

Visualization of Two-dimensional Single Chains of Hybrid Polyelectrolytes on Solid Surface

Lan-Lan Zhang^a, Wen-Ke Miao^a, Li-Jun Ren^a, Yu-Kun Yan^a, and Wei Wang^{a,b*}

^a Center for Synthetic Soft Materials, Key Laboratory of Functional Polymer Materials of the Ministry of Education and Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

^b Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China

Electronic Supplementary Information

Abstract The polyacidic character of polyoxometalate (POM) clusters endows high ionic conductivity, making these clusters good candidates for solar and fuel cells. Covalent bonding of clusters to polymer chains creates poly(POM)s that are polyelectrolytes with both cluster functions and polymer performance. Thus, solution-processable poly(POM)s are expected to be used as key materials in advanced devices. Further understanding of poly(POM)s will optimize the preparation process and improve device performance. Herein, we report a study of the first linear poly(POM)s by directly visualizing the chains using scanning transmission electron microscopy. Compared with traditional polymers, individual clusters of poly(POM)s can be directly visualized because of the resistance to electron-beam damage and the high contrast of the tungsten POM pendants. Thus, cluster aggregates with diverse shapes were observed. Counting the number of clusters in the aggregates allowed the degree of polymerization and molecular weight distribution to be determined, and studying the aggregate shapes revealed the presence of a curved semi-rigid chain in solution. Further study of shape diversity revealed that strong interactions between clusters determine the diverse chain shapes formed during solution processing. Fundamental insight is critical to understanding the formation of poly(POM) films from solutions as key functional materials, especially for fuel and solar cells.

Keywords Polyelectrolyte; Polyacidic cluster; Functional hybrid; Chain; Scanning transmission electron microscopy

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INTRODUCTION

Nanoscale and atomically precise clusters are an attractive class of molecules with structural and compositional diversity, which impart unique properties and functions that are significantly different from those of atoms and bulk materials.^[1–5] Notably, recent research on clusters of gold and other noble metals has progressed very rapidly owing to their exciting properties and/or functions.^[3–5] Naturally, they are ideal building blocks for the fabrication of novel functional materials with the desired properties and functions of clusters.^[6–12] Currently, developing methods other than crystallization to prepare cluster-based materials remains a challenge.

The incorporation of inorganic clusters, such as silicon oxide, metal oxides, and carbon clusters, into organic polymers is an important strategy for fabricating cluster-polymer hybrid materials featuring the promising functions of clusters and excellent performance of polymers.^[9–12] The use of clusters as building blocks also has the advantage of realizing

a nanoscale distribution of clusters in the polymer matrix, which maximizes cluster functions. Thus, the best way to avoid cluster aggregation is to prepare poly(cluster)s by covalently linking clusters to a polymer. Thus far, several hybrid materials have been fabricated using cluster-based monomers or initiators by various polymerization techniques.^[9] However, our understanding of their nanostructures is limited owing to the lack of effective characterization methods.

Polymer science research has revealed that the randomly coiled conformation of linear flexible polymers defines the most basic properties and performance of polymers and related materials.^[13,14] Therefore, intensive experimental and theoretical investigations have been carried out on this polymer conformation. The methods used normally include light and X-ray scatterings,^[13] and occasionally atomic force microscopy (AFM).^[15,16] The direct observation of single chains of these polymers by transmission electron microscopy (TEM) is quite challenging because samples containing only light elements (H, C, N and O) give images with very low contrast and are, in most instances, damaged by electron beams.^[17,18]

On the other hand, dendronized or bottlebrush polymers have significantly extended and thickened chains because

* Corresponding author, E-mail: weiwang@nankai.edu.cn

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of the steric hindrance of large or long side groups, enabling direct visualization by AFM or scanning tunneling microscopy.^[19–23] These studies revealed that their basic properties and performance are completely different from those of linear flexible polymers. Recently, 3D chains of a dendronized polymer were directly visualized by cryogenic TEM to resolve conformations of individual macromolecules.^[24] Further analyses verified that conformations can be described by a wormlike chain model.

The principles of TEM imaging indicate that incorporating heavy elements into the backbones or pendants of polymers facilitates contrast-enhanced TEM imaging, particularly for characterization by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM),^[18] because the intensity is proportional to the square of the atomic number (Z-contrast).^[25–27]

Polyoxometalates (POMs) are a class of anionic metal-oxygen clusters of early transition metals with polyacidic character.^[28] Because of their unique and multiple functions, linear or cross-linked poly(POM)s have been synthesized and studied.^[29–47] In our previous work, we pioneered the design and subsequent synthesis of the first linear hybrid polyelectrolyte—poly(POM) in which the POM clusters are covalently attached to the polymer backbone as pendants.^[41] In addition to exhibiting catalytic function, linear poly(POM)s can be potentially solution-processed into thin films that are completely different from that of POM clusters. These thin films can be used to prepare proton-conductive membranes for fuel cells,^[38,43] and hole-collection interlayers for organic solar cells,^[48,49] owing to the high proton conductivities of POM clusters. Unfortunately, a fundamental understanding of poly(POM)s or other poly(cluster)s is almost non-existent.

