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A new approach to produce polystyrene monoliths by gelation and capillary shrinkage

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ABSTRACT Polymeric monoliths are of great interest in a variety of applications. A new gelation approach to produce a mechanically stable polystyrene (PS) gel directly from its microemulsion is reported. To produce a PS gel, the as-prepared microemulsion is first demulsified by adding selected watermiscible organic solvents. The small PS latex particles liberated from the surfactant are assembled into a piece of bulk material at an appropriate temperature with a high degree of entanglement of the polymer chains. It is found that the d^2T/η value is an important parameter to evaluate the gelation ability of the organic solvents and helps determine the gelation conditions. Finally, PS monoliths are obtained by capillary drying and their pore structures can be effectively tuned by changing the gelation time and the amount of solvent exchanged with water. This allows the controlled preparation of bulk PS artefacts with densities in the range of 0.06 to 1.14 g cm⁻³. This simple method of PS monolith production avoids the use of shaping tools or chemical templates, needs less energy, and is a promising alternative approach to design either integrated porous or compact polymer materials.

Keywords: polystyrene, monolith, demulsification, gelation, capillary shrinkage

INTRODUCTION

A bulk material rather than a powder is preferred for many material applications especially when used as a support or matrix, since it takes full advantage of the mechanical stability and easy reuse [1]. Polystyrene (PS) is a common polymer and has been widely used in many fields, such as plastic products, insulation materials, catalyst supports, chromatographic separation, gas or oil absorption [2–8]. Like many thermoplastics, extrusion, compression or injection molding is usually used for shaping PS in industry, but many attempts have been made to produce a functional polymeric monolith without complex shaping equipment and high energy consumption.

One of the most commonly used methods to produce a porous PS monolith is high internal phase emulsion (HIPE) polymerization [9], which relies on the selection of a surfactant or solid particle to stabilize the emulsion where a large amount of the volume, more than 74 vol.% of the dispersed aqueous phase (i.e. internal phase), is encapsulated by a small amount of the continuous monomer phase [10,11]. Bulk PS is then obtained by the copolymerization of the styrene (St) monomer and a crosslinking agent in the continuous phase with the internal phase acting as a template. Since the pioneering work by Morbidelli's group [12,13], reactive gelation has been extensively used to prepare various macroporous polymeric monoliths with a highly crosslinked structure. This method features two important processes, pore formation by the use of porogens and post-polymerization of the residual monomer. An alternative route, phase separation induced by cooling or solvent evaporation has also been widely used to fabricate polymer monoliths [14,15]. Macroporous PS foams can also be fabricated by the UV-initiated polymerization of foamed emulsions with the help of photoinitiators [16]. Most of these methods are highly dependent on the assistance of a mold, templates, porogens, toxic solvents or complicated crosslinking and stabilizing agents to produce polymeric monoliths with the desired structure for different appli-

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cations. Therefore, more effort needs to be made in exploring alternative methods for PS monolith production with less reliance on the preparation conditions and more choice in tailoring its microstructure.

Here, we report a new PS gelation process which is effective in preparing a monolith starting from its oil/ water microemulsion. PS gelation occurs upon the addition of a water-miscible organic solvent, which acts as an effective demulsifier of the microemulsion. Rapid gelation in only a few minutes at ambient temperature was observed with acetone as the demulsification solvent (Video S1). Note that heating is necessary for most cases. Moreover, densification of the as-prepared gels was successfully achieved, indicating the possibility of tailoring the pore structure of the PS monolith and preparing porous or compact polymer bulk materials by capillary shrinkage, a method previously used for graphene-based hydrogels [17,18].

