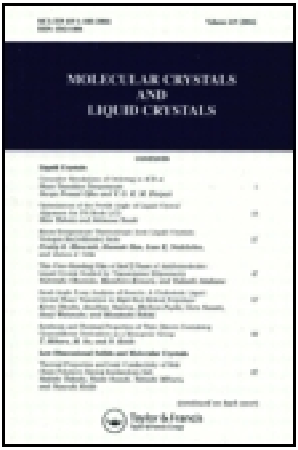

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Transcription of Near-Field Induced by Photo-Irradiation on a Film of Azo-Containing Urethane-Urea Copolymer

O. Watanabe [a] , T. Ikawa [a] , M. Hasegawa [a] , M. Tsuchimori [a] , Y. Kawata [b] , C. Egami [b] , O. Sugihara [b] & N. Okamoto [b]

[a] Toyota Central Research and Development Inc., Nagakute, Aichi, 480-1192, Japan

[b] Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu, 432-8561, Japan

Version of record first published: 24 Sep 2006

To cite this article: O. Watanabe, T. Ikawa, M. Hasegawa, M. Tsuchimori, Y. Kawata, C. Egami, O. Sugihara & N. Okamoto (2000): Transcription of Near-Field Induced by Photo-Irradiation on a Film of Azo-Containing Urethane-Urea Copolymer, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 345:1, 305-310

To link to this article: http://dx.doi.org/10.1080/10587250008023936

Mol. Cryst. and Liq. Cryst., 2000, Vol. 345, pp. 305-310
Reprints available directly from the publisher
Photocopying permitted by license only

Transcription of Near-Field Induced by Photo-Irradiation on a Film of Azo-Containing Urethane-Urea Copolymer

O. WATANABE[a], T. IKAWA[a], M. HASEGAWA [a], M. TSUCHIMORI[a],
Y. KAWATA [b], C. EGAMI [b], O. SUGIHARA [b] and N. OKAMOTO [b]

[a]*Toyota Central Research and Development Inc., Nagakute, Aichi, 480–1192, Japan and* [b]*Faculty of Engineering, Shizuoka University, Johoku,Hamamatsu, 432–8561,Japan*

We present that an intensity distribution of optical near field induced around photo-irradiated polystyrene spherical nanopariticles was transcribed on a film of azo-containing urethane-urea copolymer. The transcription was attained by a topographical change of the polymer surface, and the change was observed using an atomic force microscope. We have observed distinguishable dent surface structure using particles 28 nm in diameter.

Keywords: optical near field; azo polymer; photo-induced reaction; nanoparticle; transcription

INTRODUCTION

Taking advantage of an optical near field is one of the most promising technique for a nanometer scale fabrication such as high density optical storage and super fine lithography, because of overcoming the diffraction limit.[1] Photo-sensitive materials could be needed to develop the near-field technology, since an intensity of near field is mostly low. Many azobenzene derivatives, which transform the chemical structure by trans-cis photoisomerization, were investigated extensively due to their variable photo-sensitive phenomena, for example, reorientation of molecules[2], controlling an orientation of liquid crystal[2], inducing a phase transition of liquid crystal[3] and forming a surface relief grating.[5][6] We synthesized polyurethanes, urethane-urea copolymers and polyesters[7][8] , those are containing azo chromophore in their main chain structure, as nonlinear polymers. We fabricated a mode selective waveguide[9] from the urethane-urea azo copolymer by controlling an anisotropic refractive index change caused by photobleaching. Furthermore, we have developed non-optically probing near-field microscopy using the urethane-urea copolymer containing azo moiety as photosensitive material and demonstrated to transcribe an intensity distribution of optical near-field around polymer spherical nanoparticle.[10] In this letter, we report the dependencies of the optical power and particle diameter on the deformation process.

