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Interface-Directed Web-to-Pillar Transition of Microphase-Separated Siloxane Gels

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Received May 9, 2003. In Final Form: September 10, 2003

A unique pillar structure of methylsiloxane gel in microfabricated grooves was developed through the competition of phase separation and wetting. In the course of the phase separation in the methylsiloxane sol–gel system, the siloxane phase completely wetted the surface of the grooves while forming material transfer channels, which were arrested as a permanent structure by the sol–gel transition. The phase-separated structure shows an isotropic weblike bicontinuous structure in the grooves wider than the critical value. However, in the narrower grooves, only the pillar structure remained, showing a web-to-pillar transition. The critical value is nearly equal to the characteristic length of the bulk.

Introduction

Phase separation, especially spinodal decomposition (SD), in polymeric systems near a symmetric composition usually results in an isotropic bicontinuous structure,^{1,2} in which both separated phases are interconnected. When a system is confined in a small space, the phase separation behavior is significantly affected by the preferential wetting of one component on the existing surface.^{3–9} The relationship between morphology evolution via phase separation and wetting has been extensively studied because of its importance for various applications and its rich physics.^{10–14} In a liquid polymer solution or blend systems, preferential wetting by one component on a contacting surface during phase separation has been reported to lead to a temporary pillarlike structure by Tanaka. The pillars are thought to act as material transfer channels for the hydrodynamic pumping of a more

wettable phase on a confining surface.^{15–17} In the early step in SD in a confined space, isotropic bicontinuous phase separation develops first, and soon after that, a more wettable phase flows to the confining wall through bicontinuous channels, forming pillarlike material transfer channels. This transient structure will grow or decay in accordance with the shape of the surface and compositional symmetry.¹⁷

So far, we have investigated the phase separation behavior in confining molds in methylsiloxane sol–gel systems,^{18–20} in which significant structural deformation occurs as a result of the preferential wetting of the siloxane phase onto the surface of the mold. In a “closed” confined space, elongated gel skeletons usually form perpendicular to the surface in the proximity of surfaces, while the bicontinuous structure remains in the near-center region of the space. In these closed systems, the transition to complete wetting (wetting transition) occurs when the characteristic length of the bulk gel, Λ_m , exceeds the scale of the mold, D ; that is, D/Λ_m becomes less than unity.²⁰ The detailed definition of D/Λ_m is described in the following section.

In the present letter, a distinct transition from an isotropic bicontinuous structure to a “pillar structure” in fine “open” grooves is demonstrated. This web-to-pillar transition is significantly affected by the wetting dynamics of the methylsiloxane gel as well.

Experimental Section

The experimental procedure was quite simple. A template glass chip with a varied width of microfabricated grooves was put in the starting solution. The molar ratio of the starting solution was 1:2.3:2.5 methyltrimethoxysilane (MTMS)/formamide (FA)/H₂O, and the sample was prepared as follows. First, 7.23 g of FA and 3.37 g of 1.0 M nitric acid were mixed in a glass sample tube, and then, 10 mL of MTMS was added under vigorous stirring and ice-cooled conditions. After stirring for 5 min, the template chip was put in the solution, and the whole solution was allowed

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(1) Binder, K. In *Materials Science and Technology, A Comprehensive Treatment*; Cahn, R. W., Haasen, P., Kramer, E. J., Eds.; VCH: Weinheim, 1990; Vol. 5, p 405.

(2) Nakanishi, K. *J. Porous Mater.* **1997**, *4*, 67–112.

(3) Jones, R. A. L.; Norton, L. J.; Kramer, E. J.; Bates, F. S.; Wiltzius, P. *Phys. Rev. Lett.* **1991**, *66*, 1326–1329.

(4) Bruder, F.; Brenn, R. *Phys. Rev. Lett.* **1992**, *69*, 624–627.

(5) Krausch, G.; Dai, C.; Kramer, E. J.; Bates, F. S. *Phys. Rev. Lett.* **1993**, *71*, 3669–3672.

