

Preparation of single-molecule particles of water-soluble polymers

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Abstract

Single-molecule particles of a series of water-soluble polymers are prepared via a spray dryer from dilute polymer aqueous solutions. Two of these polymers, poly(acrylic acid) and polyacrylamide, are used as examples to illustrate the preparation and identification of single-chain molecules. Scanning electron microscopy shows that these dried particles possess diameters ranging from 1 to 4 μm . Transmission electron microscopy reveals that each particle consists of numerous distinctly separated small particles with a radius of a few nanometers. Each of these particles consists of a single-chain molecule, a conclusion based on calculations of volume involving the polymer molecular weight. This method lends itself to the preparation of single-molecule particles of water-soluble polymers in mass quantity, which may provide a gateway to studying the chemistry and physics of polymer single-molecules in a condensed state. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The studies of macromolecules in the first half of the twentieth century began to recognize the role played by the size and shape of single-chain molecules in dilute solutions [1]. With increasing interests of potential applications in science and engineering, an understanding of the chemistry and physics of bulk polymers in their condensed states has been one of the main directions of polymer materials research. The bulk polymers possess a high degree of entanglement among chain molecules and form structures and morphologies on different length scales. Various relaxation processes corresponding to these length scales have been extensively investigated. These multiple scale structures and dynamics lead to complicated structure–property relationships in bulk polymers [2]. Many physical phenomena,

such as the glass transition temperature, crystallization and melting, mesophase transitions, sub-molecular and molecular relaxation processes and viscoelastic behavior of polymers, are specifically defined in relationship to the condensed states in bulk polymers. We address these traditional concepts to determine how they are connected with a single-chain molecule. The approach to answering this question lies in the understanding of the chemistry and physics of single-chain molecules. It is expected that many of these current concepts in bulk polymers must be redefined or modified for a single-chain molecule.

The first obstacle is to prepare a mass quantity of single-chain molecules of flexible-chain polymers which are separated from one another in the absence of solvent. In the past, most of the investigations reported used a procedure of dropping the dilute solution ($\sim 10^{-5}$ wt%) on the surface of water or other liquid substrates [3–5]. Hence, the amount of sample obtained was very small, and the studies focused primarily on ordered morphologies and sizes of the single-chain molecules using transmission electron microscopy (TEM), atomic force microscopy, and in some cases, electron diffraction [6–11]. In this communication, we report a method of preparing single-molecule particles of water-soluble polymers by spray drying.

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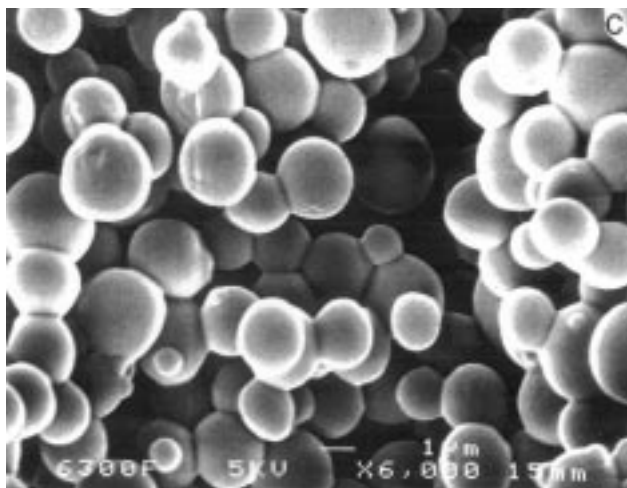


Fig. 1. SEM photograph of spray dried PAA particle aggregates from 10^{-4} wt% aqueous solution.

The single-chain molecules and their aggregates are studied using scanning electron microscope (SEM) and TEM.

2. Experimental

Two of the water-soluble polymers used in this study are poly(acrylic acid) (PAA) and polyacrylamide (PAL) with molecular weights of $M_v = 450,000$ and $5,000,000$, respectively (Aldrich Chemical). Aqueous solutions of polymers

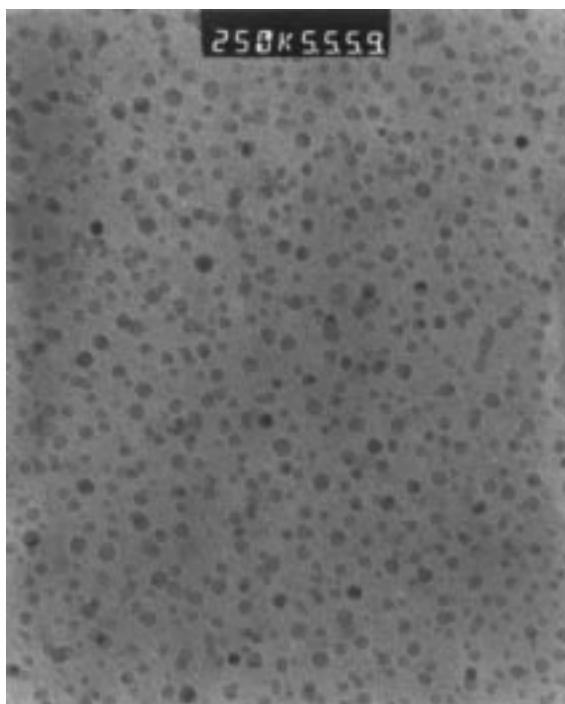


Fig. 2. TEM micro-photograph of PAA at a high magnification after the sprayed and dried sample (as shown in Fig. 1) was imbedded in epoxy and cross-sectioned.

of 10^{-4} wt% were prepared for spray drying. The dilute polymer solution was fed through a rotary pump to the Niro spray dryer and atomized (Gladsaxevej 305, DK-2860 Soeborg, Denmark). The processing temperatures in this study were controlled at 170°C for the inlet temperature, with a 100°C chamber temperature for evaporating the water, and 90°C for the outlet temperature. Polymer powders were produced after the spray drying and further treated in a vacuum oven at 50°C for 48 h.

