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Topographical Nanostructure Patterning on the Surface of a Thin Film of Polyurethane Containing Azobenzene Moiety Using the Optical Near Field around Polystyrene Spheres

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ABSTRACT: An indented nanostructure was formed on the surface of azobenzene-functionalized polyurethane thin films by the induced migration of polymer chains using the optical near field generated around polystyrene (PS) spheres. The PS spheres, which had a diameter ranging from 98 to 990 nm, were arranged on the surface of a photoresponsive polymer film using a self-organization process, and the films were then exposed to a linearly polarized Ar^+ laser at 488 nm. A hexagonal array of indentations reflecting the original geometry and arrangement of the spheres was observed on the polyurethane surface by atomic force microscopy. The indented structure that was formed had a resolution of ∼95 nm. This structure was stable at room temperature and could be erased by heating the films above their glass transition temperature (T_g). The modification depth and diameter of the dents formed depended on the size of the original PS spheres. In particular, deeper dents were formed by using PS spheres with a diameter of over 505 nm, due to the optical lens effect they created, and the irradiation onto spheres of greater than 505 nm diameter with linearly polarized light induced an anisotropic modification on the surface of the polymer films. The thickness of the polymer film significantly affected the modification depth of the dent. We prepared three different kinds of photoresponsive polyurethane, each containing a slightly different azobenzene moiety. Although these polymers all had virtually the same molecular weight, T_g, and absorptivity at the wavelength of the irradiated light, the modified depth of the dent observed for each of the films was very different. Furthermore, a dependence between the irradiated light intensity and the size of dent achievable was observed, which was due to the difference in the trans−cis−trans isomerization behavior of the azobenzene moiety.

Introduction

Over the past decade, polymeric systems containing azobenzene moieties have been attracting a great deal of attention because of their potential uses in various photonic applications.[1−12] It is well-known that azobenzene derivatives can exist in two configurations. The first of these is the cis form, which has a bent formation, and the other configuration is the more stable trans form, which is rodlike in shape. When exposed to light of a certain wavelength, the trans form can be photoisomerized to the cis form. Cis−trans back-isomerization can occur thermally or/and photochemically. This property of the azobenzene derivatives leads to a drastic change in the physical and optical properties of the polymer matrix, which has aroused the interest of many research groups. In this field, one of the most intriguing topics in recent years is the fabrication of artificial surface relief structures in azobenzene-functionalized polymer films by exposure to an interference light pattern or a single-laser beam, which occur due to the photoinduced mass transport process of the polymer chains.[13−21] This process is quite different from other conventional microscopic surface processing techniques for resist, ablation, and stamping[22−24] and is attracting interest as a novel technique for surface modification processes that use visible light, e.g., photolithography and optical data storage. However, with conventional light sources, the size that can be modified is restricted by wavelength considerations because of the diffraction limit of the exposed light.

Use of the optical near field, which is not constrained by diffraction limits, is one effective method for solving this problem. Currently, near-field optics have been extensively investigated from the viewpoint of nanoscale optical science and technology.[25−44] If surface modification can be induced by the optical near field, applications to superfine photolithography and high-density optical data storage media would be expected. Recently, we found that a topographical change could be induced on the surface of azobenzene-functionalized polymer films by means of the optical near field generated around polystyrene (PS) spheres of submicron diameter.[45] The experimental procedure to display this phenomenon is very easy, as described below. A monolayer of the PS spheres was formed on the surface of a polymer film, which was then irradiated with a laser beam with a wavelength that could be absorbed by the photochromic moiety. After removal of the PS spheres, hexagonally arrayed dents are formed on the surface of the polymer films. These optically formed dents have a diameter nearly the same as the spheres used to form the pattern, and the formation of indentations with a resolution of ∼20 nm could be achieved.[45a] Moreover, the indentations formed in the structure were thermally stable at room temperature but could be erased by heating the polymer film until it was above its glass transition

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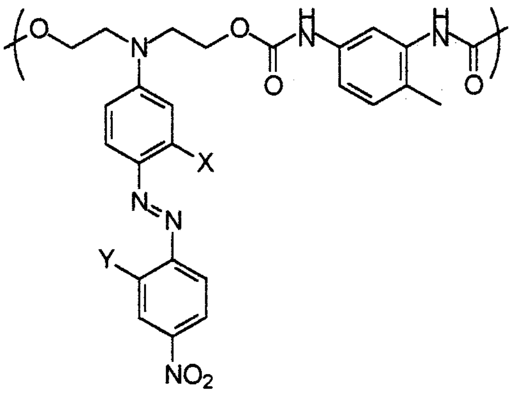

Figure 1. Chemical structure of polymers used in this study.

temperature.

