

PNIPAAm grafted particle monoliths: parameters affecting structure and morphology

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Abstract Crosslinked polystyrene latex particles generated with surfactant free emulsion polymerization were functionalized with thin layer of ATRP initiator on the surface. The functionalized particles were aggregated as physical networks using high shear techniques. The latex particles as well as the aggregated particles were used to successfully generate thermo-responsive monoliths by grafting PNIPAAm brushes from the surface of the particles by atom transfer radical polymerization and simultaneous crosslinking of these brushes. Different solid fractions and drying conditions were used in the generation of the monoliths and the effect of these variations on the structure and morphology of the monoliths was analyzed. Surprising morphologies consisting of tubes or channels were observed when higher solid fractions were used. This behavior was enhanced when the monoliths were dried at higher temperatures. By using proper solid fractions and drying conditions, homogenous porous monoliths could be achieved.

Keywords Atom transfer radical polymerization · Poly(*N*-isopropylacrylamide) · Monoliths · Polystyrene

1 Introduction

Solid phase synthesis and chromatographic separation technologies extensively employ polymers as supports. The polymer particles in these supports are joined together as a porous network or monolith where the surfaces of these particles provide specific reaction or adsorption sites based on charge, affinity, etc. To achieve suitable porosity in the structures, many studies have focused the use of porogens during polymerization of styrene [1–3]. During suspension polymerization of styrene with divinylbenzene as cross-linker, the polymer chains become incompatible with the porogen and precipitate out to arrange themselves as microspheres. As the microspheres grow, they aggregate into random structures thus forming porous networks. Another approach called ‘reactive gelation’ has been reported in the literature which was observed to control the properties of the network in a better way [4]. This process included the swelling of the preformed latex particles with monomer followed by their gelation using salt and post polymerization of the swelling monomer. Controlled morphology and porosity of the structures could be attained.

Recently, a number of studies focused on grafting of functional thermo-responsive poly(*N*-isopropylacrylamide) (PNIPAAm) brushes from the spherical latex particles by using atom transfer radical polymerization of *N*-isopropylacrylamide [5–8]. The particles were first functionalized with a thin layer of ATRP initiator followed by grafting of PNIPAAm brushes from the surface of the particles. Because of the controlled nature of atom transfer radical polymerization, the amount of grafting and hence subsequent properties of the grafted particles could be easily controlled. PNIPAAm is a material of choice because below its lower critical solution temperature (LCST) of

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about 32 °C, the polymer chains exhibit chain extended conformations and random coil structure and above LCST, the chains transform into more collapsed globular form. The intermolecular hydrogen bonding with the water molecules due to the chain extended morphology below LCST generates the hydrophilic nature of the chains. The intramolecular bonding between the CO and NH groups above LCST dominate over the external hydrogen bonding [9–12]. Owing to this nature of PNIPAAm, the particles modified with PNIPAAm were confirmed to hold tremendous potential for separation processes solely controlled by temperature [8]. As the free particles hold less importance than the macroporous networks or structures as chromatographic media, as a special functionalization of the monoliths, PNIPAAm chains can also be grown from the particles forming the network or monolith. This can lead to chromatographic separations of media like proteins, viruses, etc. just by changing the network or eluent temperature. This would help in avoiding the use of harsh adsorption and desorption conditions used conventionally which may sometimes affect the quality of the biological media. One important thing to note here is that the particles in these studies were prepared by surfactant free emulsion polymerization thus resulting in large particle sizes of approximately 500 nm. To generate monoliths from such particles using the earlier reported 'reactive gelation' approach would require large amounts of salt for gelation. Therefore, an alternative way is required which may overcome the use of salt during the monolith generation. One possibility is to generate loosely held aggregates from the latex particles followed by simultaneous grafting of PNIPAAm and crosslinking of these formed PNIPAAm chains [13].

This paper reports the synthesis of the monoliths by grafting of PNIPAAm brushes from the aggregated particles or free latex particles and simultaneously crosslinking them in order to provide the monolith structure. The PNIPAAm functionalized monoliths were prepared without the salt gelation step. Different monoliths were generated by varying the solid fraction as well as drying conditions and the effect of these variations on the resulting monolith structure and morphology was analyzed.

