

Studies on the Self-Assembly of Neat DBS and DBS/PPG Organogels

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Received 28 October 2008; accepted 19 July 2009

DOI 10.1002/app.31149

Published online 15 September 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The self-assembly behavior of neat 1,3:2,4-dibenzylidene-D-sorbitol (DBS) and DBS/poly(propylene glycol) (PPG) organogels has been investigated by scanning electron microscopy, polarizing optical microscopy, and rheological measurements. DBS molecules are capable of self-organizing into fibrils and exhibit the birefringent spherulitic textures during cooling from the melt. On the other hand, DBS can self-assemble into a fibrillar network in PPG to produce organogels. DBS/PPG organogels also reveal a spherulite-like morphology. When a small amount of DBS is dispersed into a PPG matrix, we find that the spherulite sizes are much smaller than those of neat DBS. This is because the dilution of DBS causes DBS to self-assemble in PPG at a lower

temperature. Therefore, more nucleation sites and smaller spherulite sizes are found in the DBS/PPG organogel system. The rheological measurements demonstrate that the elastic modulus (G') in DBS/PPG organogels increases as the DBS concentration increases. However, the increase in G' is less obvious, as the DBS content exceeds 3 wt %, suggesting that the DBS networks become saturated. Also, it is found that these organogels require a certain period of time to reach thermodynamic equilibrium, depending on DBS concentrations. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1113–1119, 2010

Key words: self-assembly; gels; spherulite

INTRODUCTION

Organogels generally consist of low concentrations of low molecular weight organic gelators that self-assemble into networks within a specific organic media.^{1,2} As shown in Figure 1, 1,3:2,4-dibenzylidene-D-sorbitol (DBS) is a butterfly-shaped amphiphile derived from the sugar alcohol D-glucitol. It is known as a gelator. It can self-organize to form a 3D network, stabilized by hydrogen bonds at relatively low concentrations in a variety of organic solvents and polymers, to produce organogels.^{3–14} The resulting network consists of DBS fibrils, ranging from 10 nm to 0.8 μm in diameter, as measured by scanning electron microscopy (SEM) or transmission electron microscopy. DBS organogels prove useful in a variety of commercial applications such as wood stains, gel antiperspirants, fuel cells, and chemical sensors.^{15–20} In our recent research (unpublished results), we found that DBS organogels can be used as self-assembled templates to prepare nanoporous

materials, by polymerizing the liquid monomer and removing the gel fibrils.

The characteristics of DBS/poly(propylene glycol) (PPG) organogels have been reported.^{21,22} Using polarized optical microscopy (POM), DBS/PPG organogels were found to exhibit birefringent spherulitic textures. These spherulite morphologies are similar to those reported for DBS in silicone-based polymers^{6,7} and PPG-*b*-PEG-*b*-PPG triblock copolymers.²³ Transmission electron microscopy verified that these features were formed due to the presence of a DBS fibrillar network, with nanofibrils measuring approximately 10 nm in diameter.²² Previous studies have focused on the morphologies of DBS/PPG organogels. However, there are no references discussing the differences between neat DBS and DBS/PPG organogels.

In this article, attempts have been made to discern the morphology and microstructure of neat DBS and DBS/PPG organogels. Both neat DBS and DBS/PPG organogels are found to exhibit spherulite-like textures, indicating a connection between them. Thus, it is proposed that the DBS fibrils formed a network structure in DBS/PPG that consequently gave rise to the gelation behavior, which may provide a better understanding of these systems and the possibility of tuning the properties. Moreover, the morphological differences between neat DBS and DBS/PPG organogels are discussed.

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Contract grant sponsor: Taiwan National Science Council; contract grant number: NSC 95-2218-E-032-001.

The rheological behaviors of DBS/PPG organogels are also examined in this article. According to the previous literature, the matrix polarity, molecular weight, and DBS concentration influence gel formation and the rheological properties of the DBS-induced organogels.^{5,10,21–24} Here, we report the effects of DBS concentration on dynamic rheological data (elastic modulus G' and viscous modulus G'') of DBS/PPG organogels. Moreover, we find that there is a certain period of time required for DBS/PPG organogels to reach equilibrium.

EXPERIMENTAL

Materials

DBS was obtained from Milliken Chemicals. DBS is a crystalline powder, and the melting point is 225°C, as provided by the company. PPG with a number-average molecular weight of 4000 was obtained from Alfa Aesar. PPG is a viscous liquid, and the sample information provided by the company states that the melting point is not determined.

