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# *Articles*

## Fluorescence Studies of the Hybrid Composite of Segmented-Polyurethane and Silica

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In this work, we describe a new type of composite material made from segmented-polyurethanes and silica. The silica is incorporated into a hard segment phase of the segmented polyurethane to make a "hybrid domain". The composite formation between segmented polyurethane and silica was prepared via a general sol−gel process. The fluorescence emission spectra from dansyl probe molecules bonded to the silica gave us information about crystallization behavior of the hard segments in the hybrid domain. According to the emission signals from the probe, the rearrangement temperatures ($T_r$) of the hard segments of 2,6-TDI polymer composites increased with increasing silica content from TDI polymer/silica 100:1 to 100:5, indicating that the silica associated with the HS domain hindered the HS from completing their rearrangement. The hybrid domains with the ratios of 100:10 and 100:30 retained the well-ordered structure similar to that of the original 2,6-TDI polymer above the crystallization temperatures ($T_c$), even when the SS matrix is frozen. The silica component destroyed the ordered structure of HS when the ratio of silica content in the hybrid domain exceeded the amount of HS.

### Introduction

It is widely recognized that the elastic properties of segmented urethane block copolymers arise from a two-phase microstructure, in which hard-segments (HS) are separated from the soft segments (SS) to form domain structures.[1−5] The HS of segmented polyurethanes have hydrogen-bonded groups that promote aggregation into domains.[5] It is presumed that these domains act as physical cross-links, imparting the observed elastic properties. A considerable amount of research has been devoted understanding the structure and properties of segmented polyurethane elastomers, which suggested the existence of domains of the order of 100 Å in size.[1,2,4] In particular, two series of segmented polyurethanes, one based on tolulene-2,6-diisocyanate (2,6-TDI) and another on tolulene-2,4-diisocyanate 2,4-TDI, have been extensively investigated to determine crystalline or amorphous domains resulting from the symmetric or asymmetric monomer unit structures of HS.[6−10] From the differences observed in small angle light scattering, small-angle X-ray scattering, and differential scanning calorimetric (DSC) studies, 2,6-TDI polymers were found to have well-ordered crystalline HS domain structures and 2,4-TDI polymers have amorphous HS domains.[6,7,9]

Hybrid nanocomposite materials between inorganic glasses and organic polymers have been developed recently.[11−16] The sol−gel reaction basically involves two steps: (1) hydrolysis and (2) condensation polymerization reaction. The hydrolysis and condensation steps are

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very much affected by the catalytic conditions. When basic catalysts were used to cure silica, the rate of condensation is fast compared to hydrolysis, resulting in the formation of dense, colloidal particles. On the other hand, the rate of condensation is slow relative to the rate of hydrolysis under acid catalysis; i.e., the resulting silica has a highly ramified structure with many silanol groups on the silica surface. The typical domain sizes observed using sol−gel processes are on the scale of nanometers. To promote high levels of molecular mixing, it is useful to use polymers possessing hydrogen bond acceptor groups that can form hydrogen bonds with the silanol groups on the silica surface. In fact, segmented polyurethane has a high concentration of urethane groups in the HS domains, which can interact with silanol groups through hydrogen bonding.[5,8−10] In this study, we have attempted to create a new type of nanocomposite system between HS organic domains and silica in the SS continuous matrix.

This paper reports the investigation of the “local environment” in the interfacial region between the silica and HS domains, using fluorescent probes on silica. Fluorescence techniques have been established to monitor the local environment of chromophores, especially local polarity and rigidity. Experimental work on the molecular structure using optical probes has been done on many kind of molecular composites and sol−gel material.[18−20] Derivatives of the 5-amino-1-naphthalenesulfates, particularly the dansyl (5-(dimethylamino)-1-naphthalenesulfate) group, are suitable for fluorescence probes of the structure and dynamics of macromolecules.[21−24] These molecules have the emission properties that are strongly dependent on environmental polarity. They exhibit a large red-shift when their environment changes from nonpolar to polar.[25,26] We report insight regarding the structural aspects of the HS domains in contact with silica, from the emission spectroscopy of the dansyl probe molecule binding to the silica.