In this study, we further investigated linear poly(POM) chains through the very effective direct visualization of individual clusters; thus cluster aggregates were observed by HAADF-STEM using samples prepared by spreading the dilute solutions. The degrees of polymerization (DPs) and molecular weight distributions were determined from the number and distribution of clusters in the aggregates. Analysis of aggregates with multiple shapes, ranging from straps to discs, revealed that poly(POM) chains prefer a curved semi-rigid conformation that lies between fairly extended and coiled conformations in good POM-cluster solvents. Finally, the formation of multi-shaped single chains in these samples is attributed to the strong interactions between two or more clusters located at different positions in a chain confined in a single solution droplet during solvent evaporation.

EXPERIMENTAL

Materials

We have shown the synthetic methods and proofs of the poly(POM)₁₀₀ sample in our previous publications.^[41] The molecular weights and polydispersities of the mono-POM and poly(POM)₁₀₀ samples are shown in Fig. S1 and Table S1 (in the electronic supplementary information, ESI). Acetonitrile (absolute, over molecular sieve) was purchased from Tianjin Heowns Institute and used without any further purification.

Sample Preparation

Acetonitrile solution of poly(POM)₁₀₀ (100 μ L, 5 mg/mL) was added quickly to the 5 mL spray bottle, then 4.9 mL of acetonitrile was added into the spray bottle to obtain the sample solution (0.1 mg/mL).

Sample Observation

Bright-field transmission electron microscopy (BF-TEM) images were obtained using a field-emission TEM (FEI Talos F200X G2) operating at an acceleration voltage of 200 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) characterization was performed using a TEM (FEI Talos F200X), operated at 200 kV in STEM mode using HAADF detector. The TEM samples were prepared by spraying the poly(POM)₁₀₀ solution (0.1 mg/mL) onto the ultra-thin carbon film of TEM grids, and the solvent acetonitrile was evaporated at room temperature and further in a vacuum oven at 25 °C.

Image Processing

In order to count the bright dots in the original Z-contrast images of the poly(POM)₁₀₀ sample more clearly, we used Photoshop and ImageJ to process the images. The details are summarized in SI-7 (in ESI).

RESULTS AND DISCUSSION

Poly(POM)

The poly(POM) used has a polynorbornene backbone with POM pendants in each repeating unit (Fig. 1a). The predesigned DP and molecular weight (M_n) are 100 and 583.3 kDa, respectively. The fully extended chain has a length of ~ 60 nm and width of ~ 6.8 nm. The absolute weight-average molecular weight, $\overline{M}_w = 774.9$ kDa, and polydispersity index, $\overline{M}_w/\overline{M}_n = 1.15$, and radius of gyration, $R_g = 15.34$ nm, were determined by size exclusion chromatography (SEC) equipped with both refractive index and online light-scattering detectors (Fig. S1 and Table S1 in ESI).^[41] Therefore, the experimental DP and length are $\overline{DP} = 116$ and ~ 70 nm, respectively.

More importantly, the POM pendant is a $(\text{Bu}_4\text{N})_6\text{H}_3\text{P}_2\text{-W}_{15}\text{V}_3\text{O}_{62}$ complex composed of a $(\text{H}_3\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62})^{6-}$ trivanadium-substituted Wells-Dawson-type polyoxotungstate anionic core (Fig. 1b) and six tris(hydroxymethyl)aminomethane cations (Bu_4N^+).^[50] Herein, we introduce three features of the POM cluster. First, the electrostatic interactions between the complexes are stronger than the van der Waals interactions between the organic backbones and linkers. As a result, the solubility of the POM cluster will dominate over that of poly(POM). Second, fifteen tungsten and three vanadium atoms in the POM cluster facilitate the direct visualization of individual clusters by HAADF-STEM because the squares of their atomic numbers are 5674 and 529, respectively, which are much higher than those of carbon (36), nitrogen (49), and oxygen (64) in the backbone. Consequently, the POM clusters are much brighter in the Z-contrast images, and the imaging quality is much better than that obtained by bright-field TEM (Fig. S2 in ESI). Third, the cluster core is a truncated ellipsoid with long and short axes of ~ 1.2 and ~ 1.0 nm, respectively. There are three and two layers of tungsten atoms along the long and short axes, respectively.