In our previous work, the diameter of the dents formed by this process had been the main criterion for the evaluation of the materials. The modification depth of the dent, however, is also an important parameter because it can provide useful information on the surface modification behavior and mechanism. Moreover, the only urethane–urea copolymer with the ortho positions substituted by the DR19-type azobenzene moiety was employed.[45] To evaluate the role of each of the structural elements contributing to the surface modification on a submicron scale, a simple polymer structure is desirable. In this article, the surface modification induced by the optical near field was explored on a thin film of polyurethane containing the ortho positions and no substituted azobenzene moieties in the side chain. The effect of the introduction of substituents on the photochromic moiety of the surface modification behavior was investigated. Furthermore, several other important parameters, such as the effects of the size of the PS spheres, the film thickness and the intensity of the irradiated light on the modification depth, and the diameter of the indented structure, were explored, and a possible mechanism is discussed.

Experimental Section

Figure 1 shows the chemical structures of the photoresponsive polyurethane polymers (polymers **1**–**3**), which were used in this study. The synthetic route to manufacturing polymer **3** had been described elsewhere,[46] and the other polymers were also prepared according to the same method as used for polymer **3**. The number- and weight-average molecular weights (M_n and M_w) of the polymers were measured by gel permeation chromatography (GPC; Tosoh SC-8010; column, Shodex OhpakSB-G + SB-806M HQ × 2; eluent, *N*,*N*′-dimethylformamide) calibrated with standard poly(ethylene glycol). The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC; Perkin-Elmer DSC-7 and TAC 7/DX thermal controller; heating rate, 10 °C/min). The measurement of the inherent viscosity of the polymers was performed at 30 °C in 1-methyl-2-pylorridone (Ubbelohde viscometer). The general properties of these polymers are summarized in Table 1.

Table 1. Composition, Molecular Weight, Glass Transition Temperature, and Viscosity of the Polyurethanes Used in This Study

polymer	X	Y	M_n[a]	M_w[a]	M_w/M_n[a]	T_g (°C)[b]	η (dL/g)[c]
polymer **1**	H	H	4440	8137	1.83	128	0.11
polymer **2**	H	CH_3	3488	5585	1.60	120	0.10
polymer **3**	CH_3	CH_3	3388	6239	1.84	124	0.09

[a] Determined by GPC using a poly(ethylene glycol)-calibrated column set. [b] Determined from DSC measurements. [c] Determined from viscosity measurement using 1-methyl-2-pyrrolidone at 30 °C.

Sample films were prepared by spin-coating from ~8 wt % pyridine solutions of each polymer. These solutions were passed through a 0.20 μm filter (Millipore) to remove impurities before spin-coating. Optically clear films were formed on the glass substrates. The films that we obtained were placed in a vacuum oven at 130 °C for over 24 h to obtain solvent-free-samples. The thickness of the polymer films was measured by using a surface profiler (a subsidiary of Veeco Instruments Inc. Dektak3 ST).

Photoinduced surface modification of the polymer films was performed by the following procedure. An aqueous solution including the PS spheres (Moritex Co.) was dropped on the surface of the polymer films, and then the spheres were allowed to arrange themselves by a self-organization process. After drying the samples at room temperature overnight, they were irradiated with a linearly polarized Ar^+ laser at 488 nm (Lexel model 95 ion laser). The light was irradiated at normal incidence to the surface of the polymer films, and the sample films were held vertically to avoid the effects of gravity. The sample films were then washed with benzene for 3 days in order to remove the spheres from the surface, and then subsequently they were dried in vacuo at 25 °C for 2 days.

The surface structure of the polymer films was investigated by atomic force microscopy (AFM, Nanoscope E Digital Instruments Inc.) under ambient conditions. For all measurements, a 15 μm scanner was used in contact mode, with a microlever force constant of 0.38 N/m. A scan rate of 5 Hz was employed.

