Polymer Journal, Vol. 25, No. 2, pp 201—203 (1993)

NOTES

Cryo-TEM Observation of the "Super-Network" Structure in Polymer Solutions

Toyoko IMAE

Department of Chemistry, Faculty of Science, Nagoya University, Nagoya, Aichi 464, Japan

(Received May 21, 1992)

KEY WORDS Cryo-TEM / Sodium Alginate / Poly(ethylene) Oxide / Intermolecular Linkage / Junction Zone / Super-network Structure / Spinnability / Viscoelasticity /

Aqueous solutions of sodium alginate and poly(ethylene oxide) (PEO) are very viscous and viscoelastic, and these polymers form intermolecular linkages.[1-6] Such junction formation in polymer solutions should be related to the rheological properties.

Spinnability, a viscoelastic phenomenon, was investigated for aqueous viscoelastic polymer solutions.[7] When a rod was pulled up from the solution and a liquid was stretched to form a thread, the length of the liquid thread increased linearly with the velocity of the rod for solutions of sodium alginate at low concentrations and PEO, while the length was nearly independent of the velocity of the rod for sodium alginate solutions at high concentrations.

In this work, the cryo transmission electron microscopic (cryo-TEM) observation of polymer solutions is conducted, and polymer structure in solutions is discussed in relation to rheological properties.

Cryo-TEM, which is a direct visualization method of vitrified hydrated specimens, is a technique for avoiding some artifacts that hinder TEM observation. This technique was applied to surfactant solutions,[8] and TEM images of molecular assemblies were correlated with the rheological behavior.[9,10] Since polymer solutions have never been investigated by cryo-TEM so far as author knows, this investigation should give new insight into polymer solutions.

EXPERIMENTAL

Sodium alginate and PEO are commercial products from Scientific Polymer Products, Inc., New York. Aqueous solutions of sodium alginate (3 wt%) and PEO (6 wt%) were prepared by dissolving polymer in water at *ca.* 60°C and cooling down to 25°C.

Cryo-TEM observation was carried out on a Hitachi H-800 electron microscope at 100 kV, according to a procedure described in literature.[8] A filmy drop of polymer solution on an electron microscope grid was vitrified by jet-freezing in cooled liquid ethane at its freezing point to avoid contamination by artifacts on the freezing process. The grid with the vitrified specimen was mounted on a Hitachi 5001-C cold stage and observed in TEM under liquid N_2 cooling.

RESULTS AND DISCUSSION

Figure 1 shows electron micrographs of sodium alginate and PEO solutions. Network

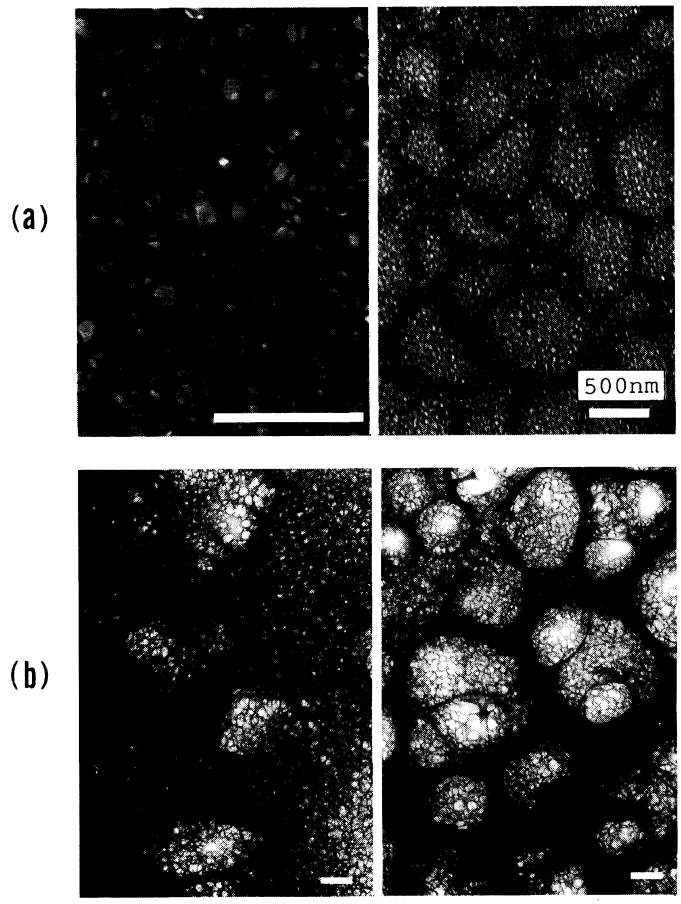

Figure 1. Electron micrographs of polymer solutions. (a), sodium alginate (3 wt%); (b), PEO (6 wt%). A bar is 500 nm.

images were observed for both polymer solutions. However, it may be noted that the networks are not homogeneous; thick network domains segregate from thin network domains. The segregation produces the "super-network" structure. Mesh size of the super-networks is ~ 500 nm and 1—2 μm across for sodium alginate and PEO, respectively.

