Polymer Bulletin 22, 617–620 (1989)

Polymer Bulletin

Influence of sample preparation on microdomain formation on some zwitterionic polymers

V.M. Castaño[1], A.E. González[1], J. Cardoso[2], O. Manero[2], and V.M. Monroy Soto[2]

[1]Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364,
México DF 01000, México
[2]Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,
Apartado Postal 70-360, México DF 04510, México

Summary

We have conducted observations of possible microstructure on some zwitterionic polymers by means of Transmission Electron Microscopy. Two different solvents, with very different evaporation rates, were used to dessicate the samples onto the carbon covered microscope grids. While no sign of microstructure was apparent in the samples prepared from the more volatile solvent, a well defined grainy appearance was observed in the samples obtained from the less volatile solvent. This shows that sample preparation plays an important role on microstructure formation on zwitterionic polymers.

Introduction

Zwitterionic polyampholytes have been the subject of a variety of studies, mainly concerned on their solution properties (1-3). Also, some recent reports on their solid state properties have appeared in the literature (4-6). One of the major interests for the study of these materials is the aggregation phenomena between the zwitterionic moieties, resulting from the dipole -dipole interactions. This aggregation of the ionic groups leads to domain formation in the solid state, as it has been observed by X-ray diffraction (4,6) and Transmission Electron Microscopy (TEM) (7).

For example, we reported results on TEM studies (7) for a series of poly (4-vinyl pyridine) homo- and copolymers, with varying contents of sulphopropyl betaine groups $(-\mathrm{N}^{+}-(\mathrm{CH}_2)_3-\mathrm{SO}_3^{-})$. It was observed that domain formation, ranging from 50 to 200 Å ocurred, depending on the zwitterionic content of the samples (7). We noticed, however, that sample preparation plays a key role on this domain formation. It is the purpose of this note to report our results on the influence of sample preparation on TEM observations.

Experimental Procedure

Various zwitterionic polymer samples were prepared for standard TEM observations. The specimens included poly (2-vinyl pyridine) homo- and copolymers with 0%, 10% and 100% degree of quaternization. In our previous report (7), the samples were prepared by suspending polymer powder in deionizated water (a non-solvent for the polymers, if no salt is present). The microstructure observed was therefore already present in the polymer powder. In the present case, since we were mainly interested in the possible influence of the preparation procedure upon the observed features, two very different liquids were chosen for dissolving the polymers. The difference being basically the vapour pressures that, at least in principle, would allow different time scales for the formation of microstructure in the solute as the solvent evaporated.

In fact, by using 2,2,2-trifluoro ethanol the evaporation time of a drop of solution onto a carbon-covered microscope grid was of about half an hour, whereas the use of dimethyl sulfoxide as a solvent resulted in evaporation times as long as a full day (∿26 hours).

The actual TEM observations were carried out in a 100 KeV machine (JEOL-100CX) and no stainning agent was used in order to avoid any possible artifact in the microstructure due to strange substances.

Results and Discussion

As explained elsewhere (7), we dessicated the polymers onto the carbon coated grids from highly dilute solutions. In this way, we obtained well separated polymer pieces instead of a single continuous film. We preferred to dry the samples in this way instead of from a more concentrated solution, because the evidence for a microphase separation (or ion-pair aggregation) is more apparent on the edges of these polymer chunks, as it will be evident in the following figures.

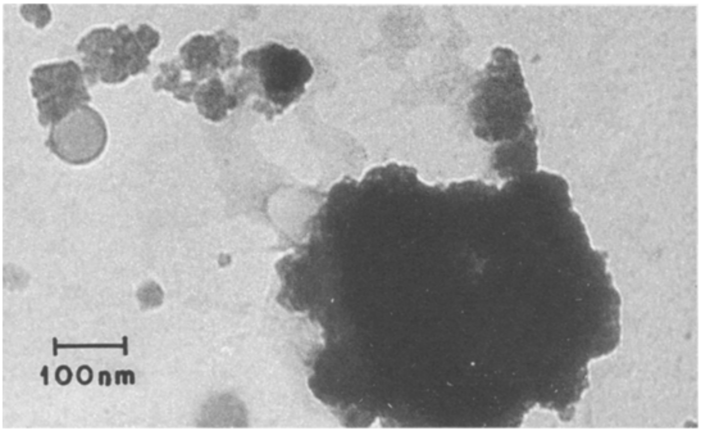

Figure 1. A micrograph of the 0% sample, casted on the grid from a dimethyl sulfoxide solution.

For the first solvent (2,2,2-trifluoro ethanol), no sign of microstructure was observed for the three polymers, no matter the length scale investigated. Results similar to the one shown in Fig. 1 were obtained and we didn't deem it necessary to include photographs for the trifluoro ethanol case.