## Experimental Section

**Polymers.** Two series of polyetherurethanes, one based on 2,6-TDI and the other based on 2,4-TDI, were used (Figure 1). The SS unit was poly(tetramethylene oxide) (PTMO $M_n$ = 2000, Polyteach Inc.) followed by chain extension with 1,4-butanediol (BD, Aldrich). Polymerization followed a two-step procedure in DMF, and solid concentration was 15 wt %.[27] The molecular ratio of TDI/BD/PTMO was 1.000:0.832:0.200. The stoichiometric number average molecular weight of the polymer is approximately 20 000. The weight ratio of HS/SS was calculated to be 39:61.

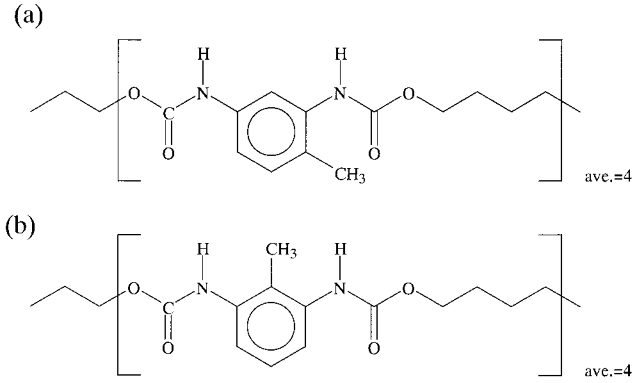

**Figure 1.** Structures of studied polymers: (a) 2,4-TDI polymer, (b) 2,6-TDI polymer.

**Materials.** Tetraethoxysilane (TEOS, Aldrich Chemical) and *N*-(triethoxysilylpropyl)dansylamide (Gelest) were used without further purification.

TEOS was added to the polymer DMF solution and then stirred for 5 min with various weight ratios (solid polymer weight/calculated silica weight =100:1, 100:3, 100:5, 100:10, 100:30, 100:50, and 100:70 for 2,6-TDI polymer and 100:30 and 100:50 for 2,4-TDI polymer). In addition, *N*-(triethoxysilylpropyl)dansylamide (1.0 × 10−5 mol/total solid weight 1 g) was mixed into the solution. Formic acid aqueous solution (pH = 2.0) made from distilled water was added with a stoichiometric ratio of water molecules per ethoxy group. The mixtures were stirred thoroughly until clear solutions were made at room temperature. Portions (2.5 mL) of these viscous solutions were poured into polyethylene embedding molds (1.5 cm × 1.5 cm × 1.5 cm). These samples were cured at 100 °C under nitrogen for 24 h and were dried for 48 h under vacuum at the same temperature. The films removed from the molds were washed in ethanol to remove unreacted dansyl molecules and TEOS. Finally, the films were dried at 50 °C in a vacuum for 48 h. The composite films were used in the subsequent DSC and emission spectroscopy measurements.

Adding 1.0 g of the formic acid aqueous solution to 5.0 g of the polyurethane solution and then curing under the same conditions, we made a polyurethane film without silica. The number average molecular weight of the polyurethane film was measured approximately 20 500 by GPC. Therefore, we recognized the polyurethane is chemically stable in the presence of the acid catalysis and the curing condition mentioned above.

**Measurements.** DSC was carried out with a Perkin-Elmer DSC. The normal scanning speed was 20 °C/min, and the weight of the material was approximately 10 mg. The temperature range is from −100 to +50 °C.

Fluorescence measurements were performed with an Edinburgh Analytical Instruments FS900CDT fluorometer with a Xe 900kmp with slit widths of 0.5 mm. The temperature of the sample was controlled by an Oxford Instruments variable-temperature liquid nitrogen cryostat optistat in the range from −93 to +37 °C after the initial cooling.

