

Graft Copolymers Having Hydrophobic Backbone and Hydrophilic Branches XXXIV. Fabrication and Control of Honeycomb Structure Prepared from Amphiphilic Graft Copolymers

Ken-ichiro HIWATARI, Takeshi SERIZAWA, Fusako SETO,* Akio KISHIDA, Yoichiro MURAOKA,* and Mitsuru AKASHI†

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

**Department of Home Economics Education, Faculty of Education, Kagoshima University, 1-20-6 Korimoto, Kagoshima 890-0065, Japan*

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ABSTRACT: Well-controlled polymeric honeycomb structures were made from graft copolymer prepared by free radical polymerization of a poly(ethylene glycol) (PEG) macromonomer and styrene with *N,N*-azobisisobutyronitrile (AIBN) as radical initiator in ethanol/water (4/1, v/v) solvent. Macroporous polymeric films were formed when chloroform solution of the freeze-dried nanospheres was dip-coated under controlled conditions of humidity and while controlling the composition of the graft copolymer and the type of substrate. Highly-ordered and monodispersed pores were formed on polymeric film surfaces from the graft copolymer (St/(PEG macromonomer) ratio = 105/1, mol/mol) under controlled conditions (humidity, 70% (RH); pulling up speed, 500 cm min⁻¹). Control of humidity during the dip-coat process was essential for formation of the ordered porous structure. Macroporous structures were formed possibly by condensed water-droplets as templates. The formation of pores on the film was dependent on concentration of the solution. When dip-coated in a 3 (w/v) % solution, the pores did not penetrate the substrate. In contrast, pores penetrated it from a 1 (w/v)% solution. Graft copolymers formed a unique structure under controlled regulatory conditions.

KEY WORDS Nanospheres / Macromonomer Method / Core-Corona / Honeycomb / Porous Film / Graft Copolymer / Dip-Coating /

The production of macroporous materials is presently under intense study for a wide range of applications in chemistry.^{1,2} Macroporous polymer matrices can be used as catalytic surface and supports,^{3,4} biomaterials,^{5,6} separation and adsorbent media,^{7,8} etc. Ordered porous film over a wide range of pore size can be applied to optical filters,⁹ linear and nonlinear optics and chemical sensors.^{10,11}

A number of techniques have been studied for the production of well-controlled macroporous polymer matrices. These include emulsions¹² or silica particles as templates,^{2,13} self-assembly of diblock copolymers^{14,15} and various amphiphilic polymers.^{16–18} François *et al.* reported a method to generate polymer films with monodispersed pores, in which pores existed as hexagonal arrays. These films are produced by evaporating carbon disulphide solutions of poly(styrene-*b*-polyparaphenylene) diblock copolymers under a flow of moist gas.¹⁴ The chemical function of diblock copolymers is synchronized with the honeycomb structure.¹⁹ Shimomura *et al.* reported the production of a honeycomb-structured film, prepared by solution casting of several types of amphiphilic polymers in volatile solvent on a substrate. Honeycomb structure of the

polymer films was formed using water droplets at the air-solution interface as an ordered template. Size and structure of the honeycomb patterns could be regulated by the altering concentration, atmospheric humidity, etc.^{16–18,20}

We previously investigated the macromonomer method for the preparation of polymeric nanospheres.^{21–23} Hydrophilic macromonomer chains accumulated on the surface of nanospheres prepared by dispersion copolymerization of styrene with a hydrophilic macromonomer. We previously described platinum nanocolloids immobilized on polystyrene nanospheres coated with poly(*N*-isopropylacrylamide), which are thermo responsive polymers.^{23,24} Nanospheres immobilizing a metal catalyst serve not only as stabilizer, but also as functional component that influences the activity and thermoresponsiveness of the catalyst. The accumulation of functional macromonomers on surfaces enables applications as captors of human immunodeficiency virus-1 (HIV-1)²⁵ and as peptide drug carriers *via* oral administration.^{26–28} The graft copolymer in nanospheres was composed of a hydrophobic backbone and hydrophilic graft chains. During polymerization, the graft copolymers self-assembled to form a sphere