Methods

The DBS/PPG organogel samples were prepared by dissolving various amounts (0.25–6 wt %) of DBS in PPG at 200°C on a hot plate, under constant agitation (200 \times g). After DBS was completely dissolved, the solution was removed from the hot plate and cooled to room temperature to induce gelation. The gelled samples were then stored at 25°C for 1 week before the measurements.

The gelation time (time required to form a gel) of various DBS/PPG organogel samples was determined by inverting the vials every 30 s after the stop of heating to see when the samples were capable of holding their weights without flowing down.

The morphological characteristics of neat DBS and DBS/PPG organogels were observed using a Precisa XT-200A POM and a Leo-1530 field emission scanning electron microscope (FE-SEM). For the POM experiment, the DBS melt or DBS/PPG solution was dropped onto a glass pate, covered with a cover slip, and held at 225°C for 3 min to erase previous thermal history (the sample information provided by the company indicated that the melting point of DBS was 220°C), using a Linkam THMS600 hot-stage equipped with a Linkam CI94 programmable temperature controller. The sample was then cooled to room temperature and images were taken. To determine the gel dissolution and formation temperatures (T_d and T_f , respectively) by POM, the DBS/PPG organogel sample was first heated from 25 to 225°C at a rate of 3°C/min and then cooled to 25°C at the same rate. For the SEM experiment, a drop of mol-

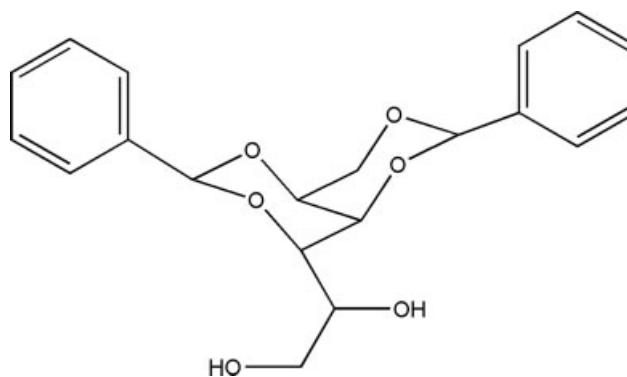


Figure 1 Chemical structure of DBS.

ten DBS sample was placed on a glass plate, using a Linkam THMS600 hot stage at 225°C for 3 min. The sample was then cooled down to room temperature and was coated with gold before SEM observation.

The rheological properties of DBS/PPG organogels were measured using a Rheolab MC 100 instrument (Paar-Physica, Stuttgart, Germany) under oscillatory shear. The frequency spectra were collected over 0.01 to 100 rad/s at 25°C with strain amplitudes maintained at 2%. The strain-dependent measurements were carried out in a strain range of 1–10% at 25°C, at a frequency of 100 rad/s.

RESULTS AND DISCUSSION

Self-assembly of neat DBS

Figure 2(a,b) present the POM and SEM micrographs of neat DBS at room temperature. In Figure 2(a), the spherulite-like texture appears after cooling from the melt. Nucleation starts at a point near the central region of the sample and then nucleus grows into spherical entities. SEM micrograph in Figure 2(b) shows that the DBS molecules self-assemble into fibrils. Many of these fibrils are entangled around the nucleation center of the sample (Fig. 3). Figure 4 shows a high-magnification SEM micrograph of neat DBS. It is found that a network forms in the neat DBS and that the diameters of the aggregated fibrils range from 100 nm to 1 μ m.

Self-assembly of DBS/PPG organogels

Figure 5 demonstrates the relationship between the gelation time and the DBS concentration in DBS/PPG organogels. The formation of the gels is observable by the naked eye. If you invert a vial, it can be seen that the solution does not flow because of its high viscosity; thus it could be termed the gels. In Figure 5, the gels form as the concentration of DBS reaches 1 wt %. The gelation time for DBS/PPG organogels decreases as the DBS concentration increases, which means that gels form more easily at

