CHEMISTRY of MATERIALS

VOLUME 5, NUMBER 5 MAY 1993

Communications

Azo Oxide Gels for Optical Storage

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Received January 6, 1993
Revised Manuscript Received March 3, 1993

It is now well-known that organic molecules can be incoporated in sol–gel oxide matrices prepared at room temperature in either bulk or film forms by inorganic polymerization of alkoxides monomers.[1,2] Depending on the sol–gel process, the molecules can be freed in the pores or completely trapped in the matrix offering new attractive possibilities in the context of optical information storage and non linear optics.[3,4] For second-order nonlinearities, different organic–inorganic sol–gel precursors have recently been used in which the nonlinear chromophores (2,4-dinitroaniline, *p*-methoxybenzaldehyde, and disperse orange 3) were directly attached to the silicon atom.[5–7] The chemical bonding of the chromophore to the polymer backbone leads to higher concentrations of organic molecules in the polymer and a better orientational stability after the electric field poling employed to introduce noncentrosymmetry required for second-order nonlinearity.

Azo polymers are generally used for the writing records and in reading and erasing steps. Until recently, the samples were made from organic polymers as host passive matrices where the active dye molecules as methyl orange, methyl red, or disperse red 1 were introduced as guest units. These materials are cast on various substrates to provide thin films in which the doping molecules are either dispersed in[8–10] or grafted on[11–13] the polymer backbone. These layered structures are used as polarization holograms or for making channelised waveguides and various patterns. Finally, the optical information is revealed by the observation of the photoinduced anisotropy and dichroism, due to the trans–cis–trans photoisomerization of the active units.[14,15] The birefringence is created when the azo material is illuminated with a monochromatic polarized beam, the wavelength of which is located inside the absorption band of the active azo molecules. The trans–cis–trans isomerization process results in the reorientation of the dipole moment of the active entities. This appears as an alternative poling procedure in soft conditions.

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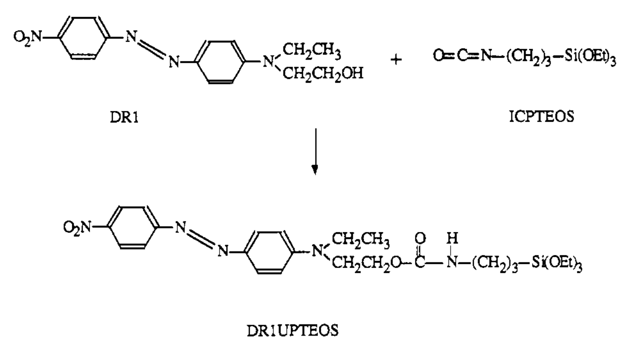

Figure 1. Synthesis of the organosilane monomer (DR1UPTEOS) by reaction between the disperse red 1 (DR1) and the isocyanatopropyltriethoxysilane (ICPTEOS).

In this paper we firstly report the sol–gel preparation of a new organic–inorganic composite material in which the optically nonlinear disperse red 1 (DR1) is covalently bound into the silica network by the coupling of DR1 and of the (3-isocyanatopropyl)triethoxysilane (ICPTEOS). Second, the orientation of organic molecules via the photoisomerization process is demonstrated for the first time inside sol–gel matrices.

Two reference thin-film samples were prepared beforehand for which DR1 molecules are only incorporated in the polymer network without covalent bonding. The first guest/host system (DR1/PMMA at 10 wt %) was prepared by mixing DR1 molecules in a solution of poly(methyl methacrylate) (PMMA) in methyl isobutyl ketone. The second reference system (DR1/ΦTEOS) was a solid solution of DR1 molecules in a xerogel matrix prepared by using the phenyltriethoxysilane precursor. The azo dye was only dissolved in the initial reacting mixture with a silicon:DR1 molar ratio of 250. For these samples, a disadvantage is the limited concentration of active molecules that can be introduced into the sol–gel or organic polymers owing to the tendency for segregation. Moreover, the azo groups were only confined by matrices and orientational relaxations can be probably induced because the azo dye has a rather high mobility in the free volume of the host network.

