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Polymer 46 (2005) 3538
polymer
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Reply to the paper 'Comment on Gelation mechanism of agarose and κ-carrageenan solutions estimated in terms of concentration fluctuation' [Polym 2002;43:5299]

Their paper [1] as the comment to our paper [2] deals with the ESEM observation of agarose solution. The investigations by ESEM are still very few and they shall be expanded to polymer field, especially to study the crystallization mechanism from solution and melt state. Accordingly, I evaluate their work due to the importance to apply this new technique to polymer investigations. However, we believe that their comment [1] to our paper [2] is wrong.

First of all, our DSC measurements were carried out by using a solution pan whose exposed sample area is not larger as compared to its volume. Before putting the gel into the pan, the weight of pan was measured, and no weight change between the before and after the measurements was confirmed. The heating was done up to 90 °C to assure perfect dissolution of agarose chains as much as possible. Furthermore [1], when the sample pan was opened, it was confirmed that the gel still remains original state. In their comment, "Finally, it reaches a state where it can't be melt but burnt" is nonsense. As additional experiments, the pan was waved at ca. 90 °C to assure better resolution of agarose chains in solvent and set on DSC instrument kept at ca. 90 °C. The curve on the cooling process was confirmed to be similar to the curve shown in Fig. 5(a) in our paper [2]. Incidentally, DSC curves of agarose solution has no endotherm and exotherm peaks under heating and cooling process reflecting no existence of crystallites, which is different from the gelation mechanism of ultra-high molecular weight polypropylene (UHMWPP) solutions [3].

I am afraid that if their ESEM observation was done by using very thin thickness of solution, the surface tension for the 2.5% solution is thought to be very strong and furthermore the surface of their solution tends to dry up, due to evaporation of small amount of water under heating process. If this is the case, it is evident that no morphological changes at room temperature and 80 °C. The well-blended polymer/solvent mixture at 80 °C is the solution with high viscosity. Here, we must emphasize that when the mixture was put on the glass plate at 80 °C, the flow occurred.

In their other comment [1] to our paper [2], they quoted the paper by Bulone et al. [4]. We also agree that gel formation of crystalline polymer takes complicated steps and cross-linking points formed by very few amount of paracrystallites, whose diffraction peaks cannot be detected by X-ray measurement, plays an important role to form gel structure. The problem, however, is concerned with the different gelation behaviors between agarose and κ-carrageenan solutions. As shown in Figs. 1, 2, 7 of our paper [2], the logarithm plots of the scattered intensity increased linearly against time for agarose solutions, while for κ-carrageenan solutions the plots showed no change with elapsing time. Accordingly, it was concluded that the gelation of agarose is attributed to the phase separation due to the concentration fluctuation of the solution, while gelation of κ-carrageenan solutions is independent of liquid–liquid phase separation but is due to the cross-linking formation. Of course, we must point out that the driving force to form cross-linkings of ararose gels is attributed to the phase separation, since the cross-linking points appeared in the polymer-rich phase. Unfortunately, their comment is only the criticism of our paper [2] by quoting several papers [4,5].

Incidentally, we would like to refer to the more detailed explanation. To pursue the light scattering measurements, the solution in glass tube was prepared by heating the well-blended polymer/solvent mixture at 80 °C for 20 min under nitrogen. At that time, I was afraid that the agarose and κ-carrageenan chains are dissolved in distilled water perfectly at the above condition. The mixture at 80 °C, however, was inevitable to avoid a drastic convection and to obtain smooth data of the light intensity in the shorter time ca. <1 min.

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Received 1 September 2004 Received in revised form 9 December 2004 Accepted 7 February 2005

doi:10.1016/j.polymer.2005.02.066