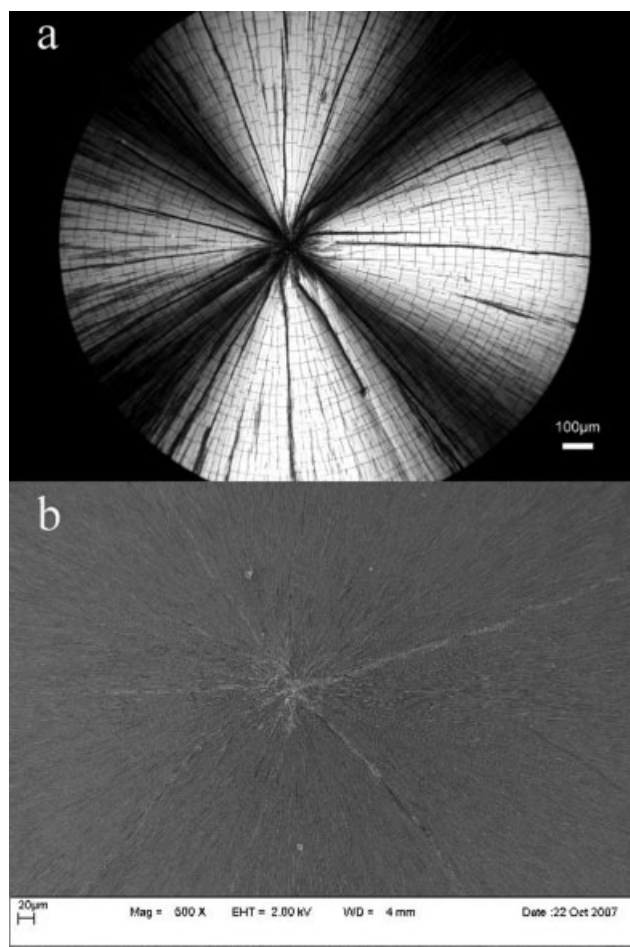


Figure 2 (a) POM and (b) SEM micrographs of neat DBS at room temperature.

higher DBS contents. However, DBS/PPG organogels become heterogeneous when their DBS concentrations exceed 4 wt %. “Heterogeneous” means that the DBS precipitation occurs or macroscopic phase separation happens as observed by optical micros-

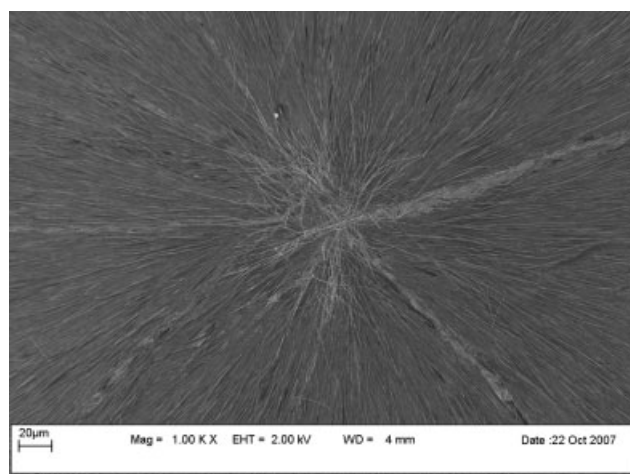


Figure 3 A SEM micrograph of neat DBS at room temperature around the nucleation center of the sample.

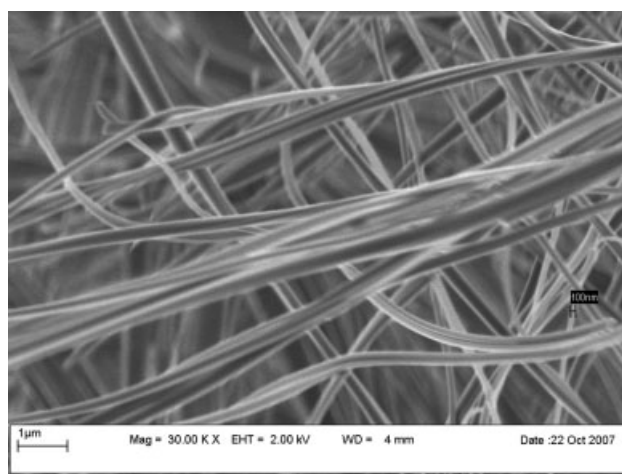


Figure 4 A high-magnification SEM micrograph of neat DBS at room temperature.

copy. Consequently, DBS/PPG organogels with 1–4 wt % DBS are chosen for further investigation.

To characterize the viscoelasticity of DBS/PPG organogels, dynamic rheological analysis was used. Figure 6 displays representative dynamic rheological data (elastic modulus G' and viscous modulus G'' vs. frequency ω) for DBS/PPG organogels with 1 and 4 wt % DBS at 25°C. This figure shows that G' only depends weakly on ω and that G' is greater than G'' for all ω . These results affirm that the produced substances are really gels.²⁵ Therefore, it is obvious that DBS is capable of self-assembling into a network within the PPG. Representative frequency spectra of the elastic modulus G' for DBS/PPG organogels with various DBS contents are presented in Figure 7. It can be seen that G' increases as DBS concentration increases, which implies that the stiffness of the sample increases as its DBS content increases.

