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SHORT COMMUNICATION

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Fabrication of nanoscale latex arrays based on hydroxylated poly(butyl methacrylate-*b*-glycidyl methacrylate)

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Abstract We succeeded in fabricating nanoscale arrays of polymers based on hydroxylated poly(butyl methacrylate-*b*-glycidyl methacrylate) which was prepared via a novel atom-transfer radical polymerization technique. Nanosized latex particles of the copolymer were obtained in the tetrahydrofuran/toluene solvent system. By evaporation of the latex solution on a substrate, the ordered self-organization monolayer was formed. Rather regular, two-dimensional arrays of nanopaticles with diameters down to approximately 12 nm were observed by means of transmission electron microscopy. The regular nature of the arrays can be controlled well by depositing the monolayer at a lower temperature.

Keywords Self-organization · Nanocrystals · Ordered arrays

Introduction

Owing to potential applications in schemes of arrays for electronic and electrooptic devices, membrane filters with controllable pore sizes and waveguides, fabrication of colloidal crystals on the nanoscale is attracting considerable attention [1, 2, 3, 4]. Several authors have developed techniques to create such colloidal crystals [5, 6, 7, 8, 9, 10]. They usually prepared the latex particle monolayer by the evaporation of a solution on a substrate, but special devices [5, 6] or substrates with surface treatment [4] are usually required. Moreover, the monodisperse polymers used for fabrication of ordered arrays were traditionally synthesized by ionic polymerization [8, 9, 10]. The ionic polymerization technique, however, suffers from the stringent requirement for moisture removal and monomer purity.

A novel “living” radical polymerization method termed atom-transfer radical polymerization (ATRP) without these drawbacks has aroused considerable interest recently [11]. ATRP is easier to execute and can also control the polymerization well. Nevertheless, the formation of nanoparticles from polymers prepared by ATRP remains rare although many studies describing various ATRP systems have been reported [12, 13, 14]. And more regrettably, as far as we are aware, there have been no reports on nanoscale arrays of polymers via prepared by the ATRP technique. Hence, it is expected that one could obtain such ordered arrays of polymer nanoparticles with the use of ATRP.

We reported here a recent investigation in which ordered arrays of polymer nanoparticles were produced. The polymer used for fabrication of the ordered arrays was synthesized by ATRP. Also, we do not need special devices to deposit the film, nor do we need to treat the substrate to get a hydrophilic hydrophobic surface. Because the arrays are easy to control and require no particular skill or precise instruments, they can find applications in many modern industries, for example, in data storage, microelectronics, optical units.

Experimental

The block copolymer investigated (Fig. 1), namely hydroxylated poly(butyl methacrylate-*b*-glycidyl methacrylate), was prepared via ATRP (Table 1). A detailed description of the synthesis was presented in a previous publication [15]. Tenfold excess toluene was added dropwise with stirring to a tetrahydrofuran (THF) solution

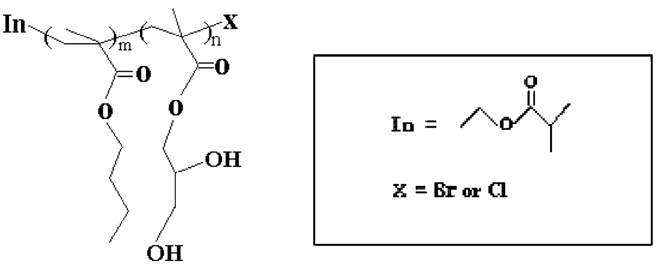


Fig. 1 The chemical structure of the block copolymer investigated prepared via atom-transfer radical polymerization

of the copolymer to reach a final micelle concentration of about 5 mg/ml. The micelle solution was stirred overnight and then dialyzed against pure toluene over 2 days to remove THF. Then the solution was filtered through a 0.5-μm poly(tetrafluoroethylene) filter. When one drop of the micelle solution was deposited on a copper grid support coated with carbon and the carrier solvent was evaporated at a certain temperature, the arrays were produced. The molecular weight and its distribution of the polymers were measured using a size-exclusion chromatograph based on standard polystyrene calibration. The surface morphology of the nanoscale arrays was obtained using a JEOL-2000EX transmission electron microscope operated at 120 kV. The size polydispersity of the nanoparticles was determined by calculating their standard deviation for certain amounts of particles in the observation area of the transmission electron microscope image.