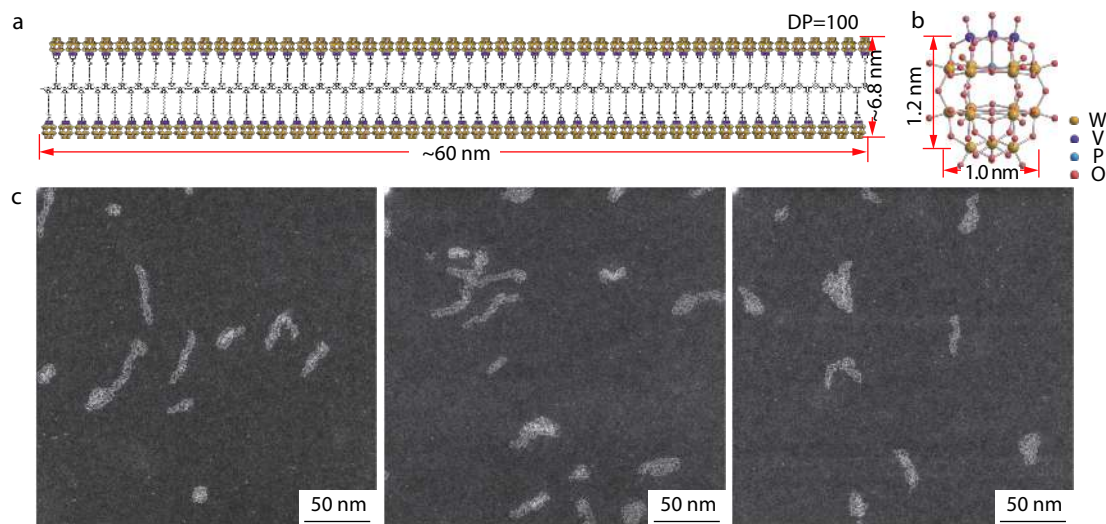


Fig. 1 Structures and dimensions of (a) poly(POM)₁₀₀ and (b) the anionic core of the POM cluster. Note that the six Bu₄N⁺ cations are omitted for clarity. (c) Three original Z-contrast images of poly(POM)₁₀₀ chains showing aggregates of POM clusters (bright dots) with various shapes and/or sizes.

Poly(POM) Aggregates

First, poly(POM) dissolves well in acetonitrile, thus the STEM samples were prepared with acetonitrile solution. In our work, we characterized thin films prepared by dropping dilute acetonitrile solutions (0.7 mg/mL) onto the surface of water. Unfortunately, although individual POM clusters are seen in the Z-contrast images, individual chains cannot be identified (Fig. S3 in ESI). Therefore, we know that the key to successfully observing single polymer chains by microscopy is to separate them from each other and then solidify them. The STEM samples were further prepared by spreading dilute solutions of the polymer in acetonitrile (0.1 mg/mL) onto the ultra-thin carbon film of TEM grids and then observed by HAADF-STEM. Fig. 1(c) displays three typical Z-contrast images. The bright aggregates are composed of dots, which are POM clusters with diameters of about 1 nm. Hence, the number of POM clusters in the aggregates, N_{POM} , can be counted. Thirty-five original images are shown in Fig. S4 (in ESI), from which 257 aggregates of different shapes were identified. The identification process is indicated in Fig. S5 (in ESI), and all grayscale images of the aggregates are illustrated in the left columns of Figs. S8–S10 (in ESI).

Multi-shaped Aggregates

First, the Z-contrast images obviously display multi-shaped aggregates. In order to further facilitate the analysis of these aggregates, the image quality was improved using the Fire LUT option of the “Interactive 3D Surface Plot” plugin of ImageJ to convert the grayscale images into pseudo-colored ones. After the conversion, the images were smoothed to reduce noise and 3D-colored to improve both 3D visualization and quantitative resolution. This process is also described in detail in SI-7 and Fig. S5 (in ESI). Hereafter, pseudo-colored images will be shown in this work for better presentations. The pseudo-colored images of all aggregates are also illustrated in the right columns of Figs. S8–S10 (in ESI). Note that the conversion for 257 aggregates was completed under the same conditions.

The pseudo-colored images in Fig. 2 were selected to show the multi-shaped character of the aggregates. We found at least two common features. First, the POM clusters are not well-distributed in the aggregates because a few “holes” can be seen. Second, the individual POM clusters are not completely uniform in brightness, clearly reflecting differences originating from the orientation and overlap of these ellipsoidal clusters. In Fig. 2, the orientation causes differences not only in the size and shape of the ellipsoidal clusters, but also in the number of layers of tungsten atoms: three and two layers along the long and short axes, respectively. Thus, the clusters should be 1.5 times brighter and slightly smaller when viewed along the long axis. Moreover, the overlap of POM clusters causes a more obvious difference. Compared with the grayscale images, the pseudo-colored images allow easy identification of the overlapping clusters with double or triple brightness (Figs. S8–S10 in ESI).

The aggregates can be mainly classified into five categories according to shape (Fig. 2 and Figs. S8–S10 in ESI): 77 straps, 59 discs, 76 intermediates between strap and disc, 37 complex-shaped aggregates, and 8 aggregates with $N_{\text{POM}} < 30$. The N_{POM} is shown in each image. When N_{POM} values are counted from these images, all bright spots in a grayscale image are considered the same since it is difficult to distinguish the differences in brightness. A few bright dots in the pseudo-colored images are considered as having $N_{\text{POM}} = 2$ or 3 on the basis of their brightness. Thus, there is a difference between the N_{POM} values obtained from the two methods (Figs. S8–S10 in ESI). In this case, the N_{POM} obtained from the grayscale images is somewhat smaller than that obtained from the pseudo-colored images.