(6) Krausch, G.; Dai, C.; Kramer, E. J.; Marko, J. F.; Bates, F. S. *Macromolecules* **1993**, *26*, 5566–5571.

(7) Krausch, G. *Mater. Sci. Eng. Rep.* **1995**, *R14*, 1–94.

(8) Geoghegan, M.; Jones, R. A. L.; Clough, A. S. *J. Chem. Phys.* **1995**, *103*, 2719–2723.

(9) Cherrabi, R.; Saout-Elhach, A.; Benhamou, M. *J. Chem. Phys.* **1999**, *111*, 8174–8181.

(10) Steiner, U.; Klein, J.; Eiser, E.; Budkowski, A.; Fetters, L. J. *Science* **1992**, *258*, 1126–1129.

(11) Böltau, M.; Walheim, S.; Mlynek, J.; Krausch, G.; Steiner, U. *Nature* **1998**, *391*, 877–879.

(12) Kielhorn, L.; Muthukumar, M. *J. Chem. Phys.* **1999**, *111*, 2259–2269.

(13) Moffitt, M.; Rharbi, Y.; Li, H.; Winnik, M. A. *Macromolecules* **2002**, *35*, 3321–3324.

(14) Steinhart, M.; Wendorff, J. H.; Greiner, A.; Wehrspohn, R. B.; Nielsch, K.; Shilling, J.; Choi, J.; Gösele, U. *Science* **2002**, *296*, 1997.

(15) Tanaka, H. *Phys. Rev. Lett.* **1993**, *70*, 53–56.

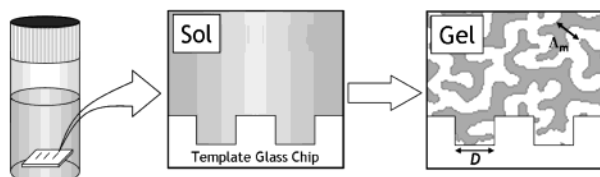
(16) Tanaka, H. *Phys. Rev. Lett.* **1993**, *70*, 2770–2773.

(17) Tanaka, H. *J. Phys.: Condens. Matter* **2001**, *13*, 4637–4674.

(18) Kanamori, K.; Ishizuka, N.; Nakanishi, K.; Hirao, K.; Jinnai, H. *J. Sol-Gel Sci. Technol.* **2003**, *26*, 157–160.

(19) Kanamori, K.; Nakanishi, K.; Hirao, K.; Jinnai, H. *Langmuir* **2003**, *19*, 5581–5585.

(20) Kanamori, K.; Nakanishi, K.; Hirao, K.; Jinnai, H. *Colloids Surf., A*, submitted for publication.



Reaction Vessel

Figure 1. Schematic illustration of the sample preparation. The enlarged parts depict the near-surface region of the template glass chip, where the starting solution turns to gel accompanied by phase separation. Obviously, the outer solution (or gel) and the grooves are continuous in both the sol and the gel states. The width of a groove, D , and the characteristic length of the bicontinuous structure, Λ_m , are also shown.

