Polymer Network Fabricated by Topochemical Polymerization of Self-assembly Films Composed of a Diacetylene Derivative

Kaori Sasada, Yuko Nishiwaki, Yuko Takeoka,*[†] Masahiro Rikukawa, and Kohei Sanui
Department of Chemistry, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554
[†]*PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Hon-cho, Kawaguchi 332-0012*

Well-ordered layered structures prepared by the self-assembly method using condensing agents better facilitate the γ-ray polymerization of diacetylene units.

Creation, combination, and reorganization of nanostructures within organic thin films are of great interest in material science studies. Well-ordered organic thin films with nanometer scale thicknesses have been produced mostly by vaccum deposition, Langmuir–Blodgett technique, and self-assembly method. In particular, self-assembly methods are attracting much attention as simple operations to manipulate large area membranes for possible commercial use. The most typical self-assembly method is thin film deposition based on layer-by-layer self-adsorption of positively and negatively charged polyelectrolytes.[1] In spite of the ease of preparation, structure, and properties such as thickness, charge density, and porosity can be controlled on the nanoscale level. This approach, however, is limited to a certain extent by the poor solubility, functionality, and thermal and chemical stability of polyelectrolyte materials. For example, the molecular orientation of polyelectrolytes is nearly random and provides a relatively narrow window for fundamental researches to understand the relationship between structure and properties. In order to overcome this limitation in the self-assembly method with polyelectrolyte materials, we have been investigating the solid-state polycondensation in the self-assembly films.[2] Utilizing the solid-state polycondensation provides a higher level of versatility and processability in the self-assembly films, due to the favorable choices of film components and compositions. For example, ultra-thin films with cationic diamine and anioic dicarboxylic acid layers can be successfully fabricated by a conventional solution-dipping method of their aqueous solutions, as shown in Figure 1a. Upon the additional dipping in a condensing agent solution, the dicarboxylic acid and the diamine molecules in each layer undergo polycondensation during the dipping process (Figure 1b). It should be possible in principle to fabricate polyamide thin films with excellent control over molecular orientation and various choices of their components without the use of polyelectrolytes.

Polydiacetylene, which is well known for its high electrical conductivity and high third-order nonlinear optical properties,[3] is obtained by the radiation polymerization of diacetylene derivatives. The radiation polymerization occurs as a kind of topochemical reaction when diacetylene-containing molecules are aligned in a definite molecular configuration, which is caused by mechanical stretching and molecular templates.[4,5] In this study, to examine if our polycondensed self-assembly method results in a specific molecular organization for sophisticated polymerizations, we explored in detail the role that the polycondensed self-assembly method plays in determining the radiation polymerization.

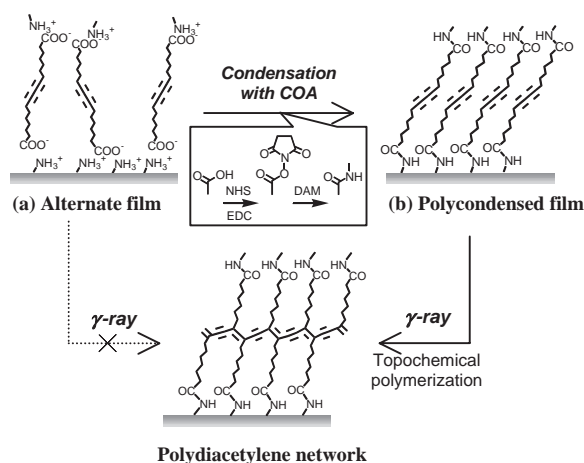Polycondensed films containing diacetylene moiety were

Figure 1. Model of solid-state polymerization of diacetylenes in DDyDA/DAM self-assembly films.

