

## Phase Separated Co-network Structure Induced by Radical Copolymerization of Poly(dimethylsiloxane)- $\alpha,\omega$ -diacrylate and *N,N*-Dimethylacrylamide

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### Introduction

Study on phase separation induced by polymerization of components in initially miscible mixture has been widely reported. Polymerization-induced phase separation occurs in multicomponent system such as polymerization monomer/polymer mixture, sol-gel reaction, and formation of rubber-modified epoxy resin, polyurethane form, thermoplastic/thermoset polymer alloy and polyester elastomer. *In-situ* measurement of polymerization-induced phase separation was conducted by some researchers using light scattering, synchrotron small angle X-ray measurement (SAXS), Rheological measurement, and FT-IR measurement. 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. Such a phase separation is caused by an increase in the molecular weight of the polymer and by the change in the interaction with monomer conversion. These changes in the course of reaction have the system crossing thermodynamic phase boundaries and result in a transition from homogeneous to a phase-separated state. 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, the structure formation of copolymer comprising of PDMS- $\alpha,\omega$ -diacrylate (telechelic polymer with  $M_n$  of 6,500) (PDMS-DA) and *N,N*-dimethyl acrylamide (DMAA) was investigated by *in-situ* SAXS during copolymerization in order to discuss mechanism of the phase separation induced by radical copolymerization.

### Experimental

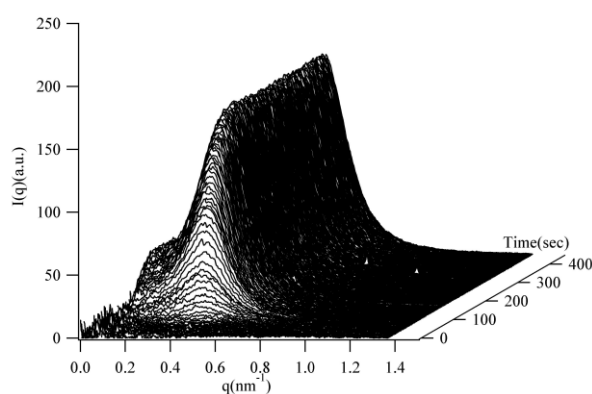
#### *In situ* SAXS measurement

First, PDMS-DA (60wt%), DMAA (40wt%), and V-65 (0.1wt%) were mixed and the mixture was put into the reaction cell (thickness of 1 mm and inner diameter of 8

mm) that was covered by Kapton films (thickness of 12  $\mu\text{m}$ ). Radical copolymerization was conducted on hot-stage of Linkam 10002 (Japan high-tech, Co., Ltd.) whose temperature was controlled within 0.1 K. *In-situ* SAXS measurement was conducted at BL15A.

### Result

Mixture of PDMS-DA and DMAA was transparent and homogeneous, which gave no peak in SAXS profile (Figure 1). The radical copolymerization of both initiated at 303 – 368 K was successfully done to form fully transparent objects and they indicated peaks in SAXS profiles which means the resulting polymers had a periodic structure. The analysis of time evolution of the SAXS profiles (*in site* measurement) revealed that the phase-separation occurred via spinodal decomposition mechanism. The structure was fixed by solidification of the sample due to cross-linking and glass transition during reaction-induced phase separation. The final structure was interpreted fairly using Teubner-Stray model. Thus, the final structure of the PDMS-DA/DMAA copolymer sample was found to be bicontinuous and periodic structure (co-network) in nanometer scale, which was also confirmed by TEM.



**Figure 1** Time-resolved SAXS profiles of PDMS-DA/DMAA during copolymerization at 338K.

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