EXPERIMENTAL

Urethane-urea copolymer containing azo chromophore was synthesized according to previous report.[7] The chemical structure of the copolymer was shown in Fig. 1 (lower). The copolymer has a glass transition temperature of 145 °C measured by a difference scanning calorimeter, a maximum absorption at 475 nm determined by an absorption spectrometer and weight-average molecular weight of 170000 measured by gel-permeation chromatography. The thin film of the copolymer was spin-coated on glass substrate from the polymer solution dissolved in

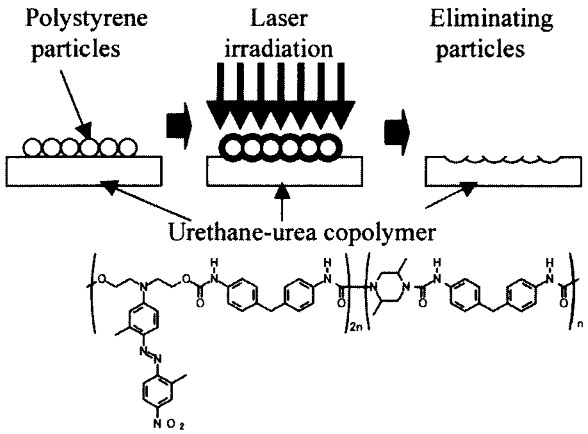

FIG. 1 Transcription process (upper) and chemical structure of the copolymer (lower)

pyridine after filtering through a 0.2 μm filter. The films obtained were dried under vacuum at room temperature for 6 h, at 100 °C for 20 h, and at 150 °C for 2 h.

An aqueous solution containing polystyrene monodisperse nanopartiles was dropped onto the polymer film and dried over night. Various kinds of particles having diameters ranging from 2000 nm to 28 nm was used The solution was purchased from MORITEX. An ordered monolayer of nanoparticles was formed on the azo polymer film by self-organizing process. Coherent light at 488 nm was irradiated to the sample using an Ar laser. After the irradiation, the nanoparticles were eliminated by washing with water, and then the sample was immersed in benzene to eliminate the residue of particles. The topographic image of the obtained film was observed using a Nanoscope atomic force microscopy (AFM). This process was shown schematically in Fig. 1 (upper).

RESULTS & DISCUSSION

Fig 2 a. b. and c show AFM images obtained from the experiments using 500-nm, 100-nm and 28-nm nanoparticles, respectively. These images showed arrayed dent structures, respectively. The hexagonal arrayed structure of nanoparticle was formed on the film by self-organizing process; however, the structure was disordered in the case of small particles, smaller than 100 nm. The arrayed structure of nanoparticles was transferred in the images obtained from the photo-transcribed process. We also observed the image of film on which the particles were remaining, so that identified the center of dent structure with the center of particle. The deepest position of dent structure corresponded to the point of contact between sphere and azo polymer. We also confirmed the images using a scanning electron microscope.

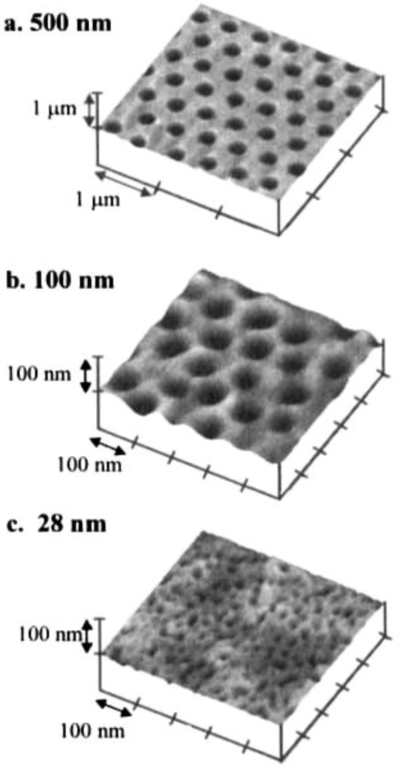

FIG. 2 AFM images of deformed film. The samples were prepared using photo-irradiated particles, a:500 nm, b:100 nm, c:28 nm

Since the diameters of both the 100-nm and the

28-nm particle are smaller than the diffraction limit, Fig.2 b and c show transcriptions of optical near field onto azo copolymer. The 28-nm distinguished dent-structure corresponds to high-density optical recording of about 1 Tbit/in^2.