The powder samples were coated with gold for the SEM (Jeol 6300) examination. For TEM (Phillips CM 20 and JEOL JEM-1200IIX) experiments, the powders were imbedded in epoxy pre-solution (EPO-TEK 301, Epoxy Technology, USA). Note that PAA and PAL in this study are not soluble in the epoxy pre-solution. The epoxy was then cured at room temperature and ultra-microtomed (Leica Ultracut R Ultramicrotome) at -120°C in liquid nitrogen. The thickness of the specimens obtained was about 70 nm. The microtome slices were used directly for TEM observation without any further treatment.

3. Results and discussion

Individual particles, with a particle size larger than $1\ \mu\text{m}$, are visible once collected after spray drying. PAA particles with spherical shapes can be observed with SEM as shown in Fig. 1. It is evident that the spherical particles have a radius of about $1\text{--}2\ \mu\text{m}$. Clear spherical boundaries can be observed, which is associated with the particle coating of heavy metals needed to make the conducting layer for SEM observations. Note that the radius is greater than the size of single-chain molecule, here it appears that single-molecule particles are not obtained (see below). Decreasing the concentration of polymer solutions below 10^{-5} wt% did not generate any visible polymer particles in the sample-collection process.

In order to explore internal structures of the particles, TEM experiments were conducted. A typical TEM observation for PAA is shown in Fig. 2 at high magnification. The sample was obtained after the particles shown in Fig. 1 were imbedded in epoxy and cross-sectioned. Interestingly enough, many small particles of PAA fixed in the epoxy matrix have a radius of around 3 nm. A simple calculation (density = mass/volume) under an assumption of a density of $1\ \text{g cm}^{-3}$ in a spherical particle of PAA leads to a radius of around 5.6 nm for $M_v = 450,000$. The obtained range of sizes of the radius may be caused by the relatively broad molecular weight distribution. Also, when the samples were ultra-microtomed, the small particles may be cut on non-diametric places, so only then spherical caps are observed, which have a smaller radius. Furthermore, it is unclear whether a single-chain molecule packs into the same volume as it would in the bulk. The observed scale and distribution of the radii is about the size of a single-molecular particle of PAA. We therefore suggest that these

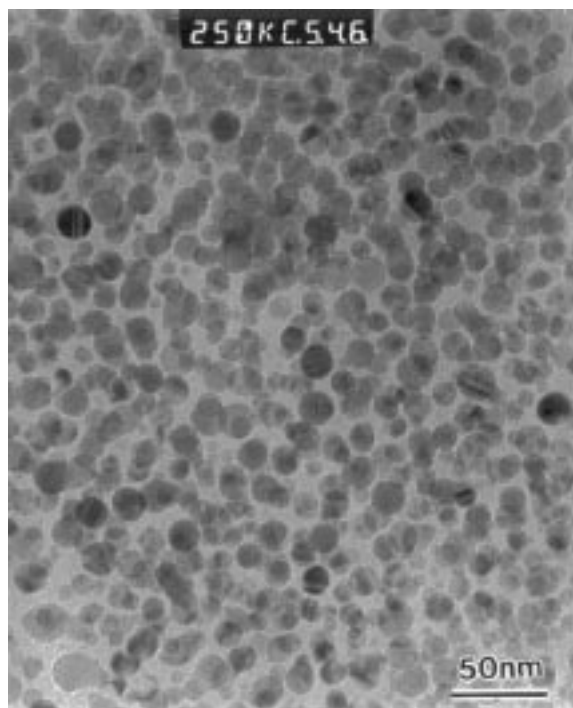


Fig. 3. TEM micro-photograph of single-chain particles of PAL after the sprayed and dried sample was imbedded in epoxy and cross sectioned.

observed small particles on nano-scale consist of individual chain molecules.

The formation of these single-molecule particles during the spray drying most likely involves at least two steps. First, each liquid droplet formed during the spray process contains many chain molecules. However, due to the low concentration of 10^{-4} wt%, these chain molecules may be completely isolated from one another in the droplets. When the water is vaporized very quickly at temperatures between 100 and 170°C, the chain molecules remain as independent entities, and inter-chain entanglement among these molecules does not occur. In a second step, the single-molecule particles aggregate together to form a particle having a radius of 1–2 μm shown in Fig. 1. The aggregation can take place when the concentration of the particles drastically increases during the very quick evaporation of the water. When the concentration of the polymer solution was decreased to 10^{-5} wt%, each liquid droplet contains fewer single molecules. Although the individual single-molecule particles can form, aggregates of these particles may be too small to be collected.

Based on the results in Figs. 1 and 2, we have observed particles of two completely different length scales. The μm -particles are aggregates of single-molecule particles, and the nm-particles are the single-chain molecules. We have also used other high molecular weight water-soluble polymers such as poly(vinyl alcohol) (PVA), polyvinylpyrrolidone (PVP) and PAL to produce single-molecule particles. Very similar SEM and TEM images of single-molecule particles and their aggregates were obtained. Fig. 3 shows a TEM microphotograph for PAL. Single-molecule particles, with a radius of around 6 nm, were observed clearly. The upper limit of the calculated radius of a single molecule with a $M_v = 5,000,000$ is roughly 12.5 nm. Therefore, we believe that these small particles also consist of single-chain molecules.

This study has provided an efficient method to prepare a large quantity of single-molecule particles suitable for future studies of the chemistry and physics of single-chain macromolecules in their condensed state. The structure and properties of single-molecule particles will be investigated using chemical, thermodynamic, diffraction and scattering, and spectroscopic methods in the near future.

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