EXPERIMENTAL SECTION

Emulsion polymerization

The St monomer (AR, Aladdin) was purified by washing in 1 mol L⁻¹ NaOH solution to get rid of trace polymerization inhibitors. As listed in Table S1, weighed amounts of St and sodium dodecyl sulfate (SDS) (AR, Aladdin) were added to 100 mL deionized (DI) water in a 250-mL four-neck flask under stirring, then 0.01 g mL⁻¹ $K_2S_2O_8$ (99.5%, Real & Lead) aqueous solution was added. After purging with Ar for 15 min under stirring to remove the remaining oxygen, the mixture was placed in a 70°C water bath where it was kept for 6 h. As it reached the target temperature, the transparent solution gradually turned a translucent blue color for microemulsions or an opaque white color for emulsions with larger PS latex sizes.

Preparation of the PS monolith

Typically, 10 mL water-miscible organic solvent (such as acetone) was poured into 2.5 mL of the prepared PS emulsion. For the case of demulsification in acetone (99.5%, GuangFu Inc) or 1,4-dioxane (99.5%, Kermel), the PS gel rapidly formed at 25°C in several minutes. After the addition of acetonitrile (ACN) (AR, Kermel), the gelation was promoted by a water bath at 25°C for 4 h. For gelation after demulsification by *N*-methyl pyrrolidone (NMP) (98%, Aladdin), *N*,*N*-dimethylforma-mide (DMF) (99.5%, Kermel), acrylic acid (AA) (AR, Real & Lead), ethanol (EtOH) (AR, Kermel), or dimethyl sulfoxide (DMSO) (GR, Macklin Inc), the lowest tem-

perature at which the gel was obtained is defined as the critical temperature (T_c). After demulsification by methanol (MeOH) (AR, Kermel), ethylene glycol (EG) (AR, Kermel) and glycerol (TG) (99.5%, Real & Lead), the mixtures were treated at 70 and 80°C, respectively. The gel was then taken out and washed with DI water to remove any residual organic solvent. Finally, the pore structure of the PS monolith could be changed by capillary drying at 70°C after solvent exchange with DI water. The gelation mechanism and the structure of the PS monolith were systematically investigated.

Material characterizations

The microstructure of the samples was observed by transmission electron microscopy (TEM, JEM-2100F) and scanning electron microscopy (SEM, Hitachi S-4800). Dynamic light scattering (DLS, Marvin-Nano ZS) measurements were used to determine the particle size distributions of the as-prepared emulsions as well as the demulsified dispersions. Note that the demulsified samples were measured after ultrasonication for 7 min to eliminate the unstable aggregation. The monolith bulk densities were measured by a density balance (Sartorious-YDK03). Fourier transform infrared spectroscopy (FTIR, Thermo Scientific-Nicolet 380) was performed in the wavenumber range of 400 to 4000 cm^{-1} . Thermogravimetry (TG, TA-Q50) curves were recorded from 30 to 700°C. Differential scanning calorimetry (DSC, TA-Q20) was conducted in the range of 25-200°C for the first 2 cycles with heating and cooling rates of 10° C min⁻¹. Considering that the first cycle data generally reflects the thermal history of the materials, the data in the second cycle was used for further analysis. Rheological properties of the gels were measured using a RheoPlus MCR301 rheometer with the distance of the two parallel plates fixed at 2 mm and the oscillation strain at 0.2%. The viscosity of water/organic solvent mixture was also detected by this rheometer, where 15 mL solution was poured into the container with the detector rotating at the constant speed of 10 rad s^{-1} .

RESULTS AND DISCUSSION

As shown in Fig. 1, rapid demulsification occurred after the selected water-miscible organic solvent was dropped into the PS microemulsion, and larger clusters or aggregates formed followed by an integrated gel under the appropriate conditions. It was found that the gelation of PS strongly depends on the size of the PS latex particles in the as-polymerized emulsion, the type of organic solvent, and the temperature of the mixture after demulsification.



Figure 1 Schematic of the preparation of a PS monolith from a PS microemulsion by adding a water-miscible organic solvent for demulsification and followed by gelation and controlled drying.

Moreover, the pore structure of the monolith could be tuned by evaporation-induced capillary drying after solvent exchange with water. That is, the PS gel could be dried to produce either a compact PS bulk or a porous PS aerogel by controlled densification.