†To whom correspondence should be addressed (Tel: +81-99-285-8320, Fax: +81-99-255-1229, E-mail: akashi@apc.kagoshima-u.ac.jp).

in a polar solvent because the hydrophobic backbone of the graft copolymer is insoluble but hydrophilic graft chains swell in a polar solvent. This amphiphilic property of graft copolymers may be utilized in the formation of specific structures on substrate surfaces.²⁹

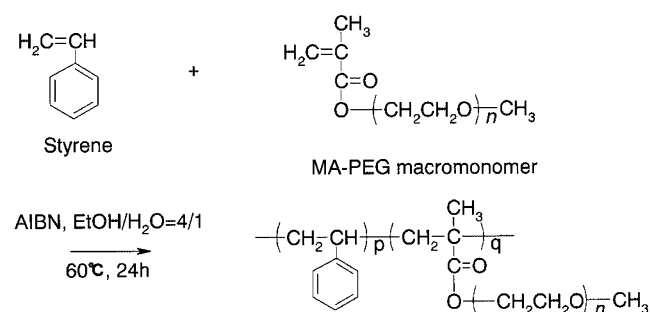
We previously reported that poly(styrene-*co*-PEG macromonomer), prepared as a component of its nanosphere, form macroporous structure prepared by dip-coat on poly(ethylene terephthalate) as a substrate, in which the morphology was dependent on the chemical composition of the graft copolymer.³⁰ It is expected that a graft copolymer with a honeycomb structure has self-supportability. The preparation of a honeycomb structure using graft copolymers has not been previously reported.

This study describes the production and control of macroporous structure from poly(styrene-*co*-PEG macromonomer) prepared by the macromonomer method. Macroporous polymeric films were prepared when chloroform solution of the freeze-dried nanospheres was dip-coated under controlled conditions of humidity, composition of the graft copolymer, and substrate. The surface of dip-coating film was observed by scanning electron microscopy. Morphology of dip-coating films was affected by any environmental factors.

EXPERIMENTAL

Materials

Methacryloyl-terminated poly(ethylene glycol) (PEG) ($M_n = 1700$) was furnished by Nippon Oil and Fats Co. (Tokyo, Japan). Styrene (Wako Pure Chemical Ind.) was purified by distillation under reduced pressure before use. *N,N'*-azobisisobutyronitrile (AIBN) was recrystallized from acetone. Poly(ethylene terephthalate) (PET) was donated by Teijin Co. (Tokyo, Japan), and washed by a Soxhlet extraction in condensed acetone for 24 h. Mica was purchased from Okenshoji Co., Ltd.



Scheme 1.

Preparation of Poly(styrene-*co*-PEG macromonomer) Nanospheres

The preparation of the poly(styrene-*co*-PEG macromonomer) nanospheres using methacryloyl-terminated PEG has been reported in several papers.^{31,32} Methacryloyl PEG as macromonomer and styrene were weighed into a glass tube, together with AIBN as an initiator and 5 mL ethanol/water (4/1, v/v) as solvent. The solution was degassed by freeze-thaw cycles on a vacuum line, and the tube was sealed off. The tube was placed in a water bath of 60°C for 24 h with shaking. The products were first dialyzed in methanol using a cellulose dialyzer tube to remove unreacted macromonomer and styrene, and polymer particles were replaced by dialyzing in distilled water and freeze-drying.

Fabrication of the Macroporous Structure on a Solid Surface

Dip-coating onto a solid surface was carried out at controlled temperature (20°C) and humidity. Freeze-dried nanospheres were dissolved in chloroform at prescribed concentration. The solution became homogeneous, since the nanospheres dissolved in chloroform. The substrate was soaked in this solution, and pulled up at constant speed (500 cm min⁻¹) with a viscoelasticity meter (SHIMADZU ez-meter). And dried in air at ambient temperature. PET films and mica were used as substrates.

Characterization of the Nanospheres and Macroporous Surface

The diameter of the nanospheres was determined by a submicron particle analyzer (COULTER model N4SD) and scanning electron microscope (SEM, HITACHI S-4100 H). Before SEM observation, gold was sputtered onto the dip-coated film. Surface morphology of the film was observed by SEM (accelerated voltage; 5 kV). Atomic Force Microscopy (AFM) images were obtained with a Digital Instruments NanoScope III operating in contact mode in air at ambient temperature.

