Exploitable Flexible Honeycomb Structured Porous Films from Sol−Gel Cross-Linkable Silicone Based Random Branched Copolymers

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This work describes the novel use of silicone based random branched copolymers, PEGDMA-*ran*-PMMA-*ran*-PMPS and PEGDMA-*ran*-PMMA-*ran*-PTRIS, in "breath figure" technique formation of honeycomb structured porous films. These branched copolymers compounds are prepared by a facile, one-pot conventional free radical copolymerization technique that is economic and scalable for industry exploitations. The branched copolymers compounds are soluble in organic solvents and high in molecular weights and were taken to high monomer conversions without gelling or cross-linking. The degree of branching and molecular weights of branched copolymers compounds was readily controlled by varying the feed concentrations and ratios of the monomers methyl methacrylate (MMA), 3-(trimethoxysilyl)propyl methacrylate (MPS), or 3-[tris(trimethylsiloxy)silyl]propyl methacrylate (TRIS), the cross-linker and ethylene glycol dimethacrylate (EGDMA), and the chain transfer agent 1-dodecanthiol (DDT) during copolymerization. The presence of alkoxysilane precursors (i.e., PMPS) inside honeycomb structured porous films prepared from PEGDMA-*ran*-PMMA-*ran*-PMPS random branched copolymers enables cross-linking of the film via the sol−gel process to improve properties of the film. Cross-linked porous films have enhanced properties including higher flexibility without breakage, higher solvent resistance, and thermal stabilities up to 85 °C. The observed phase transitions of thermal sensitive PNIPAAm solution deposited inside the pores of these cross-linked porous films exhibited the thermal conductivity property of honeycomb structured porous films. These flexible, thermally and chemically stable honeycomb structured porous films may find applications as thermal sensors or low-cost conformal digital display when coupled with thermal sensitive or light emitting materials inside the pores of these films.

1. Introduction

Featured porous thin films with hexagonally arranged spherical pores, otherwise known as honeycomb structured porous films, are readily prepared by self-assembly of polymers gelling around condensates in volatile organic solvents.[1] François et al. termed this the "breath figure" formation technique and instigated intense research in self-assembly polymeric structures over the passed decade.[2,3] The general mechanisms of "breath figure" formation technique and various distinctive characteristics of the honeycomb morphology including high surface to area ratios, light diffractions properties, and ultrahydrophobicity have been reported.[4,5] Easy accessibility to formation

techniques, good control of honeycomb array physiques (hole dimensions, film thickness), and the unique surface properties have made honeycomb structured porous films potential materials for applications in separations,[6] chemical microreactors,[7] photonics band gap materials,[8] and biological cell proliferation substrates.[9]

Many studies have suggested a variety of designer polymer compounds that support "breath figure" technique formation of regular hexagonal porous arrays in thin films. They include star polymers,[10] strategically branched polymers,[11] block copolymers,[12] conjugated

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polymers,[13] polymers blends,[14] polyion complexes,[15] and amphiphilic copolymers.[16] Although the advantages and effectiveness of using these well-architected polymer compounds in honeycomb structured porous films formations are well recognized, their synthetic methodologies are however nongeneric, uneconomic, and difficult to exploit industrially (i.e., lack of scalability). Examples of synthetic routes include controlled living polymerization techniques such as living anionic,[17] atom transfer radical polymerization (ATRP),[18] and reversible addition−fragmentation chain-transfer (RAFT)[19] polymerizations. The conditions of these polymerization techniques are often stringent and/or demanding, frequently requiring tailored molecules or precursors limited in varieties, elevated polymerization temperatures, and multiple purification procedures to isolate the desired polymer compounds.

Early this decade, Sherrington and co-workers reported a generic, one-step, batch solution synthetic strategy, termed the "Strathclyde methodology", that yields completely soluble, high monomer conversion branched or hyperbranched copolymers from routinely available vinyl monomers and organics.[20] Unlike other branched polymers synthetic strategies, such as group transfer polymerization (GTP) by Muller et al.,[21] ATRP by Matyjasewski et al.,[22] or RAFT by Davis et al.,[23] although refined, are not universal and require specialized vinyl monomers and other molecules that are either difficult to acquire or costly in large quantities. In addition, branched polymers produced by these approaches can only be polymerized to low monomer conversions, while attempts to increase conversions will lead irreversible to insoluble cross-linked polymers.[24] Consequently rendering such elegant synthetic approaches is uneconomic and unfeasible for large-scale commercial developments.

The Strathclyde methodology, complements the self-condensing vinyl polymerization (SCVP) strategy first reported by Fréchet et al. in 1995, employing additional vinyl monomers with a second or more functionalities to initiate supplementary polymerization with other vinyl monomers during polymerization to produce branched copolymers.[25] The Strathclyde approach employs simple conventional free radical copolymerization of common vinyl monomers (i.e., methyl methacrylate, styrene) and a difunctional (or multifunctional) comonomer or branching agent (i.e., divinylbenzene, ethylene glycol dimethacrylate) with cross-linking inhibited by the introduction of thiol based chain transfer agents (i.e., dodecanethiol, butanethiol) and dilution of the reactions with solvents. As reported by Isaure et al., one key factor in achieving highly branched but soluble copolymers is the introduction of appropriate concentrations of chain transfer agents during the copolymerization, particularly the feed concentration ratios of branching agents and chain transfer agents.[26] Typically a branching agent/chain transfer agent mole feed concentration ratio (divinylbenzene/dodecanthiol) of ≤1 ascertains the absence of cross-linking in the copolymers, even when the feed concentrations of branching agents were increased compared to monomer feed concentrations. Additionally, to achieve inhabitation of cross-linking in the Strathclyde approach, an adequate dilution of the whole reaction medium with appropriate quantity of solvent is essential. With adequate dilutions, increases in viscosity of reaction medium as copolymerization proceeds will be insignificant. The diffusion of molecules, especially macromolecules formed during copolymerization, although highly expanded structurally, is not inhibited, and consequently the probabilities of cross-linking due to close approximations of molecules are minimized.

The stability of honeycomb porous films in harsh environments such as organic solvents, elevated temperatures, and process handlings are important issues to address for 'real world' applications of polymer honeycomb porous films. Stenzel et al. have suggested that chemically cross-linking polymers inside the films could lead to improved physical properties and stability of honeycomb porous films.[27] Shimomura et al. and Bunz et al. reported two cross-linked polymer honeycomb porous films prepared by photochemical (Ultraviolet ∼ 265 nm) cross-link of prepolymers and azide-containing rigid-rod polymers, respectively.[28,29] However, the three-dimensional spherical pore structures in these films collapsed during cross-linking. In recent times, Karthaus et al. also reported two other cross-linked polymer honeycomb porous films, one prepared by photochemical cross-link of poly(cinnamates) and another by chemical cross-link of maleic anhydride copolymers with diamine.[30] The three-dimensional

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porous structures in these films were not damaged during cross-linking, and cross-linked poly(cinnamates) porous films were stable in a variety of organic solvents, including chloroform, tetrahydrofuran, and carbon disulfide. Cross-linked maleic anhydride copolymers porous films were also thermally stable up to 350 °C, but the inherent surface ultrahydrophobicity of honeycomb porous films was changed after cross-linking.

The sol−gel process is a widely used wet-chemical method for manufacturing hybrid organic/inorganic glass base materials.[31] Unlike traditional sintering methodologies, the sol−gel process is a low temperature and economical approach to bring together organic polymeric molecules and inorganic moieties at temperatures the organics do not decompose. This process has generated a novel class of hybrid nanocomposite materials termed "ormosils" or "ormocers" by Schmidt et al.[32] These hybrid materials exhibit exceptional syndicate properties unachievable by traditional materials or production methods.[33]

The sol−gel process initiates with liquid chemical precursors and generates complex integrated polymer networks or discrete particles. Precursors for the sol−gel process contain metal or metalloid elements surrounded by various reactive ligands such as alkoxide, which reacts readily in water. The most extensively used silicate based alkoxide precursors (alkoxysilanes) are tetramethoxysilane (TOMS) and tetraethoxysilane (TEOS). The general reaction mechanisms of the sol−gel process with alkoxysilanes precursors include hydrolysis of the precursors alkoxide groups into transition silanol groups (Si−OH) in water, followed by polycondensations of the silanol groups into siloxane bonds (Si−O−Si) with derivatives of water (oxolation) and/or alcohol (alcoxolation) based small molecules byproduct.[34] Both hydrolysis and polycondensations proceed simultaneously by nucleophilic substitutions (S_N): nucleophilic addition (A_N) of hydroxylated groups onto electrophilic metal atoms during hydrolysis, proton transfers between transition species to form bonds, and removal of protonated water or alcohol species during polycondensations.[35]

Although the sol−gel process of alkoxysilane precursors can proceed without the addition of catalyst, hydrolysis and polycondensations are more rapid and complete when a catalyst was used.[36] Sol−gel process of alkoxysilane precursors can be initiated by either an acid or base catalyzed reaction and the morphology of the generated networks depend strongly on the nature of the catalyst used, in particular the pH of the reactions.[37] In an acid
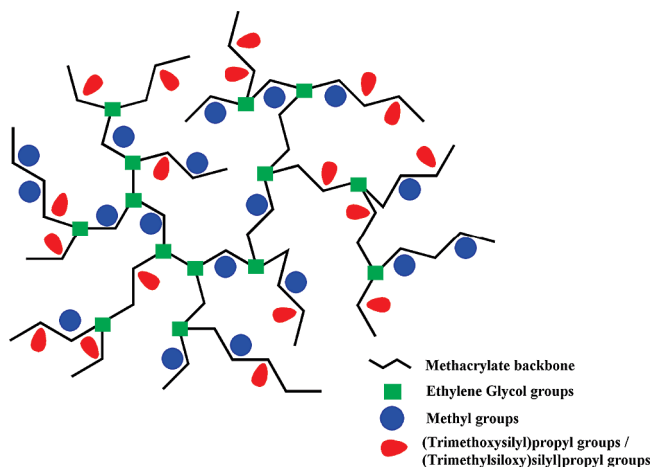

Figure 1. Graphic representations of random branched copolymer compounds of PEGDMA-*ran*-PMMA-*ran*-PMPS and PEGDMA-*ran*-PMMA-*ran*-PTRIS.

