the role of molecular weight and polydispersity of the PNIPAAM on the pore size due to LCST of polymer.

In summary, we have prepared uniformly dispersed, temperature-sensitive PNIPAAM in a dense silica matrix using the sol–gel process. Permeation and DSC experiments revealed the LCST behavior of PNIPAAM in silica–polymer hybrid materials and indicated that permeation occurred through pores that are formed due to the hydrophilic to hydrophobic transition of PNIPAAM. Cycling of the membranes between 25 and 40 °C demonstrated reversible toggling of permeability. Permeation experiments on PNIPAAM–silica membranes with various molecular weights of PEG have demonstrated that PNIPAAM molecules dispersed in the hybrid membranes act as molecular switches that can be used to control the selective permeability of the membranes. We are currently exploring ways to extend the versatility of these switches. Possible extensions of this work include the use of multiple smart polymers with different transition properties in the creation of tunable molecular filters and the development of other methods of actuation of the transition (e.g., electrochemical, electrical, or optical).

Experimental

Chemicals used were tetraethyl orthosilicate (TEOS) (Aldrich), PNIPAAM (weight average M_w = 349 200 Da; M_w/M_n = 3.64 from Polysciences, Inc), ethyl alcohol (Aaper), crystal violet (Fischer Scientific), PEG of polymer standard grade with molecular weights (M_w) of 100, 1000, 5000, 9000, and 15 000 with M_w/M_n 1.1 (Polysciences) and PEG (M_w = 400, Aldrich). All chemicals were used as received. Deionized water whose resistivity greater 18.2 MΩ cm from Nanopore was used for all the experiments.

Silica sol was prepared by mixing TEOS, ethanol, water, and HCl in a molar ratio of 1:3:1:0.0007 followed by a reaction at 60 °C for 90 min. The resulting stock sol was stored at –20 °C until use. For each membrane prepared, 0.25 mL of stock sol was diluted with 0.043 mL of water and 0.6 mL of ethanol and stirred well to yield a sol with final proportion TEOS/ethanol/water/HCl = 1:20:5.02:0.0007. Aqueous PNIPAAM solutions (4.4 mg/mL) were prepared at various pHs (2.6, 4, 5, and 7) of which 1 mL was added to the diluted stock sol and stirred to obtain a clear transparent sol. The concentration of PNIPAAM in all cases was 20 % by volume to that of silica [22]. The resultant sols and sols without added PNIPAAM, were coated on Millipore Microcon centrifugal filter units (YM-30 with 30 000 molecular weight cut-off membranes; active membrane area = 0.32 cm^2; diameter = 1.23 cm) at 1500–2000 rpm using a spin coater (Chemat Technology). Uncoated, silica-coated, and silica–PNIPAAM coated filters were sputter coated with platinum and characterized by SEM (Hitachi S-800).

To obtain bulk gels, the sol was aged at room temperature until gelation (see above for gelation times). Silica–PNIPAAM composite gels were washed repeatedly in water and subjected to thermal analytical studies to determine the LCST of PNIPAAM in silica gel matrix. Differential scanning calorimetric studies were carried out using a Universal V2.5H TA instrument. 40–50 mg of sample was used for the measurements. Experiments were carried out both in heating and cooling cycles in nitrogen atmosphere with heating/cooling rates of 1 K/min. Silica gel without PNIPAAM obtained from the sol–gel process was used as a reference.

Permeation experiments were carried out using an IEC Centra CL3R centrifuge at various temperatures ranging from 25 to 40 °C with a controlled temperature of ±1 °C. 100–300 µL of solute (crystal violet (0.1 wt.-% aqueous solution), PEGs (1–3 wt.-% aqueous solutions)) were centrifuged in uncoated, silica-coated, and silica–PNIPAAM-coated YM-30 centrifugal filters. Unless otherwise indicated, permeation experiments were done at 1000 rpm, equivalent to an estimated centrifugal field of 200 × *g* (gravities) for 3 min. Permeation experiments were carried out at various temperatures. Initially the samples were equilibrated to the test temperature in an oven for 10 min and transferred to the centrifuge, which was maintained at the set temperature and the samples were again equilibrated at that temperature and then centrifugation was carried out. The concentration of crystal violet in the filtrate was determined from ultraviolet (UV) spectrophotometric measurements at 591 nm. For PEG experiments, the concentration of the filtrate was determined from refractive index measurements using a Kernco refractrometer by comparing to the calibration curve obtained by measuring the refractive index of known concentrations of PEG. For measuring the refractive index of the filtrate, we need a minimum of 100 µL of filtrate. To obtain this amount, experiments were carried out 2000 rpm for 30 min. Prior to high temperature permeation, membranes were found to be impermeable at 2000 rpm for almost 1 h at 25 °C. The minimum concentration of PEG, which can be measured using a refractometer, was determined to be 0.3 wt.-%.