2 Experimental

2.1 Materials

N-Isopropylacrylamide (NIPAAm, 97%) and *N,N'*-methylenebis(acrylamide) (MBA, $\geq 97\%$) were procured from Aldrich (Buchs, Switzerland). Styrene (S, $\geq 99.5\%$), divinylbenzene (DVB, $\approx 80\%$) and potassium persulfate (KPS, $>99.0\%$) were purchased from Fluka

(Buchs, Switzerland) and were used as supplied without further purifications. ATRP initiator end capped with an acrylic moiety (2-(2-bromopropionyloxy) ethyl acrylate, BPOEA) was synthesized as reported earlier [14].

Reagents to run the ATRP polymerization, namely 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%), copper(I) bromide (CuBr, 99.99%), copper(II) bromide (CuBr₂, 99.99%) and powder copper (Cu, 99%, 200 mesh), were procured from Aldrich (Buchs, Switzerland). Ultra pure Millipore water was employed in all experiments.

2.2 Synthesis of polystyrene particles and surface functionalization

Polystyrene seed latex was prepared by surfactant free emulsion polymerization of styrene (14 g), divinylbenzene (0.5 g) added with 0.3 g KPS and 310 g of water [7]. The crosslinked polystyrene latex particles were washed by repeated centrifugation and resuspension cycles in millipore water and were subsequently functionalized with a thin layer of ATRP initiator on the surfaces. For this, BPOEA (0.21 g), DVB (0.065 g) and styrene (0.26 g) (0.01 g of KPS in 0.5 mL of water) were added to 15 g of preformed latex heated to 70 °C and polymerized for further 7 h [7]. Finally, the functionalized latex was washed following the similar process of centrifugation and resuspension in water.

2.3 Shear aggregation

The functionalized latex particles were sonicated for 10 min (ultrasonic horn at 70% amplitude) and shear mixed for another 10 min with a ultra-high shear mixer (Ultra-Turax T50) to destabilize the latex. The resulting porous latex aggregates were allowed to settle and the aqueous layer was decanted to concentrate the latex solid fraction.

2.4 Monolith synthesis

Different monoliths were prepared from these concentrated aggregates as well as concentrated functionalized latex particles. For monoliths prepared from aggregates, the concentrated latex (1.5 g, 15 wt.%) was transferred to a flat bottom vial, degassed and subsequently added with HMTETA (17 mg), CuBr (4.3 mg), CuBr₂ (1.4 mg) and Cu (2 mg). The solution was stirred for 2 min and NIPAAm (0.4 g) and MBA (0.4 g) were added to the solution. The viscous slurry was vigorously stirred to solubilize the monomers. The stirrer was then removed and the vial was degassed and kept for 12 h without shaking. In another trial, exactly same process and reagents were used but in this case additional 1.5 mL of water was added to the

slurry in order to see the effect of volume changes on the properties of the monolith. The formed monoliths were carefully removed from the vials and dried at room temperature. Drying of monoliths at 70 °C was also carried out in order to analyze the effect of fast drying conditions on the structure of the monolith. ATRP initiator modified particle latex was also concentrated by evaporating a fraction of water followed by monolith synthesis following the similar procedure as reported above. Effect of different solid fractions on the structure and morphology of the resulting monoliths was also analyzed.

2.5 Electron microscopy

Hitachi field emission in-lens S-900 high resolution scanning electron microscope at accelerating voltages of 10–20 kV was employed to observe the surface morphology of the particles. Carbon/collodium coated 400-mesh copper grids, freshly etched by charged oxygen plasma (10 s, 100 mV, 5 mbar of O₂) in Balzers GEA-003-S glow-discharge apparatus (Balzers), were placed on the droplets of particle suspensions for 2 min, dried on filter paper followed by sputter coating with 3 nm platinum. The SEM of monoliths was performed by fixing small pieces of dry monoliths on copper supports followed by sputter coating with 3 nm platinum.

3 Results and discussion

PNIPAAM modified networks hold tremendous potential for their use in commercial separation technologies [8, 13]. PNIPAAM grafting of particles along with simultaneous monolith generation presents an alternative approach to the earlier reported reactive gelation process in order to obtain such commercially important materials. The potential of

these PNIPAAM grafted particles as well as monoliths for such separations has been quantitatively established [8, 13]. The temperature dependant swelling/deswelling studies on the monoliths as well as adsorption/desorption of a virus sample on the PNIPAAM grafted particles was successfully reported. But an optimum porous structure and morphology is required in the porous networks for the process to be successful. Few preliminary trials in this regard to analyze the effect of various process changes on the resulting monolith network structure and morphology are detailed as follows.