catalyzed reaction (hydrochloride acid, acetic acid, hydrofluoric acid), higher rate of hydrolysis compared to polycondensations is dominant, yielding primarily linear or low-density branched polymer networks.[38] A base catalyzed reaction (sodium hydroxide, potassium hydroxide, triethylamine) generally yields clusters of hyperbranched polymer networks due to a higher rate of polycondensations.[39]

In this study, we describe the formations of cross-linkable, flexible honeycomb structured porous polymer films prepared from two random branched copolymer compounds of poly ethylene glycol dimethacrylate -*random*- poly methyl methacrylate -*random*- poly [3-(trimethoxysilyl)propyl methacrylate] (PEGDMA-*ran*-PMMA-*ran*-PMPS) and poly ethylene glycol dimethacrylate -*random*- poly methyl methacrylate -*random*- poly{3-[tris(trimethylsiloxy)silyl]propyl methacrylate} (PEGDMA-*ran*-PMMA-*ran*-PTRIS) as shown in Figure 1.
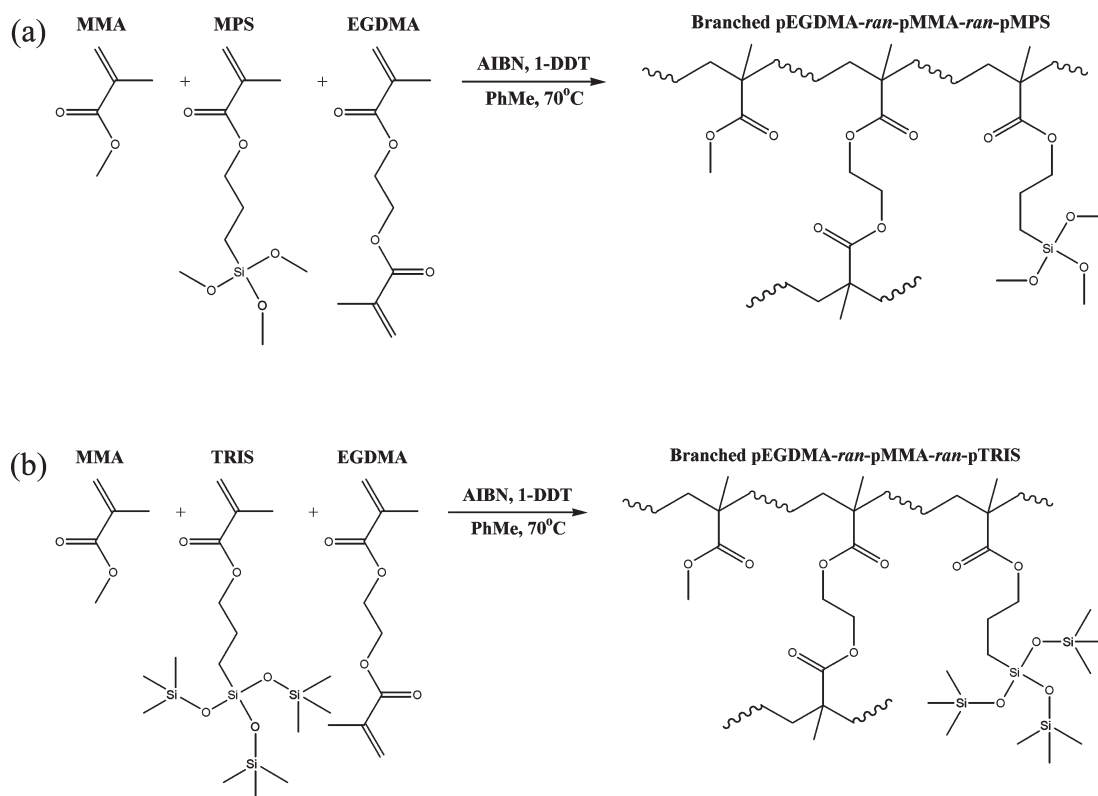
Ethylene glycol dimethacrylate (EGDMA) is a bifunctional vinyl monomer commonly employed as branching agents in polymer materials for soft ocular contact lenses.[40] 3-(Trimethoxysilyl) propyl methacrylate (MPS) and 3-tris(trimethylsiloxy)silyl] propyl methacrylate (TRIS) are methacrylate based alkoxysilane monomers that polymerize into optically transparent polymer materials. These random branched copolymer compounds were synthesized via a straightforward and inexpensive, one-pot conventional free radical copolymerization strategy, shown in Scheme 1.

Using moist airflow casting technique[41] described previously, both copolymer compounds yield honeycomb structured porous films. Honeycomb porous films prepared from PEGDMA-*ran*-PMMA-*ran*-PMPS random branched copolymer compounds were subsequently

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Scheme 1. One-Pot Conventional Free Radical Copolymerization of Random Branched Copolymer Compounds of (a) PEGDMA-*ran*-PMMA-*ran*-PMPS and (b) PEGDMA-*ran*-PMMA-*ran*-PTRIS, PhMe (Toluene)

cross-linked by sol−gel process to enhance their physical properties (toughness), thermal resistance, and stability in organic solvents. Thermal sensitive linear poly (*N*-isopropylacrylamide) (PNIPAAm) (90,000 g mol^{-1}) seeded inside the pores of the cross-linked honeycomb porous films were used to aid thermal analysis studies of these films.

2. Experimental Section

2.1. Materials. Methyl methacrylate (MMA) (99%) and ethylene glycol dimethacrylate (EGDMA) (98%) from Aldrich were deinhibited of monomethyl ether hydroquinone (MEHQ) inhibitor through several passes of basic alumina oxide packed columns. 3-(Trimethoxysilyl)propyl methacrylate (MPS) from Sigma (≥98%) and 3-[tris(trimethylsiloxy)silyl]propyl methacrylate (TRIS) from Aldrich (98%) was used without further purifications. 2,2′-Azobisisobutyronitrile (AIBN) from Du Pont was recrystallize twice from methanol, while 1-dodecanthiol (1-DDT), toluene, triethylamine (TEA), acetonitrile (ACN), methanol (MeOH), n-hexane, deionized water (DI-H$_2$O), chloroform (CHCl$_3$), and dichloromethane (DCM) were used as supplied from Sigma Aldrich without further purifications. Linear poly(N-isopropylacrylamide) (PNIPAAm) (90,000 g mol^{-1}) was synthesized according to a procedure described elsewhere.[42]

2.2. Synthesis and Film Preparation Techniques. *2.2.1. Synthesis of PEGDMA-ran-PMMA-ran-PMPS Random Branched Copolymers.* Random branched PEGDMA-*ran*-PMMA-*ran*-PMPS copolymers were prepared via a one-pot synthesis conventional free radial copolymerization procedure. AIBN (0.04 mol L^{-1}),

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1-DDT (0.33 mol L^{-1}), and toluene (15 mL) were employed respectively as initiator, chain transfer agent, and solvent. Using several concentrations of EGDMA branching agent (3.33, 0.33, 0.03 mol L^{-1}), various molar feed concentrations of MMA to MPS were employed ([MMA]:[MPS] = 3.33: 0 mol L^{-1}; 2.5: 0.83 mol L^{-1}; 1.67: 1.67 mol L^{-1}; 0.83: 2.5 mol L^{-1}; 0: 3.33 mol L^{-1}) as shown in Table 1. Into a 500 mL round-bottom Schlenk flask, the above mixtures were charged and sealed with rubber septa/copper wires. Several freeze−pump−thaw cycles were employed to degas the solution mixtures before cannulising into several sealed and degassed reaction vials. Polymerizations were completed in a 70 °C paraffin oil bath over intervals of 0.5, 2, 8, and 30 h. Quenching reaction vials in ice water bath and introduction of air into the vials by puncturing the septa stopped the polymerizations. The polymerized mixtures were purified by precipitating into a 15-fold excess of methanol, separated, and dried under reduced pressure at 45 °C over 12 h to yield the final copolymer compounds. The conversion of each monomer was determined using NMR analysis (Figure 2(a)).
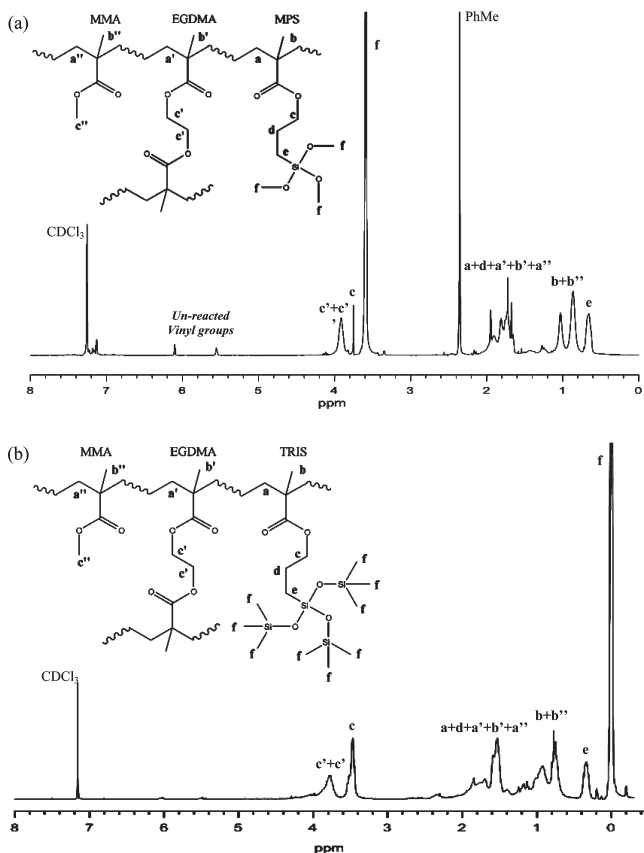
2.2.2. Synthesis of PEGDMA-ran-PMMA-ran-PTRIS Random Branched Copolymers. Random branched PEGDMA-*ran*-PMMA-*ran*-PTRIS copolymer compounds were prepared via a one-pot synthesis procedure similar to the above using equivalent concentrations. NMR analysis (Figure 2(b)) was employed for conversion determinations.