Received: May 19, 2000
Final version: July 27, 2000

---

[1] H. G. Schild, *Prog. Polym. Sci.* **1992**, *17*, 163.
[2] I. Y. Galaev, *Russ. Chem. Rev.* **1995**, *64*, 471.
[3] M. Meewes, J. Ricka, M. de Silva, R. Nyffenegger, T. Binkert, *Macromolecules* **1991**, *24,* 5811.
[4] L. C. Dong, A. S. Hoffman, *J. Controlled Release* **1991**, *15*, 141.
[5] L. C. Dong, Q. Yan, A. S. Hoffman, *J. Controlled Release* **1992**, *19*, 171.
[6] L. K. Ista, G. P. Lopez, *J. Ind. Microbiol. Biotechnol.* **1998**, *20*, 121.
[7] L. K. Ista, V. H. Perez-Luna, G. P. Lopez*, Appl. Environ. Microbiol.* **1999**, *65*, 1603.
[8] M. V. Badiger, M. G. Kulakarni, R. A. Mashelkar, *Chem. Eng. Sci.* **1992**, *47*, 3.
[9] S. J. Trank, D. W. Johnson, E. L. Cussler, *Food Technol.* **1989**, *43*, 78.
[10] A. Gutowska, Y. H. Bae, H. Jacobs, F. Mohammad, D. Mix, J. Feijen, S. W. Kim, *J. Biomed. Mater. Res.* **1995**, *29*, 811.
[11] A. S. Hoffman, *Mater. Res. Bull.* **1991**, 42.
[12] H. Kanazawa, K. Yamamoto, Y. Matsushima, N. Takai, A. Kikuchi, Y. Sakurai, T. Okano, *Anal. Chem.* **1996**, *68*, 100.
[13] M. Gewehr, K. Nakamura, N. Ise, *Makromol. Chem.* **1992**, *193*, 249.
[14] D. J. Beebe, J. S. Moore, J. M. Bauer, A. Yu, R. H. Liu, C. Devadoss, B. H. Jo, *Nature* **2000**, *404*, 588.
[15] Y. Okahata, H. Noguchi, T. Seki, *Macromolecules* **1986**, *18*, 493.
[16] T. Nonaka, T. Ogata, S. Kurihara*, J. Appl. Polym. Sci.* **1994**, *52*, 951.
[17] T. Tsuji, M. Konno, S. Sato, *J. Chem. Eng. Jpn.* **1990**, *23*, 447.
[18] D. O'Connor, P. Barnes, D. R. Bates, D. F. Lander, *Chem. Commun.* **1998**, 2527.
[19] *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing* (Eds: C. J. Brinker, G. W. Scherrer), Academic, San Diego, CA **1990**.
[20] M. J. Vanbommel, T. Wolde, T. N. M. Bernards, *J. Sol–Gel Sci. Technol.* **1996**, *2*, 61.
[21] Y. Haruvy, S. E. Webber, *Chem. Mater.* **1991**, *3*, 501.
[22] Y. Lu, G. Cao, R. P. Kale, S. Prabakar, G. P. Lopez, C. J. Brinker, *Chem. Mater.* **1999**, *11*, 1223.
[23] H. W. Schild, D. A. Tirrell, *J. Phys. Chem.* **1990**, *94*, 4352.
[24] K. Otake, H. Inomata, M. Konno, S. Saito, *Macromolecules* **1990**, *23*, 283.
[25] D. W. Urry, *J. Phys. Chem.* **1997**, *101*, 11 007.

