

MORPHOLOGICAL OBSERVATION OF SINGLE-CHAIN POLY(METHYL METHACRYLATE) PARTICLES*

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ABSTRACT

Tapping mode atomic force microscope has been applied to observe single-chain PMMA particles which were stored for six months at room temperature after sprayed from very dilute solutions in good solvents, good/poor mixed solvents, and a theta solvent. Monodisperse PMMA standards of molecular weights ranging from 7.90×10^4 to 1.3×10^6 were used to investigate the effect of molecular weight on the size of the single-chain PMMA particles. These single-chain particles showed close to spherical shapes. The morphology of single-chain PMMA particles of a given molecular weight was found to be identical in spite of different solvents used for solution spraying. Molecular weight dependence of the particle dimension was also found. The diameters of single-chain PMMA particles after correction of tip-geometry effect were compared to the values estimated from molecular weight and density.

INTRODUCTION

The state of polymer nano-particles containing single chain is expected to be different from that of the bulk polymer. Interest in the morphology of nano-particulate polymers from molecular level has promoted experiments to direct visualization of

* This work was supported by The National Key Project for Fundamental Research "Macromolecular Condensed State".

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Received April 18, 1997

the shape of single-chain polymer particles. Atomic force microscope (AFM) offers many advantages over other instruments for such measurements since it requires no surface treatment and can resolve nano sized features easily. Recently, Qian et al.^[1] used AFM to observe the morphology of single-chain polystyrene (SCPS) and found that the SCPS particles possessed a definite morphology which is irrespective of the molecular weight but depends on the solvent and the morphology changed with time during drying after spraying. It is well known that the dissolution of macromolecular coil goes through a process of swelling, coil expansion, complete dissolution, and dispersion separately in the solvent through many dissolution stages. It is easy to imagine that the solidification involved after spraying a dilute polymer solution is a reverse process of dissolution. Therefore, in principle, it will get the same size for a given molecular weight polymer after the solvent completely evaporates and the coil contraction reaches an equilibrium, even if the initial solvents may be quite different. The aim of the present work is to observe final morphology of single-chain polymethylmethacrylate (PMMA) particles sprayed from dilute solutions with long period room temperature standing to find any solvent effect. The relationship between the particle size and molecular weight will also be discussed.

EXPERIMENTAL

Materials and specimen preparation

Three standard high molecular weight atactic PMMA samples with narrow molecular weight distribution were supplied by Polymer Laboratory Ltd (U.K): $M_w = 7.90 \times 10^4$, $M_w/M_n < 1.08$; $M_w = 2.65 \times 10^5$, $M_w/M_n < 1.12$; $M_w = 1.30 \times 10^6$, $M_w/M_n < 1.04$. The solvents used were spectrograde benzene, xylene, chloroform, decalin, cyclohexane, iso-propanol and methanol (BDH) without further purification. A series of good/poor-solvent mixtures with different solubility and vaporization properties, benzene/decalin, benzene/cyclohexane, benzene/methanol, were prepared in a volume ratio of 80 : 20. The theta solvent used was cyclohexane/iso-propanol with volume ratio of 51.6 : 48.4 (θ point = 21 ~ 22°C). The dilute solutions of PMMA were prepared by weighing polymer into different solvents, stirring for three days to allow complete dissolution. All of the solutions had approximate PMMA concentration of $5 \sim 9 \times 10^{-4}$ wt%, far below the dynamic contact concentration C_s , on which the polymer coils in solution are isolated^[2]. All of the specimens were prepared by spraying solutions from a home-made glass atomizer onto a freshly cleaved mica surface. The samples were exposed and stored under ambient environments for six months prior to AFM imaging.

AFM imaging

The atomic force microscope used was Nanoscope IIIa, operated in the tapping mode. AFM images were obtained by using 125 μm cantilever with resonance frequency of 240–420 kHz. Samples were imaged with pyramidal silicon nitride tip and several spring constants (3–100 N/m). The radius of curvature was 18 nm, (from SEM measurements). AFM observation of the samples was carried out in air.

RESULTS AND DISCUSSION

Shape of single-chain PMMA particles

It is perceivable from AFM images that only well isolated PMMA particles are observed in the AFM images. The solution concentration used in the present work was $5\text{--}9 \times 10^{-4}$ wt%, far below the dynamic contact concentration C_s , therefore, the uniform and isolated particles are observed in the AFM images. After a long period room temperature standing, the lateral shape of PMMA particles is almost close to spherical shape, but slightly flattened as illustrated in Fig.1. Qian et al.^[1] found the irregular shapes of the single-chain PS particles sprayed from their dilute solutions and attributed these irregular shapes to the orientation depending on the direction of probe scanning due to the interaction between probe-tip and particles when the particles containing residual solvent were not completely solidified. This orientation effect is not found in the present work checked by changing the scanning direction of the probe when the samples were after a long period of time to completely drive off the solvent so that they could not change shape easily.