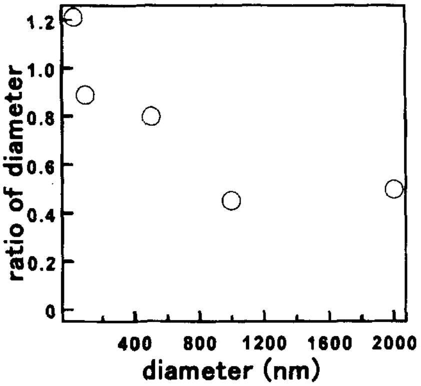

FIG. 3 Ratio of diameter between dent structure and nanoparticle as a function of the nanoparticle diameter

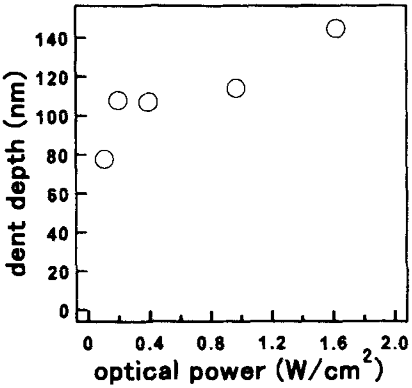

FIG. 4 Dent depth as a function of optical power. Irradiation was performed using nanoparticles of 500 nm in diameter.

The diameter of dent structure increased with that of nanoparticles, however, was not proportional to that of nanoparticles. The diameter of dent structure was unchanged with increasing the irradiated optical power under the same irradiation time, though the depth increased with the power. Fig.3 shows the ratio of diameter between dent structure and nanoparticle. The ratio decreased with the diameter of particle and saturated over 1000 nm. Fig. 4 shows the dent depth as a function of optical power. The dent depth increased depending on the power. In early stage the depth of dent structure rapidly increased with the power and then the depth slowly increased to reach saturated state. The depth also increased with irradiation time. The saturated depth was almost same, about 100-150 nm, in the case of experiments using particles of 2000, 1000, and 500 nm. On the other hand, the depth decreased with decreasing the diameter of nanoparticles in the experiments using 100-nm and 28-nm particles.

Large particle having diameter over the diffraction limit works as a lens so that optical power is focused on the area around contact point between nanoparticle sphere and azopolymer film. The results indicate that the lens effect dominates the deformation process in large - particle experiments, and near field is transcribed to the polymer film in small-particle experiments.

References

[1] M. Ohtsu Ed.; Near-Field Nano/Atom Optics and Technology, Springer (1998).
[2] T. Todorov, L. Nikolova and N. Tomova; *Appl. Opt.*, **23** 4588 (1984).
[3] K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki and K. Aoki; *Langmuir*, **4** 1241 (1988).
[4] T. Ikeda and O. Tsutsumi; *Science*, **268** 1873 (1995).
[5] D. Y. Kim, S. K. Tripathy, L.Li and J. Kumar; *Appl. Phys. Lett.*, **66** 1166 (1995).
[6] E. Batalla, A. L. Natansohn and P.L. Rochon; *Appl. Phys. Lett.*, **66** 136 (1995).
[7] O. Watanabe, M. Tsuchimori, and A.Okada,; *Polymers for advanced technology*, **10** 459 (1999).
[8] M. Tsuchimori, O. Watanabe and A. Okada; *J. Mater. Chem.*, **7** 877 (1997).
[9] O. Watanabe M. Tsuchimori, A. Okada and H. Ito; *Appl. Phys. Lett.*, **71** 750 (1997).
[10] Y. Kawata, C. Egami, O. Nakamura, O. Sugihara, N. Okamoto, M. Tsuchimori, and O. Watanabe; *Optics Communications*, **161** 6 (1999).