Structures in the Solid-state and in the Organized Molecular Films of Comb Copolymers Containing *s*-Triazine Ring

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Structures in the solid state and in the organized molecular films of comb copolymers containing 2-vinyl-4, 6-diamino-*s*-triazine (VDAT) were investigated using X-ray diffraction (XRD), differential scanning calorimetry (DSC) and surface pressure-area (π-A) isotherm measurements. The comb copolymers used in this study were synthesized by co-polymerization of fluorinated or hydrogenated long-chain vinyl compounds and VDAT with AIBN initiator in acetone solution. From the results of XRD and DSC, these copolymers formed side-chain crystals in the bulk states. Fluorinated comb copolymers had a short spacing of 5.0 Å for the two-dimensional side-chain lattice whereas hydrogenated polymers formed sub-cell structure at a lattice spacing of 4.2 Å
These comb copolymers formed stable condensed monolayers on the water surface estimated by π-A isotherms. The molecular arrangement of Langmuir-Blodgett film of comb copolymers corresponded well to that of bulk state from the results of in-plane XRD measurements.

Key words: 2-vinyl-4, 6-diamino-*s*-triazine, Comb copolymer, Side-chain crystal, Organized molecular films, Two-dimensional lattice

1. INTRODUCTION

Recently, many researchers have attempted to utilize poly-2-vinyl-4, 6-diamino-*s*-triazine (PVDAT) such as agricultural chemicals, a weed-killer agent and a candidate for drag delivery system[1] because PVDAT exhibits selective ion capturing properties and self-aggregated properties.[2] Further, PVDAT is expected to be used as an absorbing material to DNA molecules.[3]

On the other hand, it is essential to control the molecular orientation and the arrangement at the monomolecular level in order to drive these organic molecular recognizing sensors in an efficient manner. However, in many cases, it is difficult to control the molecular arrangement and the homopolymer packing because PVDAT itself readily forms an amorphous polymer.[4]

In the previous study, we have investigated to control solid-state structures and the formation of organized films of newly synthesized comb copolymers containing hydrogenated and fluorinated side-chains.[5] These comb polymers form a side-chain crystal in the bulk state due to the van der Waals interaction between the side-chains, and extremely stable condensed monolayers at the air/water interface. The incorporation of bulky and flat functional groups in the main-chains of 'side-chain crystalline polymers' may enable us to control the arrangement of bulky groups at the monomolecular level, regardless of the low crystallinity of the polymers.

In this study, fine structures in the solid-state of synthesized comb polymers containing 2-vinyl-4, 6-diamino-*s*-triazine (VDAT) in the main chains obtained by co-polymerization with hydrogenated or fluorinated long-chain compounds were investigated using wide-angle X-ray diffraction.

Further, the molecular arrangement of the organized molecular films of comb copolymers containing VDAT units was estimated using in-plane X-ray diffraction.

2. EXPERIMENTAL

2.1 Materials

The comb copolymers used in this study were obtained by the copolymerization of VDAT with octadecyl acrylate (OA) or 2-(perfluorodecyl)ethyl acrylate (FF$_{10}$EA) at various monomer ratios. Copolymerizations were carried out in an acetone solution at 50 °C for 48 h using 1 mol% azobisisobutyronitrile (AIBN) as an initiator. These monomers and the initiator were purchased from Tokyo Kasei Co. Ltd. and Daikin Fine Chemicals Co. Ltd., and were used without further purification. The precipitated polymers were washed with acetone until they were free of monomers. The syndiotactic poly-FF$_{10}$EA homopolymer was obtained from a 1 M rad ^{60}Co γ-ray irradiated post-polymerization according to the procedure described in the previous work.[6] The γ-ray irradiation was carried out at the Japan Atomic Energy Institute at Takasaki. The comb copolymer compositions were determined by ^{1}H NMR (Nihon Densi Co. Ltd. EX270 NMR) spectroscopy. The tacticity of fluorinated homopolymer obtained by ^{1}H NMR analysis according to the reference was found to be almost syndiotactic (Diad: 58 %). The molecular weights of several copolymers at higher ratios of OA units were estimated to be approximately $\overline{Mw}$ = 2.02 × 10^4 ($\overline{Mw/Mn}$ ≈ 1.01) on the basis of GPC (JASCO-860-CO) measurements. The molecular weights of fluorinated homopolymers and copolymers at higher ratios of FF$_{10}$EA units were estimated to be above thousand. These values were estimated from the intrinsic viscosity [η],