Results and discussion

As is well known, assembling nanoparticles in ordered arrays requires hard-sphere repulsion, a controlled size distribution, the inherent van der Waals attraction between particles and dispersion forces [16]. The polydispersity in particles prevents construction of such ordered structures, so external forces are often used to induce the formation of monolayers of ordered nanoparticles. Here, to form the monolayer without any external forces, we consider the narrow size distribution of the particles is a crucial factor. Comparing, for example, Fig. 2a, b and c provides clues. The first shows particles with a size polydispersity of 14.95% (average of 80 particles, with a mean diameter of 7.4 nm and a polymer polydispersity index of 1.28); in this case the particles were disorderly dispersed. The second represents a one-dimensional ordered structure where the particles have a rather narrow size polydispersity of 3.12% (average of 83 particles, with a mean diameter of 9.7 nm and a polymer polydispersity of 1.19). On further decreasing the size polydispersity to 1.93% (average of 79 particles, with a mean diameter of 11.6 nm and a polymer polydispersity of 1.06), in the third image a very regular, two-dimensional ordered array appears. Looking into the zones on the top left and bottom right where the particles have great differences in size, the array looks relatively disordered; on other regions where the particles present nearly the same size (particularly in the middle of the image), the array is sufficiently regular for our purpose. It once more depicts the important role of the size distribution of particles during the process of self-organization.

Some cylindrical particles can be observed in Fig. 2b and c although the most common morphology for block copolymer micelles is spherical [17]. Other authors have also found such structures in their investigations and attribute this to the crystalline nature of the block [18] or the different colloidal structure [16]. We tried to understand the nature of these cylindrical particles. Our strategy was mainly to change the relative block content of the polymer because in some of our experiments the number of spherical particles increased at a lower content of the hydrophilic block. However, the cause of the formation of the cylinders is not clear and is under investigation.

A sequence of transmission electron microscope images of monolayers prepared from same micelle solutions but at a different temperature is shown in Fig. 3. When the deposition temperature is 35 °C some

Table 1 Synthesis of hydrolyzed Ppoly(butyl methacrylateBMA-*b*-glycidyl methacrylateGMA) block copolymers using a macroinitiator in 4-methyl-2-pentanone at 90 °C

Macroinitiator	Sample	Conversion (%)	M_n (size-exclusion chromatography)	M_w/M_n(size-exclusion chromatography)	Feed ratio	Block composition
BW1-A[a]	BW2-A[e]	97.6	46,280	1.28	88/12	90/10
BW1-B[b]	BW2-B[f]	95.4	49,260	1.19	89/11	86/14
BW1-C[c]	BW2-C[g]	93.3	9,570	1.06	78/22	81/19
BW1-D[d]	BW2-D[h]	96.7	28,730	1.06	82/18	80/20

[a] M_n = 41,260 and M_w/M_n = 1.34 for PBMA-Br, [EPN-Br]/[CuBr]/[phen]/[Cu] = 1/2/4/4

[b] M_n = 41,480 and M_w/M_n = 1.28 for PBMA-Cl, [TSCl/[$CuCl_2$]/[phen]/[Cu] = 1/2/6/5

[c] M_n = 7,610 and M_w/M_n = 1.20 for PBMA-Br, [EPN-Br]/[$CuCl_2$]/[phen]/[Cu] = 1/2/4/10