2.2.3. Casting/Porous Film Formations. Formations of honeycomb structured porous films were conducted in a customized Perspex glovebox with controlled airflow (20 L min^{-1}), humidity (50% to 85%), and temperature (22 °C). Porous films in this study were cast according to the airflow casting technique described elsewhere[41] with minor variations (no moist airflow from funnel). An aliquot of 400 μL of each copolymer solution with a polymer concentration of

Table 1. Molar Feed Concentrations and Fractions Used in the Synthesis of PEGDMA-*ran*-PMMA (*1a*), PEGDMA-*ran*-PMPS (*5a*), PEGDMA-*ran*-PTRIS (*4b*), PEGDMA-*ran*-PMMA-*ran*-PMPS (*2a, 3a, 4a, 1c, 1d*), and PEGDMA-*ran*-PMMA-*ran*-TRIS (*1b, 2b, 3b, 2c, 2d*), Random Branched Copolymers

| sample | molar feed concentrations | | | | | molar feed fractions | | | |
	[MMA]/mol L^{-1}	[MPS]/mol L^{-1}	[TRIS]/mol L^{-1}	[EGDMA]/mol L^{-1}	[DDT]/mol L^{-1}	f_{MMA}	f_{MPS}	f_{TRIS}	f_{EGDMA}
1a	3.33	-	-	0.33	0.33	0.91	-	-	0.09
2a	2.5	0.83	-	0.33	0.33	0.68	0.23	-	0.09
3a	1.67	1.67	-	0.33	0.33	0.46	0.46	-	0.09
4a	0.83	2.5	-	0.33	0.33	0.23	0.68	-	0.09
5a	-	3.33	-	0.33	0.33	-	0.91	-	0.09
1b	2.5	-	0.83	0.33	0.33	0.68	-	0.23	0.09
2b	1.67	-	1.67	0.33	0.33	0.46	-	0.46	0.09
3b	0.83	-	2.5	0.33	0.33	0.23	-	0.68	0.09
4b	-	-	3.33	0.33	0.33	-	-	0.91	0.09
1c	1.67	1.67	-	3.33	0.33	0.25	0.25	-	0.5
2c	1.67	-	1.67	3.33	0.33	0.25	-	0.25	0.5
1d	1.67	1.67	-	0.03	0.33	0.496	0.496	-	0.009
2d	1.67	-	1.67	0.03	0.33	0.496	-	0.496	0.009

Figure 2. NMR analysis (CDCl$_3$) of (a) PEGDMA-*ran*-PMMA-*ran*-PMPS (*3a*) and (b) PEGDMA-*ran*-PMMA-*ran*-PTRIS (*2b*) random branched copolymer compounds.

100 mg mL^{-1} in chloroform (CHCl$_3$), dispensed from a gastight glass syringe, were drop cast onto either 22 mm diameter borate silicate round glass coverslips or round polypropylene (PP) disks inside the Perspex glovebox. The polymer solution was allowed to evaporate to dryness to yield porous films.

2.2.4. Sol−Gel Cross-Link of Honeycomb Structured Porous Films from PEGDMA-ran-PMMA-ran-PMPS. Honeycomb structured porous films prepared from random branched PEGDMA-*ran*-PMMA-*ran*-PMPS copolymers were subsequently cross-linked via the sol−gel process to improve mechanical stability and thermal properties of the porous films. Using a base catalyst solution of TEA/ACN/H$_2$O with volume ratios

of 0.05:0.15:0.8, porous films (on PP round disk substrates) were cross-linked into freestanding flexible porous films. In a 30 mm diameter Petri dish, porous films on a PP substrate were submerged in 2 mL of base solution (TEA/ACN/H$_2$O), sealed using a glass top cover with paraffin film wrap. After a very brief (1−2 s) sonication treatment to aid diffusion of base solution into the pores of the film, the sol−gel cross-linking process was let to proceed over 48 h with porous films delaminating themselves from the (PP) round disks. The sol−gel cross-linking process was stopped by washing with 3 × 3 mL DI-H$_2$O and air-dried under fume hood to yield flexible porous films.

2.2.5. Seeding PNIPAAm into Cross-Linked PEGDMA-ran-PMMS-ran-PMPS Porous Films. Depositions of linear PNIPAAm into the pores of cross-linked PEGDMA-*ran*-PMMA-*ran*-PMPS honeycomb structured porous films were completed by several (3×) applications by droppings of an ample amount of PNIPAAm solution (10 mg mL^{-1} of water) onto the porous films, sonicated very briefly (1−2 s) to aid solution entry into pores, and air-dried over 24 h before subsequent applications. Excess PNIPAAm, on the surface of the porous films were removed by 2 × 1 mL DI-H$_2$O rapid rinses from a glass pipet. Finally, the PNIPAAm seeded cross-link PEGDMA-*ran*-PMMA-*ran*-PMPS porous films were air-dried under the fume hood.

2.3. Characterization Techniques. *2.3.1. Gel Permeable Chromatography (GPC)/Size Exclusion Chromatography (SEC).* Molecular weights and polydispersity indexes of copolymer compounds were determined by Gel Permeable Chromatography (GPC)/Size Exclusion Chromatography (SEC) analysis in tetrahydrofuran (THF) eluent at 40 °C. A Shimadzu modular system comprising a DGU-12A solvent degasser, an LC-10AT pump, a CTO-10A column oven, and a RID-10A refractive index detector was used. Separation columns setup consisting of a Polymer Laboratories (PL) 5.0 μm bead-size guard column (50 × 7.8 mm) followed by four (PL) 300 × 7.8 mm linear columns (10^5, 10^4, 10^3, and 500 Å). Calibration was performed with narrow polystyrene standards ranging from 500 up to 2 × 10^6 g mol^{-1}. Data were acquired using a high-resolution (PL) data stream data acquisition system (software data stream monitor version 1.2), and the distribution spectra were collected and analyzed with Cirrus GPC/SEC software version 2.0 from Polymer Laboratories.

2.3.2. Nuclear Magnetic Resonance (NMR). ^{1}H NMR was used to characterize the constitutions and conversions of copolymer compounds synthesized. Spectra were recorded on a 300 MHz Bruker NMR spectrometer in deuterated chloroform (CDCl$_3$) and deuterated water (D$_2$O) with Bruker TopSpin

NMR data acquisition and processing software. Conversions of copolymers were calculated from the integration values obtained of the collective dual vinyl bonds of the methacrylate groups of MMA, EGDMA, and TRIS or MPS monomers before and after polymerizations.

2.3.3. Differential Scanning Calorimetry (DSC). The glass transition temperatures (*Tg*) of the branched polymers were obtained using Differential Scanning Calorimetry (DSC) analysis. Spectra were recorded on a Perkin-Elmer DSC 7, equipped with a TAC 7/DX Thermal Analysis controller, a CCA 7 Controlled Cooling Accessory, and a DPA 7 Photo Calorimeter, all from Perkin-Elmer. An adequate amount (10−20 mg) of polymer was sealed in aluminum sample pans (50 mL, 0.1 mm) without vents. Three heating and three cooling scanning cycles between −100 to 200 °C at a rate of 20 K min^{-1} were employed to determine the glass transition temperatures (*Tg*). The *Tg* values were analyzed and determined by the provided Pyris software also obtained from Perkin-Elmer.

2.3.4. Scanning Electron Microscopy (SEM). SEM scanning electron microscopy (SEM) images of the porous films formed was acquired using a Hitachi-S900 FESEM. Honeycomb porous films were fixed to copper stubs with carbon adhesive tape and sputter-coated with 10 nm of chromium (EMITECH K575x high resolution) before analysis.

2.3.5. Optical Microscopy. An optical microscope (Leica DMLB connected to a DC300 camera) with × 100 and × 630 magnification objectives, equipped with transmittance and reflective mode, was used to observe the hexagonal morphology of the surfaces of honeycomb porous films. An additional hot stage, Mettler Toledo FP82HT, with a FP90 Central Processor temperature controller, also from Mettler Toledo, was used to complete the thermal analysis with PNIPAAm seeded honeycomb porous films.

2.3.6. Thermal Analysis of PNIPAAm Solution Seeded Cross-Linked PEGDMA-ran-PMMA-ran-PMPS Porous Films. To analyze the thermal responses of PNIPAAm seeded in cross-linked PEGDMA-*ran*-PMMA-*ran*-PMPS porous films, the PNIPAAm was moist by 2 × rapid dip in water with any residual water on the surface of the film instantly shook off. On a hot stage under a microscope, PNIPAAm seeded porous films were heated from 20 to 85 °C at an increment of 10 °C min^{-1} to acquire transformation images of PNIPAAm at different temperatures.

3. Results and Discussions

3.1. Synthesis of Random Branch Copolymers Compounds. Good solubility of polymer compounds in organic solvents such as carbon disulfide, dichloromethane, and chloroform is essential for achieving homogeneous hexagonal porous arrays in "breath figure" technique formation of honeycomb structured porous films. In addition, polymers with starlike structures are known to result in films with higher regularity compared to their linear counterparts. While the synthesis of star polymers can be tedious, the synthesis of branched structures that can be easily obtained from a simple one-pot step from commercially available monomers has been explored as an alternative. Furthermore, the resulting branched copolymer carries reactive groups for further cross-linking to improve solvent and mechanical stability.

