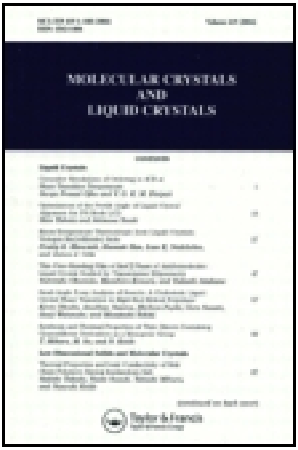

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

THE EFFECT OF POROGEN MOLECULAR WEIGHT ON PHASE SEPARATION BEHAVIOR IN POLY(METHYLSILSESQUIOXANE)/POROGEN HYBRIDS

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Version of record first published: 15 Jul 2010

To cite this article: Sung Kyu Min, Jae Man Park, Kitae Song, Hee-Woo Rhee & Moon Young Jin (2003): THE EFFECT OF POROGEN MOLECULAR WEIGHT ON PHASE SEPARATION BEHAVIOR IN POLY(METHYLSILSESQUIOXANE)/POROGEN HYBRIDS, Molecular Crystals and Liquid Crystals, 406:1, 195-202

To link to this article: http://dx.doi.org/10.1080/744819004

Mol. Cryst. Liq. Cryst., Vol. 406, pp. 195/[389]–202/[396], 2003
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390264973

THE EFFECT OF POROGEN MOLECULAR WEIGHT ON PHASE SEPARATION BEHAVIOR IN POLY(METHYLSILSESQUIOXANE)/POROGEN HYBRIDS

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Thermo gravimetric analysis (TGA) and differential TGA (DTGA) were performed to investigate phase separation behavior of organic-inorganic hybrids. The hybrids were composed of six-arm star-shaped aliphatic poly(ε-caprolactone) and methyl silsesquioxane (MSSQ). By analyzing the DTGA thermograms of the hybrids and the porogen, we could qualitatively estimate the degree of interaction between organic porogen and inorganic matrix and domain sizes of the porogen in hybrids. When porogen loading was low in the hybrids, there was only one main peak on DTGA curve and it positioned at higher temperature than that of pure porogen. This shift in decomposition temperature resulted from nano-sized porogen domains in MSSQ. As porogen loading increased over critical points, the additional peaks appeared at the lower temperatures indicated that porogen molecules began to form larger porogen domains which were confirmed by the cross-sectional FE-SEM images. The porogen with higher MW was decomposed at higher temperature but its hybrids resulted in lower decomposition temperatures due to larger domains of the porogen.

Keywords: low dielectric materials; MSSQ and porogen; phase separation behavior; TGA and differential TGA

1. INTRODUCTION

In microelectronics industry, the interconnect resistance-capacitance (RC) delay becomes increasingly dominant over intrinsic gate delay, as devices scale down to a deep sub-micron regime [1]. Power dissipation and

This work was supported by Sogang University research fund 2002.

crosstalk noise also become issues due to the decrease in wiring dimensions and pitches. International Technology Roadmap for Semiconductors (ITRS) 2001 predicts that 130 nm device generation needs low dielectrics below 2.7 in 2002 and 2.4 for the 70 nm device in 2006 [2].

One of the promising approaches for lowering the dielectric constant (k) is the introduction of nanometer-sized pores ($k = 1.0$) into the matrix. This approach is based on the incorporation of a thermally degradable organic material (porogen) into a host matrix. In recent years, porous methylsilsesquioxane (MSSQ) has been actively studied since it has low dielectric constant ($k = 2.7$), good mechanical strength and low water absorption [3]. IBM researchers reported that star-shaped poly(ε-caprolactone) (PCL) with hydroxyl end groups has been used as a porogen to generate porous MSSQ with a low dielectric constant and minimal moisture absorption [4].

Ideal porous materials would consist of a network of closed and nanometer-sized pores with narrow size distribution. However, when the loading of porogen is high, large and interconnected pores can be generated, resulting in poor mechanical properties in terms of elastic modulus, surface hardness, crack and delamination. One of the important factors to determine pore morphology is the compatibility between low-k matrix and porogen. The better the miscibility between the porogens and the matrix, the smaller the resultant pores. Another is the mobility of porogen chains after the onset of phase separation [1]. Consequently, thermodynamic miscibility and dynamic mobility should be considered for designing porous low-k materials.