RESULTS AND DISCUSSION

Preparation of Nanospheres from Graft Copolymers

The conditions and results of the preparation of the nanospheres are listed in Table I. Particle size and ratio of styrene and PEG macromonomer were related to each other, as described in previous studies,^{21,31-33} as follows. Briefly, when total concentration of monomer was constant, size of the nanosphere was proportional to content of styrene as a hydrophobic comonomer. From GPC, the nanospheres consisted

Table I. Characterization of nanospheres copolymerized from PEG macromonomer with styrene in ethanol/water (4/1, v/v) as a solvent

Run	PEG		St mmol	St/PEG mol/mol	Yield %	dm nm	c.v. %	$M_n \times 10^{-4}$ ^a	M_w/M_n ^a	Composition of Nanospheres. St/(MA-PEG) ^b
	M_n	mmol								
1	1700	0.36	3.6	10	70	62	17	56	31	17.7
2	1700	0.20	6.2	30	74	150	17	93	26	34.1
3	1700	0.082	8.2	100	85	180	16	26	23	105

^aEstimated by GPC. Mobile phase, CHCl_3 ; standard, polystyrene. ^bEstimated by $^1\text{H NMR}$ in CDCl_3 .

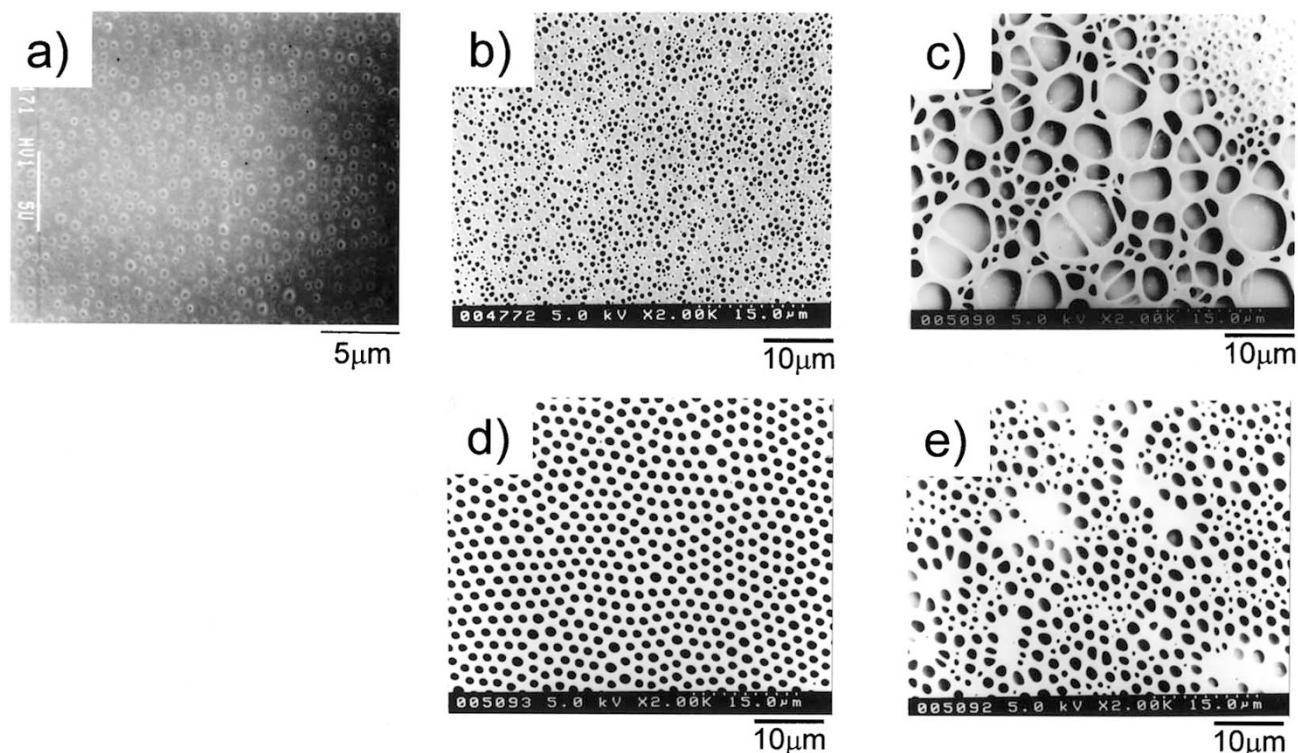


Figure 1. SEM of the surface of film prepared by dip-coating from a poly(styrene-*co*-PEG macromonomer) solution at different humidities. Characterization of poly(styrene-*co*-PEG macromonomer) shown in Table I (Run 3). Film was prepared by dip-coating on a substrate as mica under a) 20%(RH), b) 70%(RH), c) 90%(RH); and using PET as substrate under d) 70%(RH), e) 90%(RH).