The influence of the size of the primary latex particles on PS gelation was first studied. Considering the difficulty of observing this step in the rapid gelation with acetone, EtOH was used as the demusification solvent. A series of PS emulsions denoted samples 1-5 with increasing latex particle size was prepared (see Table S1 for detailed synthesis recipes). DLS studies show that the average latex particle sizes for samples 1-5 are 42, 45, 50, 70, and 470 nm, respectively (Fig. 2a and Fig. S1a), which are slightly higher than those observed in TEM images (Fig. S2), due to the solvent effect and the adsorbed surfactant layer [19]. When EtOH was dropped into the PS emulsion, the average sizes of the PS particles in these five solutions respectively increased to around 400, 275, 186, 106, and 560 nm (Fig. 2a and Fig. S1b). It should be mentioned that after demulsification, the three PS emulsions with the smaller particles showed a marked shift in size distribution compared with the two counterparts with larger particles, which might be attributed to more coalescence along with stronger Brownian motion as well as a structural change driven by a tendency to reduce specific surface energy [20]. Another factor may be due to the higher mobility of PS chains on the surface than in the bulk [21,22]. Therefore, the smaller the particle size, the higher the surface area, and the more likely the inter-particle interaction of the polymer chains, leading to a tight aggregation that is hard to break by ultrasonication before the DLS measurement. This additional interaction is partially ascribed to the π - π bonding between aromatic groups [23], but is mostly the result of the entanglement of the polymer chains, which is a kind of physical cross-linking [24,25]. This promotes the formation of a three-dimensional integrated material at an appropriate temperature (80°C for EtOH) as illustrated by the first three samples in Fig. 2b. In contrast, the two emulsions with larger primary particle sizes failed to form a PS gel due to insufficient aggregation and a lack of chain entanglement between the primary particles. Similar observations are presented in Fig. S3a when acetone was used as the demulsifier for rapid gelation. In rheological testing, the absence of a modulus change with increasing frequency implies the outstanding stability of the asformed gel structure (Fig. S3b).

Gelation is highly dependent on the organic solvent and its volume. The solution with 80 vol.% of a water-miscible organic demulsifier showed better gelation than those with a lower volume fraction (Fig. S4), indicating that a larger volume of demulsifier favours gelation. This is attributed to the formation of more crosslinks accompanied by more intense desolvation. In the following studies, the amount of water-miscible organic solvent was fixed at 80 vol.%. The type of solvent for demulsification is also a key factor in determining the PS gelation. As shown in Fig. 2c, the gelation ability of various solvents can be divided into three types: (i) a bulk gel is directly formed at room temperature for acetone, 1,4-dioxane and ACN; (ii) heating is necessary to obtain an integrated monolith for DMF, NMP, EtOH, AA, and DMSO; (iii) no obvious changes occur even at a high temperature for MeOH, EG



Figure 2 (a) Comparison of the average particle sizes of the PS emulsions before and after demulsification by EtOH. (b) Optical photograph of the PS emulsions with different particle sizes after demulsification by EtOH and subsequent gelation at 80°C for 3 h. (c) Optical photographs of the demulsification at 25°C and subsequent gelation at the lowest gelation temperature (T_c) or boiling point of the solvent mixture. (d) d^2T/η value under either ambient temperature or T_c for all the chosen organic solvents, showing that the gelation ability of various solvents can be divided into three types: gelation under 25°C, gelation at 25–80°C, and failure to gel above 80°C or the boiling point of solvent mixtures.

