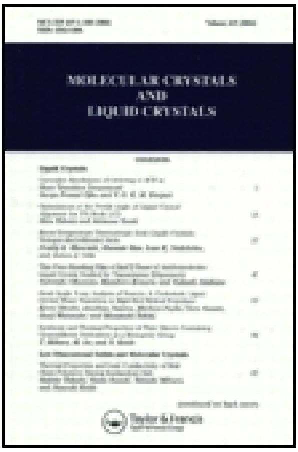

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Effect of Solvent Vapor on the Morphology of Fluorinated Block Copolymer Films from Different Casting Solvent

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Poly(ethylene oxide)-b-*poly(1H,1H-dihydroperfluorooctyl methacrylate) (PEO*-b-*PFOMA) micellar films were cast from chloroform or α,α,α-trifluorotoluene (TFT) with different copolymer concentrations, followed by TFT or PF-5080 vapor treatment. Though their initial morphologies were different, finally the same patterns were obtained under TFT or PF-5080 vapor with varying the annealing time. The time dependent phase behavior was examined at different stages.*

Keywords Block copolymers; Self-assembly; Thin film; Solvent vapor annealing.

Introduction

In the past decade, block copolymeric thin films have attracted much attention because many new nanotechnical applications, such as fabrication of high density arrays for data storage, electronics, and molecular separation, are based on thin film technology [1–3]. A number of strategies have been developed to control the nanoscopic orientation of thin films including manipulating the topology of the substrate [4] applying external fields [5], and using the directionality imposed by solvent evaporation [6].

The phase-inversion of block copolymeric thin films under various solvent vapor treatment turns out to be an effective method to control the microdomain structures [7, 8]. During such annealing, the nature of the casting solvent is one of the key factors that determine the resultant microstructures. Although tuning the micellar morphologies of thin films by applying external fields are well documented, few articles have been reported for solvent annealing effects on semifluorinated block-copolymeric films. Fluorinated polymers have many distinctive properties [9, 10].

As previously reported, semifluorinated block copolymers form thermodynamically stable morphologies after thermal annealing [11–13]. We also reported the influence of solvents on micellar architectures of the block copolymers [14, 15]. This study focused on

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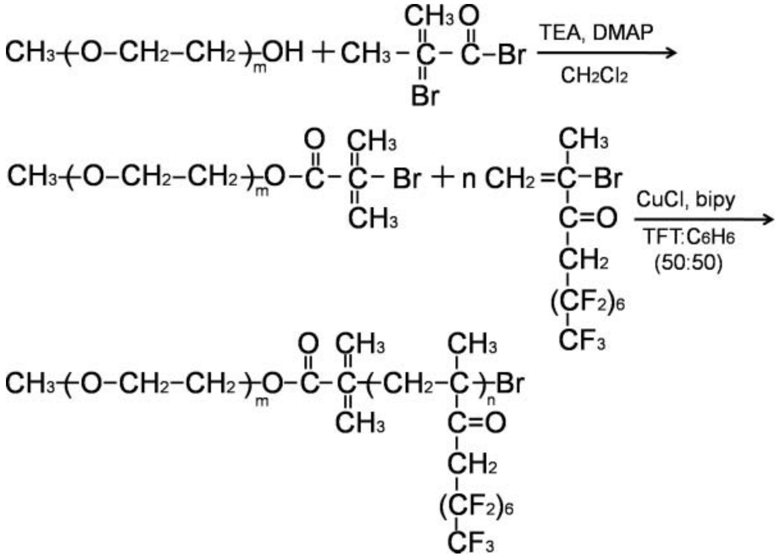
*Corresponding author. E-mail: ktlim@pknu.ac.kr establishing the effect of a casting solvent for the phase inversion of poly(ethylene oxide)-*b*-poly(1H,1H-dihydro perfluorooctyl methacrylate) (PEO-*b*-PFOMA) copolymeric thin films. The effect of different solvent vapor annealing, specifically α,α,α-trifluorotoluene (TFT) and PF-5080 (perfluroalkanes, primarily compounds with 8 carbons), on the copolymeric thin films at different time was investigated.