Surfactant free polymerization of polystyrene particles in the presence of small amount of crosslinker led to the generation of narrowly dispersed latex particles. These particles were subsequently covered with a thin shell (80 nm thick) of ATRP initiator (BPOEA). The terminal acrylic group of BPOEA molecule could be copolymerized with styrene and divinylbenzene in order to obtain this thin layer of ATRP initiator [7]. The copolymer chains were observed to be compatible with the surface of the polystyrene particles and no secondary nucleation of the copolymer particles was observed as the increase in the diameter of the seed particles after forming a shell is quantitative to the amount of monomers initially added. The amount of crosslinker can be altered in order to change the density of ATRP initiator in the shell which subsequently affects the density of PNIPAAM brushes grafted from the surface of particles. The grafting of ATRP initiator on the particle surface was also quantitatively confirmed by NMR [7]. The SEM image of these functionalized particles is shown in Fig. 1a. The particles are still fairly monodisperse though sedimentation sets in with time owing to their synthesis without the emulsifier. The average hydrodynamic diameter of the particles was estimated by laser light scattering to be 530 nm. When these latex particles were subjected to high shear forces in a

Fig. 1 (a) SEM micrograph of ATRP initiator functionalized polystyrene particles and (b) SEM micrograph depicting these particles when aggregated using high shear

