Giant Spherulite Formation in Amorphous Polyanion Membrane by Photopolymerization on Gelatin Matrix

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In-bulk photopolymerization of 2-acylamido-2-methylpropanesulphonic acid (AMPS) on gelatin matrix was made by ultraviolet irradiation at room temperature to form the crystalline and flexible membranes with giant spherulites (maximal radius: 2.2 cm). Number- and weight-average molecular weights of PAMPS were 79,500 and 138,000, respectively. The melting point of the membrane was around 200 °C. The giant spherulite formation was discussed on the basis of the PAMPS chain formation and PAMPS/gelatin complexation.

Polymerization accompanied by the self-organization has attracted researcher's attention to develop organic nanoparticles[1] and synthetic metals.[2] However, the solution environment appropriate not to monomer organization but to polymer chain organization was difficult to establish in polymerization system.[3] On the other hand, electrostatic complexation of polyanions and polycations occurred very efficiently owing to the side-by-side alignment of ionic groups on a polymer chain backbone even if corresponding monomers oppositely charged each other never assemble. Sometimes the cooperative self-assembly in the polyelectrolyte system induced to form a regularly organized structure.[4]

Solid-state polymerization (SSP) reactions induced by light irradiation have been reported.[5–7] Various polymers such as poly(methacrylamide)[8] and poly(dimethacrylate)[9] were obtained through the SSP. Poly(2-acylamide-2-methylpropanesulphonic acid) (PAMPS) polymers which was a very popular polyanion in hydrogel materials was obtained by conventional free radical polymerization.[10] However, PAMPS membrane is difficult to prepare because of high hygroscopicity. In the study, we made a unique approach of the solid-state photopolymerization to prepare the crystalline membrane in complexation of PAMPS with gelatin. Moreover, the polymerization induces the gradual spherulite growth in membrane to form giant concentric circle textures.

The typical synthesis procedure of PAMPS polymer via solid-state photopolymerization method was shown as follows. Aqueous solution (50 wt %) of AMPS monomer (10 g, WAKO pure chemical Co., Ltd.) and photoinitiator Darocure 1173 (0.1–0.3 g, Ciba Company) were mixed with aqueous gelatin solution (10 wt %, 25–40 g). The mixed solution was spin-cast on the glass surface and dried. Macroscopically separated bilayer (layer thickness: 0.5 mm) was formed; the upper translucent layer (thickness: 0.2 mm) included monomer crystals, the lower transparent one (thickness: 0.3 mm) mainly included gelatin. Then, ultraviolet (UV; high-pressure Hg-lamp, $\lambda > 250$ nm, 130 mW cm^{-2}) was irradiated over the solution for about 5 min. After irradiation, a flexible membrane was prepared, and bilayer structure and each thickness were kept. On the other hand, the monomer crystals (Figure 1) became invisible, instead, concentric circle textures with a maximal radius of 2.2 cm appeared as shown in the left photo of Figure 2. The membrane was easily peered out of the glass surface by a scalpel without breaking. A surface part of the upper layer was also shaved by the scalpel for measuring the polymer characterization.

The polymer structures were investigated by Fourier-transformed infrared spectroscopy (FTIR; FTLA2000-104), gel permeation chromatography (GPC; HLP-8120, polystyrene as standard in dimethylformamide), polarized light microscopy (PLM; Olympus BX51) and wide-angle X-ray diffraction {WAXD; Ni-filtered Cu Kα ($\lambda = 0.154$ nm), RINT 2000, Rigaku}. FTIR spectra of the upper layer surface showed no double-bond absorption (1615 cm^{-1}) which was detected in the spectrum of AMPS monomer, showing that in-bulk photo-

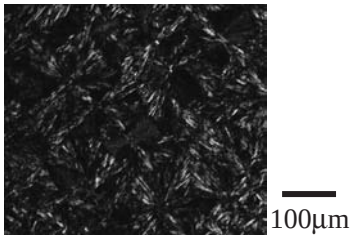

Figure 1. Polarized microscopic image of the monomer mixture before photopolymerization in the presence of gelatin matrix.

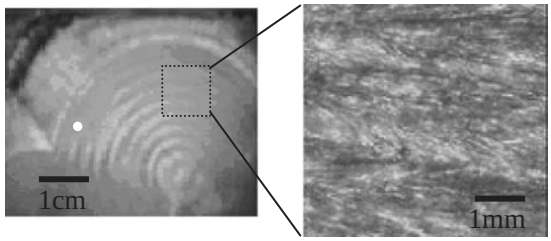

Figure 2. Optical images of spherulites generated as a result of AMPS photopolymerization in the presence of gelatin (left) and right image is close-up view by a polarized microscope. White circle (about 1 mmϕ) indicates the X-ray irradiated spot.