Experimental

Synthesis

PEO_{5k}-*b*-$PFOMA_{22k}$ was prepared by atom transfer radical polymerization (ATRP) of FOMA using PEO-Br as the macroinitiator in the mixed solvent of trifluorotoluene and benzene as described previously (Scheme 1) [16].



Scheme 1.

Fabrication of Thin Film

PEO_{5k}-*b*-$PFOMA_{22k}$ was dissolved in chloroform or TFT to yield 0.5, and 0.3 wt% of micellar solutions. For the thin film, a pasture pipette was used to cast equal-sized droplets of the block copolymer solution onto a carbon-coated copper grid. After complete solvent evaporation, it results in a thin film.

Solvent vapor treatment

For the solvent vapor annealing process, the thin film was placed into a glass vessel with the reservoir of TFT or PF-5080. The temperature of the solvent vapor was always kept at 70°C. The films were exposed to vapors by placing them several milimeters above the liquid surface of the solvent kept in the closed vessel. After the vapor treatment, the samples were taken out from the vessel and dried in air at room temperature.

Measurements

The structure of the films before and after annealing was observed by transmission electron microscopy (TEM) with a Hitachi H-7500 instrument operated at an acceleration voltage of 80 kV. The lighter phase in the TEM image is for the PEO blocks and the darker phase corresponds to the PFOMA blocks.

Results and Discussion

Micellar thin films of PEO_{5k}-*b*-$PFOMA_{22k}$ were used for phase separation under saturated TFT or PF-5080 vapor at 70°C. This temperature was chosen so that solvent vapor annealing was kept above the glass transition temperature (T_g) of the PEO and PFOMA, given complications that may arise from crystallization [17, 18]. For PEO_{5k}-*b*-$PFOMA_{22k}$ thin film, the temperature was necessary to get higher mobility of the chains in the presence of solvent vapor. The morphological changes never happened upon prolonged vapor treatment of TFT or PF-5080 at room temperature.

The different morphologies of PEO5k-b-PFOMA22k aggregates formed in chloroform and TFT solutions, before and after solvent vapor treatment are summarized in Table 1. The TEM image of as-cast asymmetric 0.5 wt% PEO-*b*-PFOMA micellar films from chloroform is shown in Figure 1a. When the soluble block is much shorter than the insoluble block, the aggregates forms a crew-cut morphology [19]. It can be seen that the as-cast film showed combined crew-cut aggregates of cylindrical and spherical. The time development of the morphology of thin films in TFT vapor was investigated by TEM (Figure 1b-c). After TFT vapor treatment for 6 h, a long range cylindrical morphology appeared in the TEM image. (Figure 1b) The topography of the whole film consists of disordered long cylinders oriented in different directions. But after 18 h, it becomes an ordered structure

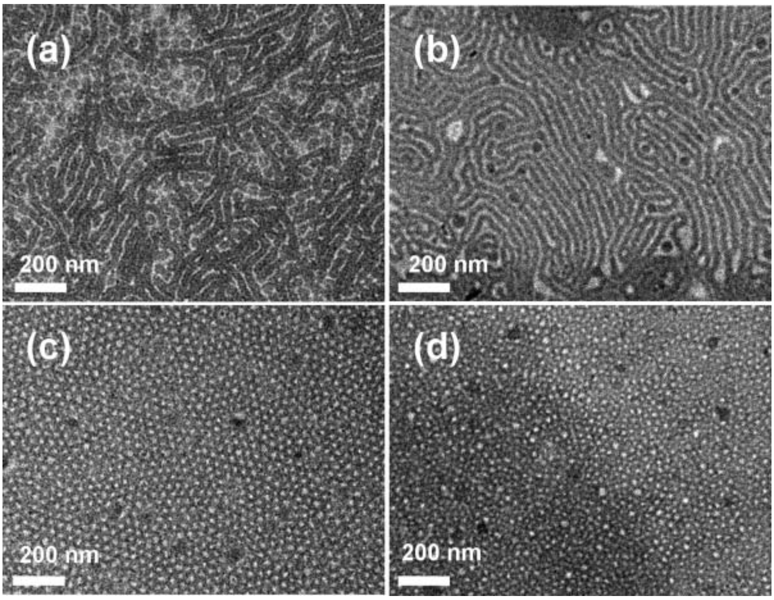


Figure 1. TEM images of 0.5 wt% PEO-*b*-PFOMA in chloroform, (a) as-cast thin films. After TFT vapor treatment for (b) 6 h, (c) 18 h; and PF-5080 vapor treatment for (d) 3 h. (Scale bar = 200 nm).

