Observation Technique of Polymer Micelle by Using Transmission Electron Microscope

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Synopsis

The method, established by Price et al. to observe the polymer micelle, was modified and applied to the region of high polymer concentration. The novelty of our method consists of the preparative method of the specimen for transmission electron microscopy. Polymer solution was diluted and solvent was evaporated rapidly before the micelle was decomposed. As a result, dilution ratio had no effect on the decomposition of polymer micelle, and the original micelle structure was conserved over 10 wt % block copolymer solution if the operations were carried out within 30 min. This time limit related to the concentration of solution.

INTRODUCTION

It is well known that block and graft copolymers that consist of two amorphous sequences generally form a micelle over critical micelle concentration. During the solvent evaporation, the micelle deforms and final microphase separated structure is fixed. This final structure is principally classified to five morphologies.[1] Recently it was pointed out that the domain shape and size expected by the theory deffered from experimental that and the reasons were discussed in connection with the growing process of polymer micelle.[2,3] Spontak et al.[4] reported that the spheric micelle formed at the beginning grew to cylindrical micelle by the increase of polymer concentration. But they supposed this process by the final structure observed by transmission electron microscope (TEM); they did not observe it directly. On the other hand, we[5] and Yamashita et al.[6] reported that the block copolymers composed of amorphous (hydrophobic)-crystalline (hydrophobic) sequences showed particular microdomain structure because micelle formation and crystallization proceeded simultaneously during formation of microdomain structure. But it has not been made clear which of the crystallization or micelle formation occurs at the beginning of the domain construction, and the detail mechanisms of the microdomain formation are not clarified. TEM observation is the best method to clarify these mechanisms, but some techniques are required in order to observe the structure in the polymer solution. Price et al.[7] reported the direct observing method for micelle by TEM. They prepared the micelle in the low concentration by using selective solvent and dried it rapidly at room temperature. But this method cannot be used for observing the micelle structure in the high polymer concentration. In order to study the processes of micelle formation and crystallization, a new method of observing the micelle in the high polymer concentration is

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required. It is known that the decomposition rate of polymer micelle by dilution is very slow. If it takes much time for the micelle to be decomposed by dilution and the micelle is not changed by evaporation of the solvent in the micelle rapidly, the TEM sample can be prepared by casting on the copper mesh, and the micelle structure in the high polymer concentration can be observed directly by using TEM. In this article we established the method of observing the micelle structure in the high polymer directly by using TEM. The method consists of dilution of the high concentrated polymer solution and evaporation of the solvent. We investigated the decomposition rate of the micelle in solution. Then we determined the suitable condition in the method and the time limit of the operations.

EXPERIMENTAL

Synthesis of Block Copolymer

We synthesized poly(tetrahydrofuran-*b*-isoprene) because we will study the morphology of crystalline–amorphous block copolymer in the future. The block copolymer was synthesized by coupling reaction between living poly(tetrahydrofuran) (PTHF) and living polyisoprene (PIP). The method was described in a preceding article.[8] The weight average molecular weight of PTHF and PIP were 118,000 and 110,000, respectively, and the content of THF was 47 mol %.

Method

Our observation technique consists of these four operations: (1) sampling of block copolymer solution, (2) dilution of the solution with the same solvent, (3) casting the diluted solution on the copper mesh covered with thin carbon film, and (4) drying the mesh rapidly in vacuum at room temperature. Then there exists a problem in these four operations. The problem is whether the time spent for micelle deformation is much longer in comparison with the time spent for the operations. In order to clarify this point, we tested the following five samples prepared by different conditions.

1. Benzene (good for both sequences) solution of the block copolymer, whose concentration was 10 wt % was prepared.
2. 1.9 mL of benzene was added to 0.1 mL of sample 1. The ratio of dilution was 20 times.
3. 9.9 mL of benzene was added to 0.1 mL of sample 1. The ratio of dilution was 100 times.
4. Benzene solution of the block copolymer, whose concentration was 30 wt % was prepared. And 9.9 mL of benzene was added to 0.1 mL of this solution. The ratio of dilution was 100 times.
5. 0.1 g of the block copolymer was thrown into 10 mL of benzene, and it was stirred very slowly. The polymer changed from solid state to 1 wt % solution finally.