Sol-Gel-Derived Mesoporous Silica Films with Low Dielectric Constants**

By *Seana Seraji*, *Yun Wu*, *Michael Forbess*,
Steven J. Limmer, *Tammy Chou*, and *Guozhong Cao**

A great deal of intensive research has been conducted on low dielectric constant materials for inter-metal-dielectric integrated-circuit (IMD-IC) applications.[1,2] A variety of

---

[*] Prof. G. Z. Cao, S. Seraji, Dr. Y. Wu, M. Forbess, S. J. Limmer, T. Chou
Department of Materials Science and Engineering
University of Washington
Seattle, WA 98195-2120 (USA)
E-mail: gzcao@u.washington.edu

[**] The authors thank the University of Washington Center for Nanotechnology for their financial support through fellowships. The authors also thank Dr. B. Flinn for his assistance in conducting the thermal analysis (NSF grant # DMR 9410981). S.S. thanks the Ford Motor Company for a fellowship. Y.W. thanks the NSF-IGERT for a fellowship.

materials have been studied and examples include non-fluorinated polymers,[3] inorganic–organic hybrids,[3,4] and porous polymers[5,6] and silica.[7–9] The dielectric constant is the physical property that describes the electric polarizability of a dielectric. There are four possible polarization mechanisms: electronic, ionic, dipolar, and interfacial polarization and the dielectric constant is the sum of the contributions from all four possible polarization mechanisms. It is obvious that in order to achieve a low dielectric constant, ionic, dipolar, and interfacial polarization would need to be eliminated; this could be achieved by carefully selecting materials that consist of highly covalent chemical bonds with non-polar crystal structure. In addition, the material should have no local electrical conduction. However, electronic polarization is present in all solid materials and is dependent on both the atomic size and the atomic density. The above consideration explains the fact that much research on low dielectric constant materials has been on various polymers.[3,10] Further reduction in dielectric constant can only be achieved by introducing porosity into the materials, since air has the lowest dielectric constant (of 1), and the dielectric constant of a composite is determined by the mixture rule.[11] However, porous structures have other problems such as mechanical integrity, moisture sensitivity, and thermal and chemical stability. For mesoporous inorganic films, one of the greatest challenges is the condensation of moisture inside pores when exposed to the ambient environment, resulting in an increased dielectric constant.

In this communication, we report our preliminary results on sol-gel-derived mesoporous silica films with low dielectric constant and possibly closed pores. The technical approach was conceptually straightforward: use a multiple-step sol-gel processing to produce a composite structure with highly porous clusters embedded into a dense matrix as schematically illustrated in Figure 1. Using this process, thin films were made by dip-coating and followed with heat-treatments at 300 °C, 400 °C, and 450 °C. The relationship between the microstructure, dielectric properties, and aging effect were discussed as well.

A multiple step sol-gel process was developed to produce a mesoporous silica–based gel. Two types of organic–inorganic hybrid sols were prepared: A sol consisting of linear oligomers, which would form a dense matrix and hereinafter referred to as sol A, was prepared by admixing tetraethylorthosilicate (TEOS), $Si(OC_2H_5)_4$, and methacryloxypropyltrimethoxysilane (MPS), $H_2CC(CH_3)CO_2(CH_2)_3Si(OCH_3)_3$, in a molar ratio of 95:5 with HCl as a catalyst, following the same procedure as described in the literature.[12] Another sol consisting of highly branched clusters (referred to as sol B) was made by mixing TEOS and methyltriethoxysilane (MTES), $CH_3Si(OC_2H_5)_3$, in a molar ratio of 1:1 with NH_4OH as a catalyst, following the same experimental procedure as published previously.[13] Both sols were allowed to age for half of their respective gelation times at room temperature and then admixed with a volume ratio of A/B = 0.3:0.7. Prior to coating, the AB sol was further diluted with ethanol in a volume of AB sol/ethanol = 1:2. The films were made by dip-coating the diluted AB sol onto either silicon or platinum sputtered silicon substrates in an ambient environment, using a withdrawal speed of approximately 14 cm/min. After each coating, the film was dried in ambient conditions for 5 min and then heat-treated at 250 °C for 5 min to remove the residual solvent. For most samples, three coatings were made. Then, the films were heated at 300 °C for 120 min in air to remove all of the residual solvent. Some films were further heated to 400 °C for 30 min and other films were fired at 450 °C for 30 min. The AB sol was also poured into a petri dish to form xerogel, which was used for thermal gravimetric and differential thermal analyses (TGA/DTA). Dielectric properties of the films were measured using a Hewlett Packard Precision 4284A LCR Meter at frequencies ranging from 20 Hz to 1 MHz by a metal–insulator–metal parallel-plate capacitance method in the ambient environment. The thickness and porosity of the films were determined by ellipsometry. The film thickness was further verified with an optical imaging profilometer and by scanning electron microscopy (SEM).