of graft copolymers, in which the molecular weight of the graft copolymer was a few hundred thousand and the distribution of molecular weight of the graft copolymers was broad. Capek *et al.* reported graft copolymers prepared by the macromonomer method have a more narrow distribution than ours.³⁴ In their experiments, nanospheres were prepared using dibenzoyl peroxide (DBP) as initiator. In our experiments, nanospheres were prepared using AIBN as an azo-type initiator. The molecular weight of the copolymer is affected by initiator used.³³

Formation of Macroporous Film on a Substrate

The graft copolymers dissolved in chloroform uniformly, since the graft copolymers consisted of chloroform-soluble segments of poly(styrene-*co*-alkylmethacrylate) backbones and PEG branches. Figure 1 shows the dependence of macroporous structure on humidity. The surface of a film dip-coated onto the

PET film under dry N_2 gas has little roughness (Figure 1a). In contrast, at around 70%(RH), a unique ordered macroporous film on PET and mica was obtained (Figures 1b and 1d). At 90%(RH), pore size of the film increased non-uniformly (Figures 1c and 1e). The size and shape of pores were affected by the substrate. In particular, the surface of polymeric film on mica prepared at 70%(RH) has monodispersed pores over a broad area. Water in the atmosphere may thus be involved in the formation of pores obtained by dip-coating.

Detailed analysis of the structures of the macroporous films was done by AFM (Figure 2). All images were observed in contact mode in air at ambient temperature. Figures 2a and 2b show the surface of Figures 1d and 1b, respectively. From a cross-section of the porous film, thickness of the film was almost constant, and the pore shape was a half sphere. In Figure 2a, pore diameter is around $1.5 \mu\text{m}$, and depth is