which is equal to 0.12~0.54, for these trifluoroacetic acid solutions at 30 °C by using the relation $[\eta] = KM^{\alpha}$, where $K = 0.24$~0.25×10^{-4} and $\alpha = 0.75$~0.78. The values of K and α were assumed from the results of the viscosity-averaged molecular weight of poly-alkyl acrylate.[7]

According to the theory of the Q-e scheme proposed by T. Alfrey and C.C. Price,[8] these comb polymers form random copolymers. In this case, the e values of VDAT and OA are 0.59 and 1.12, respectively.

2.2 Structural estimation of bulk copolymers.

The packing modes of several copolymers in the crystalline phases were examined by X-ray powder diffraction measurements using a Rigaku Rad-rA diffractometer, which was equipped with a graphite monochrometer, with Cu$K\alpha$ radiation at 40 kV and 200 mA.

Thermal analyses were carried out by using a Seiko Instruments model DSC200 differential scanning calorimeter (DSC). The DSC measurements were performed at a standard scanning rate of 10.0 °C min^{-1}. A sample mass of *ca.* 2.00 mg was used for all the DSC measurements. As usual, the scanning of DSC measurements and the heating and cooling cycle were repeated twice in order to examine the difference between the peak position and transition enthalpy in the first and second heating.

The layer structure of the copolymers was characterized with a SAXS instrument (M18XHF, MAC Science Co.) comprising an 18 kW rotating-anode X-ray generator with a Cu target ($\lambda = 0.154$ nm) operated at 50 kV and 300 mA. This instrument was equipped with a pyrographite monochromator, a pinhole collimation system ($\phi \sim 0.3$, 0.3, 1.1 mm), vacuum chamber for the scattered beam path, and a two-dimensional imaging plate detector (DIP-220). The sample-to-detector distance was adjusted to 710 mm. The exposure time for each sample was 30 min.

2.3 Formation of copolymer monolayers on water surface and estimation of molecular arrangement in the films.

The comb copolymers with VDAT were spread from chloroform solutions or chloroform/trifluoroacetic acid = 90/10 (v/v) mixed solutions (about 10^{-4} M) onto the distilled water (about 18 MΩ·cm). The surface pressure–area (π–A) isotherms of the polymers were measured on a film balance (Kyowa Kaimen Kagaku Co. Ltd., compression speed: 5 Å^2/repeating units · min) at 15 °C. These fluorinated comb copolymers formed extremely condensed monolayers. These monolayers were transferred to the solid substrates at 15 °C and at a proper surface pressure by the Langmuir-Blodgett (LB), and horizontal lifting method (HLM) to obtain alternating Y-type films and the
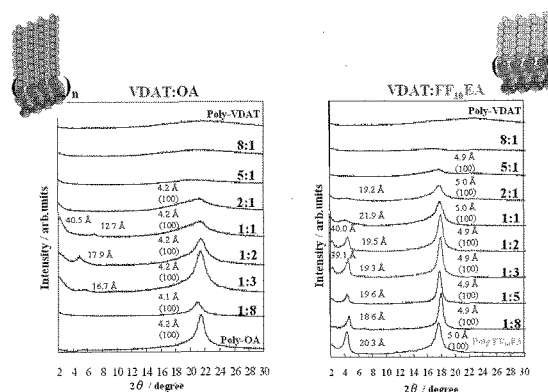

Figure 1 XRD profiles of comb copolymers containing VDAT at various monomer ratios. (a)OA:VDAT, (b)FF$_{10}$EA:VDAT copolymers.

nonalternating X- films, respectively.