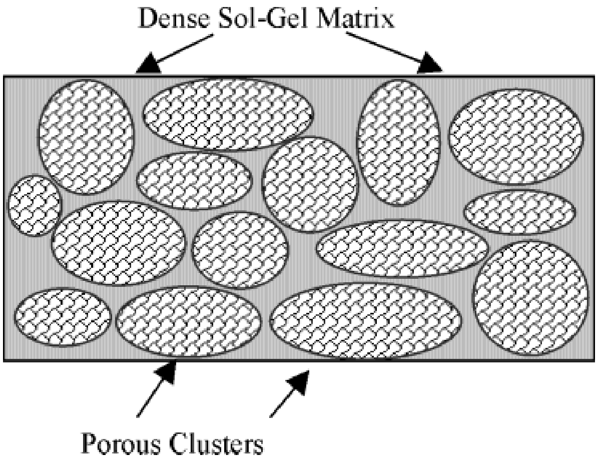

Fig. 1. Schematic illustration of mesoporous sol-gel-derived silica film.

Optical microscopy and SEM analyses indicated that the films were uniform and crack-free, and the films adhered very well to the substrates as revealed by tape testing. The thickness was found to be ~910 nm for the films with three coatings and treated at 450 °C, which implies that each coating produced a film of approximately ~300 nm in thickness. It was also found that the film thickness decreased as the temperature of heat treatment increased; the thickness of 300 °C and 400 °C films were estimated to be ~1100 and ~950 nm, respectively. Figure 2 is an SEM micrograph of a cross section of a sample with two coatings, treated at 450 °C, illustrating the thickness and uniformity of the film. TGA/DTA analysis of the xerogels from gel A[14] and gel B[15] revealed that organic ligands $H_2CC(CH_3)CO_2(CH_2)_3^{\bullet}$ and $CH_3^{\bullet}$ began to be pyrolyzed at 350 °C and 400 °C, respectively. These results were verified by performing TGA/DTA analysis on the composite gel, as can be seen in Figure 3. The film treated at 300 °C retained both organic ligands $H_2CC(CH_3)CO_2(CH_2)_3^{\bullet}$ and $CH_3^{\bullet}$, which were incorporated into the silica network during the sol-gel processing through co-polymerization. The film

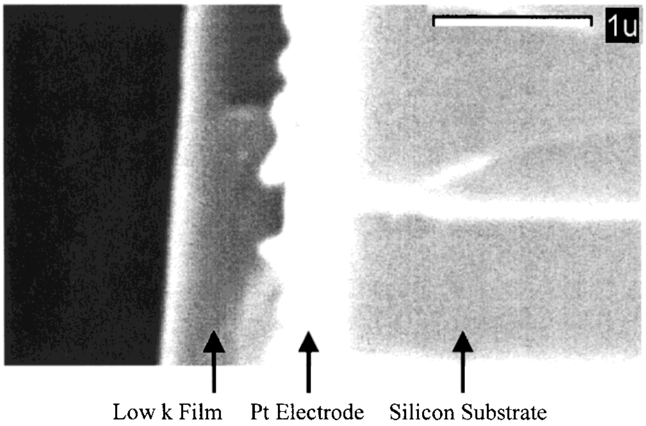

Fig. 2. SEM micrograph of cross section of sol-gel film.