Random branched copolymer PEGDMA-*ran*-PMMA-*ran*-PMPS and PEGDMA-*ran*-PMMA-*ran*-PTRIS can easily be synthesized by a one-pot free radical copolymerization approach or the "Strathclyde methodology".
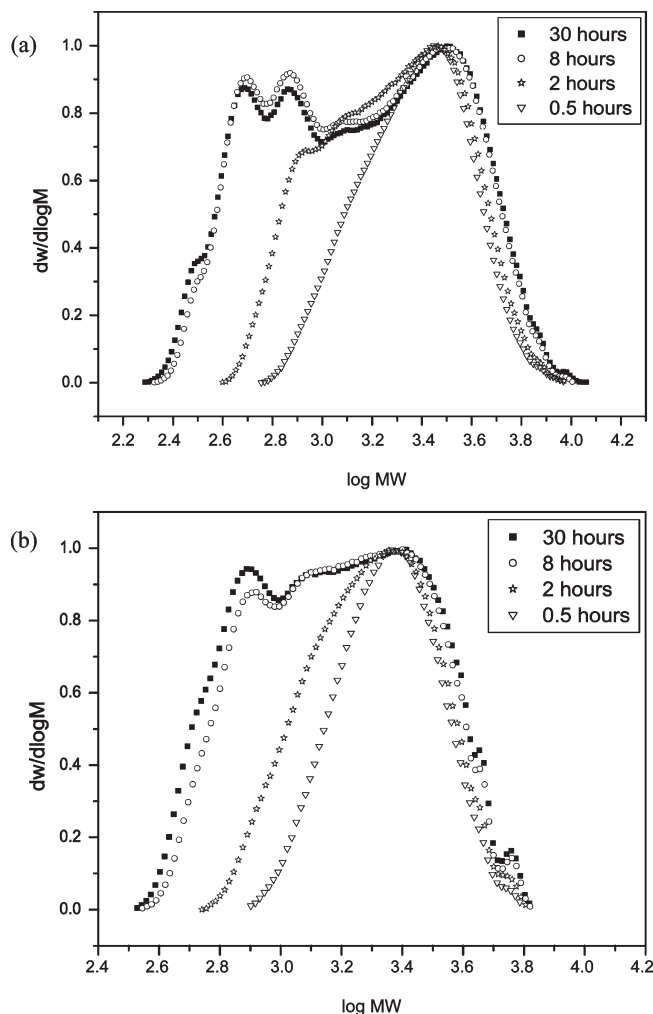

Figure 3. SEC/GPC (THF) molecuar weigth distribution spectra of polymerization of (a) PEGDMA-*ran*-PMMA-*ran*-PMPS (*3a*) and (b) PEGDMA-*ran*-PMMA-*ran*-PTRIS (*2b*) random branched copolymer compounds.

Polymerizations involving multifunctional monomers primarily generate short-branched polymers at low conversions and develops into hyperbranched polymers at higher conversions and possibly cross-linked polymers at very high conversions. In this study, with polymer conversions and molar mass distribution spectra obtained from NMR analysis and SEC/GPC analysis, respectively, the copolymerization reaction kinetics of PEGDMA-*ran*-PMMA-*ran*-PMPS and PEGDMA-*ran*-PMMA-*ran*-PTRIS random branch copolymer compounds, with EGDMA employed as the bifunctional branching agents, were studied (Figures 3 and 4). In the early stages of copolymerization, at lower conversions (≤30%), the copolymers produced are low in molecular weights (< 7000 g mol^{-1}) with a monomodal molecular weight distribution, suggesting short linear co-oligomer chains with no or very a low degree of short co-oligomer branching chains were produced. As conversion increases, the molecular weights of copolymers also increased but relatively slowly, achieving 10,000 to 15,000 g mol^{-1} at 70% conversions. Significant broadening (PDI > 4.8), due to developing higher molecular weight multipeak, in the molar mass distribution spectra
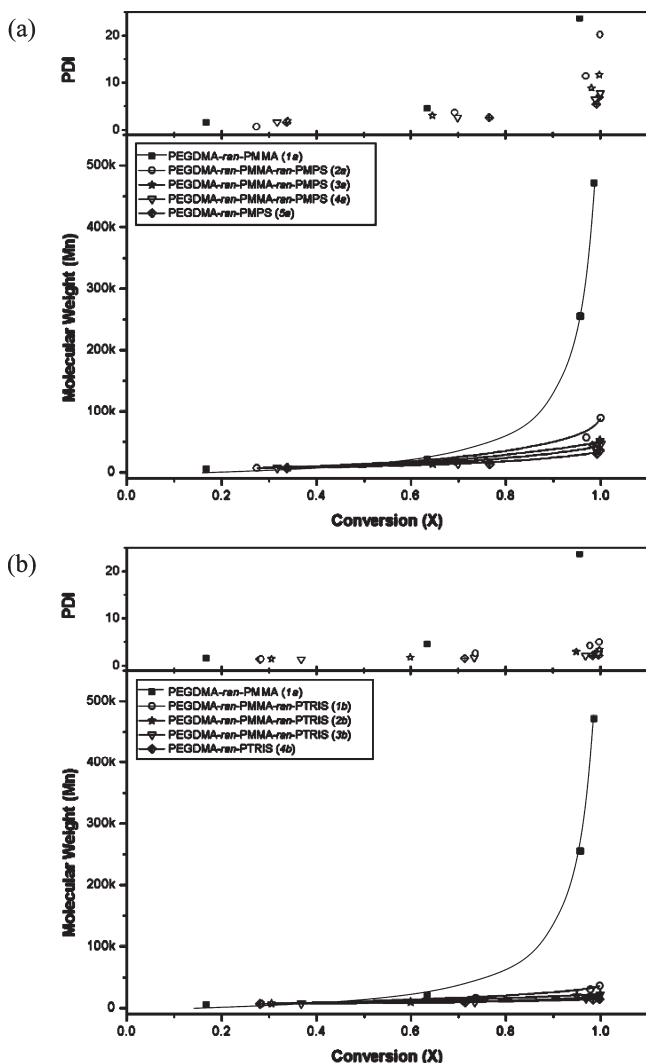
Figure 4. Conversion vs molecular weight plots of random branch copolymerization of (a) PEGDMA-*ran*-PMMA-*ran*-PMPS and (b) PEGDMA-*ran*-PMMA-*ran*-PTRIS with different molar feed fractions of EGDMA, MMA, MPS, and TRIS.

were observed. At higher conversions (>90%), the molecular weights of copolymers rapidly increased (up to 35,000 g mol^{-1}) and resulted in expansive multipeaks molar mass distribution spectra indicative of prompt interconnections of linear and branch co-oligomer chains into dense short branch or hyperbranched copolymer compounds with several fractions of different molecular weights branch copolymers. This vogue, especially the boarding and development of high molecular weight multimodal molar mass spectra with increasing monomer conversions, is in excellent agreement with kinetic studies of branched and hyperbranched copolymers reported by O'Brien et al.[43] and Turner et al.[44] The molecular weights and polydispersities of copolymers compounds synthesized in this study are listed in Table 2. It should be noted here that the molecular weights were obtained using

linear polystyrene as standards. The compact structure of branched polymers should therefore have an actual molecular weight higher than the value obtained.

Thanks to the added chain transfer agent the branched polymers remained soluble at high conversions, while cross-linked insoluble polymer networks were visibly absent. The amount of chain transfer agent was carefully tailored in concurrence to findings reported by Isaure et al., who achieved good control over the degree of branching and therefore avoided gel formation by varying the molar feed concentration ratio of branching agents/chain transfer agent.[45] Shown in Figure 5, at maximum conversions, when the EGDMA/DDT feed concentration ratio of 1 ([EGDMA] = 0.33 mol L^{-1}, [DDT] = 0.33 mol L^{-1}) was employed in the copolymerization of PEGDMA-*ran*-PMMA-*ran*-PMPS (*3a*, Table 1) and PEGDMA-*ran*-PMMA-*ran*-PTRIS (*2b*, Table 1) random branched copolymers, the produced copolymers although viscous, retain good solubility in organic solvents (THF). The broad multipeak molar mass distribution of these copolymers substantiate them as dense short branch or hyperbranched copolymers. However, a 10-fold increase in the feed ratio of branching agent/chain transfer agent ([EGDMA] = 3.33 mol L^{-1}, [DDT] = 0.33 mol L^{-1}) during copolymerization (*1c, 2c*, Table 1), yielded cross-linked copolymer gels. Additions of solvents (THF, toluene, DCM, CHCl$_3$) only swell the gels without solubilizing even after an extended period at elevated temperatures. In contrast, a 10-fold reduction in the mole feed ratio of branching agent/chain transfer agent ([EGDMA]=0.03 mol L^{-1}, [DDT] = 0.33 mol L^{-1}) during copolymerization resulted in copolymers compounds (*1d, 2d*, Table 1) that are nonviscous and narrow in molar mass distribution spectra. Indicating longer copolymer chains with a low degree of branching chains were formed in the copolymers. Therefore, in this work a branching agent/chain transfer agent mole feed ratio of 1 was employed for all random copolymerization of PEGDMA-*ran*-MMA (*1a*, Table 1), PEGDMA-*ran*-PMPS (*5a*, Table 1), PEGDMA-ran-PTRIS (*4b*, Table 1), PEGDMA-*ran*-PMMA-*ran*-PMPS (*2a−4a*, Table 1), and PEGDMA-*ran*-PMMA-*ran*-PTRIS (*1b−3b*, Table 1).

While control over the branching of copolymers can be achieved by varying the ratio of EGDMA and chain transfer agent, varying the ratios of MMA, TRIS, and MPS can also determine the branching densities, the properties (molecular weights) of the copolymer, and consequently the mechanical stabilities of honeycomb structured porous films. As shown in Figure 6, increasing the molar feed fractions ratios of MMA to MPS or MMA to TRIS (f_{MMA}:f_{MPS} or f_{TRIS} = 0:0.98, 0.23:0.68, 0.91:0) yielded branched polymers PEGDMA-*ran*-PMMA-*ran*-PMPS (*5a* = 35,000 g mol^{-1}, *4a* = 47,000 g mol^{-1}, *1a* = 470,000 g mol^{-1}, Table 2) and PEGDMA-*ran*-PMMA-*ran*-pTRIS (*4b* = 15,000 g mol^{-1}, *3b* = 19,000 g mol^{-1}, *1a* = 470,000 g mol^{-1}, Table 2) that are incrementally boarder, more densely branched, and higher in molecular weights with

(43) O'Brien, N.; McKee, A.; Sherrington, D. C.; Slark, A. T.; Titterton, A. *Polymer* **2000**, *41*, 6027.
(44) (a) Turner, S. R.; Voit, B. I. *Poly. News* **1997**, *22*, 197. (b) Turner, S. R.; Walter, F.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1994**, *27*, 1611.

(45) Isaure, F.; Cormack, P. A. G.; Sherrington, D. C. *J. Mater. Chem.* **2003**, *13*, 2701.