Due to the very small pore size (several ~ tens nanometer), the most widely used tools for observing the pore structure are field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM). The quantitative information such as pore size and size distribution as well as pore interconnectivity can be obtained with positronium annihilation lifetime spectroscopy (PALS) or small-angle neutron scattering (SANS).

In this study, simple thermogravimetric analysis (TGA) is first employed to determine the degree of interactions between MSSQ and PCL because the decomposition temperature of the porogen in hybrids is dependent on the interaction between two components. We could obtain qualitative information on the phase separation behavior of MSSQ/PCL hybrids by analyzing their differential TGA (DTGA) curves. This paper presents the effects of molecular weight and content of porogen on phase separation.

2. EXPERIMENTAL

The star-shaped PCLs with different molecular weights were synthesized by procedures described elsewhere [7] and designated as P1 (M_n: 3249 g/mol), P2 (M_n: 4160 g/mol) and P3 (M_n: 5815 g/mol). The chemical structure of the porogen is shown in Figure 1. MSSQ prepolymers were purchased from Techneglas Co., and used as received.

MSSQ prepolymer and porogens were first dissolved in n-butyl acetate, respectively, and then mixed together to make proper ratios of porogen to matrix. Porogen content in the hybrids was varied from 0 to 40 wt%. The resultant homogeneous solution was filtered with 0.2 µm Acrodisc CR PTFE filter and dropped directly onto a glass substrate placed in vacuum oven and the solvent was evaporated for 24 hours at room temperature to remove residual solvent. To obtain porous MSSQ films, the MSSQ/PCL solutions was spin-coated on a silicon wafer at 2500 rpm for 30 sec and cured at 250°C for 30 min and then porogen was completely decomposed at 430°C for 1 hour under nitrogen atmosphere.

TGA thermograms of the hybrids were obtained with a Thermogravimetric Analyzer TGA 2950 (TA instruments) and compared with that of the

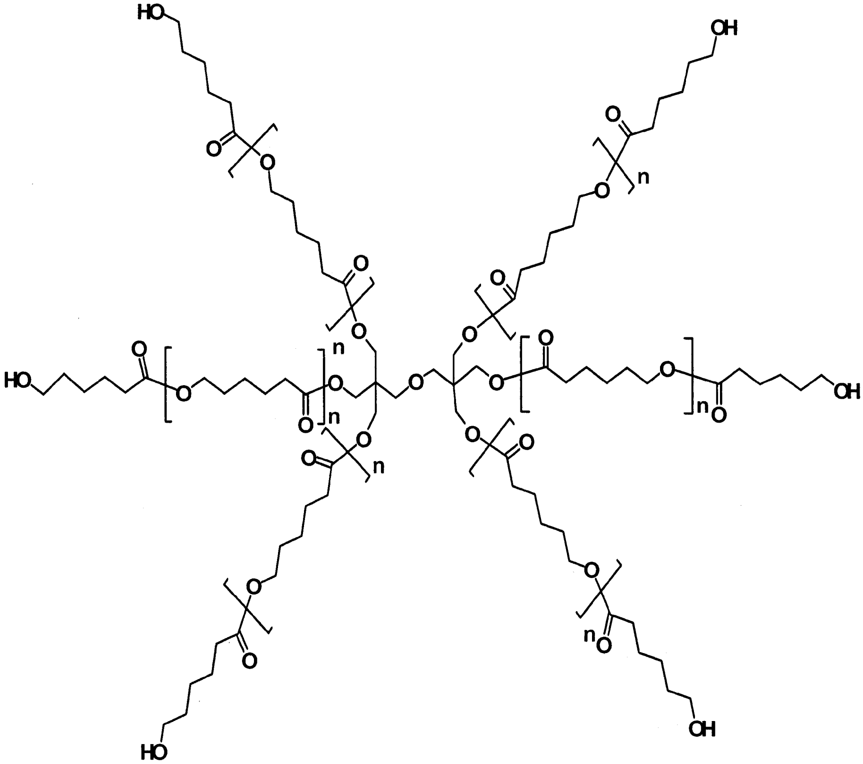

FIGURE 1 The chemical structure of 6-arm poly(caprolactone).

pure porogen. The heating rate was 3°C/min and the temperature scanned from RT to 500°C under nitrogen. The final morphology of porous MSSQ was observed with FE-SEM (JEOL JSM-633OF).