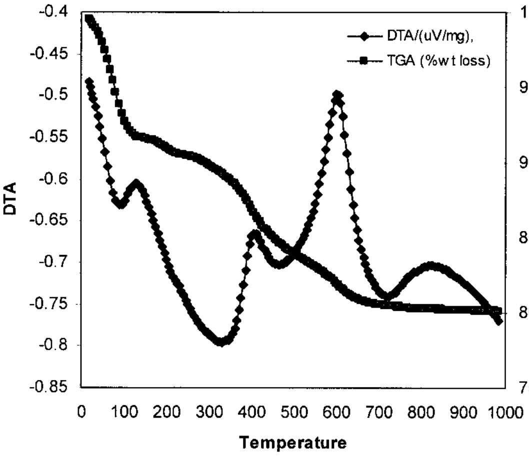

Fig. 3. TGA/DTA data from composite AB gel.

subsequently treated at 400 °C would consist of a very small amount of organic components. The pyrolysis may not have been complete, thus leaving some residual carbon components. All of the organic components were removed completely from the film that was further treated at 450 °C. The porosity of this film was found to be approximately 50 %, calculated from the index of refraction using the Lorentz–Lorenz equation.[16] Direct current (DC) conductivity of the 450 °C films was found to be $>3 \times 10^9\ \Omega$ cm at room temperature.

Figure 4 shows the dielectric constants of the films treated at 300 °C, 400 °C, and 450 °C as a function of frequency. The dielectric constants of the 300 °C film were found to be much higher than the other two samples; whereas the dielectric constants of both 400 °C and 450 °C samples were almost identical, except at low frequencies. The relatively high dielectric constants of 300 °C film could be attributed to the presence of organic components. The removal of organic components from the films when fired at 400 °C or 450 °C resulted in an increased pore volume in the films, although accompanied with small shrinkage of film thickness. An increased pore volume would explain the reduced dielectric constants of the 400 °C and 450 °C films. A sharp decrease in the dielectric constants of the 400 °C film with an increasing frequency at the low frequency range may be attributed to possible space–charge polarization, as a result of residual carbon components from incomplete pyrolysis. Although there was no space–charge polarization in the 450 °C film, slightly reduced porosity would lead to an increase in dielectric constant. As a result, similar dielectric constants were found for films treated at 400 °C and 450 °C.

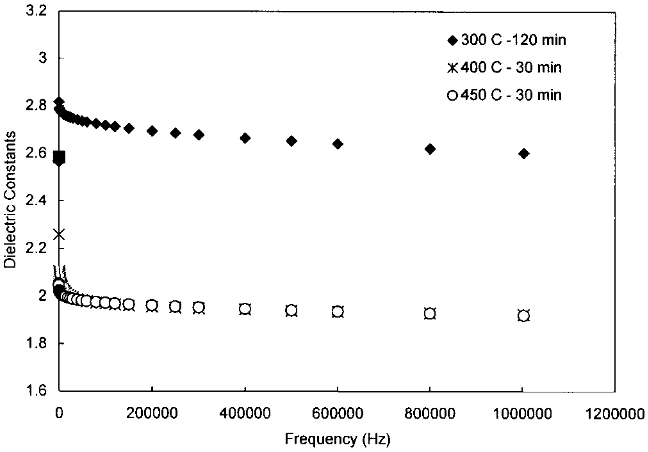

Fig. 4. Dielectric constants as a function of frequency for 300 °C, 400 °C, and 450 °C films, measured at room temperature.

Figure 5 shows the loss tangent as a function of frequency for all three films. It is seen that the loss tangent generally decreases with an increase in heat-treatment temperature. The high loss tangent at low frequencies for the 400 °C film would also be attributed to the space–charge polarization, due to the possible residual carbon components resulted from the incomplete pyrolysis. This figure also reveals that the loss tangent increased with an increasing frequency. The exact mechanism causing this increase with frequency is not known, however, the hydroxyl or silanol groups may be the cause. As the resonant frequency of the hydroxyl or silanol group is approached, an increase in loss tangent would be expected. In a separate study, Fourier transform infrared (FTIR) analyses revealed that the concentration of hydroxyl or silanol groups