Table 2. Molecular Weights, Polydispersity Index, and Glass Transition Temperatures (*T*g) of Synthesized of PEGDMA-*ran*-PMMA (*1a*), PEGDMA-*ran*-PMPS (*5a*), PEGDMA-*ran*-PTRIS (*4b*), PEGDMA-*ran*-PMMA-*ran*-PMPS (*2a, 3a, 4a, 1d*), and PEGDMA-*ran*-PMMA-*ran*-TRIS (*1b, 2b, 3b, 2d*) Random Branched Copolymers Determined by SEC/GPC (THF)

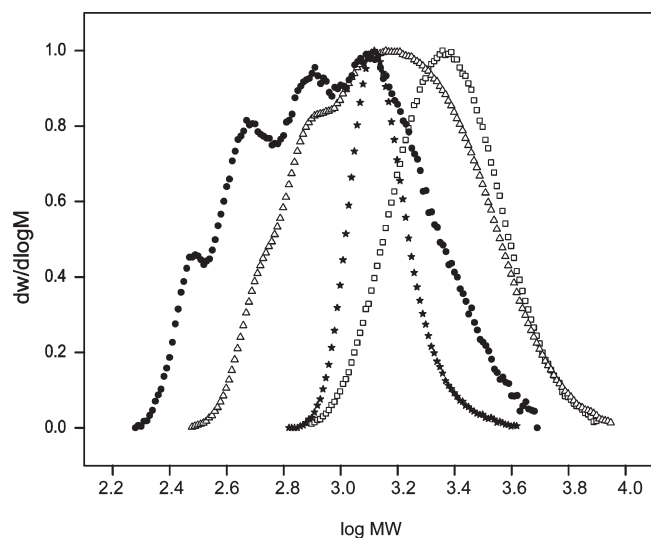| sample	molar feed fractions				GPC analysis			
	f_{MMA}	f_{MPS}	f_{TRIS}	f_{EGDMA}	Mn/g mol^{-1}	M_w/g mol^{-1}	PD	Tg/°C
1a	0.91	-	-	*0.09*	470,000	14,222,000	30.2	78.6
2a	0.68	*0.23*	-	*0.09*	88,000	1782,000	20.2	44.8
3a	0.46	*0.46*	-	-	52,000	610,000	11.7	3.2
4a	0.23	*0.68*	-	-	47,000	370,000	7.9	-30.1
5a	-	*0.91*	-	*0.09*	35,000	249,000	7.1	-34.6
1b	0.68	-	*0.23*	*0.09*	36,000	180,000	5.1	55.2
2b	0.46	-	*0.46*	*0.09*	23,000	79,000	3.4	8.2
3b	0.23	-	*0.68*	*0.09*	19,000	53,000	2.8	-19.7
4b	-	-	*0.91*	0.09	15,000	32,000	2.2	-36.2
1c	0.25	0.25	-	0.5		cross-linked		-
2c	0.25	-	0.25	0.5		cross-linked		-
1d	0.496	0.496	-	0.009	29,000	2.8	1.5	-
2d	0.496	-	0.496	0.009	18,000	2.2	1.9	-

Figure 5. Comparison of SEC/GPC distribution spectra of random branch copolymers of (●) PEGDMA-*ran*-PMMA-*ran*-PMPS (*3a*), (★) PEGDMA-*ran*-PMMA-*ran*-PMPS (*1d*), (△) PEGDMA-*ran*-PMMA-*ran*-PTRIS (*2b*), and (□) PEGDMA-*ran*-PMMA-*ran*-PTRIS (*2d*).

Figure 6. Comparing SEC/GPC distribution spectra of random branch (■) PEGDMA-*ran*-PMMA (*1a*), (+) PEGDMA-*ran*-PMMA-*ran*-PMPS (*4a*), (△) PEGDMA-*ran*-PMPS (*5a*), (☆) PEGDMA-*ran*-PMMA-*ran*-PTRIS (*3b*), and (○) PEGDMA-*ran*-PTRIS (*4b*).

additional higher molar mass peaks developing in the multi-modal molecular weight distribution. The random copolymerization of MMA and EGDMA without MPS or TRIS (PEGDMA-*ran*-PMMA (*1a*, Table 2)) yielded the broadest (PD ≈ 30) molecular weight distribution with the highest molecular weight (470,000 g mol^{-1}). In contrast, increasing the ratio of MPS to MMA or TRIS to MMA (f_{MMA}:f_{MPS} or f_{TRIS} = 0.91:0, 0.23:0.68, 0:0.98) (PEGDMA-*ran*-PMMA-*ran*-PMPS (*1a*, *4a*, *5a*, Table 2), PEGDMA-*ran*-PMMA-*ran*-pTRIS (*1a*, *2b*, *4b*, Table 2)) yielded lower branching density copolymers with lower molecular weights and narrower molecular weight distribution. The copolymerization of EGDMA with MPS or TRIS, without MMA (PEGDMA-*ran*-PMPS (*5a*), PEGDMA-*ran*-PTRIS (*4b*), Table 2), yielded copolymers with monomodal or bimodal molecular weight curves (PD ≈ 2.2 − 7.1) with the lowest molecular weight (15,000−35,000 g mol^{-1}) and low degree of branching in the copolymers.

One possible assignment to the variations in molecular weights, may be the differences in propagation rate coefficients of individual monomers. Major contributors
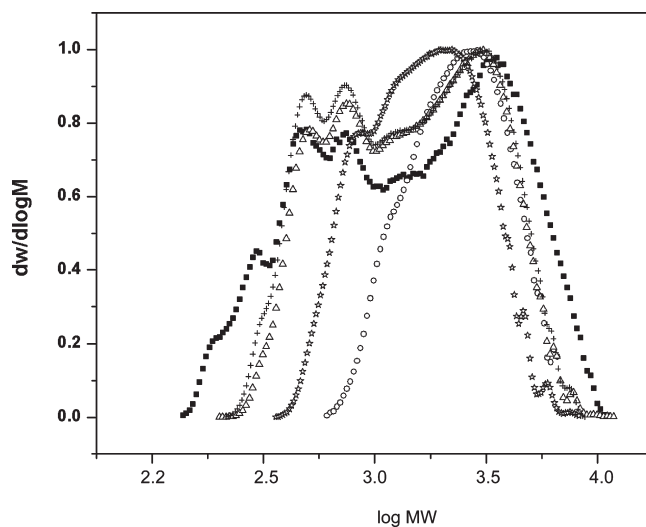
are also the different reactivity ratios with EGDMA and chain transfer constants of the different monomers with the chain transfer agent DDT. For instances, the propagation rate coefficient (k_p) of MMA (833 L mol^{-1} s^{-1}) is somewhat lower than TRIS (1092 L mol^{-1} s^{-1}).[46] This narrowing of distribution spectra is more prominent with higher feed concentrations of TRIS i.e. PEGDMA-*ran*-PMMA-*ran*-PTRIS (*3b*, Table 1, [MMA] = 0.83 mol L^{-1}, [TRIS] = 2.5 mol L^{-1}) and PEGDMA-*ran*-PTRIS (*4b*, Table 1, [MMA] = 0 mol L^{-1}, [TRIS] = 3.33 mol L^{-1}). In the PEGMA-*ran*-PMMA-*ran*-PMPS systems, due to species similarities (alkoxysilanes) and minute structural differences between TRIS and MPS monomers, it is expected and observed that the influences to the variations in molar mass distribution spectra and molecular weights were comparable to that of the PEGDMA-*ran*-PMMA-*ran*-PTRIS system. Detailed studies to investigate the effect of different monomers propagation rates and their reactivity ratios in the copolymerization systems will be

(46) Matyjaszewski, K.; Davis, T. P. *Handbook of Radical Polymerization*; John Wiley and Sons Inc.: United State of America, 2002.
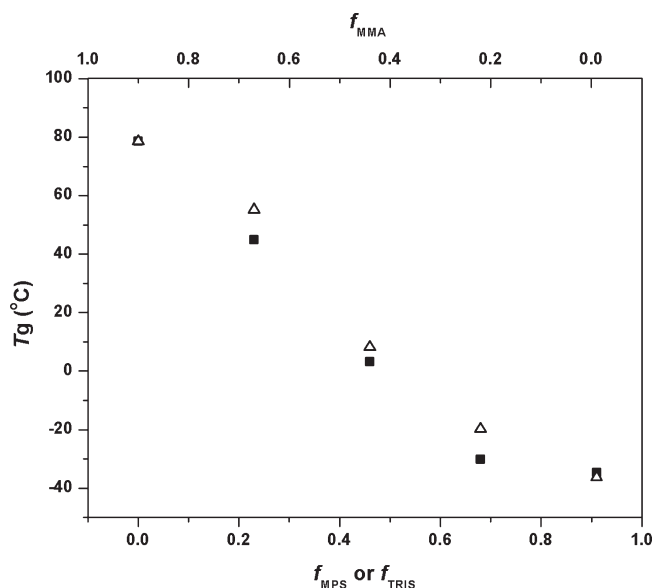
Figure 7. Glass transition temperatures of random branch (■) PEGD-MA-*ran*-PMMA-*ran*-PMPS and (△) PEGDMA-*ran*-PMMA-*ran*-PTRIS with different molar feed fractions ratios of PMMA to PMPS and PTRIS.

necessary to elucidate the observed variations but is beyond the scope of this study.

3.2. Glass Transition Temperature of Random Branched Copolymer Compounds. The properties of flexibility and impact resistance of the final honeycomb structured porous film can also be influenced by the ratios between MMA, which results in hard and brittle polymers, and TRIS or MPS, which lowers the polymer glass transition temperature. A high glass transition temperature Tg will result in brittle honeycomb structured porous films, while a very low Tg prevents the formation of stable pores.