## Results and Discussion

In Figure 2, the differences in the properties of 2,6-TDI and 2,4-TDI polyurethanes are clearly shown. The 2,6-TDI and 2,4-TDI polymers have glass transitions ($T_g$) around −75 °C and melting points (mp) near 20 °C, which is derived from the SS. In addition, only the 2,6-TDI polymer has a broad exothermic peak from −40 to +10 °C, which is attributed to the crystallization of the HS of 2,6-TDI polymer. It follows that the HS of 2,6-TDI polymer starts lining up to induce crystallization in the HS domains when the SS matrix has sufficient mobility above the $T_g$ of SS. Thus, 2,6-TDI polymer has a structural change from amorphous to

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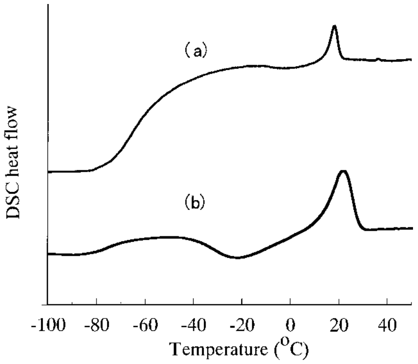


**Figure 2.** DSC runs of (a) 2,4-TDI polymer and (b) 2,6-TDI polymer.

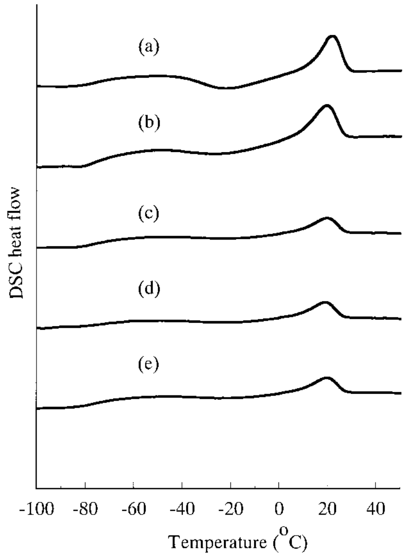


**Figure 3.** DSC runs of (a) 2,6-TDI polymer and its composites: 2,6-TDI polymer/silica (b) 100/5, (c) 100/10, (d) 100/50, and (e) 100/70.

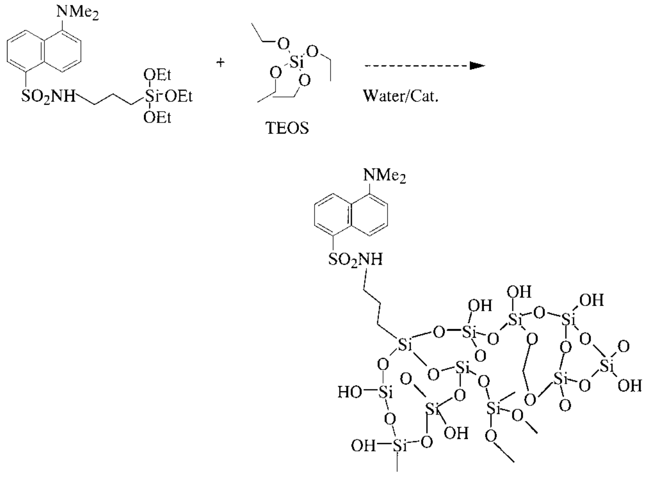
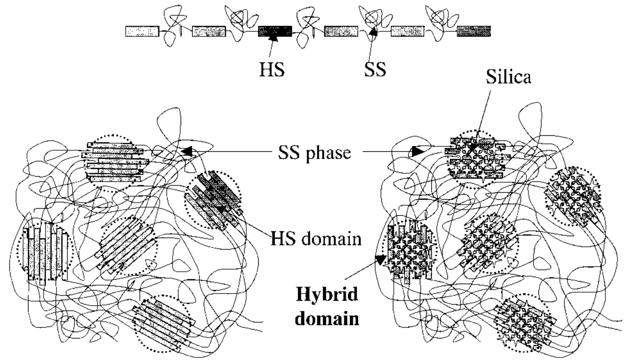


**Figure 4.** Structural model of dansyl probe bound to silica.



(a) Segmented-polyurethane (b) Hybrid composite

**Figure 5.** Structural models of microphase separation structures of (a) segmented-polyurethane and (b) hybrid composite.

crystal with increasing temperature, while the HS structure of 2,4-TDI polymer was amorphous at all temperatures.