Most straps are curved and sometimes twisted (Fig. 2a and Fig. S8 in ESI). Their lengths increase with N_{POM} , whereas their widths remain at 5–6 nm, which is smaller than that of fully extended chains (6.8 nm); consequently, they resemble two-dimensional (2D) snakes. The discs are not perfect circles, and their size increases with N_{POM} (Fig. 2b and Fig. S9 in ESI). On the other hand, brighter dots normally appear in the areas

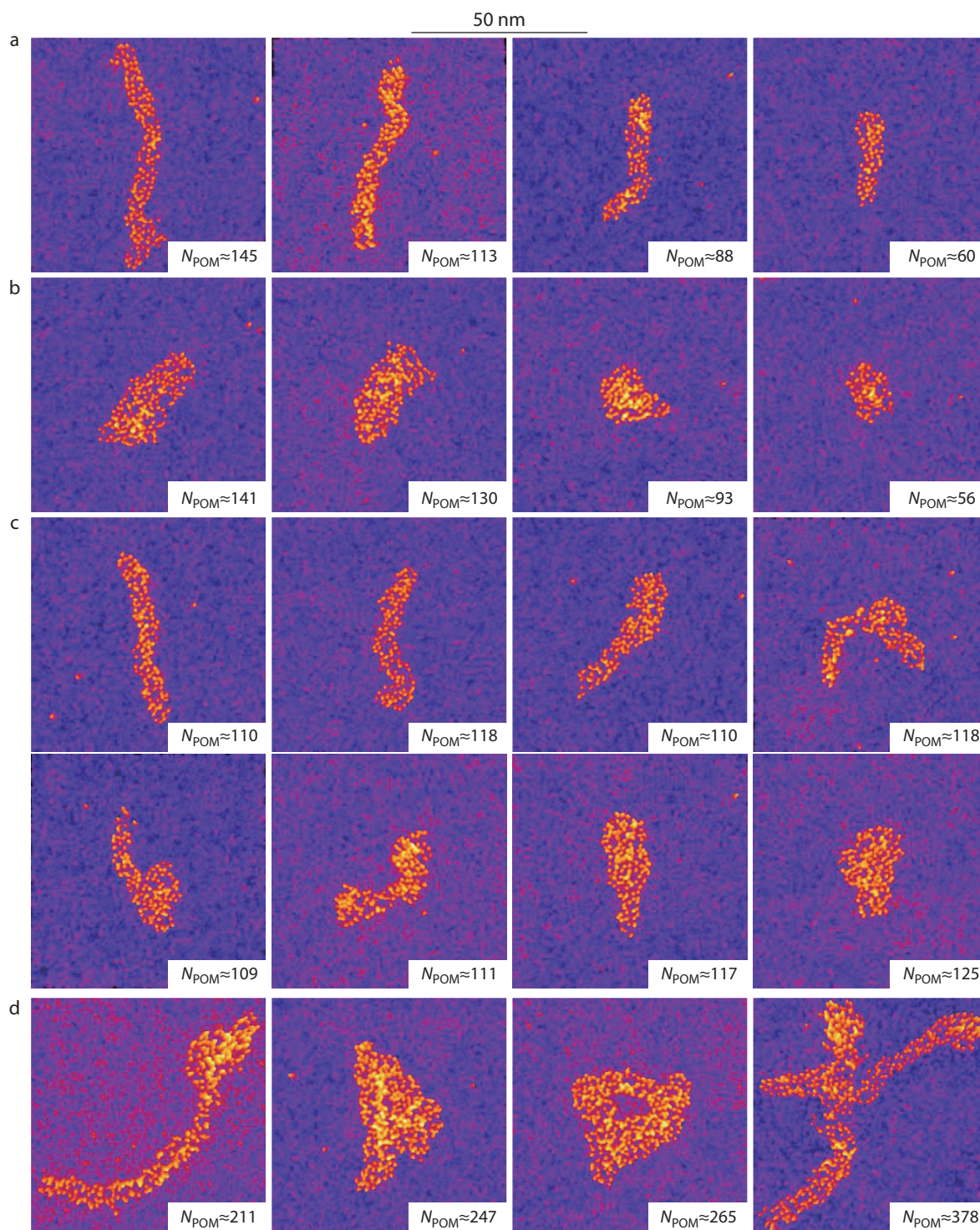


Fig. 2 Pseudo-colored images of the multi-shaped aggregates. (a) Straps and (b) discs with varying numbers of POM clusters (N_{POM}). (c) Changes in aggregate shape, from strap to disc, via intermediates with $N_{\text{POM}} \approx 110$. (d) Complex-shaped aggregates. The N_{POM} in each aggregate is indicated.

near the centers of the discs. The eight images in Fig. 2(c), which highlight the diverse shapes of aggregates with $N_{\text{POM}} \approx 110$, show the change in shape from strap to disc via different intermediates. We noticed that brighter dots appear in the areas where the aggregate shape begins to deviate

from the strap. These eight images and others (Fig. S8 in ESI) are important in understanding the shape evolution from strap to disc. We observed 37 complex-shaped aggregates with $N_{\text{POM}} > 200$, as shown in Fig. 2(d) and Fig. S9 (in ESI). On the basis of the much larger N_{POM} compared with the pre-

designed DP (100) and the aggregate shapes, we believe that the aggregates are assemblies comprising two or more straps and/or discs. Finally, the shapes of aggregates with $N_{\text{POM}} < 30$ (Fig. S10 in ESI) are difficult to determine.