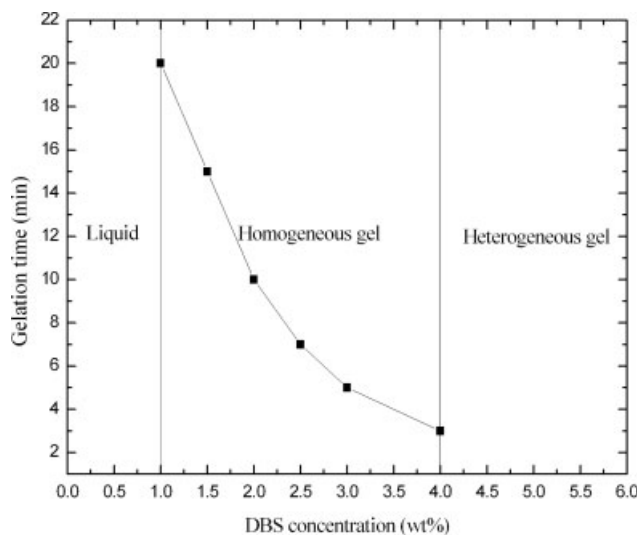


Figure 5 Relationship between gelation time and DBS concentration for DBS/PPG organogels.

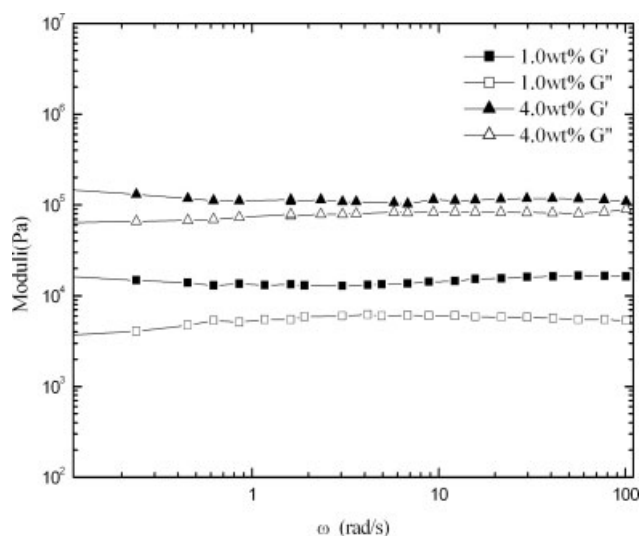


Figure 6 Elastic modulus G' and viscous modulus G'' as functions of frequency ω for DBS/PPG organogels with 1 and 4 wt % DBS at 25°C.

However, it should be noted that the difference in G' between samples containing 3 and 4 wt % DBS becomes very small, suggesting that the gel network approaches saturation beyond 3 wt % DBS. This behavior was also reported by Wilder et al.²³ for DBS in PPG-*b*-PEG-*b*-PPG triblock copolymer and by Fahrlander et al.⁵ for DBS in poly(propylene oxide) matrices.

Organogel samples were further placed in a water bath at 25°C for 30 days, after which they were taken out and tested for their dynamic rheological behaviors. Figure 8 shows the frequency dependence of G' for samples with 1 and 3 wt % DBS after 30 days in storage. Compared with Figure 7, it is found that G' increases considerably for DBS/PPG organogels with 1 wt % DBS after storing for

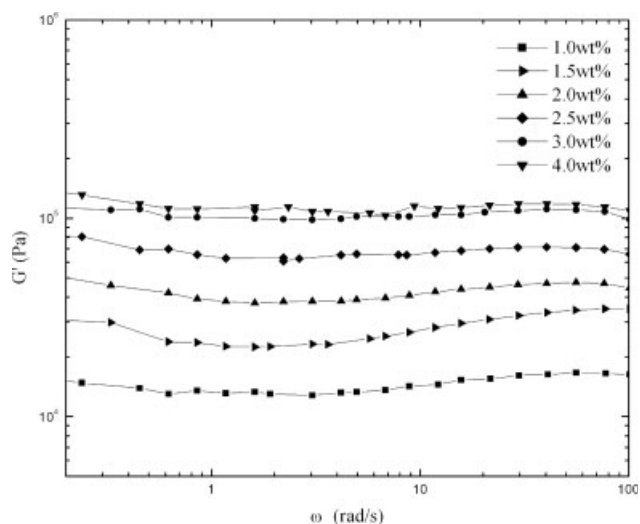


Figure 7 The frequency spectra of the elastic modulus G' for DBS/PPG organogels with different DBS contents.

