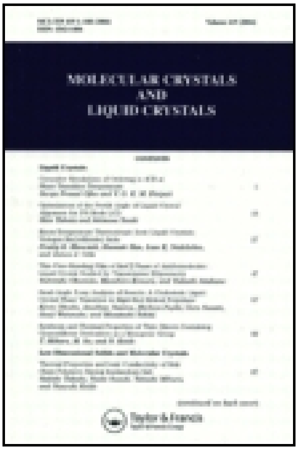

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Miscibility and Nanoporous Hybrid Film Fabrication of Methylsilsesquioxane (MSSQ) and Star-shaped Polymers

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Miscibility and Nanoporous Hybrid Film Fabrication of Methylsilsesquioxane (MSSQ) and Star-shaped Polymers

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Star-shaped polycaprolactones (PCL) with 4- or 5-arms were synthesized to be used as a porogen for nanoporous dielectric materials. Methylsilsesquioxane (MSSQ) was used as an inorganic matrix. Miscibility with MSSQ strongly depended on the molecular weight of the porogens used. Dielectric constants of the nanoporous thin films were measured using MIS cell configuration.

Keywords Methylsilsesquioxane (MSSQ); porogen; thin film; miscibility; nanoporosity; dielectric constant

INTRODUCTION

As the feature dimension in integrated circuits continues to shrink, signal delays and cross-talk between metal interconnects becomes significant problems. Low dielectric constant materials are required for the next generation logic-chips. To lower dielectric constant below 2.2 is possible only with the incorporation of air voids (k=1) in dielectric materials. Recently, we have reported that nanoporous MSSQ films could be obtained by thermally decomposing an organic material in inorganic/organic polymer hybrids[1]. In this work, MSSQ was used as a base inorganic matrix, and star-shaped poly(caprolactone) (PCL) was used as a pore-forming material (porogen). The effect of their molecular weights on the formation of nano-hybrids were investigated to obtain optically transparent and nanoporous MSSQ films. Therefore, we investigated the miscibility and phase-separation behavior of MSSQ/PCL hybrids. In addition, dielectric constants of nanoporous MSSQ films were measured.

EXPERIMENTAL

Reagents and Materials: MSSQ (GR650F, TECHNEGLAS) oligomer (M_n ~ 4,800 g/mol) was used as received. Xylitol and DL-threitol as multifunctional initiators were purified by recrystallization. $Sn(oct)_2$ (Aldrich) as a catalyst was used as-received. ε-Caprolactone (ε-CL) was dried over CaH_2 and purified by vacuum distillation.

Synthesis of Star Shaped Polymers: Xylitol or DL-threitol and ε-CL were stirred at 120 °C under N_2 atmosphere. When the reaction was finished, THF was added to the reaction mixture. Then the solution was precipitated with cold methanol. The powder was dried under reduced pressure for 24 hr. Molecular weight was determined in THF at 30 °C.

Measurements: The hybrid films were fabricated by spinning MSSQ/porogen solution on Si-wafer or glass substrates. And then hybrid films were cured according to the proper cure cycle[2]. The nanoporous thin films were obtained upon thermal decomposition at 420 °C. Capacitance-Voltage curve was obtained using a Hewlett-Packard 4194A LCR meter, and dielectric constant was calculated from the saturated maximum capacitance values in Capacitance-Voltage curve.

RESULTS AND DISCUSSION

To obtain reliable and excellent electrical properties, it is important to prepare the optically clear and organic/inorganic polymer nano hybrids. Preliminary studies showed that low molecular weight porogen was miscible with MSSQ, but phase separation was highly dependent on the curing condition. Star-shaped poly(caprolactone)s (PCL) with different molecular weights were synthesized and used as a porogen. MWs of star polymers were characterized by ^{1}H NMR (Table1). It ranged from 5,000 to 13,000. The synthesized porogens were all soluble in MIBK and decomposition of PCL started at 300 °C and finished at 400 °C.

TABLE 1. DPs of arm and Molecular Weights of Various Star-shaped PCL

Sample	^{1}H NMR Data	
	DP of arm*	M_w**
5-Arm Star-shaped PCL	9.8	5716
	12.0	7000
	24.0	13297
4-Arm Star-shaped PCL	14.3	6665
	18.2	8450
	22.0	10166

* DP of arm = (Integral at 4.1 ppm + Integral at 3.7 ppm)/(Integral at 3.7 ppm)
** Molecular weight = number of arm × M_w of monomer × DP of arm

As for the miscibility of MSSQ/porogen hybrid thin film, the star polymers having M_w < 9000 g/mol were completely miscible with MSSQ. The star polymer having more than M_w ~ 10,000 resulted in hazy hybrid films, and all their surfaces were rough compared to the miscible films.

We investigated the dielectric constants of nanoporous MSSQ thin films. Dielectric constants of the optically clear hybrids after the decomposition of PCL were measured. The values of nanoporous

MSSQ thin films with 10 vol% PCL were reduced to some extent when compared to that of the pure MSSQ film, suggesting that the nanopores were formed in the MSSQ hybrid films.

TABLE 2. Dielectric Constants of MSSQ Pure and Nanoporous Thin Films by MIS Structure

Sample		Curing Temp.	Dielectric Constant	Refractive Index
GR650F		420 °C	2.87 ± 0.13	1.342
GR650F/K5DP10*	9:1 (v/v)	420 °C	2.63 ± 0.15	1.321

* 5-Arm, DP=9.8 star-shaped polymer (M_w=5716)

CONCLUSIONS

Star-shaped poly(caprolactone)s (PCL) were synthesized and their MWs were controlled. Molecular weight of star polymers strongly affected the miscibility between the porogen and MSSQ matrix. Dielectric constants of nanoporous MSSQ hybrid films including 10 vol% PCL were 2.63.

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