Comparative Studies of the Formation of Surface Relief Grating. Amorphous Molecular Material vs Vinyl Polymer

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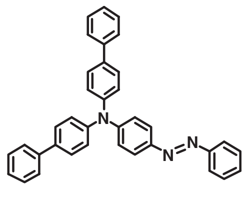
Comparative studies have been performed on the formation of surface relief grating (SRG) using an amorphous molecular material, 4-[di(biphenyl-4-yl)amino]azobenzene (DBAB), and a vinyl polymer containing DBAB as a pendant chromophore. It was found that SRG was formed more rapidly for the photochromic amorphous molecular material than for the corresponding vinyl polymer.

Formation of surface relief grating (SRG) by irradiation of amorphous films of azobenzene-functionalized polymers with two coherent laser beams has been a topic of current interest.[1–7] SRG, which is formed by the mass transport induced by the photoisomerization of the azobenzene chromophore, may find potential applications for erasable and rewritable holographic memory, polarization discriminator, and waveguide coupler. It has been suggested that the existence of a polymer chain connecting the azo-chromophore plays an important role for the formation of SRG, since molecularly doped polymer systems, where low molecular-weight azo-dyes are dispersed in a polymer binder, exhibit poor SRG-forming properties relative to azobenzene-functionalized polymers.[3,5]

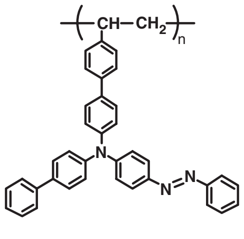
We have performed a series of studies on the creation of amorphous molecular materials.[8] As a part of these studies, we have proposed a new concept, "photochromic amorphous molecular materials,"[9] and created novel families of such amorphous molecular materials.[9–12] Photochromic amorphous molecular materials can form uniform amorphous films by spin coating and vacuum deposition. Studies of SRG formation using azobenzene-based photochromic amorphous molecular materials are of interest and significance from the viewpoints that such amorphous molecular materials, which are free from polymer chains and their entanglement, may constitute a new class of SRG-forming materials, permitting ready studies of the correlation between molecular structure and SRG formation.

In the light of these considerations, we have investigated SRG formation using an azobenzene-based photochromic amorphous molecular material, 4-[bis(9,9-dimethylfluoren-2-yl)amino]azobenzene (BFlAB), and found that it formed SRG with a relatively high diffraction efficiency of ca. 23% for a probe laser beam of 633 nm and a modulation depth of ca. 280 nm, when its amorphous film was irradiated with two coherent Ar^+ laser beams (488 nm).[13] This result indicates that the existence of a polymer chain is not necessarily required for the formation of SRG and that azobenzene-based photochromic amorphous molecular materials constitute promising candidates for SRG formation.

It is then of great interest and significance to elucidate the difference in SRG-forming properties between amorphous molecular materials and polymers. For this purpose, it is necessary to make direct comparison of SRG-forming properties between azobenzene-based photochromic amorphous molecular materials and polymers containing the same azobenzene chromophore as the pendant group under the same experimental conditions. It is also required that these two materials for comparison should exhibit nearly the same photochromic behavior. In the present study, we have investigated SRG formation using an azobenzene-based photochromic amorphous molecular material, 4-[di(biphenyl-4-yl)amino]azobenzene (DBAB), and a new vinyl polymer containing DBAB as the pendant chromophore, poly[1-(4′-{*N*-(biphenyl-4-yl)-*N*-[4-(phenylazo)phenyl]amino}-biphenyl-4-yl)ethylene] (PVDBAB).[14]