Concerning the preparation of side-chain oxide gels, the active DR1 molecules were attached to the inorganic polymer backbone via a flexible spacer. This approach allows a high concentration of the incorporated active side groups without segregation and a tailoring of molecular and optical properties via organic synthesis. In addition, as in organic polymers, a reduction of relaxations is expected after optical orientation owing to one-sided anchoring of the optically active molecules. The dye containing monomer was prepared from DR1 and (3-isocyanatopropyl)triethoxysilane (ICPTEOS). The synthetic route was as follows: under slightly elevated temperatures (50–60 °C for 24 h), the hydroxyl groups of the azo dye react with isocyanate groups of the silicon precursor in pyridine. The scheme of the chemical modification of the silicon precursor is shown in Figure 1. The grafting process has been monitored by infrared spectroscopy. During the formation of the alkoxysilane-terminated DR1 (DR1UPTEOS) (Figure 2) the isocyanate group peak (2230 cm^{-1}) disappears while absorption peaks of urethane groups (1685, 1715, and 3310 cm^{-1}) increase. The DR1UPTEOS was isolated by vacuum distillation of the pyridine, washed with toluene, and dried under vacuum. This reaction is attractive because on the one hand it does not give any byproduct and on the other hand it does not deliver any functional group (for example hydroxyls which could condense with alkoxy groups). The coating solution was obtained from copolymerization of the dye attached alkoxysilane with tetraethoxysilane (TEOS) previously hydrolyzed under acidic conditions with ethanol as common solvent. The initial molar ratios of TEOS:DR1UPTEOS:water:ethanol were 1:1:10:6. In such conditions, all the ethoxy groups are removed through hydrolysis reactions.[16]

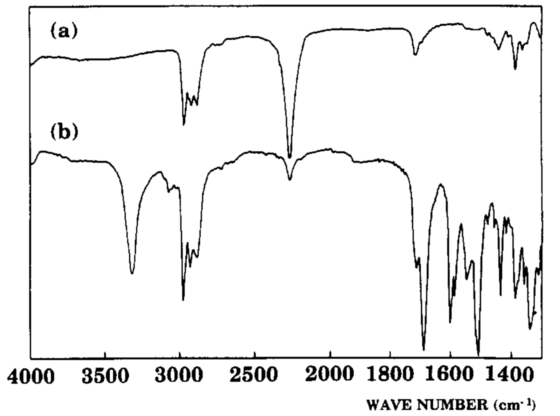

Figure 2. Infrared spectra: (a) (isocyanatopropyl)triethoxysilane (ICPTEOS) with the peak characteristics of the O=C=N— group at 2230 cm^{-1}; (b) organosilane monomer (DR1UPTEOS) with peaks corresponding to -CO-NH-R (amide I), R-O-CO-N (amide II) and NH groups at 1685, 1715, and 3310 cm^{-1}, respectively.

Crack-free sol–gel films were deposited from solution via spin coating onto glass substrates which had been previously cleaned with chromosulfuric acid and rinsed thoroughly with deionized water. The EC101 Headway Research spin coater was used to coat the sol solution on 2.5 × 2.5 cm transparent microscope slides. At the appropriate stage of the polymerization reaction, the viscous sol was poured onto the glass support. The angular velocity of the spinner was 4000 rpm. The samples were left to dry further for a few days at room temperature until the surface of the film became tack-free. The spin coated xerogel composite matrix was smooth and uniform with bright red color.

The DR1 molecules exhibit an absorption band around 490 nm inducing trans–cis photochemical isomerization with a probability proportional to $\cos^2 \Phi$, where Φ is the angle between the dipole moment of the trans molecule and the laser polarization direction. The cis-trans isomerization rapidly takes place both by a thermal relaxation due to the unstability of the cis form at room temperature and through a reverse optical pumping. Azobenzene groups which fall perpendicular to the laser direction at the end of the cis–trans isomerization will be inert to the following photochemical excitation. This leads to an excess of DR1 molecules aligned perpendicular to the laser polarization. The absorption and reorientation sequence is maintained until the molecule dipole moments are perpendicular to the polarization direction of the pump beam corresponding to the saturation of the anisotropy.

Experimental procedure to characterize the induced anisotropy consists in birefringence measurements by the pump–probe method. The samples were probed at normal

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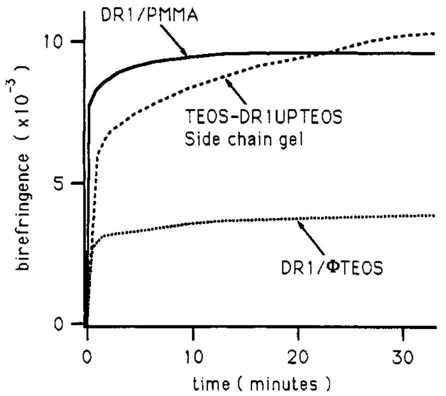

Figure 3. Birefringence as a function of time when the linearly polarized writing beam is switched on.