The in-plane spacings of the two-dimensional lattice of the films were determined by analyses using an X-ray diffractometer for different geometrical arrangements (Bruker AXS, MXP-BX, Cu$K\alpha$ radiation, 40 kV, 40 mA, an instrument specially made to order) equipped with a parabolic graded multilayer mirror. The monomolecular level resolution of this in-plane XRD apparatus was realized by applying X-ray at an incident angle of 0.2° and by slow scanning at 0.05°/20 s.

3. RESULTS AND DISCUSSION

3.1 Estimation of fine structures for comb copolymers in bulk state.

Figure 1 shows the WAXD profiles of the comb copolymers containing VDAT at various monomer ratios. From these profiles, we recognized systematic changes in the short-spacing regions with the ratios. Further, we concluded that PVDAT forms an amorphous polymer judging from the appearance of halos and the absence of any peaks.

From the profiles of poly-OA and poly-FF$_{10}$EA, short spacing peaks based on the sub-cell formation of side-chains were confirmed at 4.2 and 5.0 Å, respectively. According to Platé's review, these peaks correspond to (100) reflections.[9] The appearance of these (100) peaks in the side-chain hexagonal lattices in copolymers means the formation of side-chain crystalline polymers. In both systems, copolymers at a ratio of VDAT : side-chain = 2:1 and at lower ratios of VDAT form the side-chain crystals. The shapes of transition peaks in DSC thermograms are important evidence of formation of the side-chain crystals. In comparison with general crystalline polymers, the shapes of melting and crystallization peaks of the side-chain crystalline polymers are relatively sharp, indicating its higher thermal capacity.

In the small angle region of WAXD profiles, long spacing peaks are evident in the profile of poly-FF$_{10}$EA at approximately 20.3 Å, whereas no peaks are present in the low angle side in the profile of poly-OA. Poly-FF$_{10}$EA
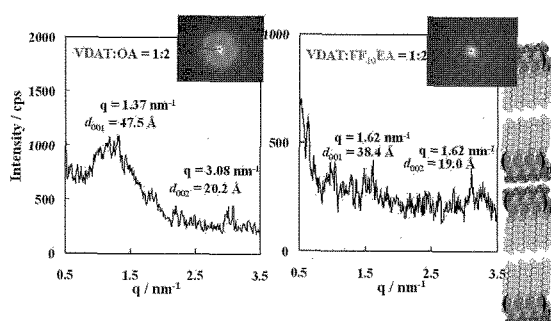
Figure 2 SAXS patterns and profiles of (a) VDAT : OA copolymers and (b) VDAT : FF$_{10}$EA copolymers at 15 °C.

forms a highly ordered layer structure along the direction of the c-axis. In accordance with the previous work, these long spacing peaks should be due to the (002) reflections[6] because poly-FF$_{10}$EA forms a double layer structure and the calculated length of the fluorocarbon side-chain is estimated at approximately 20 Å. Based on computer simulation estimations, the d-spacing from the (001) reflection peak of poly-OA was expected to be approximately 50 Å (double layer spacing), although poly-OA did not form a layer structure.

　　Figure 2 shows the SAXS patterns and profiles of VDAT : OA=1:2 and VDAT : FF$_{10}$EA=1:2 copolymers in bulk as typical examples. These results suggest the formation of double layer structures of both series of copolymers. In the VDAT : OA copolymer system, the (001) peak appears at 47.5 Å which corresponds to the double layer spacing. VDAT : FF$_{10}$EA=1:2 copolymers also form double layer structures with a spacing of 38.4 Å. The peak intensities SAXS shows differences in electron density of the samples, in the present case, the difference between the density of crystalline and amorphous regions. The SAXS peak intensities of VDAT : FF$_{10}$EA copolymers are extremely low. Although side-chains and main-chains in the polymers of this type generally correspond to crystalline and amorphous regions, respectively, relatively high density may be formed in main-chain region including VDAT units.