DBAB



PVDBAB

DBAB was prepared by the method reported in our previous paper.[9] It readily forms an amorphous glass with a glass-transition temperature (Tg) of 68 °C. A new vinyl monomer, 4′-{*N*-(biphenyl-4-yl)-*N*-[4-(phenylazo)phenyl]amino}-4-vinylbiphenyl (VDBAB), was synthesized by Suzuki coupling reaction of styrene-4-boronic acid and 4-[*N*-(4-bromophenyl)-*N*-(biphenyl-4-yl)amino]azobenzene (BrPBAB) with Pd catalyst in THF and identified by various spectroscopy, mass spectrometry, and elemental analysis.[15] BrPBAB was synthesized by the reaction of 4-(phenylamino)azobenzene and 4-iodobiphenyl in the presence of Cu, 18-crown-6, and K_2CO_3 in mesitylene, followed by bromination with NBS in $CHCl_3/CH_3COOH$. The corresponding vinyl polymer, PVDBAB, was synthesized by radical polymerization of VDBAB in toluene solution using AIBN as an initiator. The weight-average molecular weight and the molecular weight distribution of the obtained polymer were 42000 and 2.6, respectively, as determined by GPC using polystyrene as a standard. The Tg of PVDBAB was ca. 140 °C, as determined by differential scanning calorimetry.

PVDBAB shows absorption spectra similar to those of DBAB[9] in solution ($\lambda_{max}(\log \varepsilon) = 435$ nm (4.4) for DBAB and 437 nm (4.4) for PVDBAB in toluene) and as amorphous film. DBAB and PVDBAB exhibited almost the same photochromic behavior as amorphous films prepared by spin coating from benzene solution. The *cis*-fraction at the photostationary state was ca. 0.5 for both amorphous films of DBAB and PVDBAB. The *cis-trans* thermal isomerization reactions of DBAB and PVDBAB as amorphous films were also almost the same with each other. The reactions were successfully analyzed by the first-order kinetics consisting of two components ($[cis]_t/[cis]_0 = f_1 \exp(-k_1 t) + f_2 \exp(-k_2 t)$) with the kinetic parameters of $f_1 = 0.03$, $f_2 = 0.97$, $k_1 = 0.14\,\mathrm{min}^{-1}$ and $k_2 = 3.6 \times 10^{-3}\,\mathrm{min}^{-1}$ for DBAB and $f_1 = 0.06$, $f_2 = 0.94$, $k_1 = 0.14\,\mathrm{min}^{-1}$, and $k_2 = 4.3 \times 10^{-3}\,\mathrm{min}^{-1}$ for PVDBAB at 30 °C.

Almost the same photochromic behavior of DBAB and PVDBAB allowed us to compare their SRG-forming properties. When the amorphous films of DBAB and PVDBAB (thickness: ca. 15 μm) were irradiated with coherent, linearly polarized two Ar^+ laser beams (488 nm, 10 mW), SRGs were formed. By the use of two beams with the polarization directions of +45° and −45° with regard to p-polarizaition, a diffraction efficiency of ca. 8% for a probe laser beam (633 nm) and a modulation depths of ca. 200 and 310 nm were obtained for DBAB and PVDBAB, respectively. Figure 1 shows the AFM image of the irradiated sample of PVDBAB. Almost the same diffraction efficiency obtained for DBAB and PVDBAB, irrespective of the smaller modulation depth for DBAB, may result from a larger refractive index of the amorphous molecular material DBAB relative to the vinyl polymer PVDBAB.

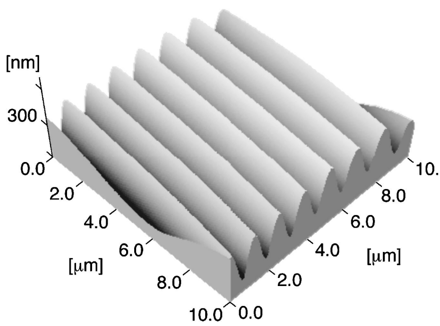


Figure 1. AFM image of the surface of the amorphous film of PVDBAB after irradiation with two coherent writing laser beams (488 nm, 10 mW) with polarization directions of +45° and −45° with regard to *p*-polarizaition.