In the case of sample 1, operations (1), (3), and (4) were carried out. In the case of samples 2–5, operations (3) and (4) were carried out. In both cases all the operations were finished within 5 min. In order to investigate the decomposition rate of the micelle, we carried out operations (3) and (4) for sample 3 and 4 after 15 min, 30 min, 1 h, 3 h, and 1 day after the dilution. We prepared the sample of the block copolymer film cast on the mesh in order to compare shape of the micelle in the solid state and the solution. This film was prepared by drying the 1 wt % block copolymer solution in atmospheric pressure and at room temperature.

Electron Microscopy

The prepared samples were stained by osmium tetraoxide and PIP was stained. TEM observation of the specimens were carried out by Hitachi H-500 transmission erectron microscope. The accelerating voltage was 100 kV.

RESULTS AND DISCUSSION

Effect of the Ratio of Dilution

Figures 1, 2, and 3 show typical TEM photographs of samples 1, 2, and 3 prepared within 5 min, respectively. The dark section corresponds to PIP domain. In sample 1, the film cast on the mesh was very thick because the 10 wt % solution was used as it was. But the film thickness was not uniform, and thin parts could be found by TEM scan operation. In Figure 1, there exists cylindrical micelles of PIP, and the domain size is about 70 nm. Also in Figures 2 and 3, there exist cylindrical micelles. There are no differences in the cylindrical micelle observed in Figures 1, 2, and 3. This result shows that the ratio of dilution has no effect on the shape and dimension of the micelle, that is, the micelle is not deformed during the operations.

Decomposition Rate of Micelle

Figure 4 is the TEM photograph of the block copolymer in solid state prepared by drying in atmospheric pressure and room temperature. Cylindrical structure

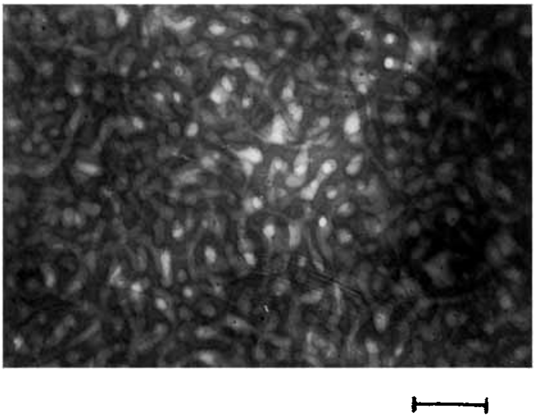


Fig. 1. TEM photograph of sample 1 prepared within 5 min (scale = 500 nm).

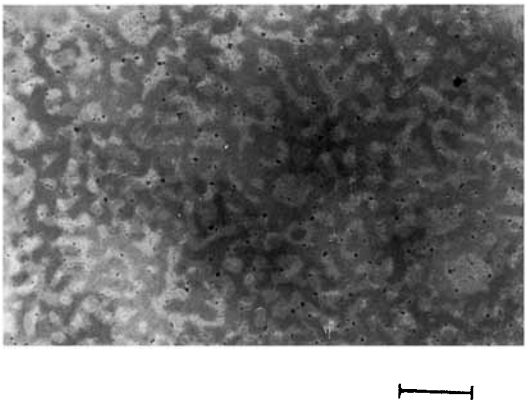


Fig. 2. TEM photograph of sample 2 prepared within 5 min (scale = 500 nm).

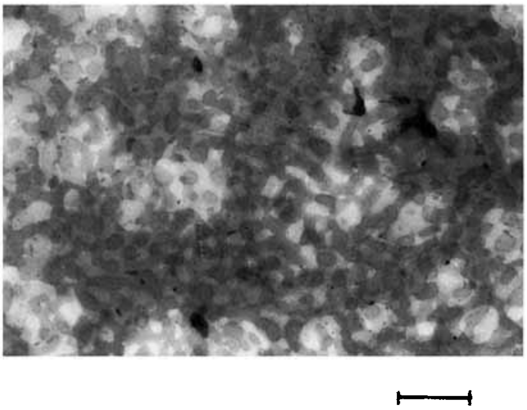


Fig. 3. TEM photograph of sample 3 prepared within 5 min (scale = 500 nm).