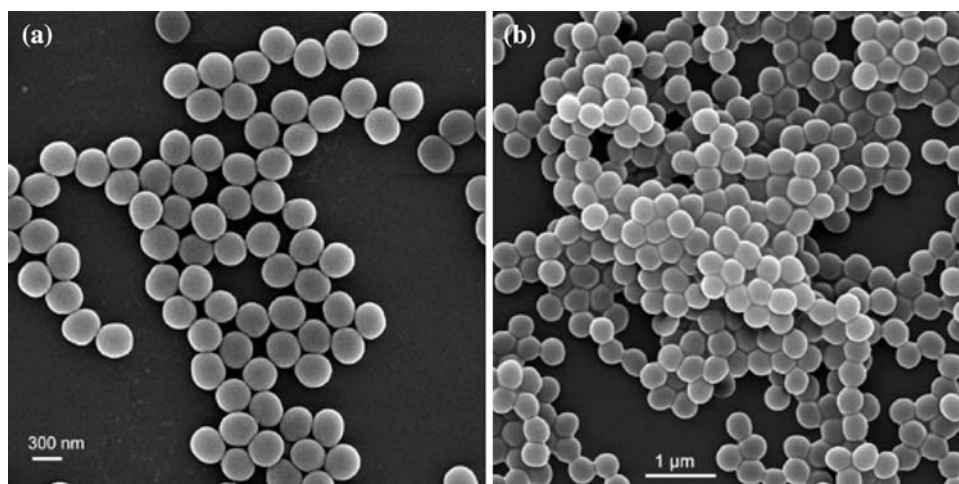
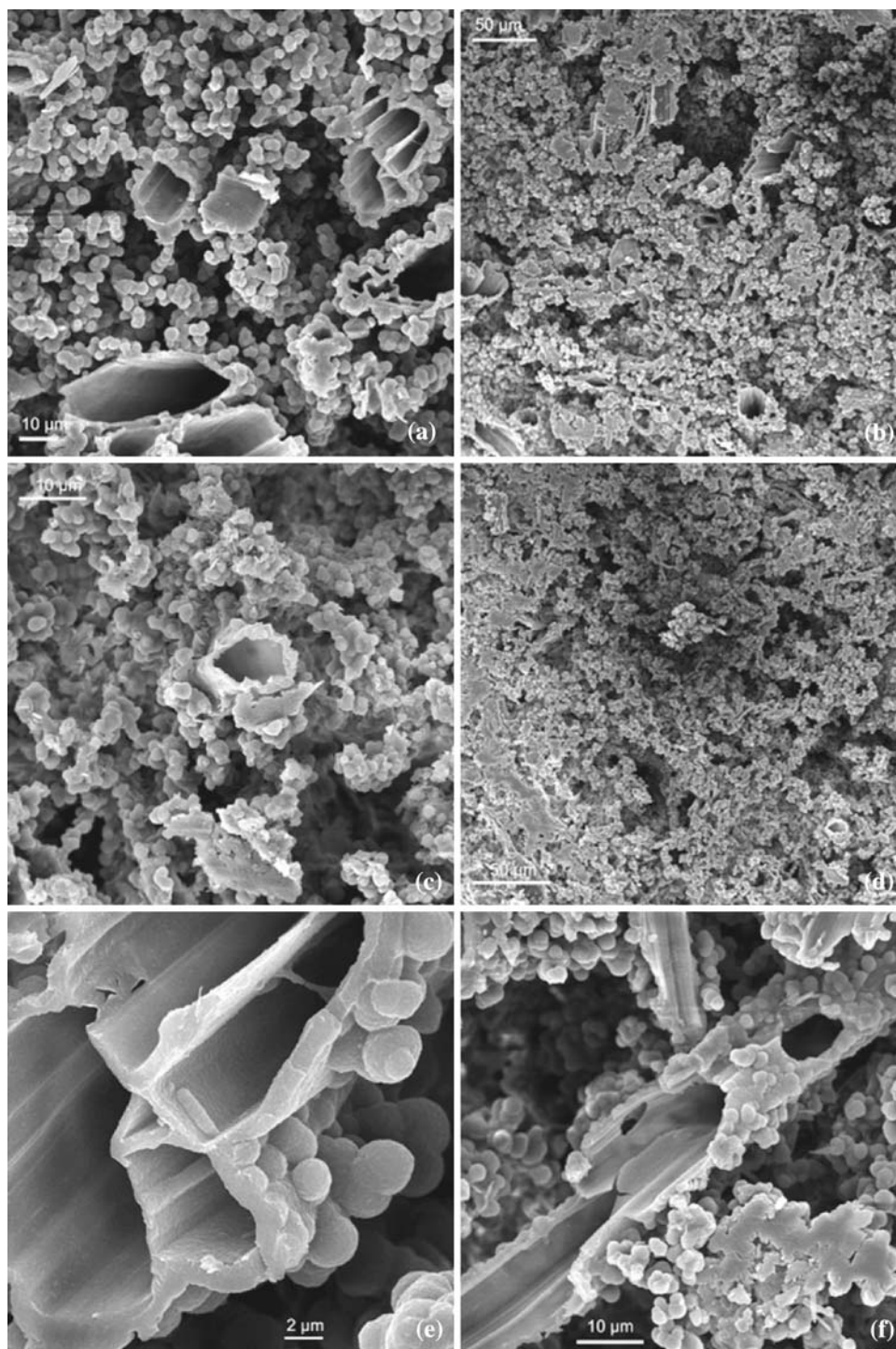


Fig. 2 (a) and (b) High and low magnification SEM image of the monolith generated from aggregated particles using higher solid fraction and dried at room temperature, (c) and (d) high and low magnification SEM micrographs of the monolith prepared using lower solid fraction and dried at room temperature and (e) and (f) SEM images representing the tubes or channels as seen in Fig. 1a, b



sonicator and shear mixer, a network of physical aggregates resulted owing to the destabilization and collapse of the latex. Figure 1b shows the SEM image of these aggregates. The aggregates are clearly visible to be porous thus providing the ideal material to generate monoliths from them. The average size of these networks was estimated to be 3–4 μm . However, as the forces holding these particles together in these aggregates are only physical,

therefore, these aggregates are not useful for commercial application and much stronger bonding forces are required to preserve the so formed porous structure.

Atom transfer radical polymerization of NIPAAm from the aggregated particles led to the successful generation of monoliths. Use of high extents of crosslinker helped to attain the required stability of the monoliths. The monoliths were hard when totally dry, whereas they turned soft and swollen