with PEO domain and PFOMA continuous phase (Figure 1c). After PF-5080 solvent vapor annealing for 3 h, the morphology of the thin film similarly shows PEO nanodomains in the PFOMA continuous phase (Figure 1d). Longer annealing times (24 h) produced almost the same morphology, indicating PF-5080 vapor treatment for 3 h is enough to reach in an equilibrium morphological state.

The TEM image of as-cast asymmetric 0.3 wt% PEO-*b*-PFOMA micellar films from the chloroform solution shows a mixed morphology, where disordered PEO domains in PFOMA matrix co-exist with disordered PFOMA cylinders (Figure 2a). The time development of the morphology of the thin films in TFT vapor was also investigated (Figure 2b-e). Interestingly, a mixed morphology containing a striped and spherical morphology appeared upon vapor treatment of TFT for 2 h (Figure 2b). After 3 h, it led to totally striped morphology showing a surface-perpendicular lamellar structure (Figure 2c). But after prolonged exposure for 6 h, the lamellar morphology completely disappeared and became nanoscale assemblies without any distinct morphology (Figure 2d). After 12 h, the film has fully developed spherical morphology of PEO nanodomains in PFOMA matrix (Figure 2e). The

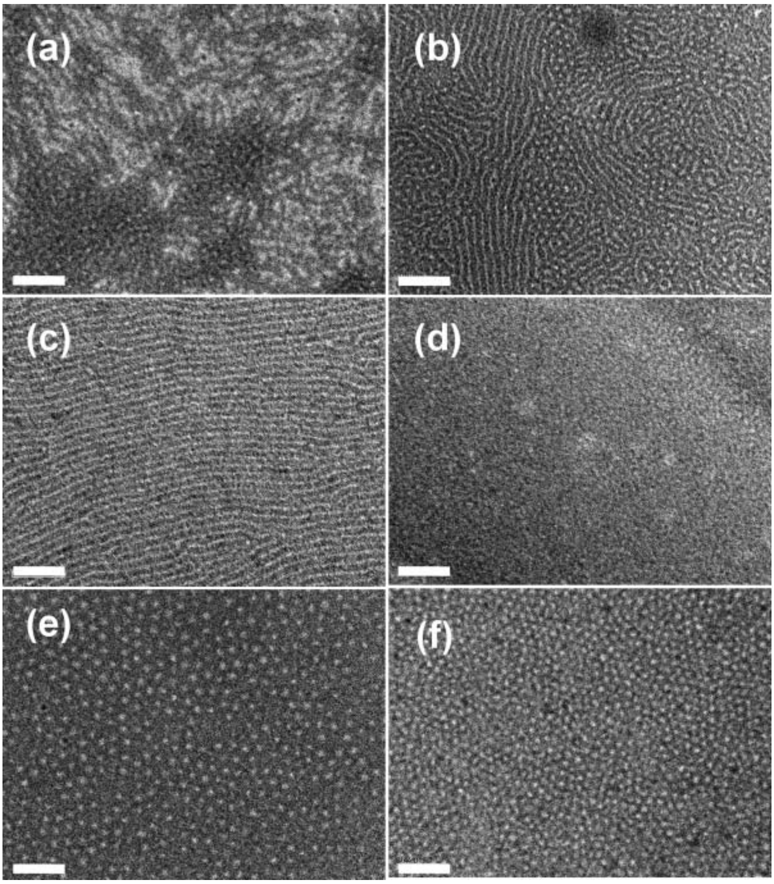


Figure 2. TEM images of 0.3 wt% PEO-*b*-PFOMA in chloroform, (a) as-cast thin films. After TFT vapor treatment for (b) 2 h, (c) 3 h, (d) 6 h, (e) 12 h; and PF-5080 vapor treatment for (f) 3 h. (Scale bar = 200 nm).