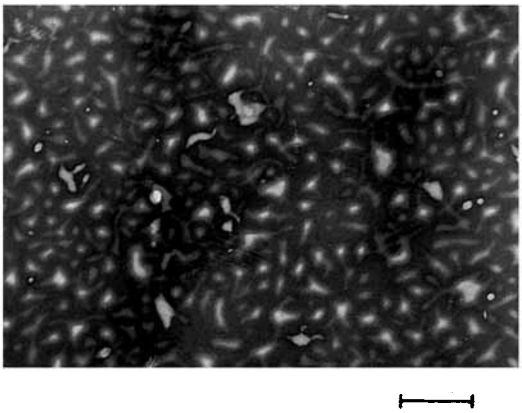


Fig. 4. TEM photograph of the block copolymer film prepared by drying the 1 wt % block copolymer solution in atmospheric pressure and at room temperature (scale = 500 nm).

of PIP could be observed. Figures 5, 6, and 7 are TEM photographs of samples 3, 4, and 5, respectively, and (a), (b), (c), (d), and (e) in the figures correspond to the samples of 15 min, 30 min, 1 h, 3 h, and 1 day after the dilution, respectively. In Figure 5, cylindrical micelles are observed in (a) and (b). But in (c) there appears many crazes in the PIP domain. In Figure 6, cylindrical micelles could be observed also in (a), (b), and (c). But in (d) many crazes appear in the PIP domain. These crazes in Figure 6 appeared later than in Figure 5. Figure 7 shows the dissolving process observed by TEM. In (a), (b), (c), and (d), the same cylindrical micelles could be seen and they are same as