when wet. Monoliths prepared by low and high solid fraction were both stable under these conditions. However, very different morphologies were observed under SEM for these two kinds of monoliths. Figure 2a, b show the SEM images of the monolith with higher solid fraction used. Surprisingly, the monolith had a number of channels or tubes clearly visible in its morphology. These channels had random dimensions and were scattered pointing in all directions. Another thing to note here is that these tubes were very smooth from inside and had particles adsorbed all around their external surface. Figure 2c, d depict the morphology of the monolith which was prepared at half the solid content of the monolith shown in Fig. 2a, b. Almost no or very negligible amount of earlier seen channels or tubes could be observed in this case and the particles were nicely connected forming a homogenous porous structures (Fig. 2d). Figure 2e, f show the channels seen in Fig. 2a, b in more detail. Absence of so formed channels in the second monolith indicates that the solid fraction may be responsible for the formation of these channels, as there was no other difference in the generation of the two monoliths. It was observed that the aggregates quickly turned solid as soon as NIPAAM and MBA solution was mixed with them thus quickly trapping all the water present in the system. It is suspected that while drying the water trapped in the system has more difficulty to escape in the monolith which is much more dense. Thus, the so formed channels formed in the former monolith can be explained to be the trails of the trapped water molecules shooting out of the structure making their path where ever they could find the way. Although water could have escaped through the pores, but the water trapped in the areas of high concentration of formed PNIPAAM polymer led to generation of these tubes with smooth inside surfaces as the polymer may be swollen in the presence of the trapped water. However, the monolith with lower solid content seem to have more porosity and subsequently less concentration of any dead areas

containing only polymer thus easing the escape of water from the monolith structure. This observation indicates that in the present operating conditions used for the generation of monoliths, there is a critical solid fraction which should not be exceeded in order to preserve the homogenous morphology of the monolith structure.

Effect of drying at higher temperatures was analyzed in order to establish optimum drying conditions. Figure 3 shows the SEM images of the monolith similar to shown in Figure 2a, b, but dried at 70 °C. On comparison of the images of monoliths dried at room temperature and 70 °C, it is clearly evident that the number of channels or tubes significantly increased when the monolith was dried at 70 °C. It also supports the earlier hypothesis concerning the escape of trapped water from the monolith structure. Heating at 70 °C is expected to accelerate this escape tremendously, thus forcing all of the water molecule to escape collectively in a much shorter period of time. This definitely is expected to increase the number of these channels or pathways through which the water molecules tend to escape. Thus it points to an another important observation to bear in mind that drying conditions have very significant effect on the final structure of the monolith and care should be taken to use optimal drying conditions.

Similar effect was also observed when the concentrated latex particles (not aggregated) were themselves grafted with PNIPAAM and simultaneous crosslinking with MBA. The particles were grafted and networked in order to analyze the effect of starting media on the final structure of the monolith. Similar tube or channel structures were observed when higher solid fractions were used (Fig. 4a), though the number of these channels were relatively smaller than those seen in the case of high solid fraction monoliths obtained from aggregated particles. This can be the result of easy escape of water from the latex particle monoliths owing to the absence of any physical network in the

Fig. 3 (a) and (b) High and low magnification images of the monoliths prepared using higher solid fraction and dried at 70 °C