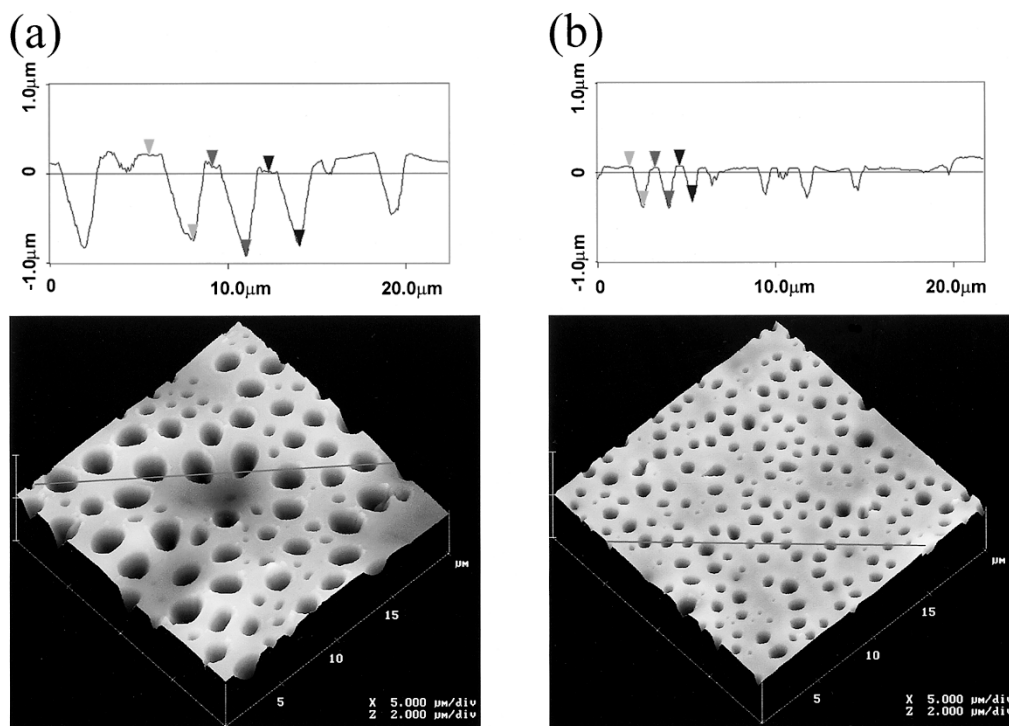


Figure 2. Surface profile of macroporous structure by Atomic Force Microscopy (AFM). Surface images of (a): Figure 1d and (b): Figure 1b.

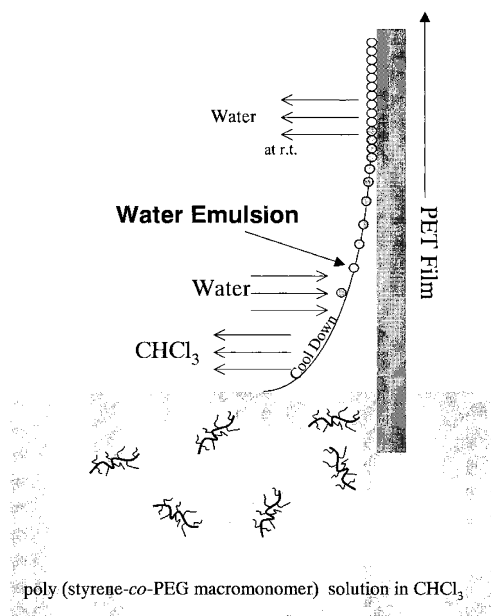


Figure 3. Schematic illustration macroporous structure on a substrate *via* dip-coating.

900 nm. Pores may thus form formatted using a spherical object as template.

The formation of the unique morphology prepared by dip-coating is almost the same to that by a solvent-casting method, of which the mechanism was proposed by Shimomura *et al.*,¹⁷ although the substrate in the present study was vertical to the solution surface. Figure 3 shows a possible mechanism of formation of macroporous structure. After the substrate was

pulled from the chloroform polymer solution, chloroform started to evaporate. The surface of the solution on the substrate was cooled by evaporation heat. Water present in the atmosphere should be condensed on the solution surface. Polymeric film was formed using the water-droplet as template, as water-droplets were not coagulated by the presence of copolymers as surfactant. When it was finished chloroform evaporation, temperature of surface is heated up to ambient temperature. Water-droplets evaporated and the traces became to pore in/on the film. It is required to formation of honeycomb structures that the evaporation rate of solvent is larger than a coagulation rate of water droplets. Polydispersed pores in Figures 1c and 1e indicate that water droplets coalesce on the air-solution interface. Honeycomb structures formed during non-equilibrium and dynamic process. The solvent evaporation rate and volume of casting solution were important factors for the formation of the honeycomb structure. In the dip-coating method, these factors can be controlled by the pulling speed and solution concentration. The dip-coating method may be applied to various polymers, in which a honeycomb structure cannot be prepared by casting. Macroporous films consisting of poly(styrene-co-PEG macromonomer) graft copolymers could not be made by the casting method.