　　These XRD profiles indicate the possibility of the structural control of bulky functional groups related to the formation of side-chain crystals and their crystallinity reflected in the peak width. These results contain very important and clear information on the formation of side-chain crystalline polymers with two-dimensional sub-cell structures.

3.2 Molecular arrangement of organized molecular films of comb copolymers.

　　On the basis of these experimental results in bulk state, we attempt to utilize the comb copolymers containing VDAT units as the material for the formation of monolayers on the water surface. Figure 3 show the surface pressure–area (π–A) isotherms of the VDAT:OA
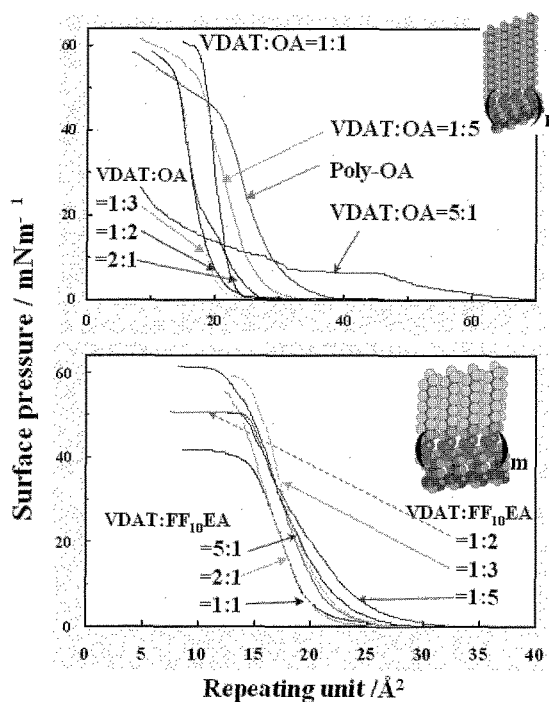

Figure 3 π–A isotherms of monolayers on the water surface of (a) VDAT : OA copolymers and (b) VDAT : FF$_{10}$EA copolymers at 15 °C.

and VDAT:FF$_{10}$EA copolymers, respectively, on distilled water at 15 °C. It is evident that these comb polymer monolayers are stabilized considerably and form condensed films, except the VDAT:OA=5:1 copolymer.

　　Figure 4 shows the in-plane X-ray diffraction profiles of several transferred films (20 layers) of comb copolymers containing VDAT. These profiles indicate the packing mode of side-chains in the organized molecular films of the copolymer systems. In the case of the VDAT:OA copolymer multilayers in the left columns of Fig. 3, all two-dimensional lattices form hexagonal packing at a lattice spacing of 4.2 Å in hydrogenated copolymer films. These values are almost identical to those obtained from the powder XRD profiles in the bulk state. Therefore, these data indicate that the packing mode of the side-chain crystal of a two-dimensional film is nearly the same as that of the three-dimensional crystal.