The glass transition temperatures Tg of random branched copolymers synthesized in this study were determined via DSC. The Tg of homo PMMA linear polymer $(10,000-20,000$ g mol$^{-1})$ is typically 105 °C, hard and brittle at room temperatures. As expected, branched PMMA has a lower glass transition temperature since the increased number of chain ends creates more free volume. As shown in Figure 7, the addition of EGDMA ($f_{EGDMA}=$ 0.09) yields PEGDMA-*ran*-PMMA branch copolymer compounds (*1a*, 470,000 g mol^{-1}, Table 2) with a Tg of 78.5 °C, 20 °C lower compared to PMMA linear polymers. The addition of MPS and TRIS during copolymerization reduces the Tg of random branched copolymers in a linear fashion with increasing feed fractions ratios of MPS or TRIS, respectively. A decreasing molar feed fractions ratio f_{MMA} of MMA in the MPS or TRIS system during copolymerization resulted in copolymers compounds with significantly reduced Tg, from 45 °C (*2a*, $f_{MMA} = 0.68$, 47,000 g mol^{-1}, Table 2) to 3 °C (*3a*, $f_{MMA} = 0.46$, 52,000 g mol^{-1}, Table 2) in the MPS system and 55 °C (*1b*, $f_{MMA} =$ 0.68, 19,000 g mol^{-1}, Table 2) to 8 °C (*2b*, $f_{MMA} = 0.46$, 23,000 g mol^{-1}, Table 2) in the TRIS system. Copolymer compounds with very high fractions of MPS or TRIS (*4a*, *3b*, Table 2 ($f_{MMA} = 0.23$) or *5a*, *4b*, Table 2 ($f_{MMA} = 0$)) were found to have Tg well below room temperature $(< -30$ °C). This reduction of Tg with decreasing fraction

of MMA is not surprising considering that PTRIS and PMPS have Tg's well below room temperature, which is typical for many silicon containing polymers. The linear relationship between measured Tg and the fractions of MMA is in good agreement with the Gordon−Taylor equation.[47]

Copolymers with glass transition temperatures around ambient temperatures are considered ideal for the preparation of honeycomb structured porous films since they are not only less brittle than PMMA but also have higher structural stability than low Tg polymers. As such it was expected and observed that random branched copolymers, PEGDMA-*ran*-PMMA-*ran*-PMPS (*2a*, *3a*, Table 1) and PEGDMA-*ran*-PMMA-*ran*-PTRIS (*1b*, *2b*, Table 1), with higher molar fractions MMA ([MMA] $\geq$ 1.67 mol L^{-1}) can form stable honeycomb structured porous films using the breath figure formation technique. On the other hand, honeycomb structured porous films prepared from PEGD-MA-*ran*-PMMA-*ran*-PMPS (*4a*, Table 1) and PEGDMA-*ran*-PMMA-*ran*-PTRIS (*3b*, Table 1) with higher molar fractions of TRIS or MPS to MMA ([TRIS, MPS] > 1.67 mol L^{-1}) were found to have very low structure stability, although the hexagonal formations of porous films was first observed after casting, but totally ruin when the copolymers rearranges and collapsed into a featureless transparent film after 1−2 h under gravitational influences.

3.3. Formation of Honeycomb Porous Films from Randomly Branched Copolymers. Numerous researchers have reported a variety of well-defined structured polymer compounds that lead to the formation of honeycomb structured porous films with "breath figure" formation technique. Figure 8a,b shows the microscope images of honeycomb structured porous films prepared from random branched copolymer compounds of PEGDMA-*ran*-PMMA-*ran*-PMPS (*2a*, Table 1) and PEGDMA-*ran*-PMMA-*ran*-PTRIS (*1b*, Table 1), respectively. As in published literature, besides achieving regular structured porous films, these porous films are robust to customizations, i.e. the size of pores can easily be tailored by adjustments to casting conditions (polymer solution concentrations, humidity or moist air-flow rates) or the structure of polymers used (polymer architectures, chain lengths or functionalities). Figure 8c−f shows honeycomb structured porous film with larger pores after casting in higher humidity (95%) (*2a*, *1b*, Table 1) and using copolymers compounds with higher feed concentration ratios of PTRIS (*2b*, Table 1) and PMPS (*3a*) ([TRIS], [MPS] $\geq$ 1.67 mol L^{-1}) to PMMA, respectively. These honeycomb structured porous films appear translucent to the naked eye due to scatterings of light by the porous structures (Figure 10).

3.4. Sol−Gel Process Cross-Link of PEGDMA-*ran*-PMMA-*ran*-PMPS Porous Films. Honeycomb porous films prepared from PEGDMA-*ran*-PMMA-*ran*-PMPS (*2a*, Table 1) random branch copolymers are relatively fragile and easily fracture upon handling. Besides the properties of the copolymers used, it can also be attributed to the morphology and features of the porous films.

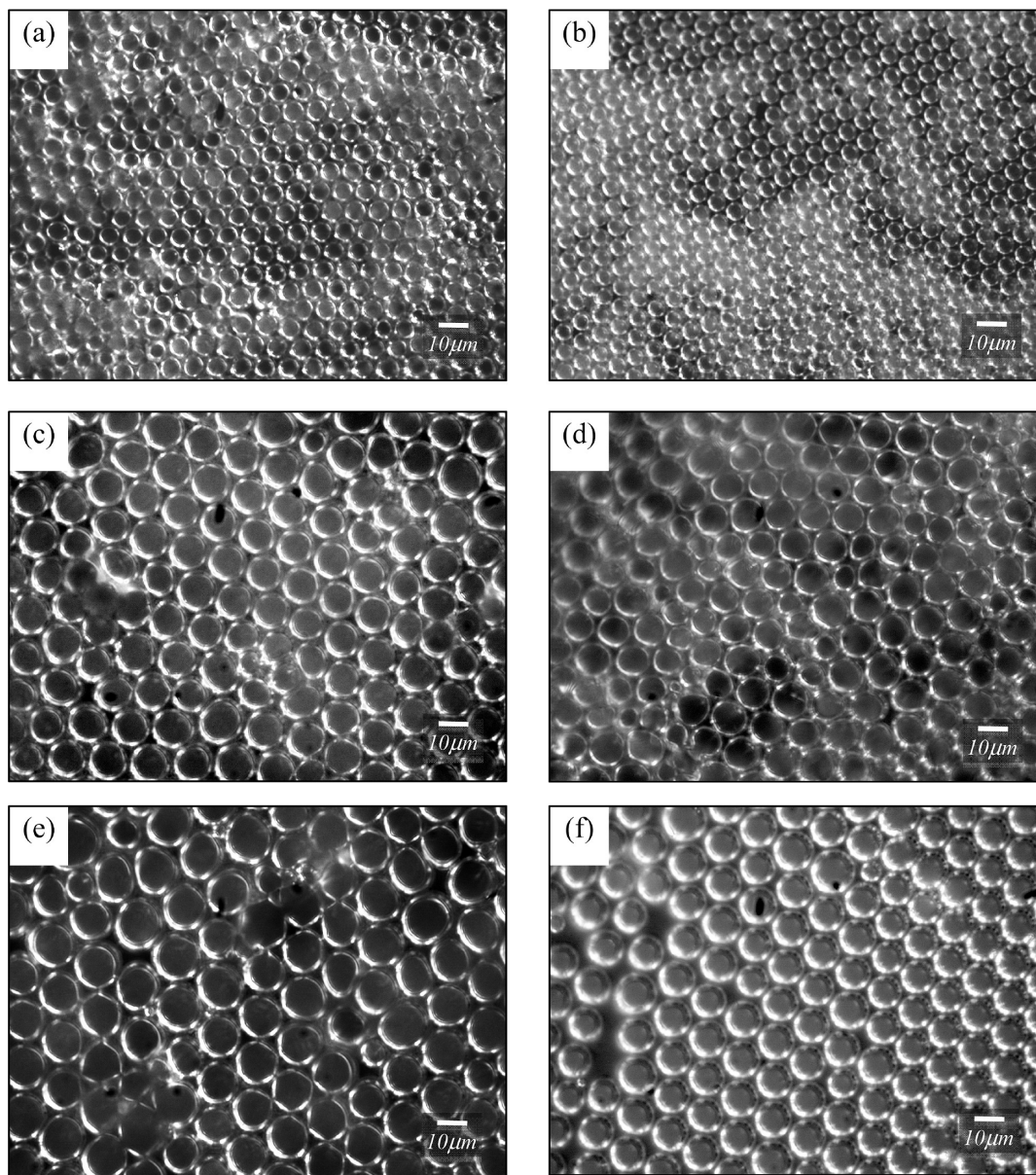(47) Wood, L. A. *J. Polym. Sci.* **1958**, *28*, 319.

Figure 8. Honeycomb porous films prepared from PEGDMA-*ran*-PMMA-*ran*-PMPS and PEGDMA-*ran*-PMMA-*ran*-PTRIS. (a) PEGDMA-*ran*-PMMA-*ran*-PMPS (*2a*) cast at 80% humidity, (b) PEGDMA-*ran*-PMMA-*ran*-PTRIS (*1b*) cast at 80% humidity, (c) PEGDMA-*ran*-PMMA-*ran*-PMPS (*2a*) cast at 95% humidity, (d) PEGDMA-*ran*-PMMA-*ran*-PTRIS (*1b*) cast at 95% humidity, (e) PEGDMA-*ran*-PMMA-*ran*-PMPS (*3a*) cast at 95% humidity, and (f) PEGDMA-*ran*-PMMA-*ran*-PTRIS (*2b*) cast at 95% humidity.

Physically, these are films of ultrahigh porosity with more voids than materials for any given area in the film, and the entire film (several micrometers thick) was held together only by skeletal sections of precipitated polymer materials. The bulk of polymer materials in these films are usually micrometers in width between pores ($< 2 \, \mu$m) as shown in Figure 9 and submicrometer in wall thickness between pores.[48]

The sol−gel cross-linking reaction using alkoxysilane (PMPS) of PEGDMA-*ran*-PMMA-*ran*-PMPS in honeycomb porous films can be an avenue to improve stability. The sol−gel cross-link process in this study was initiated by a base catalyst reaction solution of TEA in ACN/H$_2$O, as shown in Scheme 2. The sol−gel cross-linking process was carried out in the presence of a small amount of TEA (0.001 mol, pH 10) to improve the effectiveness of hydrolysis and polycondensations. The generated methanol during the process was then used to screen the progress of the cross-linking reaction. NMR analysis was used to monitor the generation of methanol using acetonitrile (ACN) as an internal standard. Subsequently, the determined molarity of MeOH was compared to the theoretical molarity of MeOH, calculated from the amount of PMPS in the honeycomb porous films, in order to establish the cross-link density of the films. An acid based catalyzed sol−gel reaction using common hydrochloric acid (HCl) or acetic acid (AcOH) solutions was evaluated but found not suitable in this study. In acid catalyzed sol−gel processes, the initial hydrolysis processes proceed very rapidly, when applied to porous film in this study,

(48) Connal, L. A.; Gurr, P. A.; Qiao, G. G.; Solomon, D. H. *J. Mater. Chem.* **2005**, *15*, 1286.

resulting in abrupt high-density cross-link of copolymers at the top surface of the film. This prevented subsequent diffusion of acid solution into the films to cross-link polymers inside the film, yielding very brittle porous films.
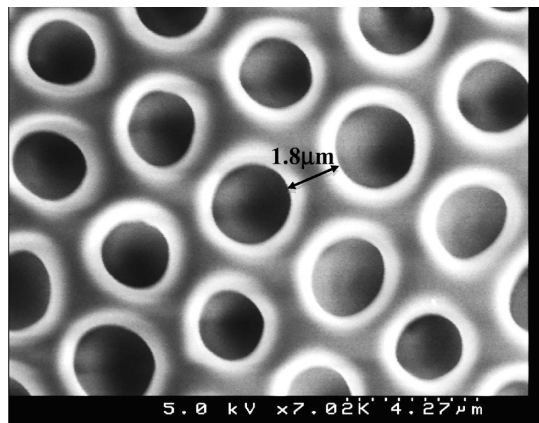

Figure 9. Scanning Electron Microscopy (SEM) image of PEGDMA-*ran*-PMMA-*ran*-PTRIS (*1b*) cast at 80% humidity, illustrating the width of copolymer materials between hexagonally arranged pores.