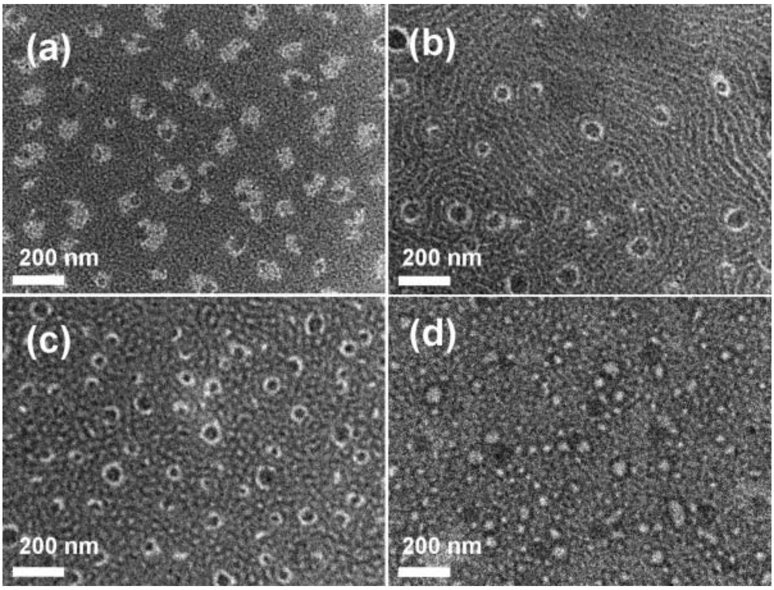


Figure 3. TEM images of 0.5 wt% PEO-*b*-PFOMA in TFT, (a) as-cast thin films. After TFT vapor treatment for (b) 6 h, (c) 18 h; and PF-5080 vapor treatment for (d) 6 h (Scale bar = 200 nm).

same PEO spherical morphology was observed after PF-5080 vapor annealing for relatively short time of 3 h (Figure 2f). The possible reason for the differences could be that the different nature of selective solvents may affect the mobility and arrangement of the blocks in the thin films.

Table 1. Different morphologies of PEO_{5k}-*b*-$PFOMA_{22k}$ aggregates form chloroform and TFT solutions, before and after solvent vapor treatment

Casting Solvent	Solution Concentration	As-cast morphology	Solvent vapor	Morphology with annealing time 3 h	6 h	18 h
$CHCl_3$	0.5 wt%	S, C	TFT	—	C	IS
			PF-5080	IS	IS	IS
	0.3 wt%	IS, C	TFT	L, IS	N	IS
			PF-5080	IS	IS	IS
TFT	0.5 wt%	N	TFT	—	C	IS
			PF-5080	—	IS	IS
	0.3 wt%	N	TFT	L	IS, C	IS
			PF-5080	—	IS	IS

key: C, Cylindrical; S, Spherical (PFOMA domain in PEO matrix); IS, Inverted-Sphere (PEO domain in PFOMA matrix); L, Lamellar; N, No morphology. If two morphologies are listed, the major one is given first.