Results and Discussion

The surface profiles of the sample films after photoirradiation were investigated by AFM observations. Parts a and b of Figure 2 show typical examples of three-dimensional views of the film surface of polymer **1**. In these cases, the diameter of the PS spheres used was 241 and 505 nm, respectively, and the sample films were irradiated for 5 min with the linearly polarized Ar^+ laser at 488 nm wavelength and an intensity of 70 mW/cm^2. In both cases, the surface of the films prior to irradiation with the Ar^+ laser showed no regular structural periodicity. After irradiation and removing the spheres, it could be observed that hexagonally arrayed dents were formed on the surface of the polymer films. For the PS spheres with a diameter of 241 nm, the modified depth and diameter of the dents formed were ~50 and ~230 nm, respectively. On the other hand, when the 505 nm diameter spheres were used, these values were ~100 and ~480 nm, respectively. The diameter of the dents obtained was about the same as the diameter of the spheres that were used. In our previous work we confirmed by scanning electron microscopy (SEM) that the dents are formed directly below the PS spheres.[47] Therefore, the dent structures observed on the polymer films reflect the shape and arrangement of the spheres placed on the film surface. This dent structure could be erased by heating the polymer film above its T_g but was stable when maintained at below T_g. The most interesting point in these figures is the large difference in the shapes of the dents that were formed. For spheres of 505 nm diameter, the periphery of the dent formed a large hump in the polarization direction of the irradiated light. On the other hand, no such anisotropic hump could be seen on the dents formed by the 241 nm diameter spheres. In our recent study, a similar result had also been observed for the photoresponsive urethane–urea copolymer system.[47] This phenomenon indicates that the shape of the dent is influenced by the polarization direction of the irradiated light falling on spheres of a certain size, strongly suggesting that the

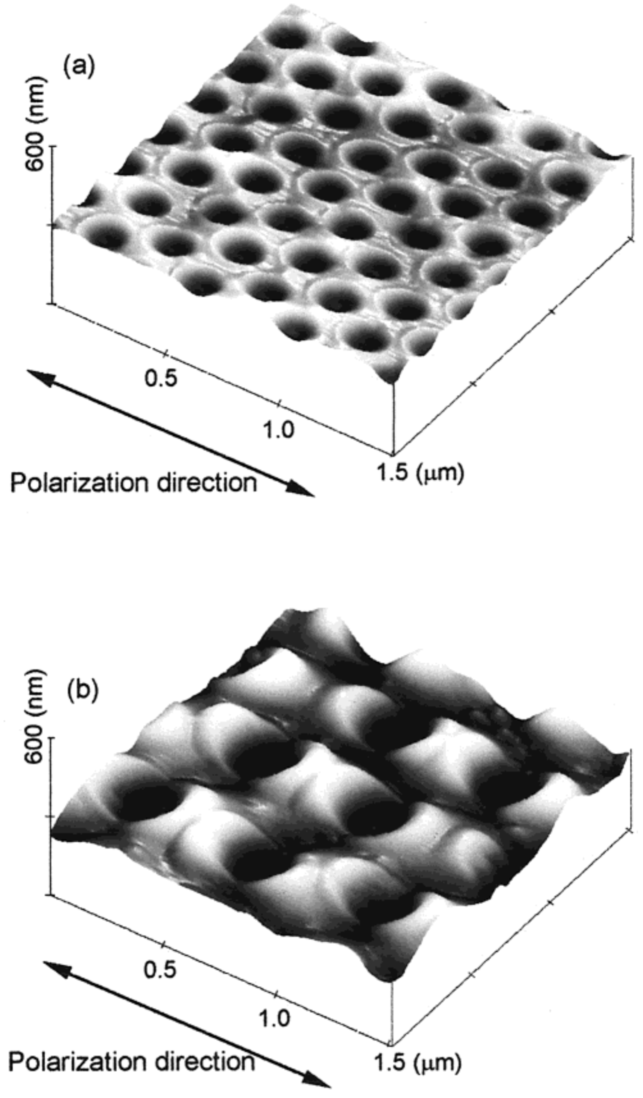

Figure 2. AFM three-dimensional view of the indented structure formed with PS spheres of (a) 241 nm diameter and (b) 505 nm diameter.

formation of the dent relates to the distribution of the electric field around the PS spheres.