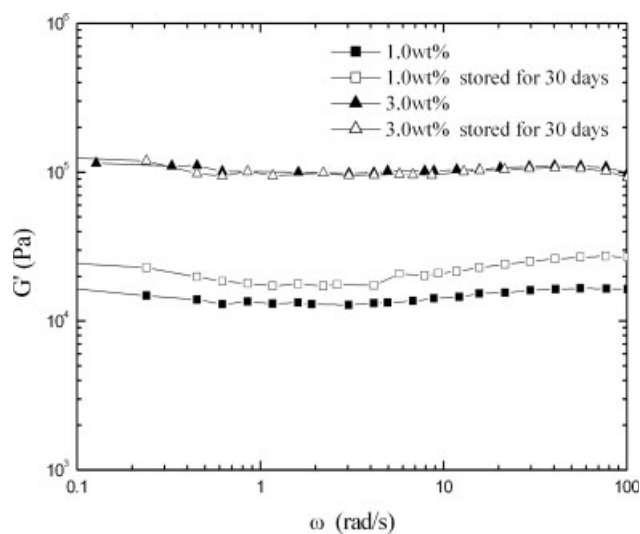


Figure 8 The frequency dependence of G' for DBS/PPG organogels with 1 and 3 wt % DBS after storing for 30 days.

30 days. However, there are no significant changes in G' for DBS/PPG organogels with 3 wt % DBS after 30 days. It is known that a certain period of time is required for DBS/PPG organogels to reach equilibrium. For the cases of higher DBS concentrations, DBS/PPG organogels reach equilibrium more rapidly, and thus G' value remains nearly unchanged after 30 days. Moreover, G' for DBS/PPG organogels containing 3 wt % DBS after 30 days is very close to that with 4 wt % DBS (Fig. 7). This is because of the network saturation behavior mentioned above. The maximum value of G' for DBS/PPG organogels is around 105 Pa.

In Figure 9(a,c), the dynamic moduli (G' and G'') are presented as functions of strain (γ) for samples containing 1–4 wt % DBS in PPG at 25°C. At low strains (< 2%), the moduli are insensitive to γ , indicative of the linear viscoelastic regime. Also, G'' is significantly lower than G' ; i.e., the gel exhibits solid-like behavior. As γ increases, the gel is collapsed and G' becomes lower than G'' i.e., liquid-like behavior. The DBS/PPG organogels undergo a transformation from solid-like to liquid-like behavior over the strain range of 3.0–5.6 %. The transformation point (γ_0) shifts to a lower strain value as DBS concentration increases [Fig. 9(c)]. Higher DBS concentrations lead to less available space for PPG molecules to move. Thus, the gels tend to collapse at a lower strain.

Figure 10 is a series of POM micrographs taken from DBS/PPG organogels with 2 wt % DBS at several temperatures. Comparison of neat DBS [Fig. 10(a)] and DBS/PPG organogels containing 2 wt % DBS [Fig. 2(a)] reveals that both samples exhibit the spherulite-like textures, although detailed observations show that the precise textures differ. The