In figure 1 we show a micrograph of the 0% sample, casted on the carbon coated grid from a solution with dimethyl sulfoxide as a solvent. In that figure we see a big dark region of about 4000 Å in size plus some smaller ones. They represent zones of high concentration of the polymer. In this first micrograph we do not see any kind of microstructure on the polymer chunks.

In the next micrograph (Fig. 2) for the 10% sample, and for the dimethyl sulfoxide case, we now see a grainy appearance, particularly on the edges of the polymer chunks, as mentioned before. The size of the grains are in the range 30 - 60 Å, which is a little bit smaller as compared to our previous results (7). It may therefore be that the evaporation time is still small to produce bigger grains. The possible structure inside these grains was already discussed in our last report (7).

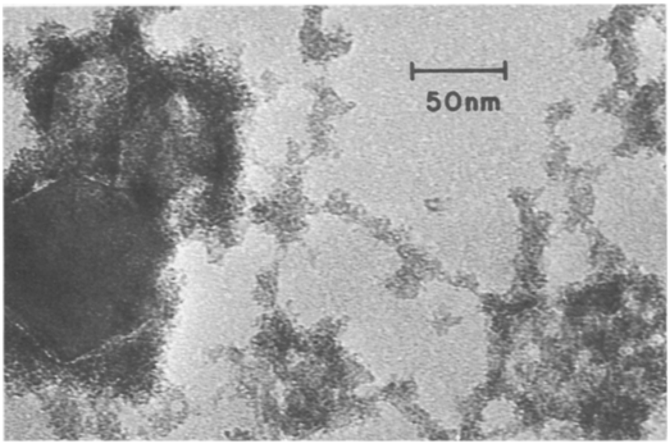

Figure 2. A micrograph of the 10% sample, also dessicated from a dimethyl sulfoxide solution.

Finally, in figure 3, we show a micrograph for the 100% sample casted from the dimethyl sulfoxide solution. We see a pronounced and closely packed grainy appearance of the polymer pieces, the size of the grains being in the range 30 - 100 Å, which is again smaller than those reported before (7). It therefore seems that, in order to produce microstructure with bigger grains, less volatile solvents are needed which allow enough time for this domain formation.

In summary, we have shown that sample preparation plays an important role on microstructure formation in zwitterionic polymers.

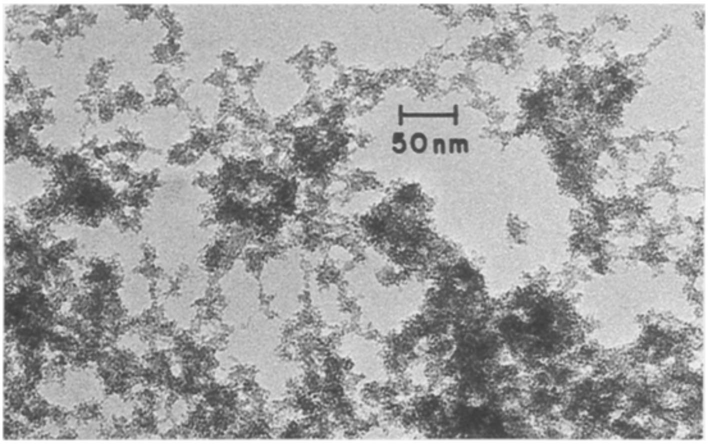

Figure 3. A micrograph of the 100% sample, dessicated again from a dimethyl sulfoxide solution.

Acknowledgments
The financial support provided by the Consejo Nacional de Ciencia y Tecnología (grant number PVT/PQ/NAL/85/3121) and the Third World Academy of S-

ciences (grant number TWAS RG 86-39) is gratefully acknowledged.

References

1.Salamone J-C, Volksen W, Israel S-C, Raia D-C (1974) ACS Polym Prepr 36 (2): 261.
2.Monroy Soto V-M, Galin J-C (1984) Polymer 25: 254.
3.Schulz D-N, Kitano K, Danik J-A and Kaladas J-J (1987) Proceedings of the ACS Division of Polymeric Materials 57: 149.
4.Monroy Soto V-M, Marchal E, Mathis A, Meurer B, Galin J-C (1984) ANTEC 84:297.
5.Marchal E, Monroy Soto V-M, Galin J-C (1985) Proceedings of the 5th Intern. Symp. Electrets, Heidelberg 1985 (avail. from IEEE, NY): 247.
6.Galin M, Marchal E, Mathis A, Meurer B, Monroy V-M and Galin J-C (1987) Polymer 28: 1937.
7.Castaño V-M, Gonzâlez A-E, Cardoso J, Manero O, Monroy Soto V-M (1989) J Mat Res (to appear).

Accepted October 18, 1989 K