The films were therefore immersed in a base solution with deuterated acetonitrile and water together with TEA as catalyst, (TEA/ACN/H$_2$O) volume ratios (0.15:0.5:0.8) and the generation of methanol as a result of cross-linking was recorded using the emerging methanol signal (CH$_3$ group, δ = 3.34 ppm). The signal intensity was then compared to the acetonitrile signal intensity at δ = 2.06 ppm. It is therefore essential to ensure than no solvent has been lost during the procedure. It is known that hydrolysis and polycondensation in sol−gel process occur quickly, but the rate of polymers cross-link in these porous films is established by the diffusion of base solution through the polymers of the porous films. It is anticipated that the cross-link process initiates from the surfaces of the porous film and ultimately through the films. However, the ultra-hydrophobicity of the surface of the honeycomb porous films resulted in reduced wetting and sluggish cross-link processes with the aqueous base solutions penetrating very gradually through the film. NMR analysis of the base catalyst reaction solution employed in the sol−gel (Table 3) cross-link of PEGDMA-*ran*-PMMA-*ran*-PMPS (*2a*, Table 1) honeycomb porous film, exhibited the initial
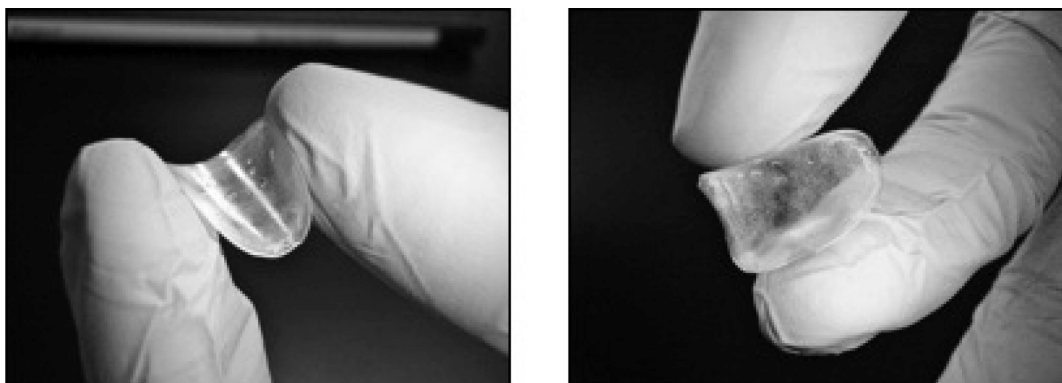

Figure 10. Images of stable and flexible translucent honeycomb structured porous films prepared from PEGDMA-*ran*-PMMA-*ran*-PMPS (*2a*) random branched copolymer compounds, subsequently cross-linked by 48 h base solution catalyzed (TEA/ACN/H$_2$O) with volume fraction ratios of (0.05:0.15:0.8) sol−gel process.

Scheme 2. Sol-Gel Process Cross-Link of TMS Groups in PMPS inside Random Branched PEGMDA-*ran*-PMMA-*ran*-PMPS Honeycomb Structured Porous Films Using the Base Catalyst Reaction Solution of TEA/ACN/H$_2$O with Volume Fractions Ratios (0.05:0.15:0.8)
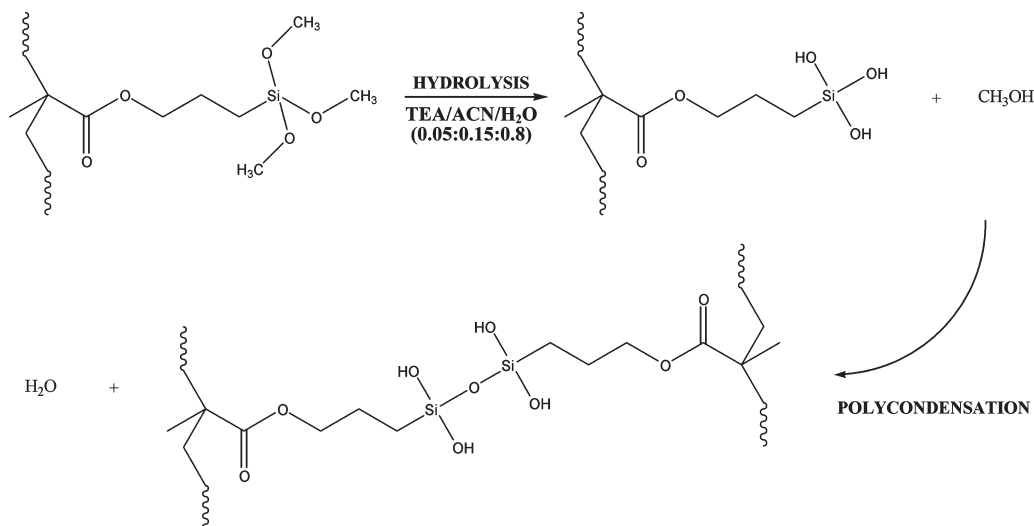
Table 3. NMR Analysis (D$_2$O) of Base Solution after Sol-Gel Processing Cross-Link of PEGDMA-*ran*-PMMA-*ran*-PMPS (*2a*) over 72 h

sol−gel cross-link duration (h)	molarity of CH$_3$ in ACN[a]	NMR integrations of CH$_3$ in MeOH[b]	molarity of CH$_3$ in MeOH[c]	molarity of pMPS in porous film[d]	theoretical molarity of MeOH from pMPS[e]	cross-link density of film (%)[f]
3	4×10^{-3}	17×10^{-3}	62×10^{-6}	159×10^{-6}	478×10^{-6}	12.98
24	4×10^{-3}	79×10^{-3}	288×10^{-6}	159×10^{-6}	478×10^{-6}	60.31
48	4×10^{-3}	99×10^{-3}	361×10^{-6}	159×10^{-6}	478×10^{-6}	75.58
72	4×10^{-3}	101×10^{-3}	368×10^{-6}	159×10^{-6}	478×10^{-6}	77.11

[a] Molarity of ACN in base solution. [b] Integrations of the CH$_3$ group ($\delta = 3.34$ ppm) of MeOH from NMR analysis, with integration of the CH$_3$ group ($\delta = 2.06$ ppm) of ACN as 1. [c] Molarity of measured MeOH in base solution obtained by $b \times a$. [d] Molarity of PMPS in 0.1 g of PEGDMA-*ran*-PMMA-*ran*-PMPS used in preparing porous films. [e] Theoretical molarity of MeOH that can be obtained from the TMS of PMPS in porous films. [f] Density of cross-link achieved in porous films by comparing c to e.

appearance of methanol's CH$_3$ group at 3 h with a cross-link density of 13%. After 24 h a cross-link density of 60% was obtained, and the porous films became less fragile. At 48 h, a cross-link density of 75% was achieved with the porous films becoming very flexible, bending without cracking but breaking upon folding. At 72 h, a very small increase in the CH$_3$ peak was observed (77% cross-link density), but the porous films became very rigid and brittle like glass, breaking upon a single bend.

Figure 10 shows a stable and flexible translucent honeycomb porous film prepared from PEGDMA-*ran*-PMMA-*ran*-PMPS random branch copolymer compounds, subsequently cross-linked by the sol−gel process for 48 h. The honeycomb porous film and its hexagonal arrays were not damaged during the cross-link process. However, extended cross-link duration (>72 h) yielded glasslike porous films with more rigid siloxane bonds formed between the trimethoxysilyl (TMS) groups of PMPS inside the porous films. Honeycomb structured porous films prepared from PEGDMA-*ran*-PMMA-*ran*-PTRIS were successfully cross-linked by an acid catalyzed sol−gel process instead of a basic solution, and the resulting porous films were too brittle for further processing.

3.5. Thermal Analysis of Cross-Linked Honeycomb Porous Films Seeded with PNIPAAm. PNIPAAm is a thermo sensitive polymer that dissolves in water resulting in optically transparent polymer solutions at room temperature. When heated to temperatures above 32 °C (the lower critical solution temperature LCST of PNIPAAm), PNIPAAm undergoes a reversible phase transition by dehydration, transforming from a hydrated swollen state to a dehydrated shrunken state (retaining 10% hydration) in the solution, resulting in the formations of opaque suspension particles. Figure 11a−e shows the microscopic images of phase transitions of a PNIPAAm solution seeded inside the pores of an optically translucent cross-linked PEGDMA-*ran*-PMMA-*ran*-PMPS (*2a*) honeycomb porous film. Through the microscope, due to a comparable reflective index of PEGDMA-*ran*-PMMA-*ran*-PMPS to PMMA or glass, the porous film appears transparent, while the PNIPAAm solution appeared multicolored. This is the result of unsystematic arrangements of pNIPAAm polymer chains, refracting a range of visible lights at different wavelengths. Upon heating to 27 °C, the colors of the PNIPAAm solution changed, and a small reduction in color intensity was observed followed by a faint white opaque front at 32 °C suggesting a prompt phase transitions of hydrated PNIPAAm into dehydrated stage. Further heating to 41 °C

exhibited a further reduction of colors intensities with increasing opaqueness, and at 48 °C, the PNIPAAm solution has been transformed in a fully opaque solution while the porous film remains transparent. At these elevated temperatures, the entire PNIPAAm seeded porous film appears opaque to the naked eye. Repeated heating studies from room temperatures to 50 °C exhibited comparable phase transitions of PNIPAAm solution in the pores. In contrast, when water has been evaporated from the pores and only dry PNIPAAm remained seeded in the honeycomb porous film, phase transitions of PNIPAAm were absent, and the pores remained colorful under the microscope (transparent by naked eyes) throughout the whole temperature range. Over the several investigations with repeated heating to 50 °C and additional experiments up to 85 °C, the honeycomb porous films, with or without seeded PNIPAAm, and the regular hexagonal arrays were undamaged as shown in Figure 11f. It is evident that the porous films in this study are thermally responsive with excellent transmission of heat and thermally stable at 85 °C.