Figure 3 shows the DSC thermograms of the composites of 2,6-TDI polymer and silica. In the case of TDI polymer/silica 100:5 of the 2,6-TDI composite, a small crystallization peak was observed, but was much smaller than that of original 2,6-TDI polymer. The crystallization disappeared in the spectra of the composites when the silica contents of TDI polymer/silica was over 100:10. The following two main results were demonstrated by the DSC measurements of the 2,6-TDI composites. First, the $T_g$ and mp of the SS of the composite materials maintained the same temperature as that of pure polyurethane. This indicates that the silica does not have a direct effect on the SS thermal characteristics with various ratios of the composite but only affects the crystallizing peak of crystal HS domains of the 2,6-TDI polymer. Second, the exothermic peak of the crystallization of HS disappeared with increasing silica content. From this result, it is obvious that the structural transition from amorphous to crystalline did not occur in the hybrid domains with TDI polymer/silica ratios of 100:10, 30, 50, and 70 silica content, as the temperature increased. From the DSC results, we confirmed that the introduction of silica to the polyurethane significantly affects the crystallization transition.

Fluorescence emission is an excellent method to get information about the polarity and the rigidity around the chromophores. We used *N*-(triethoxysilypropyl)-dansylamide as a chromophore to bind dansyl groups to the silica surface (Figure 4). It has a propyl spacer between dansyl probe and triethoxy group, allowing direct observation of the local environment of a polymer chain in contact with silica. The dansyl probe is particularly sensitive to local polarity because of its charge-transfer structure. Therefore, the dansyl probe bonding to silica would be distinguishable from the crystal domains with ordered segments from the amorphous domains, especially if silica was put into the HS phase.

In general, many hydrogen-bonding groups are needed to disperse silica in the sol—gel method. Most urethane bonds of the segmented polyurethane are localized in the HS domains. Taking advantage of silica affinity for hydrogen bonding of the HS, we selectively introduced silica into the HS domains and observed the structure of “hybrid domains” from the emission spectra of dansyl probe molecule bonded to the silica (Figure 5).

Figure 6(1) gives the emission spectra from 2,6-TDI polymer composite with TDI polymer/silica 100:1 silica content. The red shift from 470 to 520 nm observed at the crystallization peak of the original 2,6-TDI polymer confirms that the dansyl probe recognized the arrangement of the HS in the hybrid domains. The emission