and TG. It is evident that the solvent largely determines the size of secondary colloidal particle (*d*). DLS results showed that particle sizes increase significantly in acetone, ACN, 1,4-dioxane and NMP, while the particle size changes are relatively small in MeOH, EG and TG (Fig. S5). The colloidal nature of the dispersions confirmed by the Tyndall effect also suggested the limited development of secondary particles in EG and TG. More specifically, the size change of the colloidal particles and the gelation phenomena are closely associated with the three-dimensional Hansen solubility parameter (HSP, δ_t) of the solvents, which is commonly used to evaluate the miscibility of two species with each other. PS ($\delta_t \approx 19.8$) dispersed in a solvent with a similar δ_t value results in lower interfacial tension and larger secondary particles [26]. In addition, solvents with a similar δ_t value cause the PS latex to swell significantly and make the PS polymer chains more flexible [27], so there would be increased free space and more mobility for significant rearrangement and crosslinking of the polymer chains in each particle. Details of the three-dimensional HSP values of PS and the organic solvents, particle sizes and corresponding phenomena after adding the solvent are listed in Table S2 and the *d* value is plotted against δ_t for the solvent in Fig. S6. We found that *d* generally decreased with increasing δ_t , and a larger secondary particle implies more inter-particle crosslinking and thus easier gelling.

The effect of organic solvents on the gelation ability is not only related to the δ_t value but also to the diffusion coefficient (*D*) of the secondary colloidal particles. *D* is a crucial parameter reflecting the speed of the random thermal movement of the particles, i.e. the possibility of collision and fusion of the secondary particles or chains before they entangle into a bulk gel. Taking type (ii) gel formation as an example, the increased D value of the secondary colloidal particles at high temperature is beneficial for gelation. According to the Einstein-Stocks equation (Equation (S1)), D increases with temperature and decreases with viscosity η and particle size. That is, D is proportional to $T/d\eta$ (the η values for various water/ organic solvent mixtures are listed in Table S3), so that increasing the temperature leads to an increased diffusion rate, gives rise to stronger collisions and physical crosslinking between adjacent secondary particles, and macroscopic gelling is promoted. In other words, the gelation ability is determined by both diffusion of the particles (D value) and the δ_t value of the solvent which strongly influences the secondary particle mass as mentioned above, and correlates with the cube of the diameter (d^3) of the secondary particles given by Equation (S2). Therefore, the parameter $d^3 \times T/d\eta = d^2T/\eta$ can be used to predict the gelation ability of various organic solvents and quickly determine the suitable gelation condition. As shown in Fig. 2d, the d^2T/η values at room temperature fall into three categories, which is basically consistent with the classification in Fig. 2c. For example, it can be used to explain the special cases of NMP and AA, which cannot form a PS gel at room temperature even their HSP values are closer to PS than that to ACN. This is due to the lower d^2T/η value at room temperature as a result of the high viscosities of NMP and AA. In order to promote gel formation, a higher temperature is necessary to increase the d^2T/η value, which also means a lower viscosity of solvent and thus favours the movement of secondary particles and increases the amount of entanglement of the polymer chains. As a result, we define T_c as the lowest temperature at which a PS gel is formed. It is found that $T_{\rm c}$ for NMP is 70°C and a higher temperature speeds up PS gelation.

To further understand the gel formation mechanism, the thermal properties and chemical compositions of the samples before and after gelation were investigated using DSC and FTIR. The PS monolith formed at 70°C (PS-M) and PS powder obtained by filtration of the same suspension demulsified by DMF (PS-P) were collected. As shown in the DSC curves in Fig. 3a and Fig. S7, PS-M has a much higher transition temperature (~108°C) than PS-P (~89°C), which confirms the limited mobility of PS chains in the monolith due to the much larger amount of crosslinking after gelation. In addition, it was found that the demulsification induced by organic solvents is totally different from that caused by inorganic salt solutions. In both the PS-M and PS-P samples, no surfactants remained after the addition of DMF which is shown by the absence of a $-SO_3^{-}$ signal from SDS species in the FTIR spectra and a slight weight loss below 350°C in the thermogravimetric (TG) curves (Fig. 3b and Fig. S8a) [28]. This implies that the surfactant species were entirely desorbed from the PS latex and dissolved in the liquid after the addition of the organic solvent, which led to an increased affinity between the PS particles and greatly facilitated their collision and fusion. This process is quite unlike the previously reported latex swelling process for reactive gelation. In contrast, there is still obvious residual SDS surfactant for demulsified samples induced by an excess MgCl₂ solution (PS-MgCl₂) even after an extra rinse, where the particle coagulation is caused by the charge neutralization. Thus, it is difficult to form a gel under the same conditions because of the poor interparticle affinity caused by the existence of a surfactant layer [29]. Interestingly, the MgCl₂-induced precipitation still has gelation ability which is seen once the organic