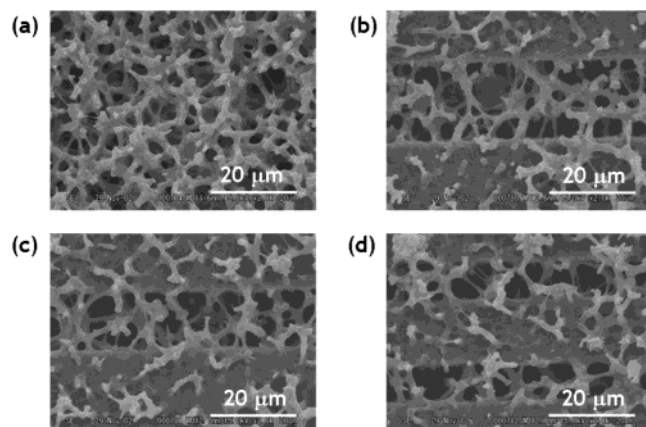


Figure 2. SEM photographs of phase-separated siloxane gels: (a) bulk portion, (b) in a 20- μm -wide groove, (c) in a 15- μm -wide groove; and (d) in 10- μm -wide grooves. The characteristic length, that is, the spinodal wavelength of the bulk, is 8.3 μm , determined by three-dimensional FFT on the digitized sliced images.²¹ The weblike bicontinuous structure developed homogeneously in the grooves as well as the bulk is confirmed.

to gel at 40 $^{\circ}\text{C}$ in a closed container. After gelation, the sample was aged for more than 24 h at 40 $^{\circ}\text{C}$ and then dried for about 72 h at the same temperature.

In Figure 1, a schematic illustration of the procedure is shown. Grooves on the template chip and outer solution are continuous, and the solution turns to a gel within the grooves. Here, we introduce the reduced scale of the mold, D/Λ_m , to compare with the result of the previous studies.^{20,22} D is the width of a groove, and Λ_m is the characteristic length (skeleton size plus pore size in this case) of the bicontinuous structure, as indicated in Figure 1.

Results and Discussion

A scanning electron microscopy (SEM) photograph of the bulk gel, which was prepared in a large enough container with effectively no confinement effect, is shown in Figure 2a, and its characteristic length Λ_m (nearly equal to the spinodal wavelength) is calculated to be 8.3 μm by three-dimensional fast Fourier transformation (FFT) of digitized sliced images. These analyses were performed by laser scanning confocal microscopy (LSCM),²¹ and the detailed procedures can be found elsewhere.^{20–21} Especially from the three-dimensional reconstructed image (not shown), the isotropic bicontinuous structure, in which both the siloxane gel skeleton and macropores are interconnected, can be clearly corroborated.

Inside the grooves that have a greater width than the bulk characteristic length (8.3 μm), the isotropic bicon-

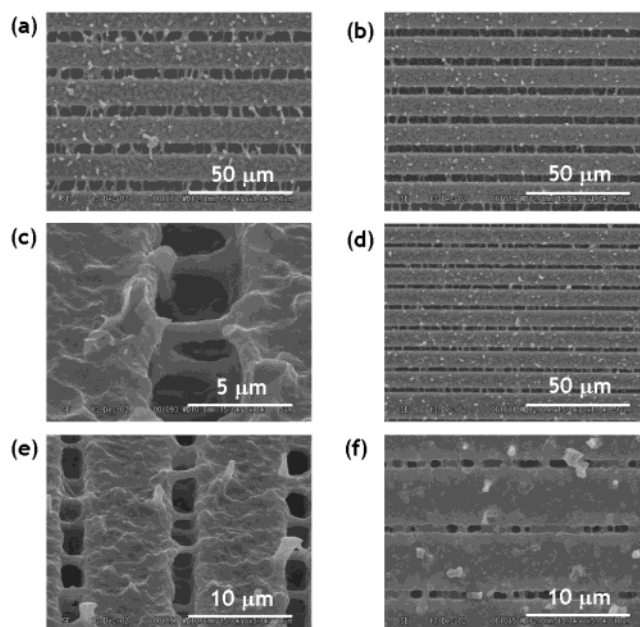


Figure 3. SEM photographs of the phase-separated siloxane gel in narrower-width grooves: (a) 7 μm , (b) and (c) 5 μm , (d) and (e) 3 μm , and (f) 1 μm . In 7- μm -wide grooves, because the weblike bicontinuous phase separation does not occur, only pillars remain in the fine grooves, exhibiting a web-to-pillar transition. In the narrower groove, more aligned gel pillars are formed (b–f). The well-aligned pillars exist not only on the surface of open grooves but also deep inside the grooves, which can be clearly seen in 45- $^{\circ}$ -angled photographs (c and e).