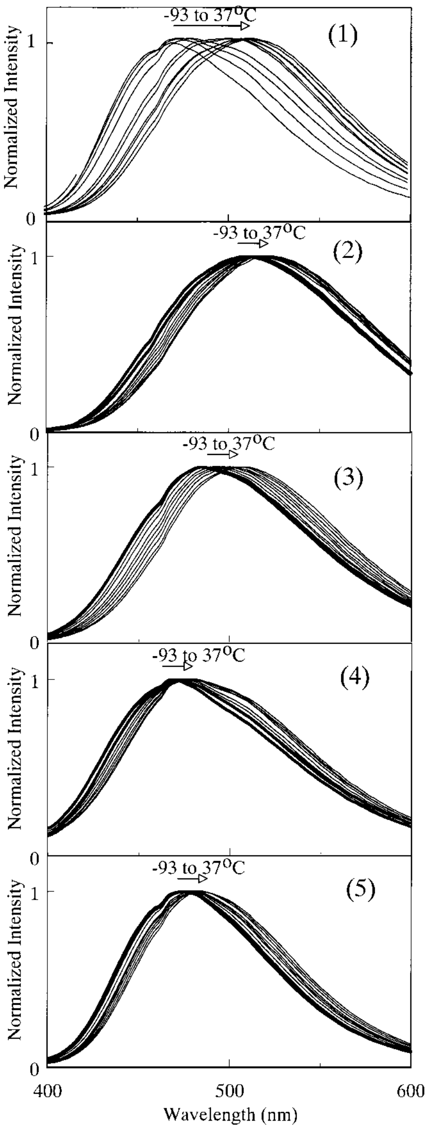


**Figure 6.** Normalized emission spectra (Ex.360nm) obtained from 2,6-TDI polymer composites with the weight ratios polymer/silica (1) 100/1, (2) 100/10, (3) 100/50, and (4) 100/70 and from (5) 2,4-TDI polymer composites with the weight ratios 100/30.

shift demonstrates that the amorphous structure of the HS has become ordered and anisotropic with crystalline structure in the domains. All these sufficiently confirms that silica containing the dansyl molecule is associated with the HS of the polyurethane.

Figure 6(5) displays the emission spectra of 2,4-TDI polymer with TDI polymer/silica 100:30 content. The 2,4-TDI polymer, as mentioned above, has amorphous domains possessing disordered HS at all temperatures. These fluorescence measurements of the 2,4-TDI polymer composites clearly demonstrate that the peaks around 470 nm are attributed to the disordered segments in the amorphous domains and that the change of rigidity in the HS causes very small peak shifts with increasing temperature over the $T_g$ of SS.

The emission spectra of 2,6-TDI polymer composite with small amounts of silica (TDI polymer/silica 100:3 and 5) have the same red sifts as TDI polymer/silica 100:3. The wavelength of the peak maxima of the emission spectra at various temperatures from the 2,6-TDI polymer composites with TDI polymer/silica 100: 1, 3, and 5 against temperatures are plotted in Figure 7(1). These plots show that segment rearrangement temperatures ($T_r$) of the HS in the hybrid domain is rising. The segment rearrangement temperatures ($T_r$) of TDI polymer/silica 100:1, 3, and 5 were observed at −18, −10, and 0 °C, respectively. From these results, the $T_r$ of the original 2,6-TDI polymer is calculated to be −25 °C, as shown in Figure 8, correlating with the $T_c$ from the DSC measurement. The rise of $T_r$ with increasing silica content indicates the silica associated with the HS domain hinders the HS from completing its rearrangement.

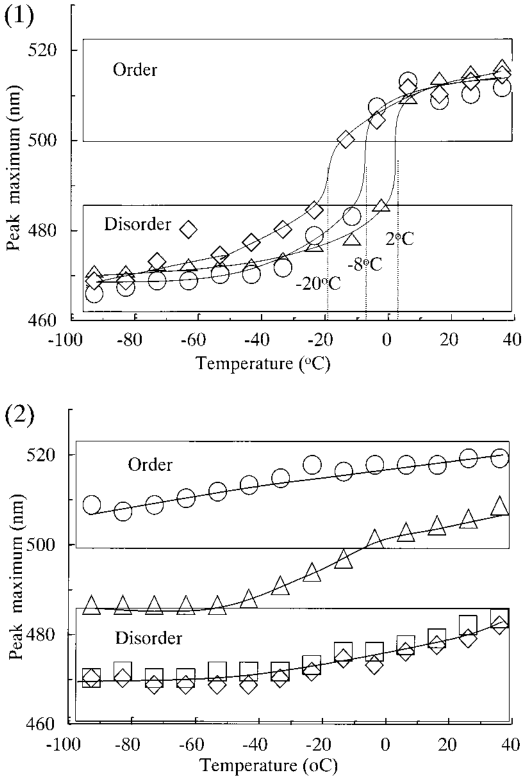


**Figure 7.** Emission maxima and weight ratio of TDI polymer/silica: (1) 2,6-TDI polymer/silica 100/1 (◇), 100/3 (○), and 100/5 (△); (2) 2,6-TDI polymer/silica 100/10 (○), 100/50 (△), and 100/70 (◇); and 2,4-TDI polymer/silica 100/50 (□).

