating that the DA reaction actually took place in the polymer hybrids.

Quantitative evaluation of the extent of DA reaction was conducted via UV absorption spectra. The films of polymer hybrids were prepared by casting the precursor mixtures onto quartz substrates. After the evaporation of the solvent, the change of UV absorption was followed. It was confirmed by UV spectroscopy that DA reaction in the dilute solution of polymers **1** and **2** was negligible within a few hours. Hence it was assumed that DA reaction hardly took place after 5 min from casting. Typical change of the absorption during the reaction can be seen in Figure 2. The decline of the absorption at ca. 300 nm is due to the conversion of maleimide and furan groups to DA adducts. The efficiency of DA reaction was evaluated according to the equation

$$\frac{A_f}{A_i} = \frac{\epsilon_M C_M(1-x) + \epsilon_F C_F(1-x) + \epsilon_{DA} C_M x + \epsilon_A C_A}{\epsilon_M C_M + \epsilon_F C_F + \epsilon_A C_A}$$

where A_i and A_f are absorbances at the initial and final, respectively; ϵ and C are the molar absorption coefficient and the concentration of the chromophore, respectively; subscripts M, F, DA, and A denote the maleimide, furan, DA adducts, and amide unit in the main chain; and x is the DA extent. As degrees of substitution of both polymers **1** and **2** are about 10 mol %, the relationship $C_A = 10C_M = 10C_F$ was applied. The DA reaction was found to end within 72 h. The DA efficiencies in each hybrid are listed in Table 2 as

Table 2. DA Efficiencies and Solvent Extraction Efficiencies of Polymer Hybrids

run	polymer **1**/polymer **2**/TMOS	DA efficiency (%)[a]	solvent extraction efficiency (%)[b]
1	100/0/1000		55
2	0/100/1000		61
4	50/50/1000	0	
5	50/50/1000	0	
6	50/50/250	27	61
7	100/100/250	30	84
8	200/200/250	47	14
9	50/50/0	63	
10	50/50/0 + polyoxazoline 100	36	

[a] Calculated from UV spectra. [b] The polymer content of the polymer hybrids before and after the extraction (p_b and p_a, respectively) was calculated from elemental analysis for nitrogen, and the solvent extraction efficiency E was calculated according to the equation: $E = (p_b - p_a)/(1 - p_a)p_b$.

well for the pure polymers. In the film composed of polymer **1** and **2**, the DA efficiency was 63%. Lower efficiencies were observed in the polymer hybrids. In polymer hybrids composed of almost the same amount of organic polymer and silica gel (run 6), an efficiency of 27% was still obtained. However, no DA reaction could be detected if the polymer content was too low (runs 4 and 5). When the film of polymers **1** and **2** was diluted with the same amount of poly(2-methyl-2-oxazoline) (run 10), the DA efficiency was diminished to 36%. This suggests that the decrease of DA efficiency in the polymer hybrids can be attributed to the dilution of functional groups with silica gel. These FT-IR and UV spectroscopy data are consistent with the occurrence of DA reaction in the polymer hybrids. The resulting polymer hybrids possess the IPN structure of organic gel and silica gel. As the DA reaction in this system is necessarily an interchain reaction, the DA efficiencies represent the cross-linking density of the organic gel as well.

The modification of solvent resistance by the formation of IPN structure was checked by means of solvent extraction experiments. The organic polymers in powdered polymer hybrids were extracted with DMF, and the portion of organic polymer remaining in the polymer hybrids was estimated. The results are also summarized in Table 2. Improvement of solvent resistance was observed in the polymer hybrids with the highest polymer content (run 8). The DA reaction efficiency of this polymer hybrid was 47%, indicating that about 5 functional groups react on each polymer chain. Gener-

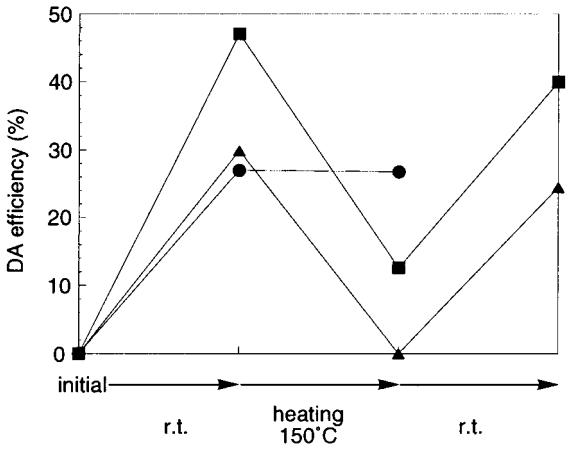


Figure 3. DA − retro-DA cycles in the polymer hybrids. (●) run 6; (▲) run 7; (■) run 8.

ally speaking, more than three or four cross-linking points per chain are necessary for gelation of organic polymers. The same trend was found in the present study, thus the critical change of solvent resistance was observed between the number of the cross-linking points 3 and 5.

The retro-DA reaction in the IPN polymer hybrids was examined by heating the polymer hybrids up to 150 °C and followed by UV absorption spectroscopy. As mentioned previously, the retro-DA reaction in the hydrogel prepared from polymers **1** and **2** took place at 80 °C.[15] In the polymer hybrids, however, a higher temperature was required for the retro-DA reaction. Figure 3 shows the results of retro-DA reaction in the polymer hybrids. In the polymer hybrid (run 6 in Table 1), no change in the UV spectrum was observed. The retro-DA reaction might be suppressed due to the surrounding rigid silica matrix. On the other hand, efficient recovery to maleimide and furan was confirmed in the polymer hybrid having larger polymer contents (runs 7 and 8). Especially, the quantitative retro-DA reaction was achieved in the sample of run 7. Furthermore, when the polymer hybrids were kept at room temperature again, the DA reaction between maleimide and furan groups took place and analogous DA efficiencies were obtained.

Conclusion

Thermally reversible formation of IPN structure in the organic−inorganic polymer hybrids was investigated by utilizing the DA reaction between maleimide and furan groups. Transparent and homogeneous polymer hybrids could be obtained by means of acid-catalyzed sol−gel reaction of TMOS in the presence of maleimide- and furan-modified poly(2-methyl-2-oxazoline)s. The DA reaction in the polymer hybrids was confirmed by FT-IR and UV absorption spectroscopy. The solvent resistance of the polymer hybrids to leaching could be improved by the formation of an IPN structure via the cross-linking of organic polymer. The retro-DA reaction also takes place in the polymer hybrids, and these reactions could be cycled. Thus, thermoresponsive polymer hybrids could be achieved.

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