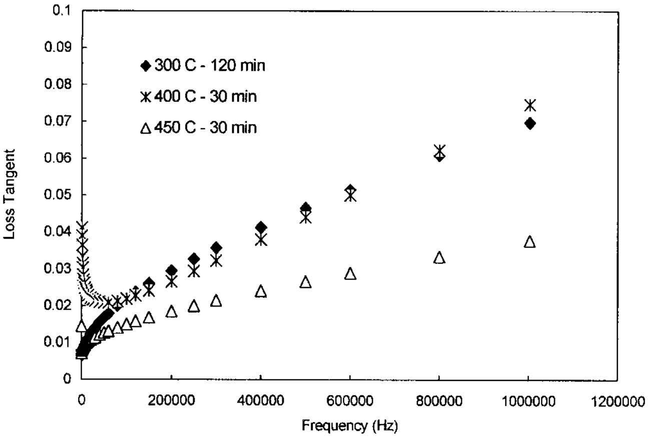

Fig. 5. Loss tangent as a function of frequency for 300 °C, 400 °C, and 450 °C films, measured at room temperature.

in sol-gel-derived silica decreases gradually with an increased heating temperature.[17] A reduced concentration of hydroxyl or silanol groups would result in a reduced loss tangent.

Figure 6 presents the dielectric constants and loss tangent of the 450 °C film as functions of aging time; the film was aged at an ambient environment: ~20 °C and a relative humidity of 56 %. It was found that there was only a slight initial increase in both dielectric constant and loss tangent in the first two-days of aging. Further aging resulted in no detectable change in both dielectric constant and loss tangent. The results imply that there was no significant moisture condensation inside pores, though there was approximately 50 % porosity (with an average pore size of ~8 nm according to our previous work[13]). Absence of moisture condensation further implies the possibility that the films have a closed pore structure; however, further analysis is required to verify the mesoporous structure.

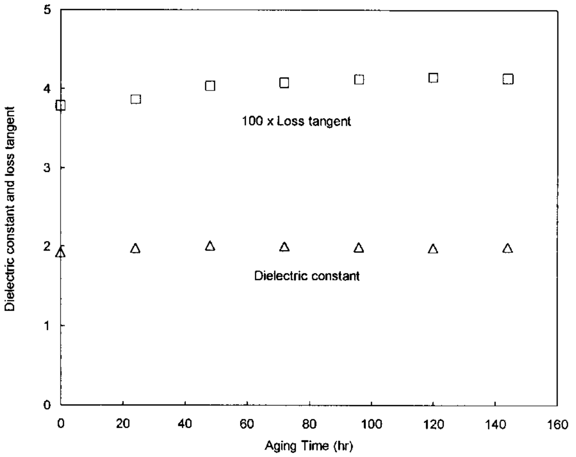

Fig. 6. Dielectric constants and loss tangent of 450 °C film as a function of aging time at room temperature and relative humidity of 56 %, measured at 1 MHz.

In summary, uniform crack-free mesoporous silica films with a dielectric constant of less than 2 were produced using multiple-step sol-gel processing. It was found that the films adhered well to the substrates and had a porosity of 50 % after removal of organic components. The dielectric properties were found unchanged when the films were subjected to aging at room temperature over 6 days with a relatively humidity of 56 %.