tinuous structure with a weblike morphology can be confirmed, as shown in Figure 2b–d. The widths and the values of D/Λ_m of these grooves are (a) 20 μm , $D/\Lambda_m = 2.4$; (b) 15 μm , $D/\Lambda_m = 1.8$; and (c) 10 μm , $D/\Lambda_m = 1.2$. In these grooves, an almost homogeneous disordered morphology similar to that of the bulk gel has formed. In the case of the “closed” mold, significantly deformed gel structures were obtained around these values of D/Λ_m mainly as a result of the preferential wetting of the siloxane phase onto the surfaces;^{18–20} however, such deformation is absent in the present case. This is probably because the upper surface of the grooves is open to the outer reacting solution, so the wetting component (siloxane phase) can be supplied continuously from the outer gelling solution. The deformed part formed in the “closed” molds was found to have large values of mean curvature,²⁰ which is unfavorable from the viewpoint of interfacial energy, so the bicontinuous structure in the “open” grooves tends to remain isotropic as long as the wetting component is supplied.

In clear contrast, upon decreasing the width of the grooves to a size comparable to the bulk characteristic length, a sudden transition from the web to the pillar structure was observed. As shown in Figure 3a, in the 7- μm -wide grooves ($D/\Lambda_m = 0.84$), only the self-organized gel pillars remain. The shapes of these pillars are still rather disordered; however, the web-to-pillar transition is clearly confirmed. When the width of a groove becomes less than the bulk characteristic length, the bulk bicontinuous structure is no more able to be coarsened as a result of the strict geometrical confinement by the grooves. As a result, the web-to-pillar transition is promoted. Though the formation mechanism remains unclear, these pillars are thought to be the remaining part of the material transfer channels.^{15–17} What is intriguing in this case is that the material transfer channels, which are normal to the basal plane of the grooves, have disappeared, and only the channels that are parallel to the basal plane remain.

(21) Jinnai, H.; Nishikawa, Y.; Morimoto, H.; Koga, T.; Hashimoto, T. *Langmuir* **2000**, *16*, 4380–4393.

(22) Jinnai, H.; Kitagishi, H.; Hamano, K.; Nishikawa, Y.; Takahashi, M. *Phys. Rev. E* **2003**, *67*, 021801.

In the previously reported “closed” confining conditions, a transition from the deformed bicontinuous structure to complete wetting was observed when D/Λ_m became less than unity. Here again, the possibility is that the difference comes from the confining conditions, that is, “open” or “closed”.

On further decreasing the width, gel pillars tend to align nearly normal to the parallel walls. Figure 3b–f shows the SEM photographs of gel pillars in 1–5- μm -wide grooves, in which more aligned pillars are corroborated. From 45°-angled SEM photographs (Figure 3c,e), it is obviously verified that these pillars form not only near the open surface of the grooves but also deep inside them, and the MTMS-derived siloxane gel phase wets the inside surface of the grooves completely. In the grooves with 1- μm widths (Figure 3e), gel pillars are rather fattened by re-absorbing the siloxane components from the wetting layer. According to Tanaka,¹⁷ pillars with diameters greater than the width of the grooves tend to be fattened because the pressure in the pillars becomes lower than that in the wetting layer, so the wetting component in the layer was retransferred into the pillar part. This is expected from the Laplace equation and confirmed experimentally.¹⁷ More precise analyses of curvatures using LSCM are required to analyze this issue completely.