Figure 3 (a) DSC curves of a PS monolith (PS-M) and PS powder (PS-P) collected from the same microemulsion after DMF demulsification. (b) FTIR spectra of PS-M, PS-MgCl₂, PS-P and PS particles obtained by direct filtration of the PS microemulsion.

solvent is introduced (Fig. S8b). The above result suggests that the complete desorption of SDS surfactant induced by the organic solvent demulsification plays a key role in PS gel formation, which is also important in avoiding any surfactant residue in the PS monoliths.

The pore structure of the as-formed PS gels can be further tailored by capillary drying, which has already proved useful for shrinking the interconnected flexible graphene network as reported in a previous paper [17]. Here, the trapped solvent in the gels was first exchanged with water, which has a high surface tension of 72.7 mN m⁻¹, and the gels were then dried at 70°C. The PS monoliths obtained showed quite different degrees of shrinkage for gels prepared using different solvents. As shown in Fig. 4a, PS foams were only obtained for the gels prepared using acetone, EtOH and ACN, while both porous and dense structures were obtained for the remainder after solvent removal. As observed from the SEM images, PS foams have a porous structure constructed by relatively uniform-sized particles (Fig. S9a-c), whose size was consistent with the size of the PS aggregations after solvent demulsification, while the very stiff monolith has a large volume shrinkage and a compact microstructure (Fig. S9d). To achieve controlled densification, both the gelation time and degree of solvent exchange must be taken into consideration. Here, DMSO was used as the demulsifying solvent to study the impact of these two factors on the final structure of the PS monolith, since this system has a long gelation time. The improved storage modulus (G'), loss modulus (G'') and shear viscosity in rheological testing, as well as a reduced gel volume, indicating the increased mechanical strength and degree of entanglement of the PS gel as the gelation time was prolonged from 5 to 10 h (Fig. 4b and Fig. S10) [30]. As shown in Fig. 4c, the densities of the PS monoliths could be changed from 0.06 to 1.14 g cm^{-3} and gradually decreased with the gelation time, while an additional solvent exchange with water did not help in achieving higher densities. For example, almost no shrinkage during drying could be observed after a second water exchange when the gelation time was longer than 8.5 h. These monoliths thus had much lower densities (less than 0.086 g cm^{-3}). Considering the above results, it is likely that increasing the gelation time and the degree of water exchange of the PS gel is detrimental to capillary shrinkage of the PS network. TG analysis was used to evaluate the amount of residual organic solvent, which is a direct indicator of the degree of solvent exchange in the PS gel. PS monoliths prepared with a shorter gelation time and less water exchange (samples of 5 h-1st, 5 h-2nd and 10 h-1st) showed much higher weight losses in the temperature range of 200-350°C (Fig. 4d), which indicates that some residual DMSO is difficult to evaporate during capillary drying and is thus trapped in channels in



Figure 4 (a) Optical photograph of PS monoliths with the two extreme structures of a porous foam (F) and a compact form (C) prepared using different solvents. (b) The rheological storage modulus (G') and loss modulus (G'') as a function of oscillation frequency for the PS gels with different gelation times in DMSO. (c) Dependence of density on the gelation time of a PS gel when the trapped solvent is exchanged with water once (1st) or twice (2nd). (d) TG curves of PS monoliths with different gelation times and degrees of water exchange.