Degree of Polymerization and Distribution

Using the measured N_{POM} , we obtained the number frequency distribution of the POM clusters in the aggregates (Fig. 3a). The green and red histograms correspond to the N_{POM} counted from both grayscale and pseudo-colored images, respectively. The histograms were fitted to Gaussian functions with $20 \leq N_{\text{POM}} \leq 160$:

$$g(N) = \frac{1}{(2\pi)^{1/2}\sigma_n} \exp\left[-\frac{(N - N_{\text{median}})^2}{2\sigma_n^2}\right] \quad (1)$$

where the median N_{median} is the number average and σ_n is the standard deviation of the number distribution:

$$\sigma_n = (\bar{N}_w \bar{N}_n - \bar{N}_n^2)^{1/2} \quad (2)$$

where $\bar{N}_n$ and $\bar{N}_w$ are the number and weight averages, respectively. We obtained number-average $\bar{N}_{\text{POM}} = 91$ and $\sigma_n = 28.0$ from the grayscale images and $\bar{N}_{\text{POM}} = 103$ and $\sigma_n = 25.0$ from the pseudo-colored images. The $\bar{N}_{\text{POM}}$ from the grayscale images (91) is smaller than the DP (100) predesigned in our

synthesis and $\overline{\text{DP}}$ determined by SEC (116) because of the underestimated N_{POM} . In contrast, $\bar{N}_{\text{POM}}$ (103) counted from the pseudo-colored images is closer to and more correctly reflects the predesigned and measured number-average DPs. Further, the number distribution, $\bar{N}_w/\bar{N}_n = 1 + \sigma^2/\bar{N}_n^2 = 1.06$, is slightly smaller than the $\bar{M}_w/\bar{M}_n$ determined by SEC (1.15). Therefore, N_{POM} corresponds to the DP of the poly(POM) chains and the N_{POM} distribution reflects the number-average dispersion of the poly(POM) chains. This is the strongest evidence that aggregates with $20 \leq N_{\text{POM}} \leq 160$ are single chains.

Packing of POM Clusters in Aggregates

The area of the aggregates, A_A , was further measured (SI-13 and Fig. S11 in ESI) and then plotted versus N_{POM} (Fig. 3b). The relationship between A_A and N_{POM} is linear with a slope of $2.60 \pm 0.02 \text{ nm}^2/N_{\text{POM}}$, which is the area of a single POM cluster in aggregates. The linear relationship indicates that the formation of the all aggregates, including the complex-shaped ones, is controlled by the same process without chain stacking. The packing density ($2.60 \pm 0.02 \text{ nm}^2/N_{\text{POM}}$) is larger than that calculated from the solution self-assembled aggregates of POM-containing building blocks ($\sim 1.5 \text{ nm}^2$ per cluster).^[51] This is a rational result because of the denser packing in assembled aggregates and the existence of “holes” in chain aggregates.

Characteristics of Strap Chains

Herein, the end-to-end distance, l_1 , and the curved chain length, l_2 , as defined in Fig. 4(a), were measured using ImageJ. Moreover, the length of a completely extended chain, l , was calculated as $l = N_{\text{POM}} \times d$, where $d \approx 0.6 \text{ nm}$ is the length of a polynorbornene repeating unit. Further, two specific ratios, $r_1 = l_1/l$ and $r_2 = l_2/l$, were defined to semi-quantitatively describe the degree of curvature and spatial characteristics of a strap on a carbon surface. If $r_1 = 1$ then $l_1 = l$, which means that the strap is completely straight. On the other hand, if $r_1 < 1$ then $l_1 < l$, which means that a curved strap is formed. Likewise, if $r_2 = 1$ then $l_2 = l$, and the strap has a perfect 2D structure, and if $r_2 < 1$ then $l_2 < l$, which means that the strap is approximately three-dimensionally structured.

The r_1 and r_2 values of 77 straps were measured, as shown in Fig. 4(b). These straps have $0.36 \leq r_1 \leq 0.85$ and $0.60 \leq r_2 \leq 0.93$, which indicate that they are not completely straight and have imperfect 2D structures. The straps with $N_{\text{POM}} \approx 113$ and 118 in Fig. 4(c) were selected to briefly discuss the significant change in strap shape reflected by the r_1 and r_2 values. The strap with $N_{\text{POM}} \approx 113$ has $r_1 \approx 0.80$ and $r_2 \approx 0.83$, which means that it is almost straight and has a nearly perfect 2D structure. An $r_1 \approx 0.38$ implies that the strap with $N_{\text{POM}} \approx 118$ is the most curved strap.

