Revisit to the old-but-totally-unknown fluorine polymer – *atactic* poly(vinylene fluoride) is amorphous ? –

So-called man-made polymers, such as polyethylene and nylon, were first produced approximately a century ago and are utilized as alternative materials for metals, ceramics, papers, wood, and so on. These synthetic polymers are expected to be developed further as soft materials that are indispensable in everyday life. Among the numerous synthetic polymers, fluorine polymers have been playing an important role in the development of polymer science and industry. Polytetrafluoroethylene [-$(CF_2CF_2)_n$-, PTFE], the most representative fluorine polymer, has a simple chemical structure: polyethylene [-$(CH_2CH_2)_n$-] with all the H atoms replaced with F atoms. However, PTFE has attracted significant research attention because of its unique properties, such as high water resistance, high heat resistance, low friction, and high chemical resistance. Various types of fluorine polymers have been developed, including fluoro-olefine polymers such as poly(vinyl fluoride) [-$(CH_2CHF)_n$-, PVF] with H/F = 3/1, poly(trifluoroethylene) [-$(CF_2CHF)_n$-, PTrFE] with H/F = 1/3, and poly(vinylidene fluoride) [-$(CH_2CF_2)_n$-, PVDF] with H/F = 2/2. Among them, PVDF was the first ferroelectric polymer to be applied to piezoelectric sensors, high-dielectric materials, etc. In this way, various types of fluorine polymers have been developed, and their structures and physical properties have been investigated in detail.

It is, however, quite curious to notice that another fluorine polymer having the same H/F ratio as PVDF, or poly(vinylene fluoride) [-$(CHFCHF)_n$-, PVLF] had been totally forgotten in the long history of fluorine polymers. Why is this polymer not interesting at all? Is this polymer totally useless nor worthless for stimulating any research?

This situation is well understood in the literature. In this half-century, only a few reports on PVLF have been published. PVDF has been characterized as chemically irregular or an *atactic* polymer with random arrays of H and F atoms along the main chain. Unfortunately, without sufficient study, PVLF was previously considered *amorphous* because of its *atactic* configuration [1]. Consequently, interest in this polymer was lost and only recently reinvigorated by us. The questions remain whether *atactic* polymers are always amorphous. There are many examples against this hypothesis. For example, the above-mentioned PVF was completely *atactic*, but it shows a highly crystalline wide-angle X-ray diffraction (XRD) pattern. This may be a good opportunity to address the problem of PVLF.

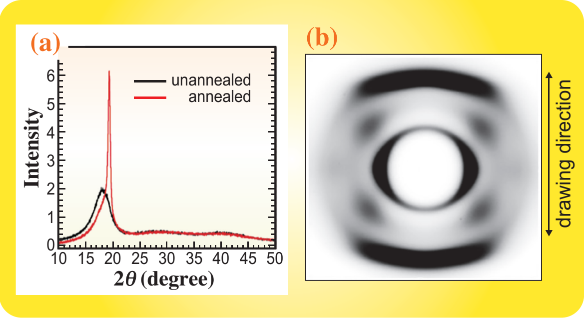

Fig. 1. **(a)** X-ray diffraction profiles of PVLF film measured before (black curve) and after the heat treatment (red curve) [3]. The wavelength of incident X-rays was 1.54 Å. **(b)** The 2D WAXD pattern measured for an oriented and annealed PVLF sample.

Recently, we synthesized a PVLF and characterized its behavior from various perspectives [2]. ^{19}F-nuclear magnetic resonance (NMR) spectral data analysis confirmed that the newly produced PVLF is still *atactic*, similar to that reported in the literature [1]. The wide-angle XRD patterns, which were collected mostly using a synchrotron X-ray beam at SPring-8 **BL38B1**, revealed that (i) the melt-quenched or solution-cast PVLF film gave only amorphous halo peaks; however, (ii) the sample annealed above 100°C or the glass transition temperature (T_g) exhibited significantly sharp and strong crystalline peaks, as shown in Fig. 1. The uniaxially oriented sample clearly exhibited a two-dimensional crystalline XRD pattern. At this moment, PVLF has come back from a long sleep as one