It is noteworthy that SRG is formed more rapidly for DBAB than for PVDBAB. As Figure 2 shows, whereas the diffraction efficiency reached the maximum in 4 min upon irradiation for DBAB, irradiation for more than 15 min was required for PVDBAB under the same conditions. It is thought that more facile mass transport for the amorphous molecular material, which is free from the restriction by the polymer chain and its entanglement, relative to the vinyl polymer rather than the difference in their Tgs is responsible for the faster formation of SRG for DBAB. In fact, we have found that the irradiation time required for the diffraction efficiency reaching the maximum for other amorphous molecular materials with different Tgs, BFlAB (Tg: 97 °C)[13] and 4-{bis[9,9-di(4-tolyl)fluoren-2-yl]amino}azobenzene (Tg: 144 °C), was nearly the same with that for DBAB. The increase in the diffraction efficiency after the turn-off of the writing beams is thought to be due to the increase of the refractive index caused by the thermal isomerization from the photogenerated *cis*-form to the *trans*-form.

In summary, comparative studies of the formation of SRG using an azobenzene-based photochromic amorphous molecular material, DBAB, and a vinyl polymer containing DBAB as a pendant chromophore, PVDBAB, have been performed. It was found that the diffraction efficiencies of SRGs formed for DBAB and PVDBAB were comparable with each other but that SRG was formed more rapidly for the amorphous molecular material than for the corresponding vinyl polymer.

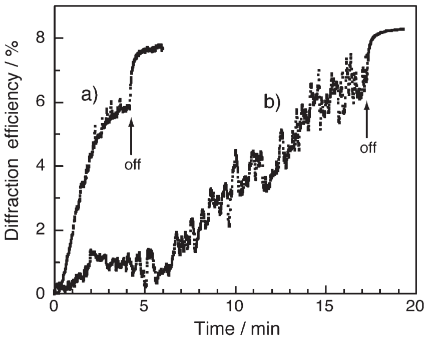


Figure 2. Irradiation time dependence of diffraction efficiency for (a) DBAB and (b) PVDBAB amorphous films.

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15 VDBAB: yield 60%. mp: 149 °C. MS: *m/z* 527 (M^+). ^{1}H NMR (750 MHz, THF-d_8): δ (ppm) = 7.86 (d, 2H, $J = 7.7$ Hz), 7.85 (d, 2H, $J = 8.9$ Hz), 7.65 (d, 2H, $J = 8.7$ Hz), 7.63 (d, 2H, $J = 8.4$ Hz), 7.63 (d, 2H, $J = 8.1$ Hz), 7.62 (d, 2H, $J = 8.3$ Hz), 7.49 (d, 2H, $J = 8.3$ Hz), 7.47 (dd, 2H, $J = 7.6, 7.7$ Hz), 7.41 (t, 1H, $J = 7.6$ Hz), 7.40 (dd, 2H, $J = 7.3, 8.1$ Hz), 7.29 (t, 1H, $J = 7.3$ Hz), 7.27 (d, 2H, $J = 8.7$ Hz), 7.27 (d, 2H, $J = 8.4$ Hz), 7.21 (d, 2H, $J = 8.9$ Hz), 6.75 (dd, 1H, $J = 11.0, 17.6$ Hz), 5.70 (d, 1H, $J = 11.0$ Hz), 5.21 (d, 1H, $J = 17.6$ Hz). ^{13}C NMR (188 MHz, THF-d_8): δ (ppm) = 153.9, 151.4, 148.4, 147.2, 147.1, 141.3, 140.6, 137.9, 137.5, 137.5, 137.3, 131.1, 129.8, 129.5, 128.8, 128.7, 127.9, 127.5, 127.4, 127.4, 126.5, 126.5, 125.1, 123.3, 122.8, 113.7. Calcd for $C_{38}H_{29}N_3$: C, 86.50; H, 5.54; N, 7.96%. Found: C, 86.45; H, 5.62; N, 7.84%.

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