Multi-shaped Chains

The diversity of chain shapes is semi-quantitatively described by determining the aspect ratio, $r_3 = l_3/w$, where l_3 and w are the length and width of the chains, respectively. For strap chains, $l_3 = l_2$ (length of a curved chain) and w is the average width. For round discs, $r_3 = 1$. For almost oval-shaped discs, l_3 and w are equal to the lengths of the long and short axes, respectively. As the intermediates are usually composed of straps and discs, their aspect ratios are determined as shown in Fig. 4(d): $r_3 = r_{3s}f_s + r_{3d}f_d$, where r_{3s} and r_{3d} are the aspect ratios of the

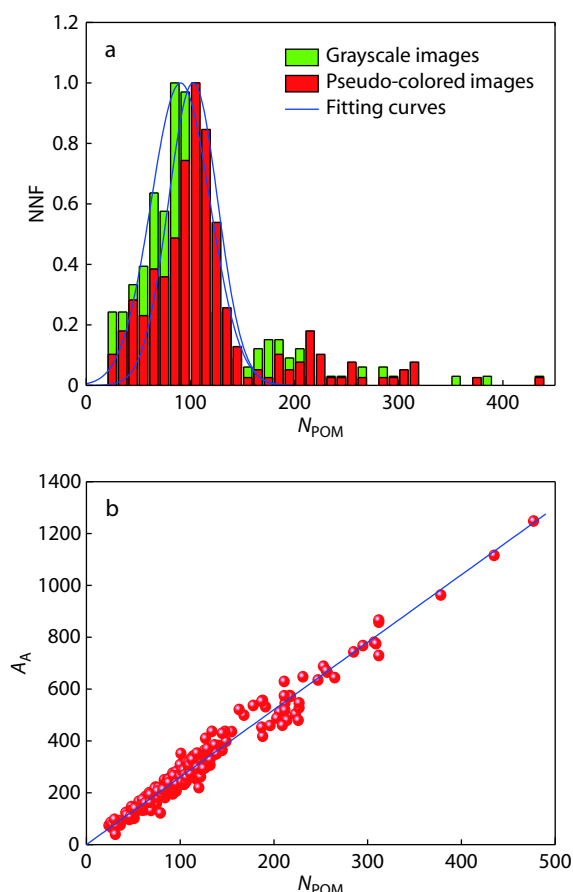


Fig. 3 (a) Normalized number frequency (NNF) distribution of the number of POM cluster in the aggregates, N_{POM} . (b) Plot of the aggregate area, A_A , versus N_{POM} . The blue curves or line are fitting results.