Sodium alginate molecules form intermolecular linkages mediated by cations in water.[4,5] PEO chains form helical structures in water and link with each other through hydrogen bonding between polymer and water.[1-3,6] Such linkages are formed on parts of polymer chains and constitute junction zones. Thus, the networks consist of junction zones and free residues of polymer chains. It can be inferred that junction rich domains construct thick networks, and free residue rich domains result in thin networks. The segregated network domains form super-networks, as illustrated in Figure 2.

When a three-dimentional network structure is formed through intermolecular aggregation as discussed above, such linkage structure leads to viscous and viscoelastic behavior. Then the viscoelasticity displays long lifetime processes, and the motions of networks relax with long relaxation times.

Although storage and loss moduli of sodium

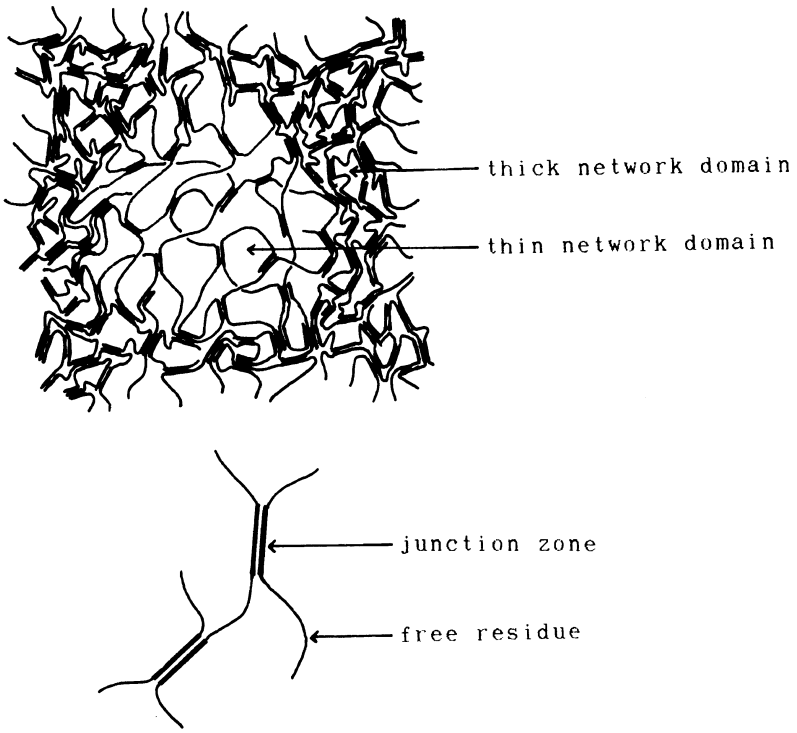

Figure 2. Schematic illustration of the "super-network" structure of polymer solutions.

alginate solutions gradually increased with angular frequency, the increase of moduli was much slower than expected for a Maxwell liquid.[11] In a spinnability experiment, sodium alginate solutions at low concentrations including 3 wt% and PEO solutions provided linear increase in length of liquid thread against the velocity of a rod.[7] Spinnability is an elastic deformation superposed on a viscous flow and is related to the pseudo-network formation. Then it may be presumed that the characteristics of the viscoelastic and spinnable solutions of sodium alginate and PEO are due to the "super-network" structure discussed in this work.

REFERENCES

1. K-J. Liu, *Macromolecules*, **1**, 213 (1968).
2. K-J. Liu and J. L. Parsons, *Macromolecules*, **2**, 529 (1969).
3. A. Sarkar and K. Ghosh, *Kolloid Z.-Z. Polym.*, **236**, 140 (1970).
4. E. R. Morris and D. A. Rees, *J. Mol. Biol.*, **138**, 363 (1980).
5. R. Seale, E. R. Moris, and D. A. Rees, *Garbohedr. Res.*, **110**, 101 (1982).
6. N. B. Graham, M. Zulfigar, N. E. Nwachuku, and A. Rashid, *Polymer*, **30**, 528 (1989).
7. K. Hashimoto and T. Imae, *Polym. J.*, **22**, 331 (1990).
8. J. R. Bellare, H. T. Davis, L. E. Scriven, and Y. Talmon, *J. Electron Microsc. Technique*, **10**, 87 (1988).
9. T. M. Clausen, P. K. Vinson, J. R. Minter, H. T. Davis, Y. Talmon, and W. G. Miller, *J. Phys. Chem.*, **96**, 474 (1992).
10. T. Imae, Y. Takahashi, and H. Muramatsu, *J. Am. Chem. Soc.*, **114**, 3414 (1992).
11. K. Hashimoto and T. Imae, *Langmuir*, **7**, 1734 (1991).