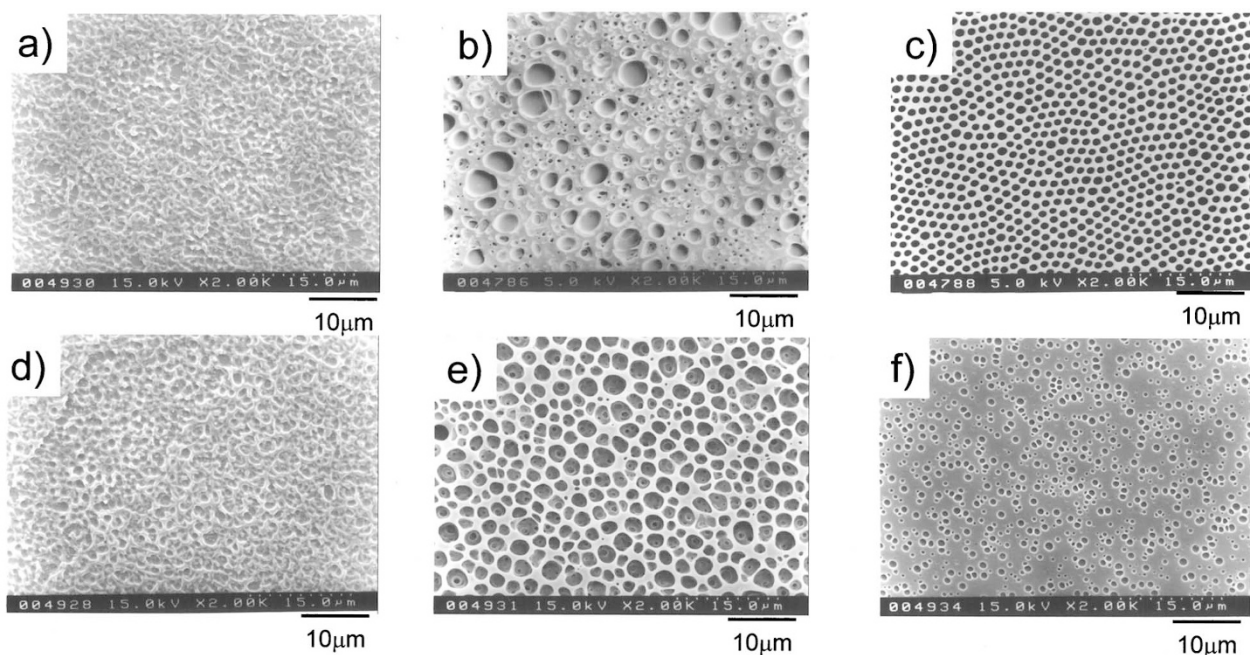


Figure 4. Scanning electron micrographs of surface morphology of poly(styrene-*co*-PEG macromonomer) film prepared from graft copolymers with different composition. a) Sample 1 on mica, b) sample 2 on mica, c) sample 3 on mica, d) sample 1 on PET, e) sample 2 on PET, and f) sample 3 on PET (as shown in Table I).

Control of the Macroporous Structure

The role of the graft copolymer in the formation of macroporous structure is stabilization of the water droplet as templates. The macroporous structure prepared by dip-coating is affected by amphiphilic property of the graft copolymers. Figure 4 shows the surfaces of the films prepared from graft copolymers with different chemical compositions on PET and mica. Surface morphology of graft copolymer with a large PEG macromonomer segment was much like a sponge structure. In contrast, graft copolymers with fewer PEG segments formed ordered pores on the surface. Graft copolymer with a medium PEG composition formed a non-uniform structure. Surface-active properties of the graft copolymers seem to affect the formation of macroporous structures. According to the present mechanism, surface-activity of the graft copolymers may affect emulsion size and form on solution surface during dip-coating. It is likely that difference of properties alter macroporous morphology.

A cross-section of the macroporous film (Figure 4c, St/(PEG macromonomer) = 105/1, mol/mol, humidity; 70% (RH)) was also observed by SEM (Figure 5). The images suggested that pores on the polymeric films did not penetrate through the film. The thickness of the bottom of the pores was around 200 nm (Figure 5c). The shape of the cross-section of the macroporous film is illustrated in Figure 5d.

The effect of solution concentration on the morphol-

ogy of the film was analyzed. Figure 6 shows a SEM image of the porous film prepared from a 1% solution. Pores on this film have lower monodispersability than that of films prepared from a 3% solution under identical conditions. Morphology of the film was affected by the substrate. Figure 7 illustrates differences in formation at different concentrations. In the case of dip-coating from a 3 (w/v)% solution, the water-droplet templates did not contact the surface of the substrate. However, in the case of dip-coating film from a 1 (w/v)% solution, the shape of the water-droplets affected was possibly by the surface properties of the substrate. Control of polymer concentration induces the variation of pore shape on the film. The surface of mica is more hydrophilic and flatter than that of PET, and thus the shape of the water-droplets on the surface should reflect surface properties of the substrate. The morphology of polymeric film dip-coated from a 1 (w/v)% solution thus seems non-homogeneous.