fabricated from 9,11-docosadiyn-1,20-dicarboxylic acid (DDyDA) and 4,4′-diaminodiphenylmethane dihydrochloride (DAM). 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDC) and *N*-hydroxysuccinimide (NHS) were used as condensing agents. Positively charged quartz substrates prepared with 3-diethoxymethylsilylpropylamine were first dipped into a 20 mM DDyDA aqueous solution (pH 11.5) for 1.5 h. After immersing in deionized water for 30 s to remove excess DDyDA, dipping into a mixed aqueous solution of 15 mM NHS and 75 mM EDC for 1.5 h (as abbreviated COA aqueous solution, pH 7.0) followed, and then rinsing with deionized water. The substrates, in turn, were dipped into an aqueous solution containing 20 mM DAM (pH 4.0) for 1.5 h, and then rinsed with deionized water. No drying step was used in this procedure. The multilayer deposition of each molecule was monitored by UV–vis absorption spectroscopy, quartz crystal microbalance (QCM) and FT-IR reflection–absorption spectroscopy (RAS). DDyDA/DAM alternate thin films without the COA deposition were also preparerd for comparison. The radiation polymerization of DDyDA/DAM films was carried out using a [60]Co γ-source (dose rate 16.1 kGy/h).

To optimize the condition of the film preparation, we investigated adsorption behavior of each monomer (DDyDA, DAM, and COA) by QCM. Remarkable frequency changes occurred as a substrate was immersed into each solution. Since the frequency changes reached a constant value after 60 min, and the deviation of the frequency changes was nearly negligible after 90 min, we determined that the dipping time should be 90 min. A linear increase in the film mass ($-\Delta F$ is proportional to mass) for all the dipping process was also confirmed by QCM.[6] The averaged adsorption of DDyDA and DAM were calculated from the averaged ΔF values to be 61.2 and 20.8 ng cm^{-2}, respectively. These results supported the reproducible deposition of each
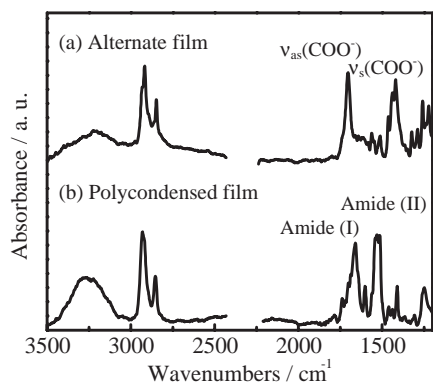
Figure 2. FT-IR spectra of (a) DDyDA/DAM alternate and (b) polycondensed films with 20 layers.

monomer. Figure 2 shows the FTIR-RAS spectra of (a) alternate and (b) polycondensed thin films with 20 layers. Alternate films show COO^- asymmetric and symmetric vibration bands at 1703 and 1438 cm^{-1} with an NH_3^+ deformation band at 1562 cm^{-1}. This results show that the alternate films was formed by electrostatic interaction between DDyDA and DAM. On the other hand, DDyDA/DAM polycondensed film exhibited the amide I band at 1659 cm^{-1} and the amide II band at 1531 cm^{-1}. These results indicated that amide bonds were formed between carboxylic acid groups of DDyDA layer and amine groups of DAM layer by using the condensing agents. The mechanism of the amide formation is depicted as follows. When a film with DDyDA as the outermost layer is dipped into a mixed solution of NHS and EDC, the NHS esters of DDyDA form. Then displacements of the NHS group by the amines of DAM and the adsorption of the DAM layer occur as the film was immersed into a DAM solution, as shown in Figure 1.