Next, the effect of the size of the PS spheres on the modification depth and diameter of the dents was explored for films (1.5 μm thickness) of polymer **1**. In this study, the diameter of the spheres used were 98, 241, 505, and 990 nm. As shown in Figure 3, increasing the size of the PS spheres increased the diameter of the optically formed dents. The value of the diameter of the dents was nearly equal to that of the spheres that we used, and a minimum diameter of ~95 nm was achieved in this study when the size of the sphere was 98 nm. On the other hand, the depth of the dents also depended on the size of the PS spheres. However, the magnitude of the modification depth drastically changed between 241 and 505 nm diameter.

This phenomenon could be ascribed to the difference in the scattering behavior of the light by the difference in the size of the PS spheres. As mentioned above, the wavelength of the irradiated light was 488 nm. In this condition, when the diameter of the spheres is smaller than 241 nm, irradiation of the spheres by the light will increase the optical electric field around them. The spheres do not diffract the irradiated light in this case because their size is smaller than the wavelength of the light used. Such an increase in optical electric field around the spheres is usually known as the optical near field, which is a newly produced electric field caused by the polarization induced in the matter by the photoirradiation. This optical electric field is localized around the irradiated matter, and its intensity decays exponentially with increasing distance from the surface of the specimen.[48] Therefore, any interaction between the optical field and the polymer will mainly happen at the near-surface of the sample film, resulting in the formation of shallower indentations. On the other hand, when spheres with a diameter of larger than 505 nm are irradiated with the 488 nm light, the light would be focused beneath each sphere because of the traditional diffraction effect. In other words, each sphere acts as an optical lens. In fact, from calculations based on Mie scattering theory, it had been found that the optical field just under the spheres with a diameter of 505 nm was enhanced by several tens of times more than the irradiated light.[45b] Moreover, the higher intensity optical field would penetrate more deeply into the inner film. Consequently, the depth of the indentations formed using the larger diameter 505 nm spheres will be deeper than those formed by spheres of less than 241 nm.

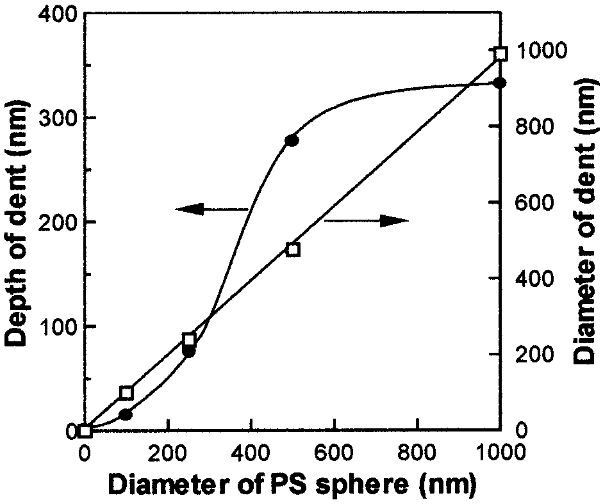

Figure 3. Effect of the diameter of the PS sphere on the modification depth and diameter of the dents formed upon irradiation with linearly polarized light at 488 nm and a power of 150 mW/cm^2 for 5 min.

Figure 4 shows the effect of the film thickness on the size of the optically formed dents. In this case, the PS spheres with a diameter of 241 nm were used to avoid the optical lens effect of the spheres, as described above. The film thickness was controlled by varying the rotational speed of the spin coater, and the thicknesses of the films obtained were ~90, ~160, ~360, ~730, and ~1500 nm, respectively. Although the diameter of the dents was nearly constant for all film thicknesses, the modification depth was increased when we increased the thickness of the sample film and became saturated at a film thickness of ~730 nm. This saturation value for the modification depth is related to the existence of the optical near field in this region. Thus, the influence of the optical near field can reach a depth of ~75 nm from the surface of the polymer film under these conditions. If the formation of the dent structure is ascribed to the ablation process, the modification depth of the dent will not be dependent on the film thickness. Consequently, this process scarcely contributes to the formation of the dent structure on the polymer film, and this phenomenon suggests that the deformation of the