CONCLUSIONS

The macromonomer method prepares polymeric nanospheres composed of graft copolymers with a hydrophobic backbone and hydrophilic branches. Graft copolymer of macroporous films on the substrate by dip-coating in chloroform solution. The honeycomb structures were affected by the composition of the copolymer as well as humidity. The unique morphology is almost similar to that by the solvent-casting

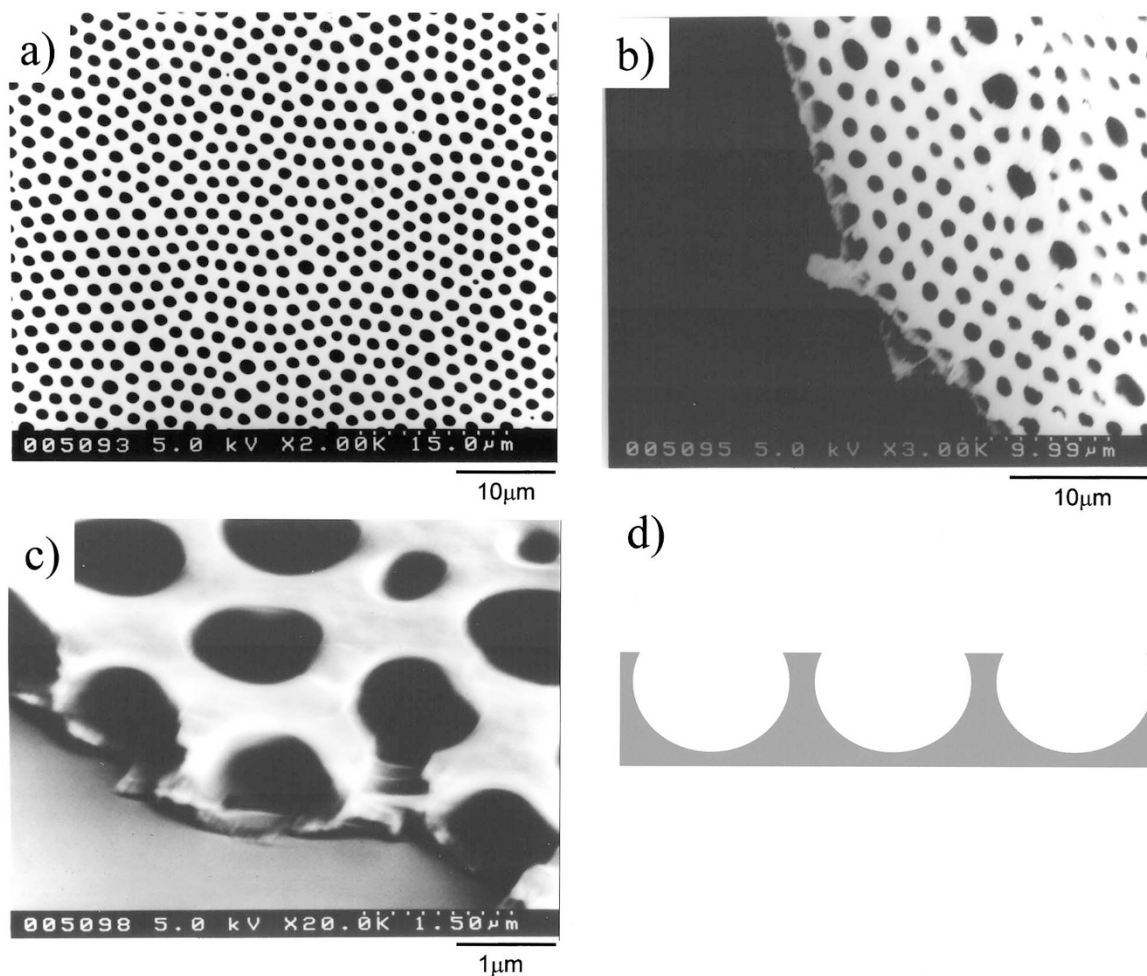


Figure 5. SEM of morphology of polymeric films prepared from poly(styrene-*co*-PEG macromonomer) (Table I, Run 3). Conditions of the dip-coating are as follows; solution concentration: 3%; humidity: 70%(RH). a) TOP view, b) quarter view, c) cross-section, d) illustration of cross-section.