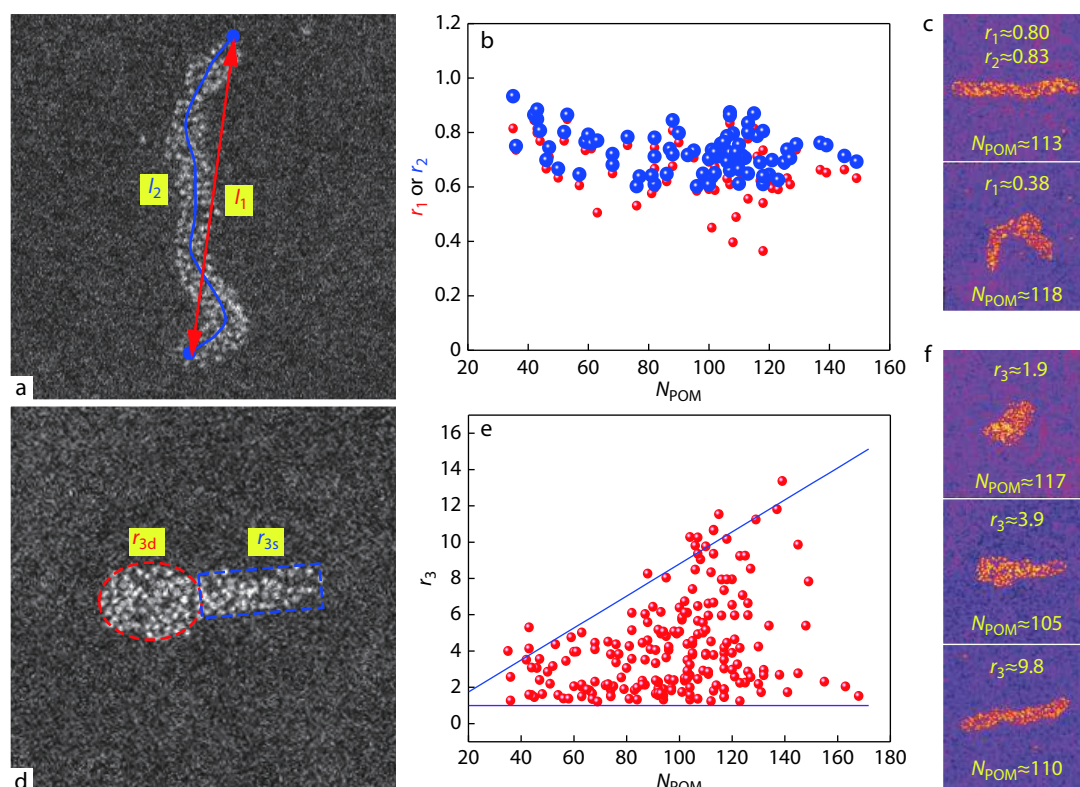


Fig. 4 (a) Grayscale image illustrating the end-to-end distance, l_1 (red line), and length, l_2 (blue curve), of the chain. (b) Plots of r_1 and r_2 versus N_{POM} . (c) Two straps with $r_1=0.80$ and $r_2=0.83$ (top) and $r_1=0.38$ (bottom). (d) Schematic showing the r_3 of an intermediate composed of a disc and strap. (e) Plot of r_3 versus N_{POM} . The purple and blue lines correspond to the r_3 of perfect disc chains and fully straightened chains with a theoretical width of 6.8 nm, respectively. (f) Three chains with $r_3=1.9$ (top), 3.9 (middle), and 9.8 (bottom). The N_{POM} values are indicated in (c) and (f).

strap and disc components, respectively and $f_s = N_{s,\text{POM}}/N_{\text{POM}}$ and $f_d = N_{d,\text{POM}}/N_{\text{POM}}$, where $N_{s,\text{POM}}$ and $N_{d,\text{POM}}$ are the N_{POM} values of the strap and disc components, respectively. Additionally, the aspect ratio of completely extended chains (Fig. 1a) was calculated as $r_3 = (N_{\text{POM}} \times 0.6) / 6.8$, where 0.6 nm is the length of a polynorbornene repeating unit and 6.8 nm is the width of a fully extended chain. In Fig. 4(e), the purple and blue lines show the relationships between r_3 and N_{POM} for round discs and completely extended chains, respectively. The r_3 values are clearly distributed in the sector between the blue and purple lines, indicating that the shape of the chain varies from an almost complete disc to a strap. At the same time, shape diversity also increases with increasing N_{POM} . Fig. 4(f) shows three typical chains with $r_3=1.9$ (top), 3.9 (middle), and 9.8 (bottom) with the N_{POM} values indicated. Finally, it is worth noting that several dots are above the blue line, the theoretical aspect ratio, because the width of the strap chains is 5–6 nm, which is smaller than the 6.8 nm width of a fully extended chain.

Poly(POM) Chains in Solution

In a good solvent, conventional polymers, such as polystyrene, exhibit very important statistical self-similar conformations, which obey scaling laws and can normally be studied by scattering methods. This self-similarity further implies that if chains are visible in real space, they will show a variety of shapes that are also defined by scaling laws. When large dendron or

bottlebrush pendants are well distributed around the polymer backbone, they form thick layers that uniformly cover the backbone.^[19–24] Thus, thickened chains in dry samples can be visualized by AFM and those in solution by cryogenic TEM. Further studies indicate that wormlike conformations existing in both the solution and solid states are the same mainly owing to the steric hindrance of the pendants.

For poly(POM), however, we found it impossible to define the chain shapes using known theoretical models. Herein, we further studied the effect of cluster pendants on chain shapes, which significantly differs from that of dendron or bottlebrush pendants in at least two respects. The first aspect is that interaction between POM pendants in acetonitrile is negligible due to solvation; thus, the POM complexes with a volume of $\sim 1.5 \text{ nm}^3$ are discretely distributed around the backbone. In this case, the conformation of the poly(POM) chain is largely determined by the polynorbornene backbone in dilute solution. Considering $R_g=15.34 \text{ nm}$, we therefore suggest that poly(POM) chains adopt a curved semi-rigid conformation in solution between a fairly extended and coiled conformation (Fig. 5a). The diversity of chain shapes observed in this study does not express the true conformations in solution because poly(POM) chains cannot possibly adopt multiple shapes (from strap to disc). The second aspect is that long-range electrostatic interactions between the POM pendants will become the key factor in controlling the chain conformation at the critical concentration at which the distance