3. RESULTS AND DISCUSSION

TGA thermograms of MSSQ and porogens with different molecular weights (P1, P2, P3) are shown in Figure 2(a). MSSQ prepolymers began to crosslink at ~100°C to form Si-O-Si linkage and the total weight loss is about 12%, which result from the condensation of hydroxyl groups in MSSQ. All the porogens were fairly stable up to 220°C and then began to be

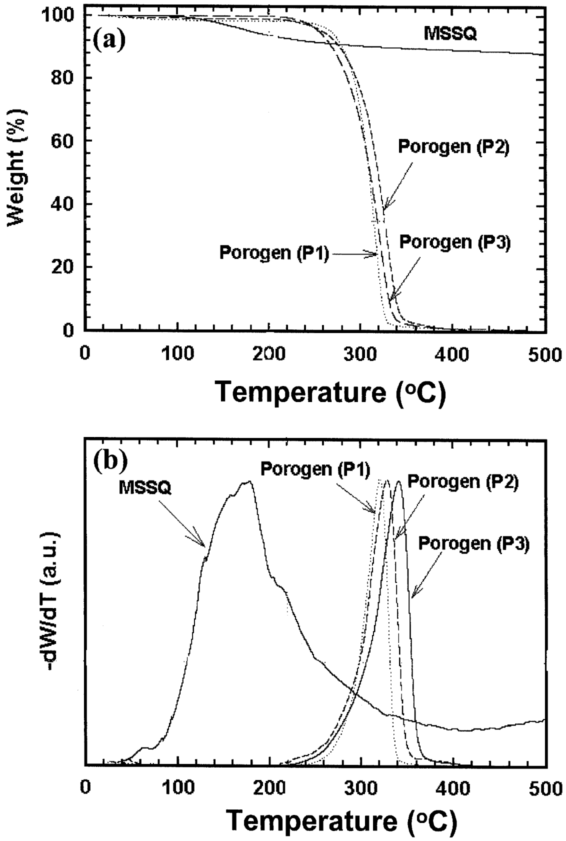

FIGURE 2 Thermal behaviors of MSS and porogens: (a) TGA and (b) DTGA thermograms.

decomposed above 250°C. Figure 2(b) also shows that the DTGA curves of MSSQ and various porogens. It was found that the maximum weight loss of MSSQ was occurred around 180°C and porogens showed very narrow decomposition temperature between 250°C and 370°C depending on the molecular weight (MW) of porogens.

Figure 3 shows the effect of porogen loading on the decomposition behavior of porogen (P2) in MSSQ prepared by solution casting technique. Interestingly, the decomposition temperature of porogen in MSSQ was dependent on the porogen loading. When porogen loading is 10 wt%, decomposition of porogen in MSSQ was occurred at higher temperature than that of porogen itself by ~85°C. But, with increase in porogen loading from 20 wt% to 30 wt%, porogen began to be decomposed at corresponding temperature of pure porogen. For 40 wt% of porogen loading in MSSQ, one big peak was centered at around 355°C with small shoulder at 415°C.

Figure 4 shows the cross-sectional FE-SEM images of porous MSSQ prepared by sintering 10 wt% and 30 wt% of porogens at 430°C for 2 hours. When porogen loading is 10 wt%, a pore structure was not found in FE-SEM images, indicating that pores size is smaller than FE-SEM resolution limit (~10 nm). However, 30 wt% porogen caused in pores with larger than 10 nm. This implies that such a decomposition behavior may be due to the change in size of the porogen domains in MSSQ. At low porogen loading, the porogen was formed with nano-sized domains favorably where