the monolith. These three samples all had high densities due to the effective shrinkage and were characterized by a compact microstructure as observed in the SEM images (Fig. S11). In contrast, the ultralight 10h-2nd sample has a highly porous structure with abundant macropores, which corresponded to negligible residual DMSO as confirmed by the TG analysis. These results suggest that shortening the gelation time and reducing the water exchange time cause more residual DMSO and a higher density. This is largely because the gel with less chain entanglement absorbs more DMSO to make the PS skeleton flexible, which permits easier shrinkage of the PS network during capillary drying. Moreover, a certain amount of residual organic solvent in the PS gel with less water exchange retains the stretching ability of the PS chains and thus also helps realize capillary shrinkage during subsequent removal of the trapped solvent. That is to say, the degree of shrinkage of the PS gel is associated with the state of the PS skeleton. The PS gel with a less entangled chain structure and more absorbed organic solvent is more readily shrunk during capillary drying. Consequently, the pore structure of the PS monoliths can be finely tuned by varying the above factors. A combination of partial capillary-drying and subsequent freezedrying to remove the trapped water in the assembled gels can also be used to achieve the structure control of the PS monoliths. As shown in Fig. S12, an increase of the capillary-drying time leads to larger degree of shrinkage and significant changes in the microstructure as the loose porous structure changes to a more compact microstructure.

CONCLUSIONS

In summary, a new strategy for the gelation of PS latex from a microemulsion with an emphasis on the gelation mechanism was proposed. A stable PS gel is obtained by the gelation of the PS latex after demulsification initiated by a selected water-miscible organic solvent, which, to the best of our knowledge, is the first report on PS gelation resulting from a demulsification-induced chain entanglement. It was found that the gelation ability of the organic solvents can be evaluated by the d^2T/η value, which takes into account the influence of both the solvent and the diffusion ability of the aggregates. In addition, the strategy proposed here has a great advantage in the structure control of PS monoliths, which can be easily regulated by controlling the gelation time, degree of water exchange of the gel, and the capillary-drying time, etc. This new gelling strategy avoids the use of shaping equipment or templates as well as the addition of a crosslinking agent. It eliminates the needs of a porogenic solvent or a large amount (5 wt.%–50 wt.%) of surfaceactive material for stabilization. It is believed that this simple alternative PS gelation method provides a promising way to produce functional polymer monoliths and may be extended to a wide range of other polymers for bulk material production.

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Author contributions Yang QH, Tao Y and Li D conceived and designed the experiments. Li D and Xia J conducted the material synthesis and characterization. Li D and Tao Y took charge of the data collection and analysis. Wu Z and Han J performed the SEM and TEM experiments. Deng Y, Li P and Shang T helped with the data analysis. Li D and Tao Y wrote the paper with further inputs from other authors. All the authors discussed the results and contributed to the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.



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聚苯乙烯微乳液的凝胶化及其块体的快速制备和 结构调控

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摘要本文利用一种新的聚苯乙烯(PS)微乳液的凝胶化现象,制备 了结构稳定的PS凝胶,并通过可控的毛细收缩过程获得了具有不 同孔隙结构的PS块体.对PS微乳液的凝胶化机制的系统研究表明, 在PS微乳液中加入适量特定的水溶性有机溶剂后,可实现PS微乳 液的破乳,PS乳胶粒子周围的表面活性剂完全解吸附,并自发团聚 成二次颗粒,在适当温度条件下可通过分子链缠结组装形成三维 多孔凝胶.不同溶剂实现PS微乳液凝胶化的能力可以通过d²T/ŋ参 数的大小衡量和评估.通过进一步调整成胶时间与溶剂置换程度, PS凝胶可在后续的干燥过程中实现不同程度的收缩,从而得到密 度范围在0.06-1.14g cm⁻³的多孔或致密PS块体.这种PS凝胶化策 略是一种简单高效的PS成型方法,避免了成型设备、模板、成孔 剂以及大量表面活性剂的应用,有望成为制备功能高分子聚合物 块体材料的新方法.