The polycondensed films containing a diacetylene derivative changed from colorless to red after γ-ray irradiation. Figure 3 shows the optical absorption spectra of a DDyDA/DAM polycondensed film before and after the γ-ray irradiation (15 Mrad). After γ-ray irradiation, a broad peak due to the existence of the π–π^* transition of polydiacetylene appeared at around 546 nm. The wavelength of the π–π^* transition band was in agreement with that of the red-phase.[7] This implies that topochemical polymerization within the polycondensed films containing a diacetylene moiety successfully occurred and that new π-conjugated backbones were formed via the γ-ray irradiation. G. Wenz et al. and other researchers have reported a method of estimating conjugation length from the observed solid-state absorption peak of the π–π^* transition.[8] The conjugation length of polydiacetylene backbones was estimated to be about 20 monomer units by fitting the absorption data obtained for the polycondensed films to their model. In addition, the absorption of π–π^* transition showed a polarized anisotropy, exhibiting that the polydiacetylene backbones oriented parallel to the film surface. The resonance Raman spectrum of the polycondensed films after γ-ray irradiation is shown in Figure 4. The bands assigned to the unsaturated double and triple bond stretching vibrations in polydiacetylene backbone were observed at 1477 and 2029 cm^{-1}, respectively. According to the report by G. Wenz et al., it is also possible to estimate the conjugation length of the polydiacetylene backbones from the significant diminution in frequency of these bands relative to isolated double and triple bonds (1620 and 2260 cm^{-1}, respectively).[8] From the frequency shift of double bond vibrations observed in
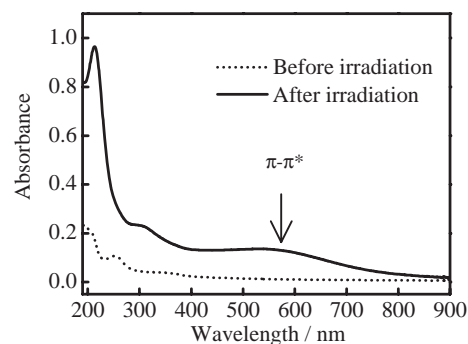

Figure 3. UV–vis absorption spectra of a DDyDA/DAM polycondensed film with 50 layers before and after γ-ray irradiation (15 Mrad).
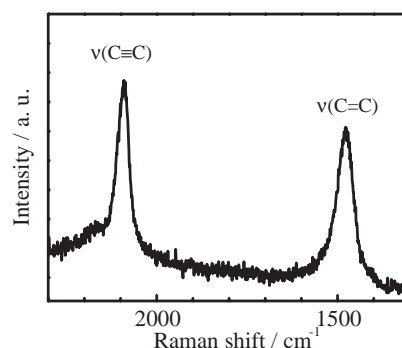

Figure 4. Resonance Raman spectrum of a DDyDA/DAM polycondensed film after γ-ray irradiation (15 Mrad).

Figure 4, the conjugation length was also determined to be 21 monomer units. This result is in excellent agreement with that obtained from the UV–vis absorption measurements.

To explore the spatial effect of polycondesed films as a molecular template, we also tried the radiation polymerization of DDyDA/DAM alternate films prepared by the above method without any dipping step of the condensing agent. These DDyDA/DAM films exhibited no change in UV absorption and Raman spectra after γ-ray irradiation, indicating that the topochemical polymerization does not occur in the DDyDA/DAM unpolycondensed films. The different reactivitites between the two reflects the fact that there is less molecular organization that can promote the topochemical polymerization in the DDyDA/DAM unpolycondensed film. In contrast, the DDyDA molecules in the DDyDA/DAM polycondensed films orient well and tightly pack in a favorable manner for γ-ray polymerization. As demonstrated here, self-assembly films with high molecular organization of functionalized polymer materials can be produced by using only our simple chemical adsorption process.

References
1   Y. Lvov, G. Decher, and H. Moewald, *Langmuir*, **9**, 481 (1993).
2   Y. Nishiwaki, Y. Takeoka, M. Rikukawa, and K. Sanui, *Synth. Met.*, **137**, 931 (2003).
3   A. Sarkar, S. Okada, H. Nakanishi, and H. Matsuda, *Macromolecules*, **31**, 9174 (1998).
4   "Polydiacetylenes," ed. by D. Bloor and R. R. Chance, Martinus Nijhoff, Dordrecht (1985), p 1.
5   B. Tieke, G. Wegner, D. Naegele, and H. Ringsdorf, *Angew. Chem., Int. Ed. Engl.*, **15**, 764 (1976).
6   T. Serizawa, S. Kamimura, N. Kawanishi, and M. Akashi, *Langmuir*, **18**, 8381 (2002).
7   K. Kuriyama, H. Kikuchi, and T. Kajiyama, *Langmuir*, **14**, 1130 (1998).
8   G. Wenz, M. Muller, M. Schmidt, and G. Wegner, *Macromolecules*, **17**, 837 (1984).