3.6. Stability of Cross-Linked Porous Films in Organic Solvents. PEGDMA-*ran*-PMMA-*ran*-PMPS random branched copolymer compounds are readily solubilized in organic solvents such as chloroform and dichloromethane, ideal for "breath figure" technique formation of honeycomb porous films. However, for many applications stability in solvents is required. The stability of sol−gel process cross-linked honeycomb porous films prepared from PEGDMA-*ran*-PMMA-*ran*-PMPS (*2a*) random branched copolymers, cross-linked over 48 h, were studied by depositing chloroform and dichloromethane on the surfaces of the porous films for over 24 h. The initial introduction of solvents did not cause any solubilizations of the film materials or its hexagonal structures. After 12 h, the porous films swelled with the honeycomb structures array intact, but a small reduction of pores sizes (5 to 3 μm) as shown in Figure 12 was observed. This swelling can be assigned to the irreversible physical changes that occurred during absorption and evaporation of solvents by PMMA inside the films, while the cross-linked PMPS preserved the integrity of the films, preventing the hexagonal arrays from collapsing. However, after 24 h the entire film and its honeycomb structures were ruined, rupturing into many solid fragments, due possibly to expansive swelling. On the contrary, when a rigid glasslike cross-linked porous films (72 h sol−gel process cross-link) was exposed to similar organic solvents and durations, minimum swelling was
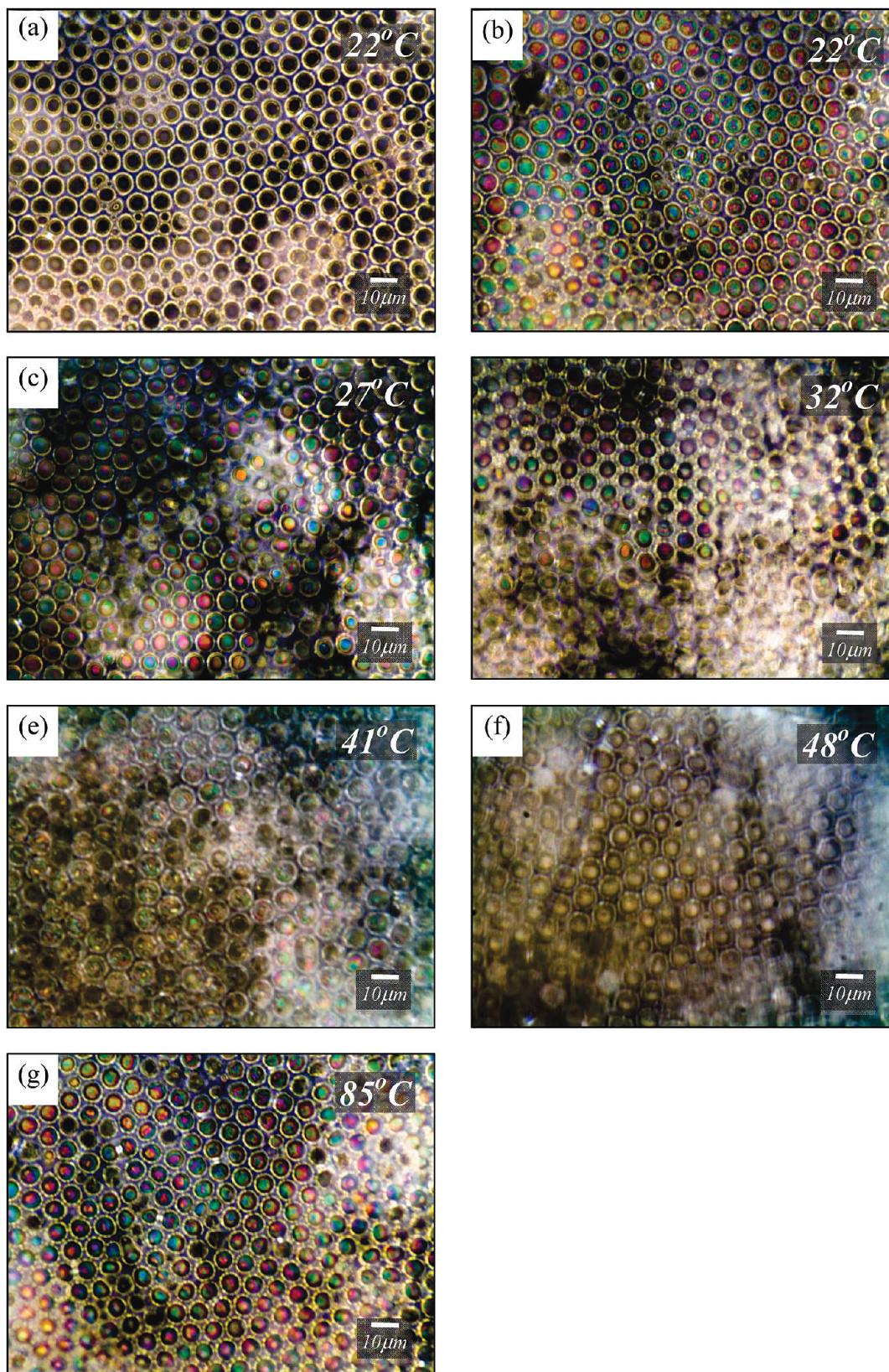
Figure 11. Images of linear PNIPAAm seeded inside pores of cross-linked PEGDMA-*ran*-PMMA-*ran*-PMPS porous films: (a) without PNIPAAm, with PNIPAAm (b) at 22 °C, (c) at 27 °C, (d) at 32 °C, (e) at 41 °C, and (f) at 48 °C, and (g) nonhydrated PNIPAAm at 85 °C.

observed with the honeycomb structures and films undamaged up to 5 days in the studies. The stability of sol−gel process cross-linked porous films in organic solvents was improved compared to noncross-linked copolymers or noncross-linked porous films. It is evident that the resistivity of porous films to organic solvents is influenced profoundly by the cross-link densities of polymeric materials inside the porous films and increasing the
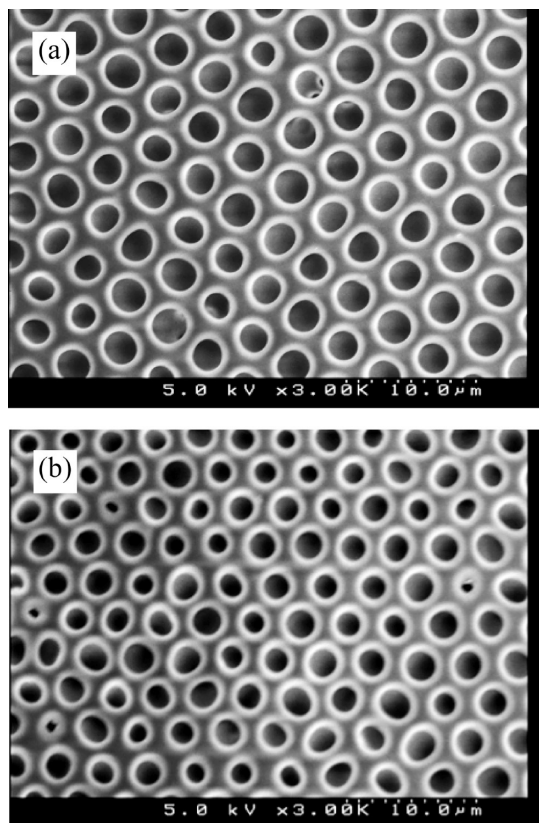
Figure 12. SEM images obtained from the organic solvent (chloroform) stability analysis of 48 h cross-linked PEGDMA-*ran*-PMMA-*ran*-PMPS (*2a*) honeycomb porous films: (a) not exposed to chloroform and (b) exposed to chloroform.

cross-link densities yield chemically more resistance porous films.

4. Conclusions

Completely soluble random branched copolymers of PEGDMA-*ran*-PMMA-*ran*-PMPS and PEGDMA-*ran*-PMMA-*ran*-PTRIS taken to high conversions were synthesized by an easy and cost-effective, one-pot conventional free radical copolymerization strategy. The copolymer compounds are shortly branched copolymers, made up of co-oligomer chains and branched using multifunctional comonomers. Reductions in the feed concentrations of TRIS and MPS during copolymerization resulted in more intensely short branched copolymers while increasing the bifunctional branching agent

(EGDMA) and a reduction of chain transfer agent (DDT) feed concentrations conferred cross-link copolymer compounds after copolymerization. Random branched copolymers obtained in this study are highly soluble in common organic solvents (DCM, CHCl₃), while cross-link copolymers prepared are insoluble in organic solvents. Both PEGDMA-*ran*-PMMA-*ran*-PMPS and PEGDMA-*ran*-PMMA-*ran*-PTRIS random branched copolymer compounds supported the "breath figure" technique formation of honeycomb structured porous films using the moist airflow methodology. The sizes of pores in these porous films can also be tailored easily by variations in casting conditions and the concentration ratios of PMMA to PMPS or PMMA to PTRIS in the copolymer compounds employed during porous film formations. Casting porous films in higher humidity and using copolymer compounds with reduced PMMA to PMPS and PMMA to PTRIS concentration ratios yield porous films with larger pores. A sol−gel processing step completed on honeycomb porous films prepared from PEGDMA-*ran*-PMMA-*ran*-PMPS random branched copolymer compounds cross-link the copolymers in the films, improving their flexibility, resistance to organic solvents (chloroform), and thermal stability up to 85 °C without damages to the films or its hexagonal porous arrays. Thermal analysis studies employing thermal responsive PNIPAAm seeded inside the pores of cross-link PEGDMA-*ran*-PMMA-*ran*-PMPS porous films exhibited the thermal conductivity property of these honeycomb structured porous films. Finally, this work may very well suggest a more comprehensive range of honeycomb structured porous films applications, such as thermal sensitive polymer sensors and more significantly the prospective of foreseeable commercial developments in the near future.