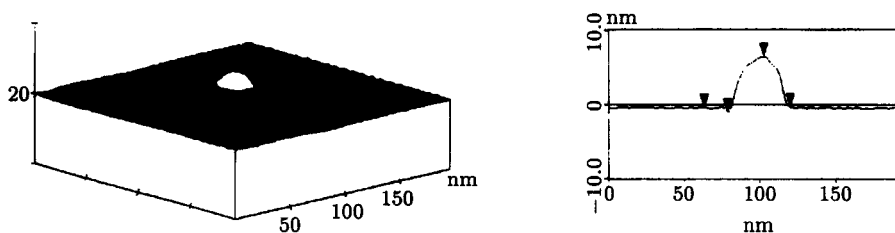


Fig.1 AFM 3D image of individual particles of single-chain PMMA on mica six months after spraying from dilute PMMA solutions. $M_w = 2.65 \times 10^5$, scale bar: 50 nm

Solvent effect

We prepared the PMMA solutions in good solvents: chloroform, benzene, xylene; in the mixture of good/poor solvents with different boiling point and solubility: benzene/cyclohexane, benzene/decalin, benzene/methanol respectively. In the case of benzene/decalin pair, the mixed solvent gradually transforms into poorer dur-

ing evaporation since decalin has a higher boiling point. On the contrary, in the case of benzene/methanol, the mixed solvent gradually transforms into better. Otherwise, in the case of benzene/cyclohexane, the composition of the mixed solvent was approximately maintained, for their similar boiling points. A theta solvent of PMMA was also used: cyclohexane/iso-propanol (θ point = 21–22°C), in which the macromolecular coils keep in unperturbed dimension. Therefore, the initial conformation of the polymer coils in various solvents and their contracting process to solid are quite different. It is noted that as the reverse process of dissolution, the contraction especially in the final stage from swelling to solid is a very slow process, so that the specimens in this work were stored for a long time before AFM observation. Although the initial solvent and then the contraction pathways are quite different, the results showed that the size of nano-particles for a given molecular weight PMMA is identical based on the AFM observation whether sprayed from good solvents, mixed solvents, or theta solvent. This indicates that the contraction process reached approximately an equilibrium state and gave the uniformed images of single-chain PMMA particles.

Molecular weight dependence of particle size

As well known, polymer coil size depends on its molecular weight both in dilute solution and in solid bulk. It is interesting to confirm the molecular weight dependence of the particle size for single-chain polymer originated from their dilute solutions of monodisperse PMMA. The AFM images of the individual particles sprayed from dilute solution showed that the size of single-chain PMMA is increased with increasing the molecular weight. The early literature^[3] pointed out that the lateral dimensions can be broadened by geometry of the tip, while the height of AFM measurements is precise. The diameters of the particles after correction listed in Table 1 are close to the calculated values of single-chain PMMA estimated from the bulk density and molecular weight, this fact indicated that all the particles sprayed from very dilute solution are single-chain ones. The density values (ρ) of the particles can be calculated from molecular weight and spatial volume, and then listed in Table 1.

From Table 1, it is found that the density of the particles for the high molecular weight sample is close to that in the bulk, while the density of the particles for the lower molecular weight sample is smaller than that of the bulk. It further confirms the loosen segment aggregation in the single-chain particles. On the other hand, the shapes of the single-chain particles are slightly flattened, especially for the high molecular weight samples. From AFM images, the mean height of those

particles, ranged in 6—7 nm, is nearly independent of molecular weight as mentioned by Zhang et al.^[4] and in agreement with the theoretical predictions of Brownian dynamics simulation.^[5] The flatness is most likely related to the surface energy and/or adsorptive interaction between the polymer and the substrate surface.

Table 1 Single-chain PMMA particle size and density

	M_w	L^a (nm)	d^b (nm)	d^c (nm)	h^a (nm)	ρ (g/cm ³)
1	1.30×10^6	59.4	24.5	15.1	5.83	1.18
2	2.65×10^5	41.6	12.0	8.9	6.90	0.85
3	7.90×10^4	32.0	7.1	6.0	5.90	0.84

a. measured directly by AFM images

b. corrected by AFM geometry-tip effect

c. calculated from the density of the bulk

Acknowledgements The authors are grateful to Professor Renyuan Qian for valuable discussions.

Keywords:

Atomic force microscope; Morphology; Single-chain particle; Polymethylmethacrylate

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