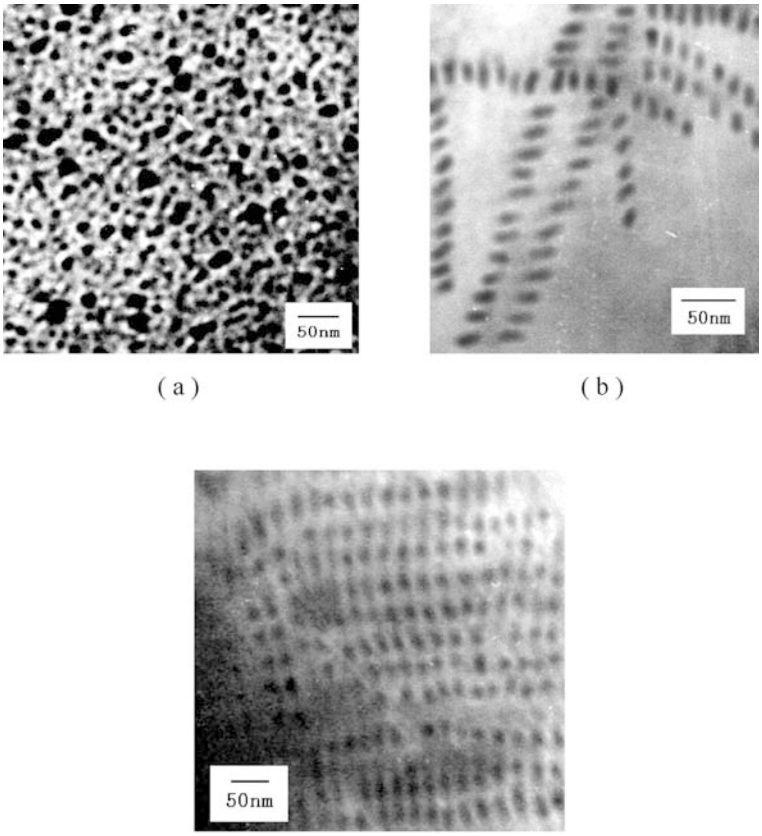
[d] M_n = 22,470 and M_w/M_n = 1.19 for PBMA-Br, [EPN-Br]/[$CuCl_2$]/[phen]/[Cu] = 1/1/3/5

[e] [macroinitiator]/[CuCl]/[phen]/[Cu] = 1/2//6/10

[f] [macroinitiator]/[CuBr]/[phen]/[Cu] = 1/2//6/10

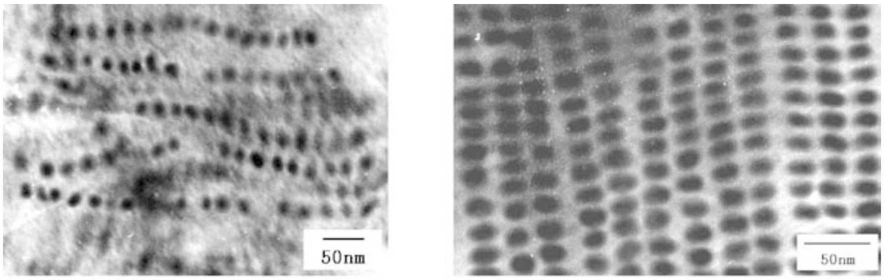
[g] [macroinitiator]/[$CuCl_2$]/[phen]/[Cu] = 1/1/3/10

[h] [macroinitiator]/[$CuCl_2$]/[phen]/[Cu] = 1/2//4/10



(a) (b) (c)

Fig. 2 A comparison of the structure of latex nanoparticles with different size distributions. The size polydispersity, as determined for the particles in the observation area, is **a** 14.95%, **b** 3.12% and **c** 1.93%, respectively. The array looks more and more regular with decreasing size polydispersity of the particles



(a) (b)

Fig. 3 A sequence of transmission electron microscope images of monolayers deposited at **a** 35 °C and **b** 15 °C. Some empty spaces are observed between the arrays at the higher temperature. When the deposition temperature is lower, a more ordered array can be observed and those empty spaces do not appear again

empty spaces are observed between the array in Fig. 3a. We propose that the irregularity may be dependent on how homogeneous the evaporation process is. To confirm this, we deposited the monolayer at a lower temperature of 15 °C to make the evaporation process slower and more homogeneous. As depicted in Fig. 3b, the array looks more ordered and those empty spaces do not appear again. Because the samples used and their preparation methods are the same, the improvement of the irregular features is probably attributed to the interaction of particles during a slower evaporation process. The more detailed mechanism of this influence is under investigation.

Conclusions

On the basis of what we have experienced, we think that the regular features of the ordered arrays are essentially due to the narrow size distribution of the particles. A more regular deposition can be obtained when the evaporation of the solvent is carried out at lower temperature. We believe that many different applications of these arrays may be found.

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