In the phase-separating sol–gel system, phase-separated structures can be obtained if the phase separation takes place first, and, subsequently, the sol–gel transition occurs. Therefore, the systems have a time lag between the onset of the phase separation and the sol–gel transition (i.e., the complete structural freezing point). The separated phases are mobile, driven by the hydrodynamic flow during the time lag. For this reason, wetting tends to be promoted when (1) the time lag is elongated, that is, the bulk structure is more coarsened, and (2) either of the separated phases has a strong affinity for the confining surface (large wetting asymmetry). In the present system because the time lag is as long as a few tens of hours and the affinity between the phase-separated siloxane phase and the surface of the grooves is thought to be relatively high, the wetting effect became more significant. Moreover, in contrast to the “closed” confining condition,¹⁹ the wetting component is continuously supplied from the outer bulk to inside the grooves by hydrodynamic flow during the phase separation. Consequently, the homogeneous bicontinuous structure could be preserved in the grooves wider than the bulk characteristic length, resulting in the sharp transition from web to pillar in the grooves with widths between 7 and 10 μm . The difference in the morphological transition between the present “open” and “closed” conditions is schematically shown in Figure 4. As described above, the “wetting transition” occurs in a “closed” confining mold, whereas the “web-to-pillar transition” occurs in an “open” condition.

We also performed the real space analysis of a phase-separating deuterated polybutadiene (dPB)/polybutadiene (PB) polymer blend sandwiched between two parallel coverslips by LSCM. In this case, when the characteristic length of the blend exceeded the separation of the coverslips (D/Λ_m became less than unity), the *sequential* transition from a rather isotropic bicontinuous structure

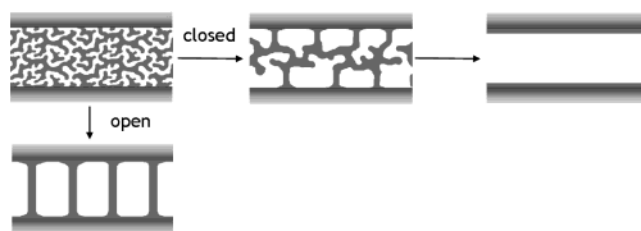


Figure 4. Schematic illustration of examples of the “wetting transition” and “web-to-pillar transition” in “closed” and “open” conditions, respectively. Bicontinuous siloxane skeletons flow onto the surfaces, forming material transfer channels perpendicular to the surfaces, and then transform into complete wetting in the case of the “closed” condition. The channels tend to remain in the case of the “open” condition.

to a columnar structure connecting wetting layers was observed.²¹ In the dPB/PB polymer blend system, the fact that the transition starts when the bulk spinodal wavelength exceeds the dimension of the mold agrees with the present case; however, the transition is rather continuous because of (1) the weak asymmetry of wettability of the components and (2) the absence of a supplementary wetting component from the outer bulk portion. Moreover, the elongated columnar pillars are characteristic in the present case; this is due to the viscoelastic deformation^{23,24} of the siloxane gel phase during morphological development.

Our approach to synthesize well-aligned siloxane gel pillars with from a few hundred nanometers to 1 μm in diameter inside grooves is quite simple and easy, so it is expected that this type of unique porous material holds extended applicability. For example, in applying it to lab-on-a-chip technology, the porous structure can be altered only by changing the width of the flow channels and the phase separation tendency. Moreover, our approach may hold the key to interpret the relationship between phase separation and wetting phenomena exactly in a wide range of multiphase systems undergoing phase separation, which will enable more precise design of materials.

Acknowledgment. Financial support by a Grant-in-Aid for Scientific Research (15206072) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, is gratefully acknowledged. Also, this work is partially supported by the 21st century Center Of Excellence (COE) program, COE for a United Approach to New Material Science, which is financially supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan. The glass chip templates were kindly supplied by Techno Quartz (Yamagata, Japan). H.J. is partially supported by the Grant-in-Aid for Scientific Research on Priority Areas (A), “Dynamic Control of Strongly Correlated Soft Materials” (413/14045246) from the Ministry of Education, Culture, Sports, Science and Technology.

LA0347962

(23) Tanaka, H. *J. Phys.: Condens. Matter* **2000**, *12*, R207–R264.

(24) Nakanishi, K.; Yamato, T.; Hirao, K. *Mater. Res. Soc. Symp. Proc.* **2002**, *726*, Q9.7.1–Q9.7.6.