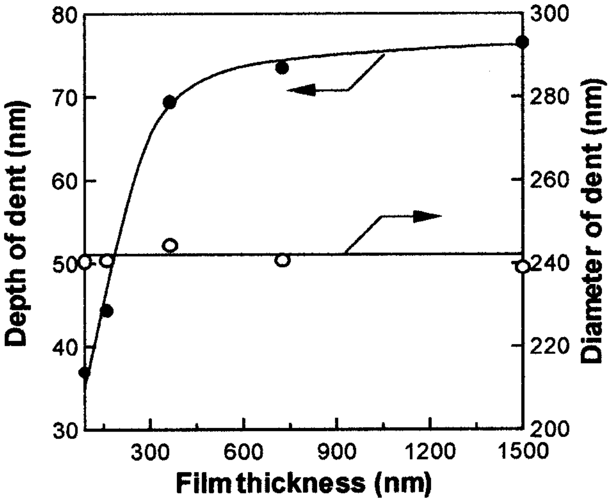

Figure 4. Effect of film thickness on the achievable depth and diameter of the dents on a polymer film irradiated with an intensity of 150 mW/cm^2 for 5 min.

polymer film is depressed at the near-interface between the glass substrate and the polymer film. Therefore, a mass transport process would be the most likely and most plausible explanation for the formation of the dent structure on the surface of the polymer films. As described above, theoretical as well as experimental data have been acquired from investigations into the optically driven mass transport of the polymers containing an azobenzene moiety. However, some additional considerations exist relating to the driving force of the mass transport.[13−21] In our previous study, we found that there is a difference in density between the inside and the periphery of the optically formed dents. The density of the inside of the dents was lower than that of the periphery of the dents.[45a] This would be strong evidence for the movement of the polymer chains from just below the PS spheres to the periphery. Furthermore, a similar film thickness dependence was also reported during the formation of SRGs on a thin azobenzene-functionalized polymer film using the optically driven mass transport technique.[20,21] Therefore, the formation of the dent structure in the region of the near field is due to a mass transport process involving the polymer chains that is induced by the optical near field, and such a large-scale molecular motion would be highly restricted at the near-surface of the glass substrate.

This optically formed dent structure could only be obtained in those polymers containing the azobenzene moieties, so it is clear that the azobenzene contributes to the formation of the dent structure on the surface of the polymer film. As mentioned above, we prepared three kinds of photoresponsive polyurethane, i.e., polymers **1**, **2**, and **3**, which are similar structurally, with their main dissimilarity being the bulkiness of the position close to the azo group. These polymers showed little difference in M_n, M_w, T_g, and viscosity. Moreover, polymers **1**−**3** exhibited similar shapes on the absorption spectra, and their maximum absorbances were at 460, 460, and 465 nm, respectively. The absorptivity of these polymers at the wavelength of the irradiated light showed nearly the same values, which were 5.73×10^4, 5.35×10^4, and 5.51×10^4 cm^{-1}, respectively. This system would be well-suited for an evaluation of the effects of the chemical structure of the azobenzene on the surface modification behavior. Therefore, as part of our study, the effect of slightly different chemical structures for the azobenzene moiety on the surface modification behavior was investigated. Figure 5 illustrates the irradiation time dependence on the depth and the diameter of the optically formed dents of polymers **1**−**3**.