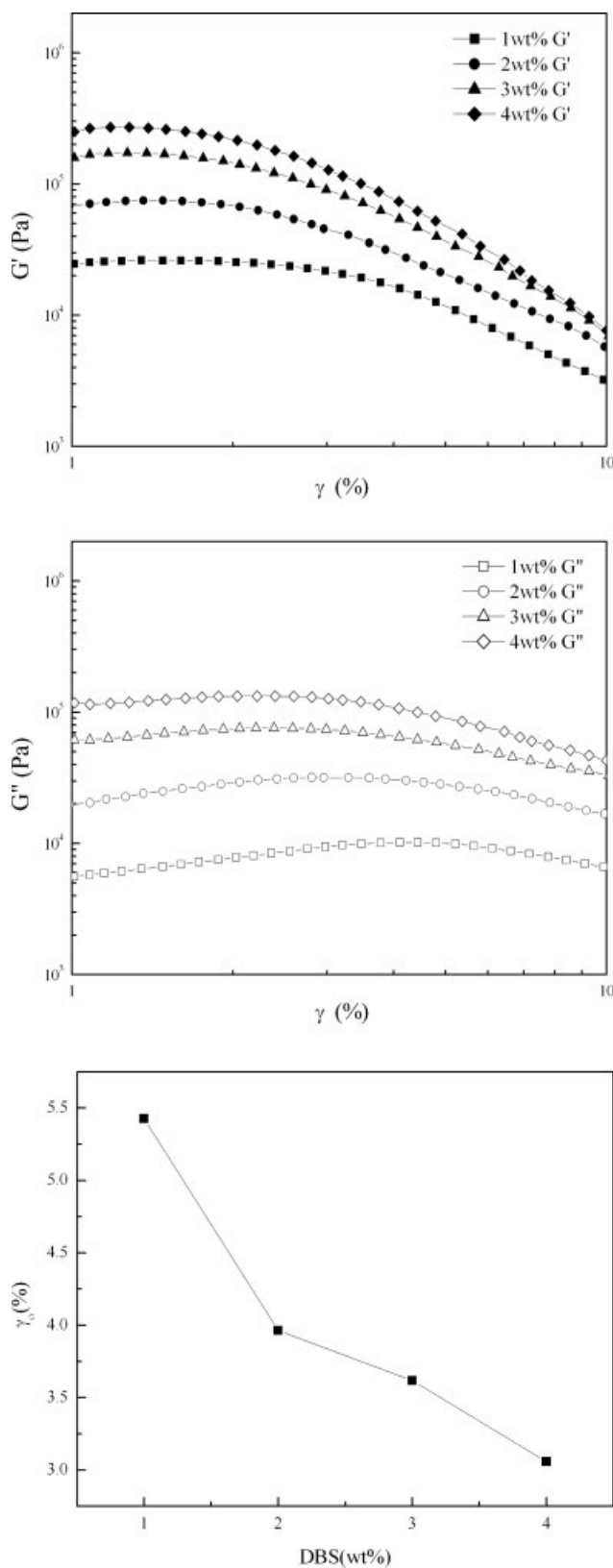


Figure 9 (a) The strain dependence of G' for samples containing 1–4 wt % DBS in PPG at 25°C. (b) The strain dependence of G'' for samples containing 1–4 wt % DBS in PPG at 25°C. (c) The transformation point (γ_{tr}) for samples containing 1–4 wt % DBS in PPG at 25°C.

features of the PPG/DBS organogels are less distinct, and more nucleation sites are observed. The spherulite sizes of DBS/PPG organogels are much smaller than those of neat DBS. The densities of DBS and PPG are 1.300 and 1.004 g/cm³, respectively, as shown in Ref. 5. Because the weight percentage of DBS in PPG is 1–4, its volume percentage should be around 0.8–3.1. However, POM observations show that the DBS/PPG organogel samples are almost filled with the spherulite-like textures generated by DBS fibrils. This volume percentage is several tens of times higher than 0.8–3.1. This implies that the spherulite-like morphologies of DBS/PPG organogels are much more loosely packed and less dense than those of neat DBS. Compared with the transmission electron micrographs of DBS/PPG organogels,²² the density of DBS fibrillar network of neat DBS (Fig. 4) is indeed much higher. The reason why the morphologies are different will be discussed later.

In Figure 10(b,d), as the temperature increases, the spherulite-like morphologies become less distinct. Birefringence starts to fade out at approximately 83°C, and eventually it disappears completely at approximately 130°C. The disappearance of birefringent microstructure is presumed to be the dissolution of the DBS fibrillar network in PPG matrix. These morphologies would form again upon subsequent cooling, and thus these organogels are considered thermally reversible. The gel dissolution and formation temperatures (T_d and T_f , respectively) of DBS/PPG organogels with different DBS contents are shown in Figure 11. The samples are heated or cooled at 3°C/min over the temperature range of 25–225°C; values of T_d are obtained from POM as the temperature at which birefringence initially disappears during heating, and values of T_f are defined as the temperature at which the birefringence initially changes during cooling. In Figure 11, both T_d and T_f increase as DBS concentration increases. Fahrlander et al.⁵ reported that the gel dissolution and formation are first-order transitions. The temperature of a first-order transition is given by $T_{tr} = H_{tr}/S_{tr}$, where H_{tr} and S_{tr} are the enthalpy and entropy of the transition, respectively. The enthalpy of gel dissolution and formation increases with the increase in DBS contents, because the gels need more thermal energy to dissolve and release more energy to form. On the other hand, as DBS contents increase, the conformations of nongels (solutions) increase and those of gels decrease. Therefore, with higher DBS amounts, the entropy of gel dissolution is more positive and that of gel formation is more negative. From the result, the enthalpy is the dominant factor influencing T_d and T_f . Furthermore, T_d and T_f depend only slightly on DBS content as the contents are beyond 3 wt %. Such plateau behavior