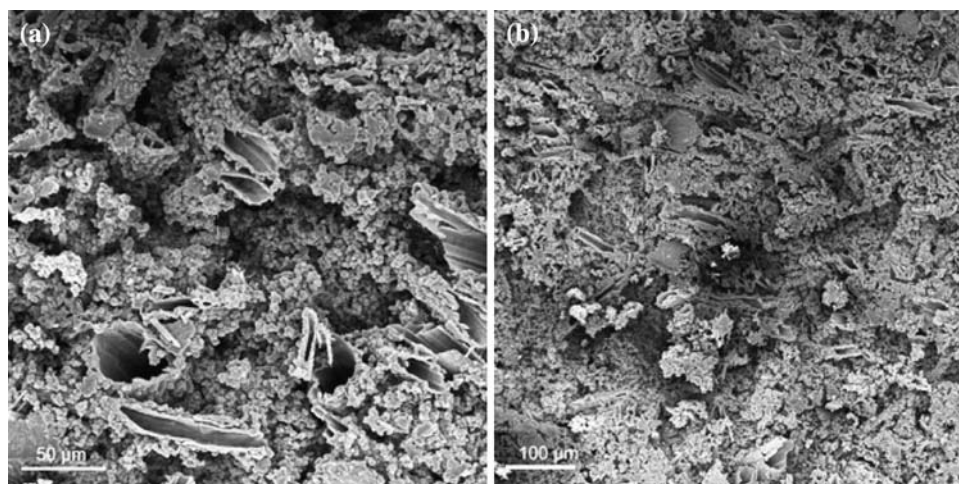
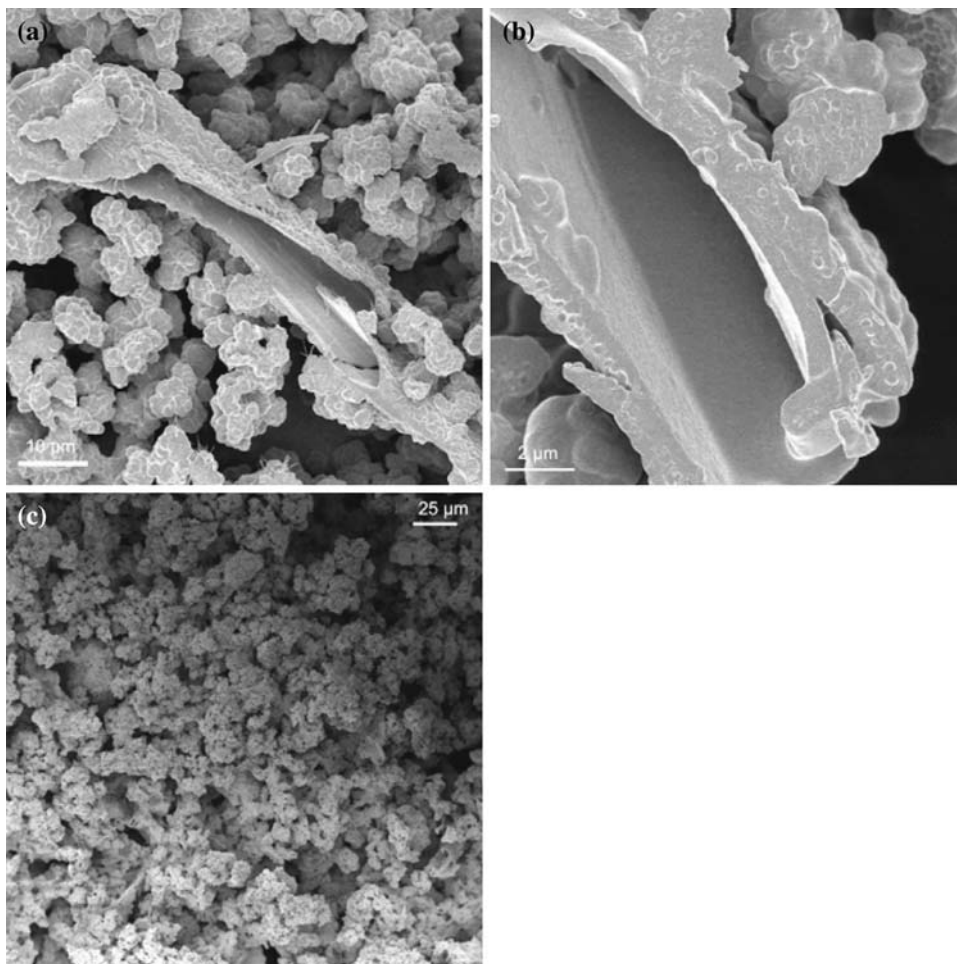


Fig. 4 (a) SEM micrograph of the monolith prepared from latex particles using high solid fraction and dried at room temperature, (b) high magnification image of the channel structure observed in figure (a), and (c) SEM image of the monolith prepared from latex particles using lower solid fraction and dried at room temperature



beginning to trap the water of the system. The cross-section of the channel structure was also similar as shown in Fig. 4b, with smooth inside surface and particles adsorbed on the outer walls. The monolith generated with lower solid content was observed to be totally free from any of the channels or tubes owing to the similar reasons mentioned above (Fig. 4c).

The results obtained thus indicate that successful generation of the monoliths could be achieved by aggregate or particle grafting process and various factors affecting the final structure of the monolith could be established. In order to obtain homogenous and porous network, thus to avoid the tubes or channels in the structure, optimum values of solid fraction and optimal drying procedures are required. Another point to note here is that in the conditions used to generate the monoliths, higher amounts of crosslinker was used. However, this amount can also be varied according to the requirement of the process thus indicating controlled fine-tuning of the process. Apart from that, density of the ATRP initiator on the surface of the functionalized particles can also be easily controlled according to the requirement of the process. The formed monoliths represent the separation supports which can have tremendous

potential for use in adsorption and desorption processes solely assisted by temperature.