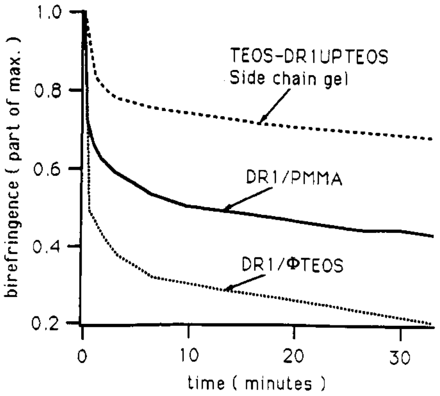

Figure 4. Time dependence of the normalized birefringence when the writing beam is switched off.

incidence with a He–Ne laser beam at λ = 632.8 nm between two crossed polarizers and pumped by an argon laser beam at λ = 488 nm (corresponding to the maximum absorption of DR1), linearly polarized at 45° from polarizers, with a power density of 220 mW/cm^2. In these conditions, the output intensity is given by

$$I = I_0 \sin^2(\pi h \Delta n/\lambda) \tag{1}$$

where I_0 is the transmitted intensity of the He–Ne beam when the two polarizers are parallel, h is the thickness of the film, and Δn is the birefringence.

Figure 3 shows the evolution of the birefringence during the pumping for the three following film samples: (a) 1.5-μm-thick DR1/PMMA guest/host, (b) 2-μm-thick DR1/ΦTEOS guest/host, and (c) 1-μm-thick TEOS-DR1UPTEOS side-chain oxide gel. When the pump was established, the birefringence rapidly increased up to saturation. For the two guest host systems (a) and (b), birefrigence values at saturation ($\Delta n_{\max}$) were 9×10^{-3} after 20 min of pumping and 3×10^{-3} after 40 min of pumping, respectively. The weak value obtained for the guest/host gel could be related to the low concentration of chromophores. In the case of the side-chain gel, the evolution of Δn was very slow and saturation was not reached after 4 h of pumping. At this time, the birefringence value was $\Delta n = 1.5 \times 10^{-2}$.

Figure 4 presents the decay of birefringence when the pump was switched off. For each sample, a first fast relaxation process was observed. As previously explained,[12] this is a consequence of the cis–trans transition of DR1 molecules which were in the cis configuration while the pumping beam was on. The resulting trans groups were randomly oriented and the overall birefringence decreased. Depending on the mobility of molecules in matrices, different slower relaxations were then observed, associated with thermal diffusion. For the DR1/ΦTEOS gel sample, the birefringence decreased to about 70% of saturation after 1 s, 40% after 1 min, and totally disappeared after 2 h. This fast relaxation process is due to the mobility of molecules in the free volume offered by the pores. The relaxation of Δn was much slower in the DR1/PMMA thin film (80% of saturation after 15 s and 40% after 30 min) and, as previously observed,[10] a low value remained at long times (10% after 1 day). In fact, a more important point was that a large memory effect was noted in the TEOS-DR1UPTEOS side chain oxide gel: more than 60% of the maximum birefringence remained 14 h after that the pumping beam was out. This value ($\Delta n = 9 \times 10^{-3}$) was stable for a long time, showing that the memory effect was close to the one previously reported in organic polymers.[13,17]

Finally, a surprising fact is that the absorbance of the TEOS-DR1UPTEOS sample, before pumping, at 490 nm, is only four times higher than the one of the DR1/ΦTEOS sample which has a DR1 concentration which is, at least, 100 times lower. However, it is well-known that electronic absorption spectra of azobenzene units are strongly influenced by their aggregation modes[18] which probably depend on the molecule–matrix interactions. As expected, the shape of the absorption spectrum of the TEOS-DR1UPTEOS sample appears as highly modified in comparison with the one of the DR1/ΦTEOS and further experiments are required for a complete analysis.

In conclusion, we have shown that DR1 nonlinear molecules, and probably many others, can be covalently grafted into an inorganic gel network by using initial coupling of chromophores and of a functionalized silicon alkoxide in which an isocyanate group is connected to alkoxy groups via an inert spacer. By mixing the DR1 attached organosilane with TEOS, dense films can be prepared. From a preliminary optical study, we have demonstrated the ability of DR1 containing gels to store optical information. This suggests possible applications in optical memory, waveguides and second harmonic generation. Further experiments are required to optimize the thin film processing and to synthesize new azo organosilane monomers.

Acknowledgment. The authors wish to thank Dr. Sekkat for the fruitful discussions and valuable advice.

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