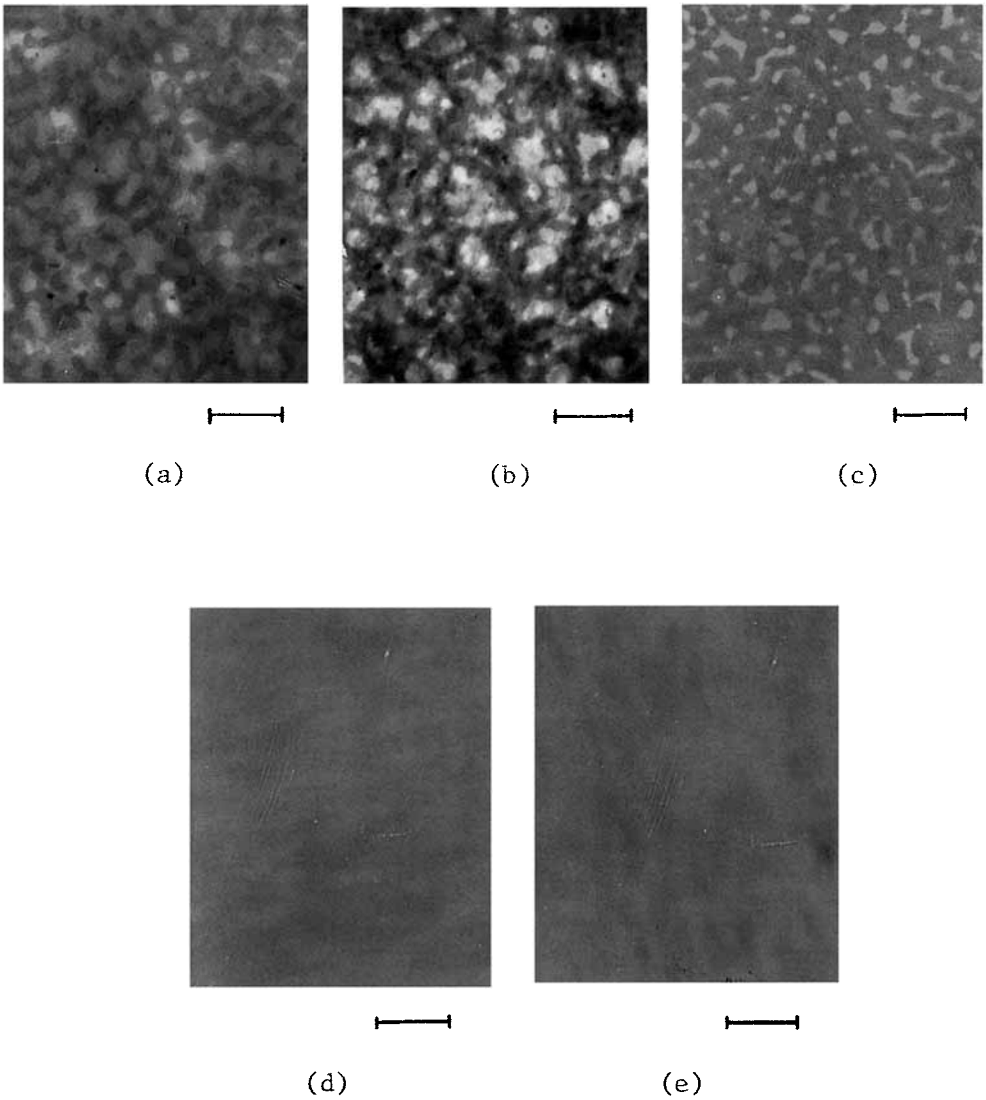
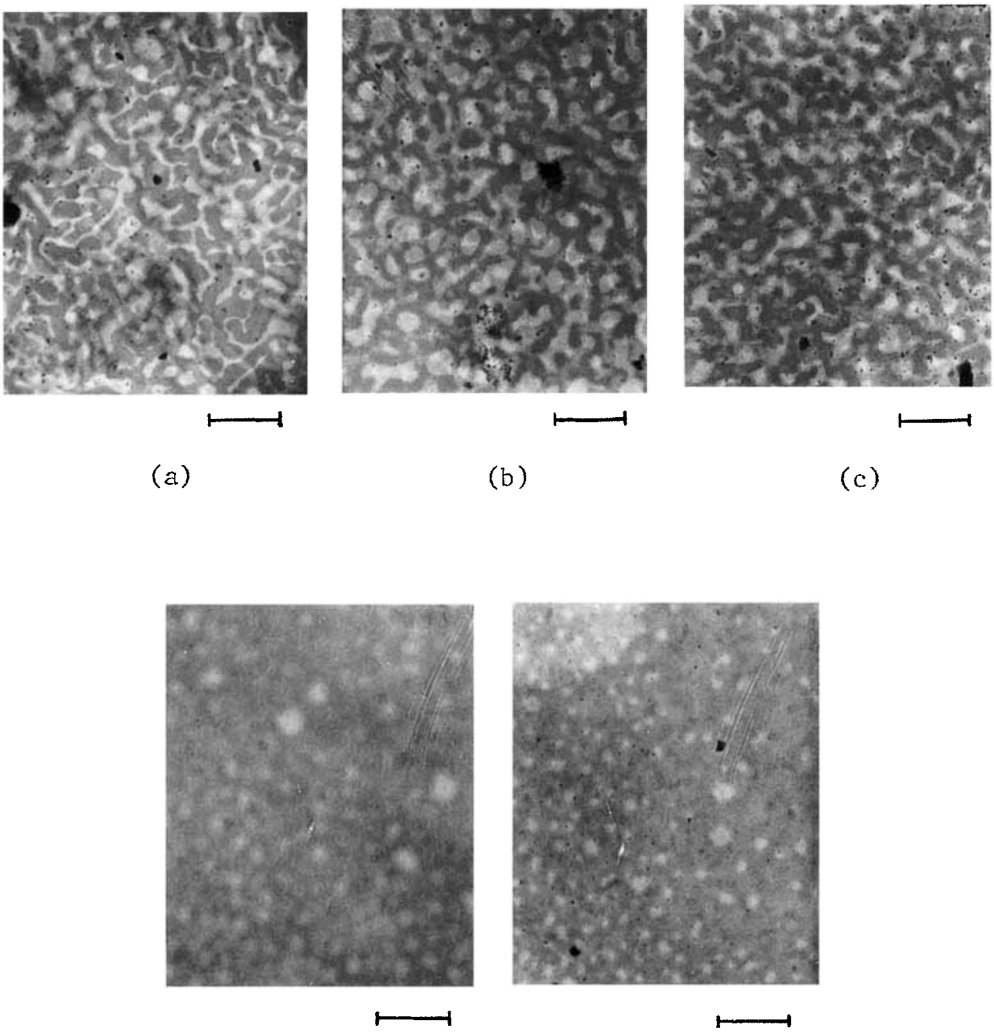


Fig. 5. TEM photographs of sample 3 prepared by changing the time between dilution and drying (scale = 500 nm): (a) after 15 min; (b) after 30 min; (c) after 1 h; (d) after 3 h; (e) after 1 day.