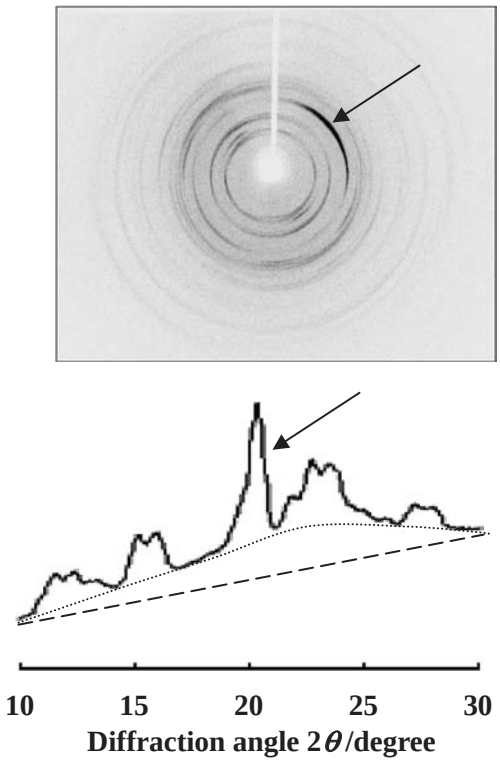

Figure 3. WAXD patterns of spherulites generated as a result of AMPS photopolymerization in the presence of gelatin matrix. Upper photo is X-ray diffraction image of the portion marked as the white circle in Figure 2. Lower diagram is the intensity profile obtained by circular averaging of the upper photo (dash line: amorphous halo, alternate short and long dash line: baseline). Arrows indicate the main diffraction used for orientation-degree determination.

polymerization successfully proceeded by UV-light irradiation for 5 min. Number-average molecular weight (M_n) and weight-average molecular weight (M_w) of PAMPS were 79,500 and 138,000 g/mol, respectively.

The right picture of Figure 2 shows PLM image of the spherulite. The picture showed an extinction ring contrast but the stripe line was very wide (about 1 mm). Although entire spherulite figures were unable to take using the microscopic view in one-shot, we observed the spherulite texture typical of the crystalline polymers by sliding the sample stage. The Maltese cross was slightly observed and the spherulite boundary was very clear. In order to investigate the spherulite structure, WAXD image of the spherulite surface sample was taken (top of Figure 3). This image did not showed nonoriented Debye–Scherrer ring but many diffraction arcs between $2\theta = 5$–40° (θ: diffraction angle), indicating the sample orientation. The orientation degree was calculated as 0.70 using the strongest diffraction arcs at $2\theta = 20.1^\circ$. The bottom pattern of Figure 3 is the intensity profile obtained as a result of circular averaging of the top image, showing more than 10 diffraction peaks. The main peaks appeared at $2\theta = 12.1$, 15.6, 20.1, 22.7, and 27.0° corresponding to d spacings of 0.73, 0.57, 0.44, 0.39, and 0.33 nm. This diagram demonstrates that the membrane is highly crystallized (crystallization degree: 61%). The spherulite melting occurred at about 200 °C on the heating scan of DSC.

Although PAMPS was an amorphous polyanion, PAMPS formed the well-organized complex with cationic amphiphiles, showing a few diffraction peaks.[11] Gelatin is amphiphilic and might be positively charged by high proton concentration from AMPS sulfonate groups. Then, PAMPS may form crystalline ionic complexes with cationized gelatins. The spherulites generally become large as a result of their slow growth.[12] The present phenomenon of such a giant spherulite formation in a short time (5 min) is very unique. Here, we discuss the phenomenon. When monomer solution was dried, most of AMPS was separated to form the upper layer presumably because of lowering the surface tension since AMPS has much lower molecular size than gelatin. UV irradiation induced very rapidly to form the polymer chains which can deposit on the cationic gelatin surface to create the spherulite nucleus. The number of the polymer chains can be increased gradually with the polymerization progressing according to the polymerization theory, and then the amount of deposited chains can increase gradually. If the PAMPS chains attach predominantly on the edge of the spherulites with the aid of the interchain interaction, the spherulite can grow as rapidly as the polymerization progress.

Thus, the solid-state photopolymerization of AMPS on gelatin matrix creates the crystalline and flexible membrane with giant spherulites. This polymerization technology hybridized with electrostatic complexation provides a new method for the acquirement of concentrically or divergently oriented membranes.

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