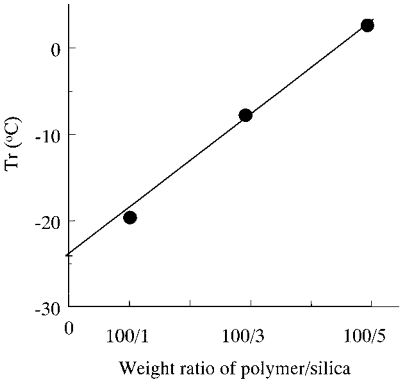


**Figure 8.** HS rearrangement temperature (Tr) of hybrid films (silica contents 100/1, 100/3, and 100/5).

Figure 6(2) shows the fluorescence emission spectra of the composites based on 2,6-TDI polymer with TDI polymer/silica 100:10. There is no structural transition from disorder to order in the spectra from these composites with silica content of TDI polymer/silica 100:10 and 100:30.

The peak maxima of the composites with TDI polymer/silica 100:10 and 30 is located around 520 nm at all temperatures, indicating the formation of well-ordered crystal domains. The hybrid domains with the ratio of 100:10 and 30 can remain well-ordered structures similar to that of the original 2,6-TDI polymer above $T_c$, even when the SS matrix is frozen. These results prove that the mobility of HS associated with silica is inhibited by hydrogen bonding with silanol groups.

The total amount of HS domains consists of about 40 wt % of the total polyurethane weight, assuming that the HS is approximately equal to the weight ratio of the (TDI + BD)/total polymer. From the results as shown in Figure 6(3), it is clear that silica starts to destroy the ordered structure of the HS when the ratio of silica content in the hybrid domain exceeds the amount of HS. Therefore, the emission peak maximum, as shown in Figure 7(2), located between the disordered area and the ordered area, included a red-shift indicating the change of rigidity with increasing temperature as in the case of TDI polymer/silica 100:50 of 2,6-polymer composite. This behavior is caused by the coexistence of ordered and disordered HS in the hybrid material at all temperatures.

Finally, the emission spectrum and the peak maximum plots in the composite with TDI polymer/silica 100:70 silica content are shown in Figures 6(4) and 7(2). This spectrum is consistent with the observed amorphous domains of 2,4-TDI polymer composites. These results indicate that silica completely eliminates the ordered structure as shown by the plots of the 2,4-TDI polymer composite in Figure 6(5). This suggests that silica, when mixed with the HS at the molecular level, disrupts hydrogen bonds between polymer chains and destroys all order in the HS domains.

## Conclusions

The structural relation of silica and HS in the hybrid domains was determined from the fluorescence emission spectra of dansyl probe bound to the silica. A very small amount (TDI polymer/silica 100:1, 3, and 5) of silica has much influence on the rearrangement behavior of the HS domains. Excess TDI polymer/silica content above 100:10 gave no structural transition on the hybrid domains. If silica particles are formed apart from the HS domain, it would be impossible to observe crystallization of the HS using an emission probe bound to silica. We conclude that silica and HS interpenetration results in mixing at the molecular level to form the hybrid domains.

When acid catalyst was used to cure TEOS, a highly ramified, low fractal-dimensional structure was formed. The most likely explanation is that the silica is not dispersed as particles, but is simply inserted between polymer chains forming hydrogen bonds, while retaining its ramified form.

In the process, we have created a new type of composite material possessing dispersed hybrid domains of HS interpenetrating with silica in the SS continuous phase. We predict that these composite films will have good mechanical and thermal properties because the hybrid domains are much harder and more heat resistant than the original HS maintaining flexibility of the SS.

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