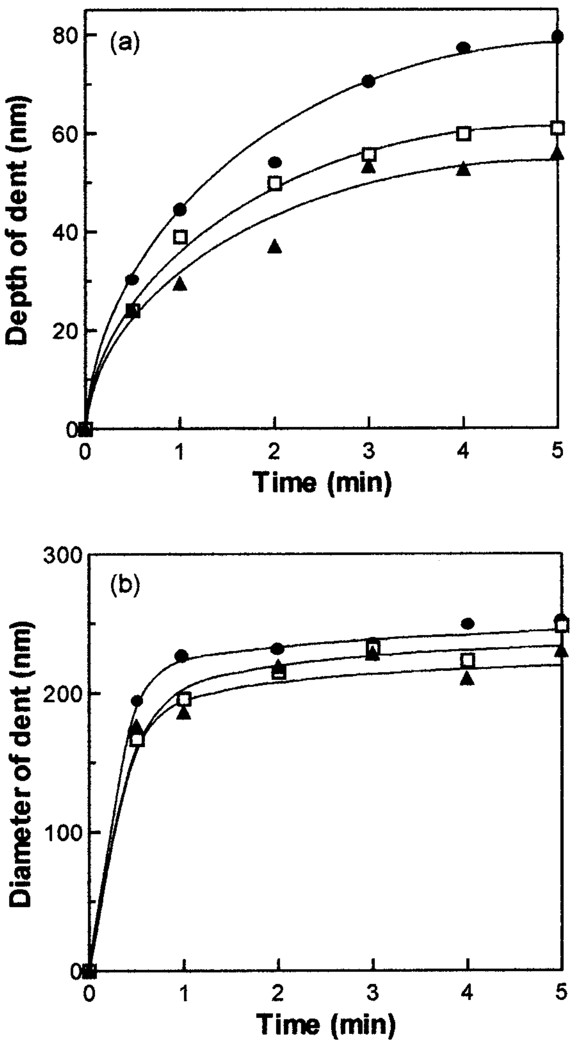

Figure 5. (a) Modification depth and (b) diameter as a function of the irradiation time for polymer **1** (closed circles), polymer **2** (open squares), and polymer **3** (closed triangles).

The polymer films were of similar thickness (~600 nm), which was irradiated several times with the linearly polarized Ar$^+$ laser (150 mW/cm^2) using the 241 nm diameter PS spheres. The modification depth and diameter of the dent increased with increasing irradiation time and saturated after about 5 min for all of the polymers. Moreover, it was found that there are differences in both the depth achievable and diameter of the dent between the polymers when we use different azobenzene ring substituents. Both values for the dents in polymer **1** were large compared to that of the other polymers. In this work, the thermal effects due to light absorption on the optical surface deformation behavior are considered to be negligible, because the absorptivity of these polymers at the wavelength of the irradiated light is nearly the same as described above. It has also been suggested that the mass transport behavior of the polymer chains is affected by their molecular weights, T_g, and their viscosity.[13b] However, in our case, there is little difference in these parameters, as shown in Table 1. Consequently, this result may be closely related to the difference in the photoisomerization behavior of the azobenzene moieties of each polymer. Polymer **1** contained the DR19-type azobenzene moiety in the side chain, while polymers **2** and **3** included azobenzene moieties that introduced methyl groups at their 2- and 2-,2′-positions, respectively. It is well-known that those substituents of the azobenzene which do not influence the spectroscopic type do not change the isomerization yield in the solution.[49] However, in the condensed phase, the introduction of bulky substituents onto positions close to the azo group depresses the photochemical trans−cis isomerization cycle of the azobenzene moiety as a result of the decrease in the free volume around the azo-chromophores.[50,51] Specifically, the amount to which the azobenzene moieties undergo the photoisomerization cycle for polymers **2** and **3** would be less than that for polymer **1**, which leads to the formation of a shallower dent structure.

In polymer **1**, the effect of the irradiated light energy on the behavior of the optical surface modification was explored. The sample films were exposed to 488 nm light at different intensities (280 and 70 mW/cm^2) while maintaining the same overall influence of the total irradiated energy by varying the irradiation time. Although the irradiated energy was kept constant, the degree of modification of the depth and diameter of the dents on the sample films exposed to a higher light intensity was larger than that in the sample film exposed to lower intensity light (Figure 6a,b).

A similar tendency could be observed also in polymers **2** and **3**. It is expected that differences in the intensity of the irradiated light would have an effect on the efficiency of the photoisomerization cycles of the azobenzene moiety because the amount of *cis*-azobenzene photochemically produced in a unit time depends on the intensity of the irradiated light. When a high-intensity light was used for the exposure, a large amount of the *cis*-azobenzene would be produced in a unit time, leading to the establishment of effective isomerization cycles. On the contrary, irradiation with a lower intensity light would generate a lower amount of the *cis*-azobenzene, resulting in a decrease in the amount of the azobenzene performing the isomerization cycles. The photoisomerization cycle of the azobenzene derivatives causes a softening of the polymer films (the azobenzene moiety acts as a plasticizer that is activated upon photoirradiation).[14e,49] Such softening of the polymer films would allow the effective migration of the polymer chains. Therefore, such a difference in the surface modification behavior would be due to differences in the amount of the azobenzene moiety undergoing the isomerization cycles.