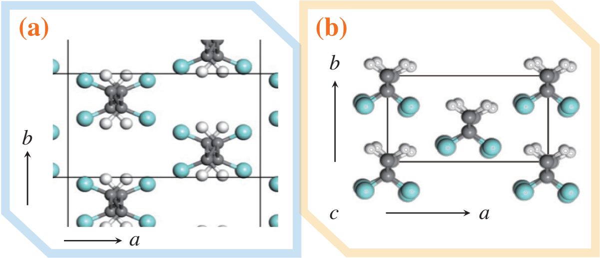

Fig. 2. Crystal structures viewed along the chain axis: **(a)** PVLF low-temperature phase [5] and **(b)** PVDF β form. In (a), the two chains are overlapped at the same lattice point at 50% probability because of statistically-disordered *atactic* configuration. In (b), the zigzag chains are packed in parallel along the *b* axis to give the polar crystal.

important member of *crystalline* fluorine polymers approximately 60 years after its initial studies.

Our research revealed extensive basic structural information such as the crystal structure (Fig. 2(a)) and higher-order structure composed of complicated aggregations of crystalline and amorphous regions (or the stacked lamellar structure) in addition to the physical properties, including the mechanical, thermal, and chemical properties. The temperature-dependent data of wide-angle (WAXD) and small-angle X-ray scatterings (SAXS), which were simultaneously measured, revealed that PVLF exhibits a thermodynamically second-order phase transition at around 100°C. The T_g is also located at about 100°C, above which the higher-order structure changed significantly.

Figure 3 shows the temperature dependence of the SAXS pattern of the as-drawn PVLF sample during heating. The pattern and its scattering intensity changed remarkably above T_g, resulting in a significant improvement in the mechanical properties. The higher-order structural changes that occurred during this process are shown in Figs. 3(a–c). The pink blocks indicate the oriented amorphous regions in the as-drawn and unannealed samples, which possess an electron density similar to that of the crystalline region (yellow), although the chains are irregular in conformation. When this sample was heated above T_g, the thermally activated chains in the oriented amorphous regions relaxed, resulting in a clear SAXS pattern corresponding to the high electron density contrast between the crystalline and amorphous regions.

Thus, PVLF is a semi-crystalline fluorine polymer with appreciably different behavior from that of other fluorine polymers. This important knowledge may allow us to develop PVLF as a novel but still primarily unknown fluorine polymer with excellent functional properties.

In addition, it is challenging to develop a novel type of VLF polymer, that is, a copolymer of VDF and VLF monomeric units. As previously discussed, PVDF is a ferroelectric polymer with a polar crystal structure composed of a parallel packing of zigzag chains (β form, Fig. 2(b)). However, VDF-trifluoroethylene (TrFE) copolymers, as members of the PVDF family, have attracted more attention than PVDF itself because the polar β form can be obtained more easily through slow cooling after melting. A ferroelectric phase transition between the polar and nonpolar phases, which is intrinsic to ferroelectric substances, was also observed for the VDF-TrFE copolymer. However, the ferroelectric transition temperature is limited to a relatively low temperature range of 60–120°C [4], above which ferroelectric properties, such as piezoelectricity and pyroelectricity, disappear. Compared with VDF-TrFE copolymers, the newly-developed VDF-VLF copolymers maintained the polar structure up to the higher temperature of approximately 140°C [5], thereby enabling the formation of a ferroelectric polymer with improved properties.

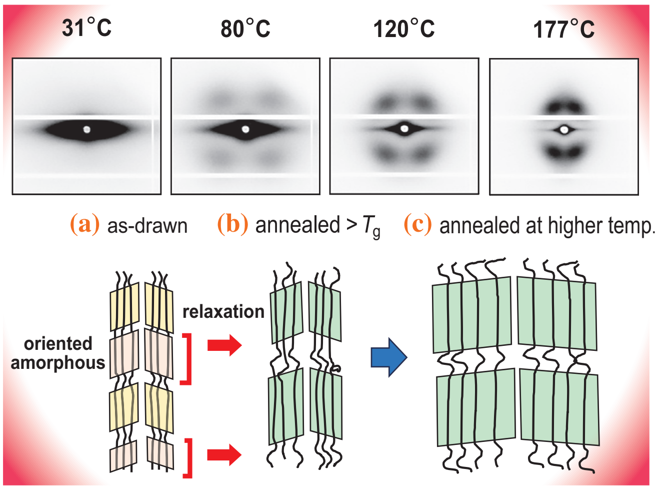

Fig. 3. Temperature dependence of 2D SAXS patterns measured for the as-drawn PVLF sample in the heating process. **(a–c)** Illustration of higher-order structure change of as-drawn PVLF by the heat treatment [5].

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