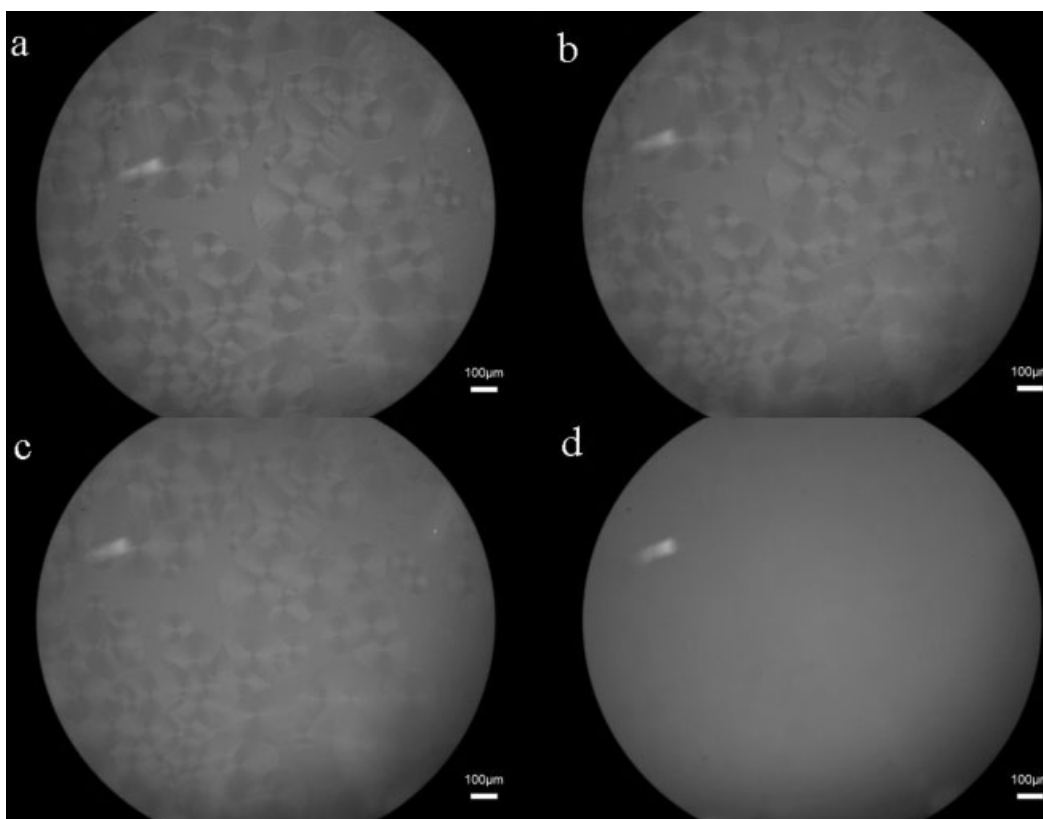


Figure 10 A series of POM micrographs of DBS/PPG organogels with 2 wt % DBS at (a) room temperature, (b) 83°C, (c) 105°C, and (d) 130°C.

coincides with network saturation and is consistent with the previous dynamic rheological analysis.

From the POM observation of neat DBS, it can be seen that the formation temperature of spherulite-like morphologies is approximately 195°C. This temperature is much higher than that of DBS/PPG

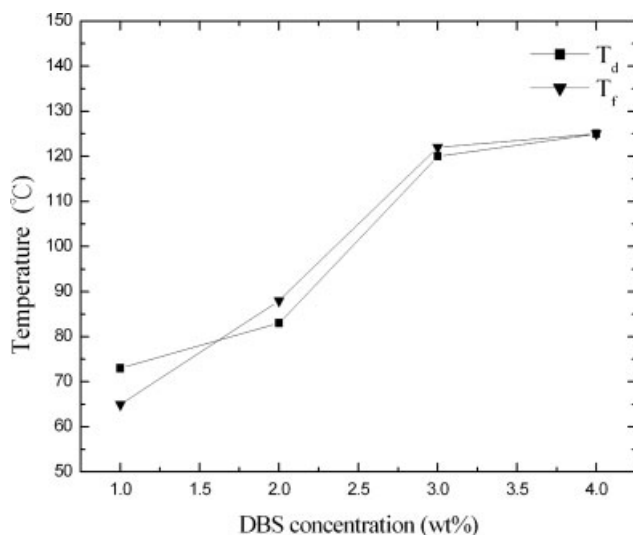


Figure 11 The gel dissolution and formation temperatures (T_d and T_f) of DBS/PPG organogels with different DBS contents.

organogels (Fig. 11). It is possible that the dilution of DBS in DBS/PPG mixtures reduces the DBS self-assembly ability in PPG, and the DBS/PPG organogels self-assemble at a lower temperature. Because the “nucleation” forms more easily at a lower temperature, DBS/PPG organogels have more nucleation sites than neat DBS. As a result, the spherulite sizes of DBS/PPG organogels are also smaller than those of neat DBS. This is consistent with our POM observations shown in Figures 2 (a) and 10 (a).