The driving force for the migration of the polymers is not understood at the present stage. In SRG formation, which involves a mass-transport process, Tripathy and co-workers proposed that the gradient of the optical electric field was the main driving force for the migration of the polymer chain. As shown in Figure 2b, it is clear that the shape of the indentation formed was closely related to the polarization direction of the irradiated light. Thus, the phenomenon observed in this study may be explained in the same way. Namely, in the initial stage, the softening of the polymer film is caused by the photoisomerization cycles of the azobenzene moieties. In the second stage, the polymer chains move from the area of stronger optical field to the weaker area of the optical near field around the PS spheres. Finally, when the photoirradiation ceases, the indented structure formed under the spheres is fixed by the cessation of the migration of the polymer chains and the photoisomerization cycles of the azobenzene moieties. However, more detailed experimental and theoretical investigation is needed in order to acquire a full understanding of the formation of the hexagonally arrayed indented structure within the optical near field.

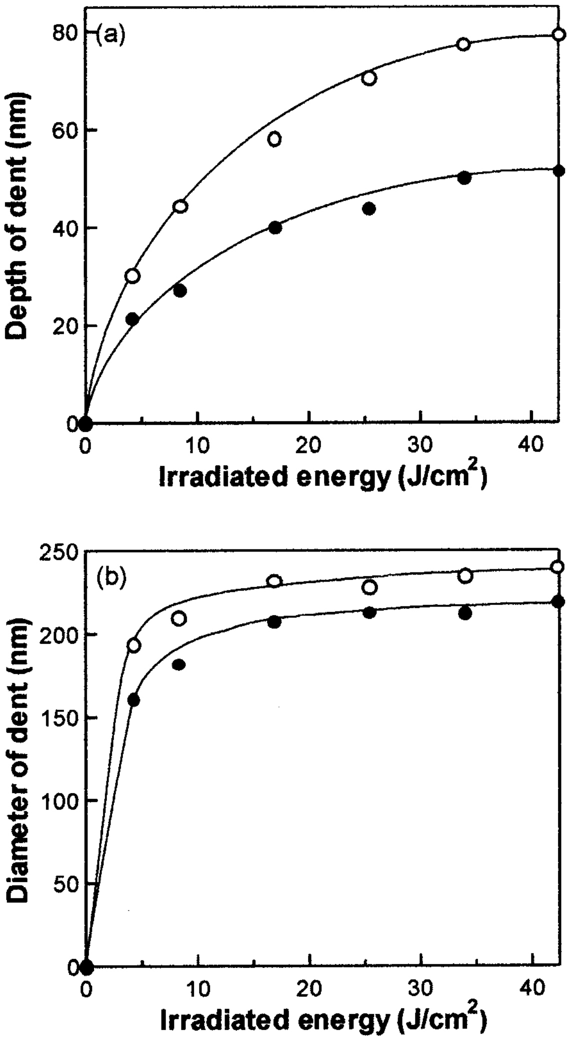

Figure 6. Effect of the intensity of the irradiated light on (a) modification depth and (b) diameter of the dent on the film surface of polymer **1**: open circle, 280 mW/cm^2; closed circle, 70 mW/cm^2.

Conclusion

In this work we studied the formation of a hexagonally arrayed indented structure that was formed on the surface of azobenzene functionalized polymer films. The mechanism for this phenomenon was the migration of polymer chains induced by the optical near field generated around a self-organized array of PS spheres with diameters ranging from 98 to 990 nm. By using the optical near field which is not restricted by the diffraction limit of the light, indented structures with a resolution ranging from several hundreds down to tens of nanometers could be formed on the surface of the polymer films if their temperature was maintained below their T_g. The modification depth and diameter of the dents strongly depended on the size of the PS spheres, due to the difference in the scattering behavior of the irradiated light caused by the difference in the sizes of the spheres. The minimum resolution of the modification diameter was ~95 nm when the size of the sphere was 98 nm. It was found that the photoisomerization behavior of the azobenzene moiety and the irradiated light intensity significantly affected the efficiency of the optical surface modification, which is an important factor in the development of optimized materials for optical data storage and superfine photolithography using visible light.

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