4 Conclusions

Shear mixing of the latex particles led to destabilization and collapse of the emulsifier-free latex particles into physical networks of the aggregated particles. These aggregates and particles could successfully be transformed into solid porous monoliths by simultaneous grafting and crosslinking of PNIPAAm from the surface. Various factors affecting the structure and morphology of these monoliths could be analyzed. Under the operating conditions used to generate the monoliths, it was found that after a critical solid fraction of the aggregates or particles used to form the monolith, a surprising channel or tube morphology in the monolith structure was developed. This channel or tube morphology was observed to be enhanced when the monoliths were dried at higher temperatures especially in the monoliths with higher solid fractions. The monolith structure can easily be fine-tuned or altered according to the requirement by changing the amount of crosslinker and the amount of ATRP

initiator on the surface of the particles thus indicating the robustness of the technique.

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References

1. O. Okay, *Prog. Polym. Sci.* **25**, 711 (2000). doi:[10.1016/S0079-6700\(00\)00015-0](https://doi.org/10.1016/S0079-6700(00)00015-0)
2. A. Guyot, M. Bartholin, *Prog. Polym. Sci.* **8**, 277 (1982). doi:[10.1016/0079-6700\(82\)90002-8](https://doi.org/10.1016/0079-6700(82)90002-8)
3. J. Seidl, J. Malinsky, K. Dusek, W. Heitz, *Adv. Polym. Sci.* **5**, 113 (1967)
4. N. Marti, F. Quattrini, A. Butte, M. Morbidelli, *Macromol. Mater. Eng.* **290**, 221–229 (2005). doi:[10.1002/mame.200400344](https://doi.org/10.1002/mame.200400344)
5. J.N. Kizhakkedathu, A. Takacs-Cox, D.E. Brooks, *Macromolecules* **35**, 4247–4257 (2002). doi:[10.1021/ma011651y](https://doi.org/10.1021/ma011651y)
6. J.N. Kizhakkedathu, D.E. Brooks, *Macromolecules* **36**, 591–598 (2003). doi:[10.1021/ma021337j](https://doi.org/10.1021/ma021337j)
7. V. Mittal, N.B. Matsko, A. Butte, M. Morbidelli, *Polymer (Guildf)* **48**, 2806–2817 (2007). doi:[10.1016/j.polymer.2007.03.050](https://doi.org/10.1016/j.polymer.2007.03.050)
8. V. Mittal, N.B. Matsko, A. Butte, M. Morbidelli, *Eur. Polym. J.* **43**, 4868–4881 (2007). doi:[10.1016/j.eurpolymj.2007.10.012](https://doi.org/10.1016/j.eurpolymj.2007.10.012)
9. H. Ringsdorf, E. Sackmann, J. Simon, F.M. Winnik, *Biochim. Biophys. Acta* **1153**, 335 (1993). doi:[10.1016/0005-2736\(93\)90424-X](https://doi.org/10.1016/0005-2736(93)90424-X)
10. Y.H. Bae, T. Okano, S.W.J. Kim, *Polym. Sci., Part B Polym. Phys.* **28**, 923 (1990). doi:[10.1002/polb.1990.090280609](https://doi.org/10.1002/polb.1990.090280609)
11. M. Heskins, J.E.J. Guillet, *Macromol. Sci. Chem.* **A2**, 1441 (1968). doi:[10.1080/10601326808051910](https://doi.org/10.1080/10601326808051910)
12. R. Yoshida, K. Uchida, Y. Kaneko, K. Sakai, A. Kikuchi, Y. Sakurai et al., *Nature* **374**, 240 (1995). doi:[10.1038/374240a0](https://doi.org/10.1038/374240a0)
13. V. Mittal, N.B. Matsko, A. Butte, M. Morbidelli, *Macromol. Mater. Eng.* **293**, 491–502 (2008)
14. K. Matyjaszewski, S.G. Gaynor, A. Kulfan, M. Podwika, *Macromolecules* **30**, 5192–5194 (1997). doi:[10.1021/ma970359g](https://doi.org/10.1021/ma970359g)