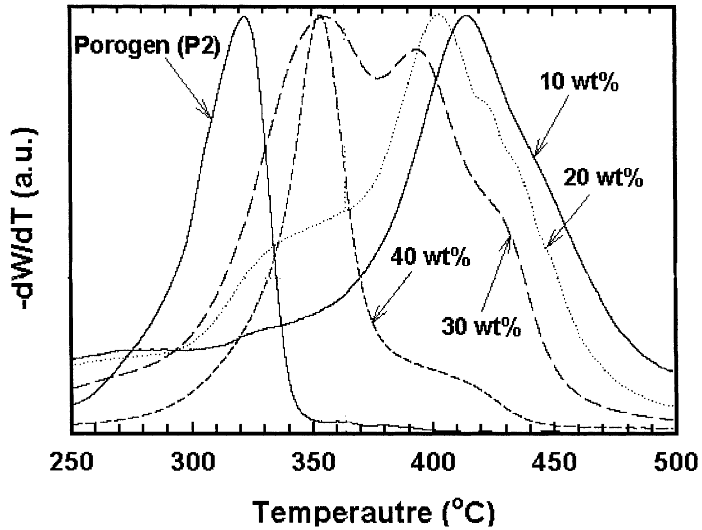

FIGURE 3 The differential TGA curves of MSSQ/porogen (P2) as a function of porogen loading.

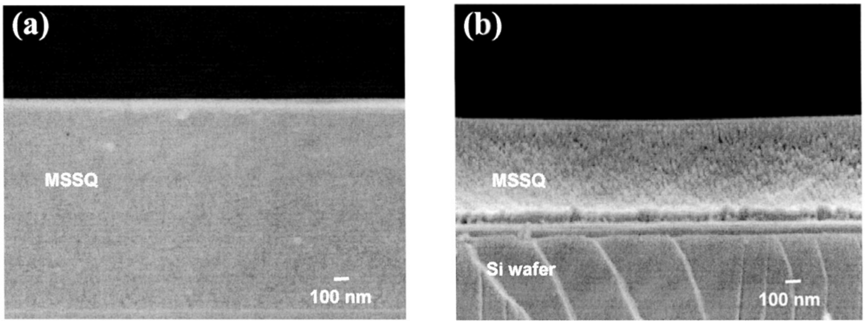

FIGURE 4 The cross-sectional FE-SEM images of porous MSSQ prepared by sintering different porogen loading: (a) 10 wt% and (b) 30 wt%.

functional groups in the MSSQ and porogen interact strongly. Since the nano-sized porogen domains provide very large MSSQ-porogen interfacial area, the decomposition temperature of porogen is expected to increase. However, as the porogen loading increases over a critical point, porogen molecules begin to form not only nano-sized domains but also larger domains. Further increase in porogen loading resulted in large porogen domains mainly which will behave like porogen itself, and the peak temperature approached that of pure porogen.

In order to prepare the nanoporous MSSQ, it is important to control porogen structure as well as porogen content. In this work, we investigated the effect of MW of porogen on the phase separation behavior. Figure 5 compares decomposition behavior of porogen at different PCL loading and MW. For 10 wt% of porogen loading in MSSQ, only one peak was observed around 428°C in both porogens as shown in Figure 5(a). This indicates again that porogens molecules may form nanoscopic domains due to the thermodynamical reason. For 20 wt% hybrids, the overall shapes were very similar and they may be deconvoluted into three peaks. The difference between them is that the thermogram of MSSQ/P3 hybrids shifted to lower temperature by 30°C, compared to that of MSSQ/P1. With increasing porogen content from 10 wt%, there are two additional peaks at the lower temperature, which are related to the larger domain sizes of the porogen. Another interesting point is that the lowest peak of the MSSQ/P1 is still higher that of pure porogen, but the corresponding peak of P3 hybrid is same as that of P3 itself. This indicates that P1 is better porogen than P3 and that we need to control the MW of porogen to make well dispersed nanohybrids. For the 30 wt% hybrids, the general trend is similar to that found in 20 wt% hybrid but the two peaks at higher temperature becomes smaller and the intensity of the lowest peak dominates as shown in