(a) (b) (c)

(d) (e)

Fig. 6. TEM photographs of sample 4 prepared by changing the time between dilution and drying (scale = 500 nm): (a) after 15 min; (b) after 30 min; (c) after 1 h; (d) after 3 h; (e) after 1 day.

observed in Figure 4. At the beginning of the dissolution, the very large bulk aggregation of the micelles divide into the unit micelle gradually, and finally the micelles are dispersed uniformly in the solution. In Figure 7(e), any definite structure is not observed. This means that the micelles are decomposed in 24 h completely. These processes are summarized schematically in Figure 8.

First, the micelle absorbs the solvent and swells. This swelling proceeds, and at last the decomposition of the micelle occurs. The amount of the solvent contained in the micelle in the 10 wt % solution is more than that in the micelle formed in the 30 wt % solution. In the solid state, of course, the micelle contains no solvent. Then the micelle in the 10 wt % solution, in the 30 wt % solution,

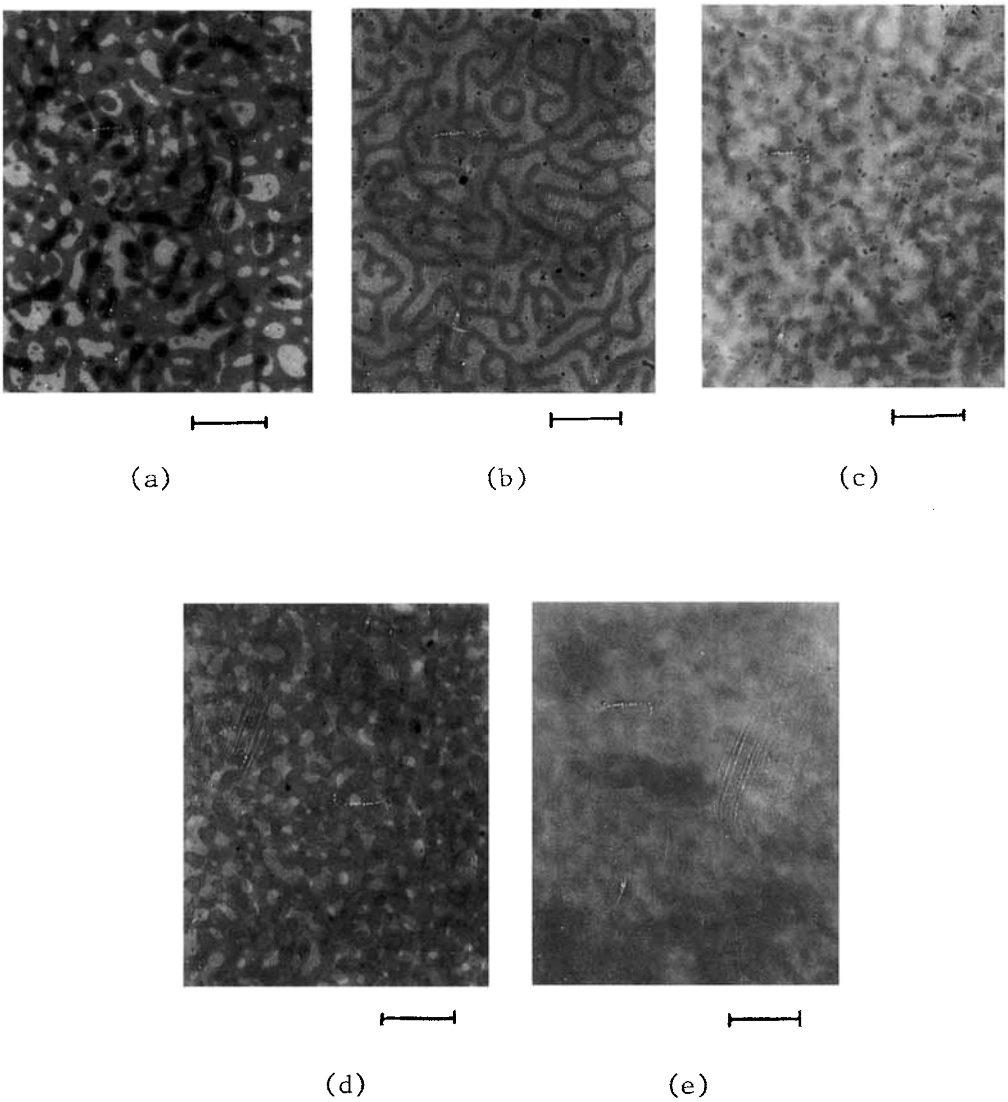


Fig. 7. TEM photographs of sample 5 prepared by changing the time between dilution and drying (scale = 500 nm): (a) after 15 min; (b) after 30 min; (c) after 1 h; (d) after 3 h; (e) after 1 day.