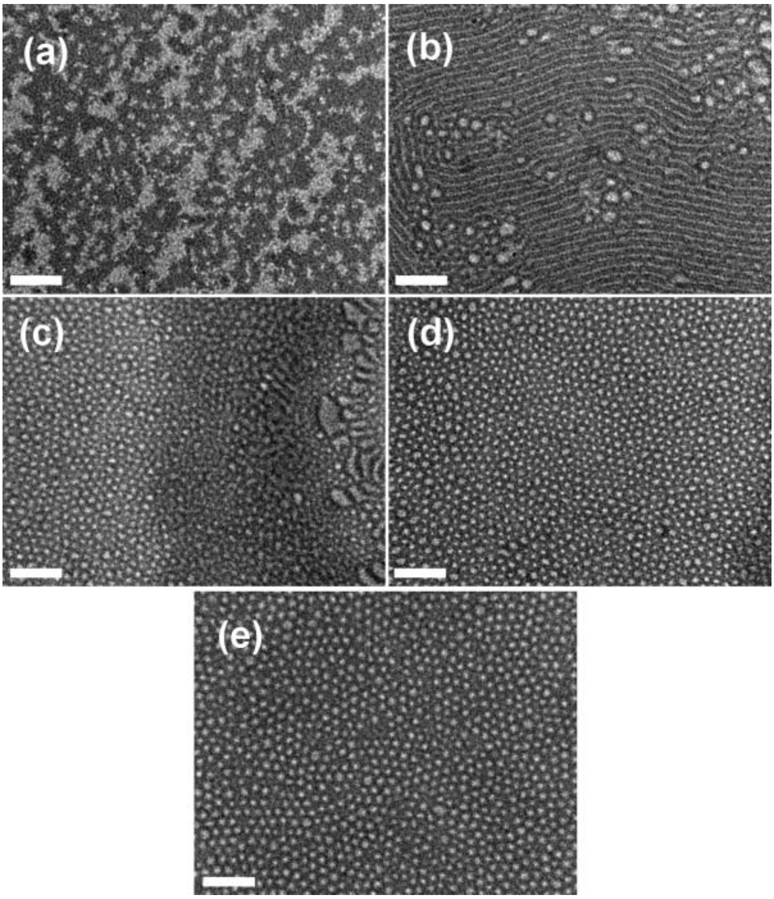


Figure 4. TEM images of 0.3 wt% PEO-*b*-PFOMA in TFT, (a) as-cast thin film. After TFT vapor treatment for (b) 3 h, (c) 6 h, (d) 12 h and PF-5080 vapor treatment for (e) 6 h. (Scale bar = 200 nm).

Since both blocks were soluble in TFT which is not a suitable solvent for micelle formation, nanoscale assemblies without any distinct micellar morphology were produced from 0.5 wt% of PEO-*b*-PFOMA in TFT (Figure 3a). Several large beadlike aggregates are seen together in the image, which may be attributed to heterogeneity of the block copolymer composition. The beadlike deformation was also present after annealing. After 6 h in TFT vapor environment, the disordered morphologies preferentially formed a long range cylindrical morphology (Figure 3b). After 18 h, PEO spheres appeared in the PFOMA continuous phase (Figure 3c). On the other hand, PEO domains of a broad size distribution in the PFOMA matrix were obtained after PF-5080 vapor annealing for 6 h (Figure 3d).

Thin films from 0.3 wt% of PEO-*b*-PFOMA in TFT also showed nanoscale assemblies without any distinct morphology (Figure 4a). However, no beadlike deformations occur for the lower concentration. After 3 h in TFT vapor environment, a long range lamellae morphology was produced (Figure 4b). After TFT vapor annealing for 6 h, the orientation of the lamellae was changed to PEO spheres. There were some cylindrical loops formed with PEO sphere (Figure 4c). After 12 h, the film has fully developed to the spherical morphology of PEO domains in PFOMA matrix (Figure 4d). Most interestingly, as-cast disordered morphology completely converted to the hexagonal spherical morphology after PF-5080 vapor treatment for 6 h (Figure 4e). For the as-cast micellar thin film from chloroform or TFT, PEO domains in PFOMA matrix appeared under PF-5080 vapor treatment in a short time. The same patterns were obtained after much longer times in the case of TFT vapor. These results suggest that a slightly preferential affinity of a good solvent for one block would strongly alter the morphological behavior.

Conclusions

The film morphologies of PEO_{5k}-*b*-$PFOMA_{22k}$ block copolymers could be manipulated by solvent annealing. PEO_{5k}-*b*-$PFOMA_{22k}$ thin films cast from 0.5 wt% in chloroform and TFT showed combined crew-cut aggregates and a featureless morphology, respectively. Both films underwent structural transitions to cylindrical and spherical morphologies, respectively, as annealing time progressed in TFT vapor. As-cast thin film from 0.3 wt% in chloroform and TFT showed disordered mixed and featureless morphology, respectively. Both film structures also transformed to lamellae and spherical morphologies, respectively, as annealing time progressed in TFT vapor. In contrast with TFT solvent vapor, all of the thin films from chloroform and TFT exhibited a highly ordered array of nanodomains upon short treatment in PF-5080 vapor. These results reveal that the initial morphologies from chloroform and TFT have little influence on the process of the pattern evolution during TFT and PF-5080 solvent vapor.

Acknowledgment

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