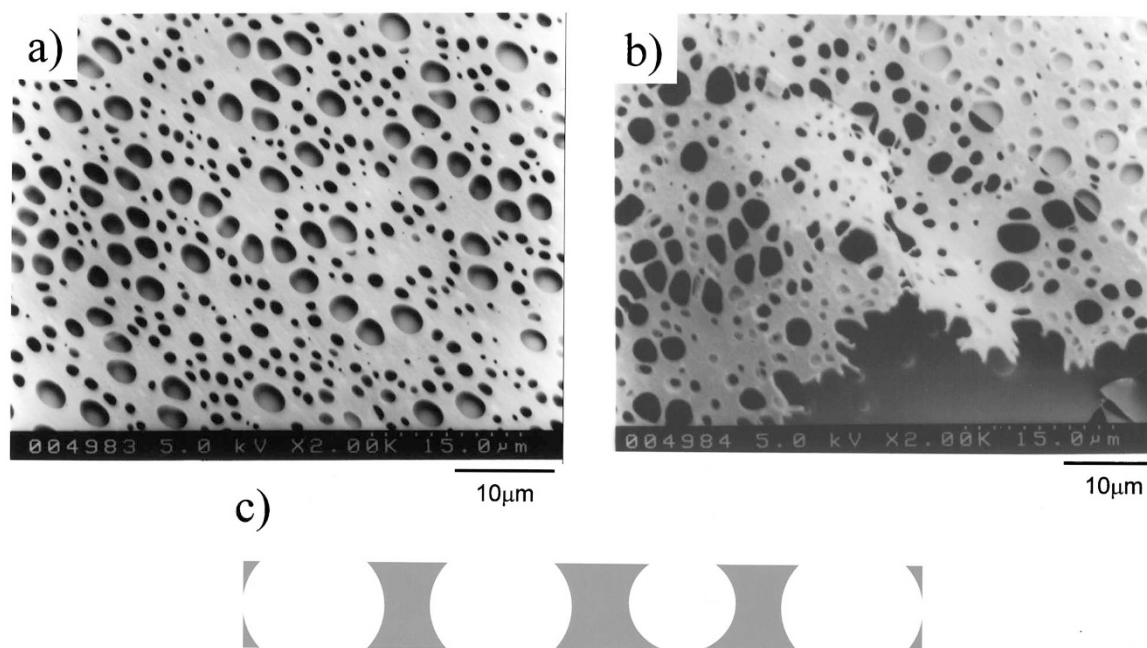


Figure 6. SEM of morphology of polymeric films prepared from poly(styrene-*co*-PEG macromonomer) (Table I, Run 3). Conditions of the dip-coating are as follows; solution concentration: 1%; humidity: 70%(RH). a) TOP view, b) quarter view, and c) illustration of the cross-section.

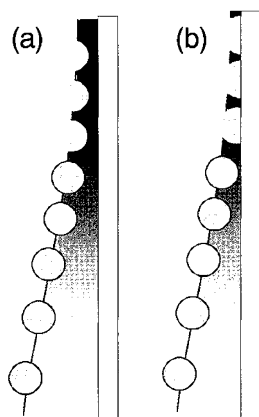


Figure 7. Schematic illustration of different topologies of films prepared of different solution concentrations. a) 3% solution concentration, b) 1% solution concentration.

method.¹⁷ Macroporous structures may form using condensed water-droplets as template. This is supported by the observation of shape of the pores, and effects of solution concentration on shape. Graft copolymers consisting of a hydrophobic backbone and hydrophilic branches may form into a well-controlled macroporous structure under controlled conditions.

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