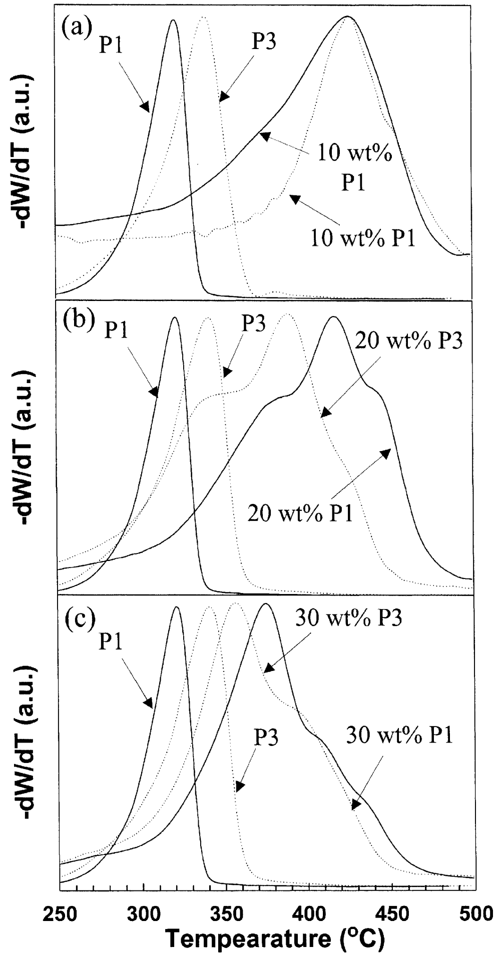

FIGURE 5 The differential TGA curves of porogens having different MW in MSSQ at various porogen loading: (a) 10 wt%, (b) 20 wt% and (c) 30 wt%.

Figure 5(c). This lowest peak is close to that of pure porogens, which may imply that polymer domains are larger with increasing content of the porogens.

4. CONCLUSIONS

We investigated thermal decomposition behavior of hybrids as function of porogen loading and molecular weight of the porogens. By analyzing the

DTGA curves of MSSQ/porogen hybrids and pure porogens, we qualitatively estimated the degree of interactions from the shift in the peak temperature of maximum decomposition rate. The peak temperature and its intensity may be quite closely related to the domain sizes of the porogens.

When the porogen loading was low, the peak temperature of porogen in hybrids was observed at the higher temperature than that of pure porogen, which resulted from the strong interaction between porogen and MSSQ. With increase in porogen content, at least two additional peaks were revealed, which suggested that there was mixed domains of several different sizes. In addition, the peak at the lowest temperature approached that of the pure porogen and its intensity increased. For the given porogen and matrix there is optimum porogen content for preparing well-dispersed nanoporous materials. We also have characterized the effect of porogen molecular weights on the phase separation of MSSQ/porogen hybrids. The porogen of higher MW decomposed at higher temperature but the corresponding temperatures of its hybrids appeared at lower temperature than its lower MW counterparts.

REFERENCES

[1] Nguyen, C. V., Robert, K. R., Miller, D., Rhee, H.-W., & Yoon, D. Y. (1999). *Chem. Mater.*, *11*, 3080.

[2] *The National Technology Roadmap for Semiconductors;* Semiconductor Industry Association, 2001.

[3] Heise, A., Nguyen, C., Malek, R., Hedrick, J. L., Frank, C. W., & Miller, R. D. (2002). *Macromolecules*, *33*, 2346.

[4] Hedrick, J. L., Miller, R. D., Carter, K. R., Hawker, C. J., Yoon, D. Y., & Trollsas, M. (1998). *Adv. Mater.*, *10*, 1049.

[5] Xu, J., Moxom, J., Yang, S., Suzuki, R., & Ohdaira, T. (2002). *Applied Surface Science*, *194*, 189.

[6] Yang, S., Mirau, P. A., Pai, C.-S., Nalamasu, O., Sun, J., & Gidley, D. W. (2002). *Chem. Mater.*, *14*, 369.

[7] Trollsas, M., Hedrick, J. L., Mecrreyes, D., Dubois, Ph., Jerome, R., Ihre, H., & Hult, A. (1997). *Macromolecules*, *30*, 8508.

[8] Bolze, J., Ree, M., Youn, H. S., Chu, S.-H., & Char, K. (2001). *Langmuir*, *17*, 6683.

[9] Huang, Q. R., Volksen, W., Huang, E., Toney, M., Frank, C. W., & Miller, R. D. (2002). *Chem. Mater.*, *14*(9), 3676.