Received: June 20, 2000
Final version: July 31, 2000

---

[1] W. W. Lee, P. S. Ho, *MRS Bull.* **1997**, *22*, 19.
[2] *Low-Dielectric Constant Materials II*, Vol. 443 (Eds: A. Lagendijk, H. Treichel, K. J. Uram, A. C. Jones), Materials Research Society, Pittsburgh, PA **1997**.
[3] N. H. Hendricks, *Mater. Res. Soc. Proc.* **1997**, *443*, 3.
[4] R. D. Miller, J. L. Hedrick, D. Y. Yoon, R. F. Cook, J. P. Hummel, *MRS Bull.* **1997**, *22*, 44.
[5] A. T. Kohl, R. Mimna, R. Shick, L. Rhodes, Z. L. Wang, P. A. Kohl, *Electrochem. Solid-State Lett.* **1999**, *2*, 77.
[6] Y. Xu, Y.-P. Tsai, K. N. Tu, B. Zhao, Q.-Z. Liu, M. Brongo, G. T. Sheng, C. H. Tung, *Appl. Phys. Lett.* **1999**, *75*, 853.
[7] S. Baskaran, J. Liu, K. Domansky, N. Kohler, X. Li, C. Coyle, G. E. Freyxell, S. Thevutharampillai, R. E. Williford, Adv. Mater. **2000**, *12*, 291.
[8] D. Zhao, P. Yang, N. Melosh, J. Feng, B. F. Chmelka, G. D. Stucky, *Adv. Mater.* **1998**, *10*, 1380.
[9] C. Jin, J. D. Luttermer, D. M. Smith, T. A. Ramos, *MRS Bull.* **1997**, *22*, 39.
[10] C. B. Case, C. J. Case, A. Kornblit, M. E. Mills, D. Castillo, R. Liu, *Mater. Res. Soc. Proc.* **1997**, *443*, 177.
[11] A. J. Moulson, J. M. Herbert, *Electroceramics*, Chapman and Hall, London **1990**.
[12] C. M. Chan, G. Z. Cao, H. Fong, M. Sarikaya, T. Robinson, L. Nelson, *J. Mater. Res.* **2000**, *15*, 148.
[13] G. Z. Cao, H. Tian, *J. Sol-Gel Sci. Technol.* **1998**, *13*, 305.
[14] G. Z. Cao, Y. F. Lu, L. Delattre, C. J. Brinker, G. P. López, *Adv. Mater.* **1996**, *8*, 588.
[15] H. Tian, *MS Thesis*, University of Washington **1997**.
[16] C. J. Brinker, G. W. Scherer, *Sol-Gel Science*, Academic, San Diego, CA **1990**, p. 803.
[17] X. H. Han, G. Z. Cao, T. Pratum, D. S. Schwartz, B. Lutz, *J. Mater. Sci.*, in press.

Photopolymerizable Cholesteric Liquid Crystals—New Materials for Holographic Applications**

By *Ulrich Theissen*, *Stephan J. Zilker*, *Thomas Pfeuffer*, and *Peter Strohriegl**

Today's information society has an increasing demand for data storage systems with high capacity and transfer rate. Organic materials such as photoaddressable polymers[1] and photopolymers[2,3] are promising candidates for holographic storage schemes that fulfill both of the above requirements. Photopolymers are write-once materials; however, their irreversibility provides excellent long-time stability. A typical system consists of a monomer and a binder polymer. Patterned exposure (either by holography or by a photomask) activates a photoinitiator in the bright regions of the pattern and photopolymerization occurs. As monomers are consumed, the concentration gradients formed prompt net migration of monomers from the dark into the bright regions. A refractive index modulation arises due to density differences between the two regions. Photopolymerization is completed by UV-irradiation and the image is permanently fixed.

Liquid-crystalline (LC) monomers that can be photopolymerized have not been widely used for holography so far.[4,5] However, such systems have been extensively studied for use as optical components (notch and color filters, reflective polarizers, and many more),[6] color-flop pigments,[7,8] and "copy safe" colors. Hereby, the specific optical properties of the cholesteric liquid-crystalline (CLC) phase, in particular its selective reflection and the angular dependence of the reflection wavelength, are used.

In this communication we present a novel photopolymer based on a CLC mixture that yields holograms even for uni-

---

[*] Prof. P. Strohriegl, T. Pfeuffer
Makromolekulare Chemie I und BIMF, Universität Bayreuth
D-95440 Bayreuth (Germany)
E-mail: peter.strohriegl@uni-bayreuth.de

U. Theissen, Dr. S. J. Zilker
Physikalisches Institut und BIMF, Universität Bayreuth
D-95440 Bayreuth (Germany)
E-mail: ulrich.theissen@uni-bayreuth.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft (SFB 481). We are grateful to the Farbenlaboratorium of BASF AG for the chiral sorbitol derivative, Ciba Speciality Chemicals for the photoinitiator, and Dr. T. Bieringer for helpful discussions.