and in the solid state correspond to (c), (b), and (a) in Figure 8, respectively. In (d), which is highly swollen by solvent, the domain surface would be very soft. And the crazes and the holes are apt to occur on the domain surface, when the solvent in the micelle is evaporated rapidly. The micelle in the 10 wt % solution contains more solvent originally than the micelle in the 30 wt % solution and the solid state micelle. So the micelle in the 10 wt % solution is swollen and decomposed sooner in comparison with the micelle in the 30 wt % solution and the solid state. Then stage (c) changed to stage (d) more rapidly in the former concentration than in the latter. But, on the other hand, since the micelle in the solid state contains no solvent, it takes more time for the micelle

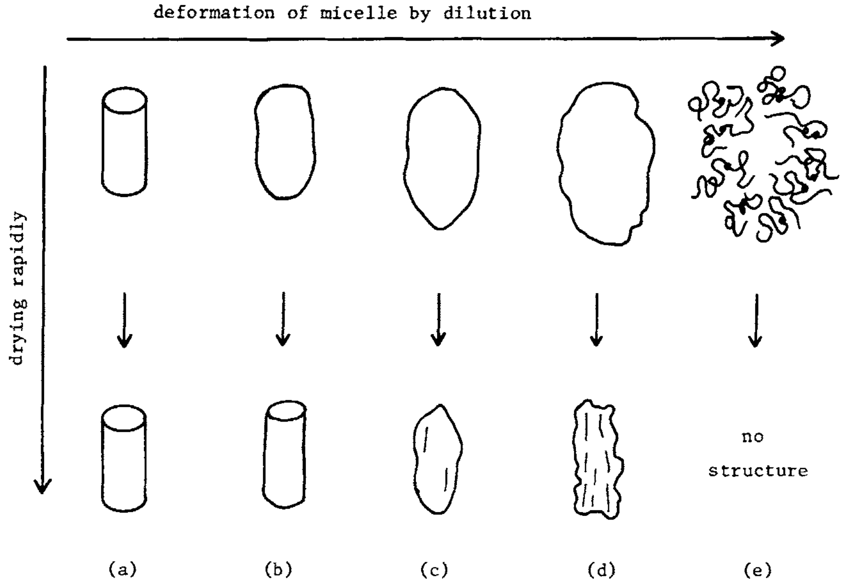


Fig. 8. Illustration of the process of the micelle deformation.

to swell and decompose in the solvent. This process corresponds to the change from stage (a) to stage (d) and (e) in Figure 8.

From these results, we determined that the time limit of the operations is 30 min over the 10 wt % concentration. If the operations are carried out within this time limit, the original micelle structure in solution can be observed, and the time limit is prolonged by the increase of polymer concentration. Since the operations can be done completely within 5 min, there is no problem. Then our method is very useful for the observation not only of micelle structure in solution but also the structure of the micelle unit in solid state. Our method can be used for the investigation on the formation and deformation of the micelle.

CONCLUSION

We have examined the method for the observation of polymer micelle in the concentrated solution by using TEM. The method consists of four simple operations: sampling of polymer solution, dilution of the solution with the same solvent, casting the diluted solution on the mesh for TEM, and drying the mesh rapidly in vacuum at room temperature. We have examined the effect of the dilution ratio and the time between the dilution and the solvent evaporation on the micelle decomposition. As the results, dilution ratio had no effect on the results and the time limit of the operations was 30 min if the concentration of the solution was over 10 wt %. This time limit was prolonged by the increase of the concentration, and this concentration dependent on time allowance originates in the decomposing process of micelle. Since the four operations can be carried out within 5 min, our method can be used for observation of polymer micelle in the solution, and it is effective for the observation of the structure of the micelle unit in the solid state. Then our method is useful for study on polymer micelle.

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