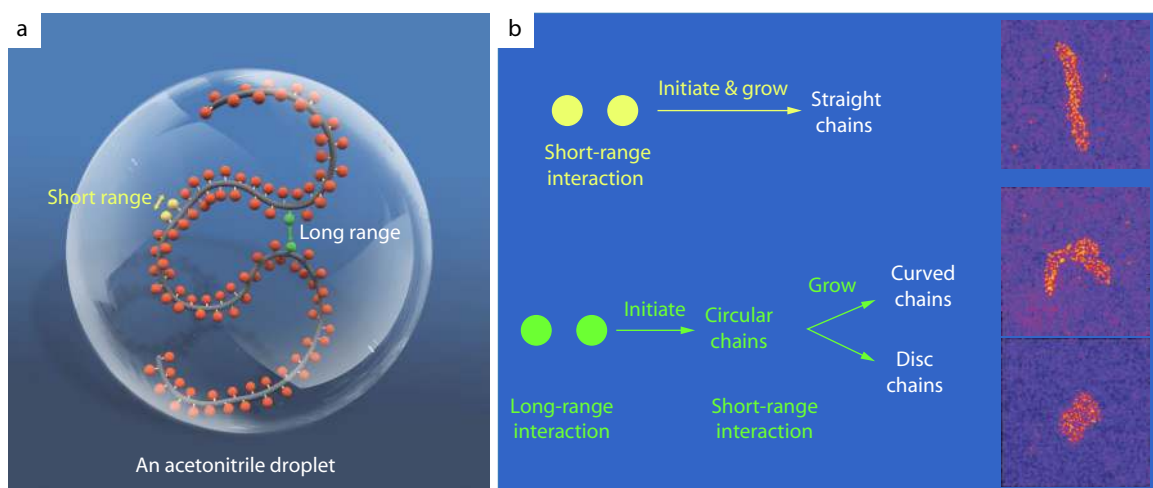


Fig. 5 Schematic representation of the conformational evolution of a poly(POM) chain during solvent evaporation. (a) Curved semi-rigid poly(POM) chain, consisting of a curved backbone (grey curve) and 100 POM clusters (100 dots), confined within a solvent droplet. Two pairs of yellow and green dots indicate the intramolecular short- and long-range interactions of two POM pendants, respectively. (b) Formation of 2D single chains and the evolution of the shape from a strap to a disc via intermediates by the coordination of two intramolecular interactions.

between the clusters is within the range of strong interactions.

Formation of 2D Multi-shaped Chains

When spreading dilute solutions in acetonitrile, a poly(POM) chain with a curved semi-rigid conformation is isolated within a solvent droplet. Normally, the droplet size is within the micrometer range, which is much larger than the dimension of a poly(POM) chain. During droplet flight and after landing on the surface of the carbon film, the solvent continuously evaporates. Once the droplet diameter is close to twice the radius of gyration of a poly(POM) chain, electrostatic interactions between the POM pendants begin to manipulate the shape of the chain.

The formation of 2D multi-shaped chains depends entirely on the position of at least two POM clusters in a curved chain that come into contact with each other; that is, their intramolecular short- and long-range interactions (Fig. 5a). The short-range interactions between the first two adjacent clusters cause the formation of a baby strap around the backbone (Fig. 5b, top). Subsequently, this strap acts as an initiator or that further interacts with the other adjacent clusters, resulting in its growth along the backbone. In this way, curved semi-rigid chains are straightened and a perfect strap chain is formed. If several initiators are formed in a chain almost simultaneously, the chain becomes a 2D snake by bending and twisting.

The long-range interactions of two spatially proximate clusters initially result in the formation of chain loops, and then the succeeding short-range interactions generate chains with shapes that are not straps. The final shape of each chain depends on the position at which the long-range interactions occur. If the interactions occur in the middle of the chain, the chain has a shape composed of two short straps at both ends and a small disc in the middle (Fig. 5b, middle). In this way, multi-shaped chains are created. If the interactions occur in two-cluster areas near the two ends of a chain, the

chain aggregates into imperfect discs (Fig. 5b, bottom). For chains with $N_{\text{POM}} < 30$, they should have a more rigid chain than that of $N_{\text{POM}} \approx 100$. In such a case, the long-range interaction should be suppressed. So, the images (Fig. S10 in ESI) should correspond to the short but fully extended poly(POM) chains.

Complex-shaped aggregates are not formed by single chains, but rather by a simple combination of a few chains. This is due to two factors: the N_{POM} of complex-shaped aggregates is much higher than the DP of the sample and single linear chains cannot form complex shapes. The hypothesis is that more than one chain is contained in a droplet and/or several droplets fuse on the surface of the carbon film. All in all, the results indicate that the shapes of single polymer chains with strongly interacting pendants are totally different to those of chain conformations in solution, even those of dendronized and bottlebrush polymers. This conclusion is very important when thin films of these polymers prepared by solution processing are used in advanced devices.

CONCLUSIONS

We directly observed multi-shaped aggregates of poly(POM) by STEM using samples prepared by spreading the dilute solution. The number and distribution of the POM clusters in the aggregates corresponded to the degree of polymerization and the molecular weight dispersion, respectively. Therefore, the aggregates are single chains of poly(POM) successfully isolated within liquid droplets and solidified on the surface of the carbon film. Further study indicated that the formation of multi-shaped chains can be ascribed to strong intramolecular short- and long-range interactions between the POM pendants on curved semi-rigid chains during solvent evaporation: short-range interactions directly generate chain straps, while long-range interactions first produce circles and then the succeeding short-range interactions generate discs and other shapes depending on the position at which long-range interactions occur. Therefore, we

postulate that poly(POM) chains adopt curved semi-rigid conformations in solution. This basic understanding provides valuable insight into the solution processing of these polymers for the preparation of functional thin films that are used to develop advanced devices, such as fuel and organic solar cells. Finally, we emphasize that *in situ* monitoring of conformational evolution with increasing concentration using scattering method will provide a deeper understanding of hybrid polyelectrolytes.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-021-2520-4>.

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