　　Here, very interesting results are shown in the profiles of VDAT:FF$_{10}$EA copolymer system. Organized molecular films of almost all VDAT:FF$_{10}$EA copolymers show the packing different from that in their bulk states. At high FF$_{10}$EA ratios, hexagonal packing is formed at a lattice spacing of 5.0 Å. However, the in-plane XRD profiles of the VDAT:FF$_{10}$EA = 1:2 and 1:1 copolymer films exhibit two kinds of short spacing peaks at 4.2 and 5.0 Å. From this result, it is inferred that a distorted orthorhombic packing of a side-chain lattice is formed. At high VDAT ratios, an isotropic hexagonal packing for a two-dimensional lattice spacing of 4.2 Å is constructed although the value of 4.2 Å
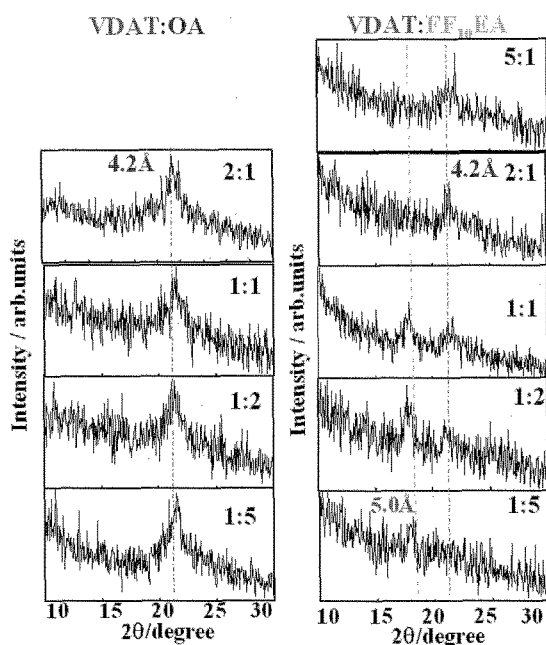
Figure 4 In-plane XRD profiles of LB multilayers of comb copolymers containing VDAT (20 layers).

Figure 5 Schematic models of structural formation for comb copolymers with VDAT.

is generally too small to pack fluorocarbons in lattice.

In order to interpret these phenomena, we propose schematic models in Fig. 6. We assume that the structural changes in fluorinated copolymers are caused due to the competition between the forces that are effective in two- and/or three-dimensional crystal, namely, the "weak van der Waals interaction between fluorocarbons" and the "relatively strong π–π interaction between s-triazine rings." Therefore, these polymer molecules are rearranged by the π–π interaction between the s-triazine rings at the air-water interface or during the transfer to the solid substrates. The side-chain packing should change with the rearrangement of the s-triazine groups. The spacing between the s-triazine groups most suitable for the π–π interaction should be 4.2 Å, which is identical to the value of the spacing between the hydrogenated side-chain crystals.

As mentioned previously, we can control the orientation of the functionalized s-triazine group using copolymerization with long-chain vinyl compounds (resultant comb copolymer) and the method of organized molecular films.

4. CONCLUSION

We investigated the molecular arrangement of monolayers and multilayers with regard to the three-dimensional crystal structures of newly synthesized comb copolymers with the s-triazine group using WAXD, SAXS, π–A isotherm, and out-of plane and in-plane XRD. In the solid state, hydrogenated and fluorinated comb copolymers containing VDAT form side-chain crystals at a lattice spacing of 4.2 and 5.0 Å, respectively. It was suggested that the
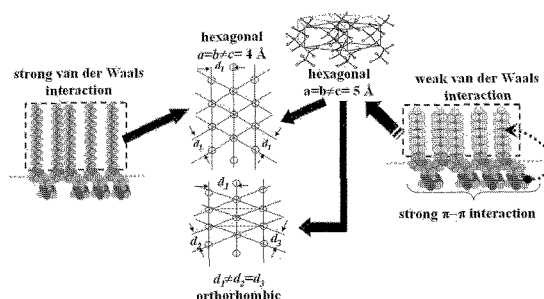
side-chain crystalline copolymers incorporating s-triazine rings formed highly ordered double layer structures. The Langmuir monolayers on the water surface of these copolymers formed extremely condensed monolayers, except for the VDAT:OA = 5:1 copolymer. From the in-plane XRD analyses of multilayers in the solids, the two-dimensional lattice structures of fluorinated comb copolymers containing VDAT units were different from those in the bulk states. These structural changes should be caused by the π–π interaction between the s-triazine rings that are stronger than the van der Waals interaction between the fluorocarbon side-chains.

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