

Nonisothermal Crystallization of a Defect-Free Polymer Network

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1 Introduction

It is well known that polymer networks can crystallize in spite of the fact that the translational motion of the constituting chains is limited by the network connectivity. Although there have been a number of reports on the crystallization of polymer networks [1, 2], crystallization might be affected by the topological defects such as loops and dangling chains that are inevitably incorporated in the randomly-crosslinked networks. Recently, Sakai and coworkers [3] found that a polymer network almost free of such topological defects could be prepared by end-linking of four-armed poly(ethylene glycol) (Tetra-PEG). In this study, we investigated the crystallization kinetics and structure formation during nonisothermal crystallization of a Tetra-PEG network to reveal the effects of network connectivity on polymer crystallization.

2 Experiment

A Tetra-PEG network (Fig. 1) was prepared by end-linking between two Tetra-PEG prepolymers having amine groups (TAPEG) and activated ester groups (TNPEG) at the chain-ends. Note that the solvent used in the end-linking process was completely removed from the sample prior to measurements. The molecular weight of each arm of the prepolymers was $5.0 \times 10^3 \text{ g mol}^{-1}$. Bulk TAPEG was also used as a control (Fig. 1). Time-resolved SAXS/WAXD measurements were conducted at the beamline BL-10C in KEK-PF. SAXS and WAXD profiles were collected during cooling from 80 °C (well above the typical melting temperature of PEG) to 10 °C at the rate of -5 °C .

3 Results and Discussion

Fig. 2 shows the development of the crystallinity of PEG chains obtained from time-resolved WAXD profiles of the network and prepolymer during cooling. The onset temperature of crystallization of the network is higher than that of the prepolymer. However, the slope of the curve, which roughly reflects the crystal growth rate, is lower for the network than for the prepolymer. These facts

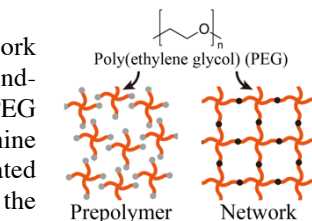


Fig. 1: Schematic illustration of the samples.

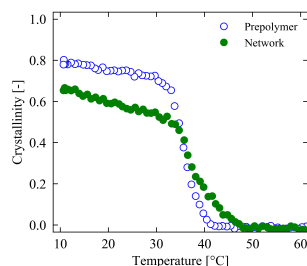


Fig. 2: Crystallinity of PEG chains during cooling.

suggest that network connectivity reduces the mobility of PEG chains and eventually accelerates the crystal nucleation but decelerates the subsequent crystal growth. Moreover, the final crystallinity of the network at 10 °C is significantly lower than that of the prepolymer, probably due to the reduced degree of conformational freedom of PEG chains imposed by network connectivity.

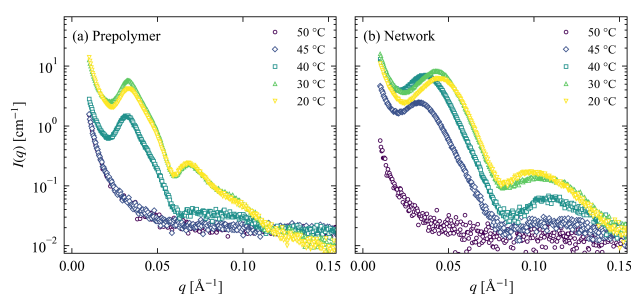


Fig. 3: SAXS profiles for the prepolymer (a) and network (b) during cooling.

Fig. 3 shows the SAXS profiles of the prepolymer and network during cooling. As soon as the crystallization begins, a peak emerges in both samples, indicating the formation of periodically stacked lamellar crystals. However, the change in the primary peak position q^* is different between the prepolymer and network. q^* of the prepolymer is almost constant at 0.035 Å^{-1} whereas that of the network gradually shifts to higher q during the nonisothermal crystallization process. The shift of q^* for the network suggests that the initially formed crystals are thicker than the thermodynamically stable one and hence slowly become thinner as the crystallization proceeds. It can be concluded that the thinning of the initially formed lamellar crystals is significantly retarded in the network compared to that in the prepolymer because of the reduced chain mobility by network connectivity.

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