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X-ray radiation effect on structure formation induced by radical copolymerization of poly(dimethylsiloxane)-α,ω-diacrylate and *N*,*N*-dimethylacrylamide

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Introduction

In-site measurement of polymerization-induced phase separation was conducted by synchrotron small angle X-ray measurement (SAXS). Reaction-induced phase separation generally proceeds from an initially homogeneous mixture (solution). Most of them, phase separation occurs via liquid-liquid phase separation except for solid-liquid separation to give regular structures during reaction if phase separation occurs via spinodal decomposition. When a reactive telechelic polymer or macromonomer having molecular weight of more than a few thousands is copolymerized with monomers whose polymer chain is immiscible with the telechelic polymer or macromonomer, it can be expected that the resulting copolymer shows inhomogeneity, e.g., indicating two glass transition temperatures which means phase separation occurs.

In this paper, we examined x-ray radiation effect on a structure formation of copolymer during measurement. The copolymer used here was comprising of PDMS-α,ω-diacrylate (telechelic polymer with M_n of 6,500) (PDMS-DA) (60wt%) and *N*,*N*-dimethyl acrylamide (DMAA) (4owt%) was investigated by *in-situ* SAXS during copolymerization.

Result

Mixture of PDMS-DA, DMAA, and V-65 (initiator 0.1wt%) was put into the reaction cell that was covered by Kapton films. Radical copolymerization was conducted on hot-stage of Linkam 10002 whose temperature was controlled within 0.1 K. *In-situ* SAXS measurement was conducted at BL9C and 15A. The sample was subjected to X-ray irradiation during the structure development. Long exposure time may damage the sample. As the polymerization temperature decreases, the generation rate of radical by decomposition of the initiator is diminished. In this way, the decreasing polymerization temperature requires a long time for a complete of the radical polymerization, resulting in long exposure time for observation of structure development. The structures generated under continuous X-ray exposure during the radical copolymerization were investigated at different polymerization temperatures. Figure 1a shows the temperature dependence of the characteristic domain size *d* (circles) and the correlation length ξ (triangles) which were obtained by analysis using Teubner--Strey model. Each scattering data was acquired on-position (open symbols) or off-position (filled symbols) of X-ray exposure after the polymerization completed. The different structural parameters between two cases are clearly seen in the case of lower polymerization temperatures. Different in ξ decreased above 335 K. The influence of X-ray irradiation on the structure formation was found to diminish considerably because of short exposure time of X-rays, but an unfavorable effect still remained. The X-ray beam was attenuated using an aluminum plate. The sata were collected on- and off-positions of the exposure at 338 K. The experimental condition at the 100% intensity is the same as that of in situ SAXS experiment at 338 K. Each structural parameter was slightly different but within an experimental error. The parameters obtained from the position without exposing of X-rays were independent of incident X-ray intensity. With reduction in intensity of X-rays, the domain spacing obtained from the X-ray exposure position decreased. It was confirmed that the X-ray irradiation eventually had no effect on the structure if X-ray intensity was appropriately controlled. However, the 0.1% of intensity in our experiment is extremely faint so that a time-resolved SAXS measurement cannot be conducted any longer. Although the unfavorable effect remained in the experiment at 338 K, the difference in the structural parameters was considered to be trifling. Thus, the experimental result on 338 K in this study is reliable to discuss the mechanism of structure development.

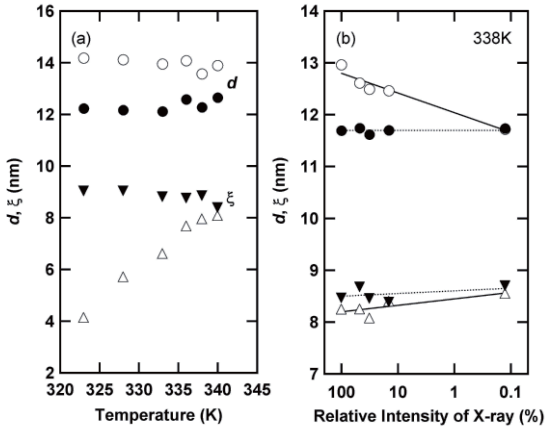

Figure 1. Structure parameters

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