CONCLUSIONS

The morphology and microstructure of neat DBS and DBS/PPG organogels are examined by POM and SEM. Both systems found that the birefringent spherulite-like features were generated by the DBS fibrils. The dilution of DBS and the reduction of DBS self-assembly ability in PPG lower the self-assembly temperature of DBS/PPG organogels. The lower temperature leads to more nucleation sites and smaller spherulite sizes found in DBS/PPG organogel system.

The viscoelastic properties of thermally reversible DBS/PPG organogels are investigated by rheological measurements. It is found that G' is independent of frequency and that G' is always greater than G'' for

all organogel systems. Also, G' increases with increasing DBS concentration. However, G' is less affected at sufficiently high-DBS contents (3 wt % DBS) corresponding to saturated gel networks. In addition, DBS/PPG organogels need a certain time to reach equilibrium. The organogels are much more stable and reach equilibrium more easily at higher DBS concentrations. Finally, the gel formation and dissolution temperatures of DBS/PPG organogels are measured by a POM equipped with a hot stage. Both temperatures initially increase and ultimately exhibit a plateau (after 3 wt % DBS), as DBS content increases. The plateau behavior is due to DBS network saturation, which is consistent with the rheological data.

References

1. Abdallah, D. J.; Weiss, R. G. *Adv Mater* 2000, 12, 1237.
2. Tan, G.; John, V. T.; Mcpherson, G. L. *Langmuir* 2006, 22, 7416.
3. Watase, M.; Itagaki, H. *Bull Chem Soc Jpn* 1998, 71, 1457.
4. Yamasaki, S.; Ohashi, Y.; Tsutsumi, H.; Tsujii, K. *Bull Chem Soc Jpn* 1995, 68, 146.
5. Fahrlander, M.; Fuchs, K.; Friedrich, C. *J Rheol* 2000, 44, 1103.
6. Smith, J. M.; Katsoulis, D. E. *J Mater Chem* 1995, 5, 1899.
7. Ilzhoefer, J. R.; Broom, B. C.; Nepa, S. M.; Vogler, E. A.; Khan, S. A.; Spontak, R. J. *J Phys Chem* 1995, 12, 69.
8. Ilzhoefer, J. R.; Spontak, R. J. *Langmuir* 1995, 11, 3288.
9. Wilder, E. A.; Braunfeld, M.; Jinnai, B. H.; Hall, C. K.; Agard, D. A.; Spontak, R. J. *J Phys Chem B* 2003, 107, 11633.
10. Wilder, E. A.; Hall, C. K.; Khan, S. A.; Spontak, R. J. *Langmuir* 2003, 19, 6004.
11. Feng, Y.; Jin, X.; Hay, J. N. *J Appl Polym Sci* 1998, 69, 2089.
12. Shepard, T. A.; Delsorbo, C. R.; Louth, R. M.; Walborn, J. L.; Norman, D. A.; Harvey, N. G.; Spontak, R. J. *J Polym Sci Part B Polym Phys* 1997, 35, 2617.
13. Kobayashi, T.; Hashimoto, T. *Bull Chem Soc Jpn* 2005, 78, 218.
14. Lipp, J.; Shuster, M.; Terry, A. E.; Cohen, Y. *Langmuir* 2006, 22, 6398.
15. Schamper, T.; Jablon, M.; Randhawa, M. H.; Senatore, A.; Warren, J. D. *J Soc Cosmetic Chem* 1986, 37, 225.
16. Nahir, T. M.; Qiu, Y. J.; Williams, J. L. *Electroanalysis* 1994, 6, 972.
17. Bhatt, D.; Rizvi, R.; Galleguillos, R. U.S. Pat. 6,132,704 (2000).
18. Isogawa, H.; Anraku, H. U.S. Pat. 5,510,237 (1996).
19. Ishiwatari, T.; Tsushima, K. U.S. Pat. 5,554,649 (1996).
20. Kasat, R. B.; Lee, W.; Mcmarthy, D. R.; Telyan, N. G. U.S. Pat. 5,490,979 (1996).
21. Mercurio, D. J.; Khan, S. A.; Spontak, R. J. *Rheol Acta* 2001, 40, 30.
22. Mercurio, D. J.; Spontak, R. J. *J Phys Chem B* 2001, 105, 2091.
23. Wilder, E. A.; Hall, C. K.; Spontak, R. J. *J Colloid Interface Sci* 2003, 267, 509.
24. Dumitras, M.; Friedrich, C. *J Rheol* 2004, 48, 1135.
25. Kavanagh, G. M.; Ross-Murphy, S. B. *Prog Polym Sci* 1998, 23, 533.