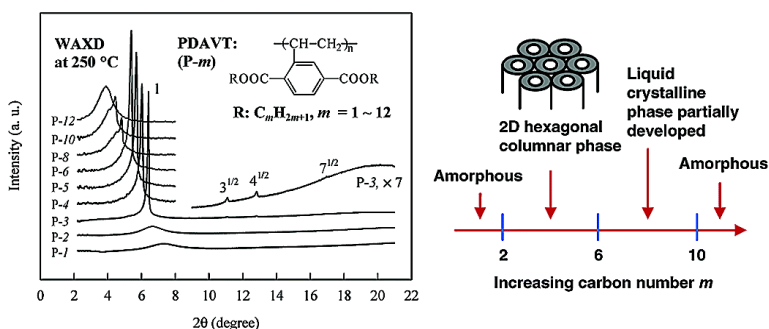


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Manipulating Supramolecular Self-Assembly via Tailoring Pendant Group Size of Linear Vinyl Polymers

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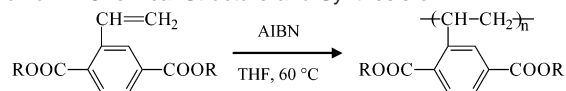
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It has been known for years that atactic vinyl polymers (random sequences of *d*- and *l*-configurations along polymer backbones) with large side groups possess a second scattering halo in the low 2θ angle region (below 10°) in wide-angle X-ray diffraction (WAXD) experiments. Some polymers, such as poly(*N*-vinylcarbazole),^{1,2} poly[dicyclohexyl vinylterephthalate],³ and poly[di(4-heptyl) vinylterephthalate] (PDHVT),⁴ exhibit sharp diffractions at low 2θ 's due to the existence of ordered structures. For example, the side group of PDHVT contains a pair of 4-heptyl groups at the 2- and 5-positions of the substituted phenyl group linked via ester bonds that are laterally attached to the backbone through a single carbon-carbon bond. Although the backbones and side groups do not display liquid crystalline (LC) behaviors individually, a two-dimensional (2D) hexagonal columnar LC phase (Φ_H) has been identified in PDHVT.⁴

Free radical polymerization generates random sequences of *d*- and *l*-configurations along the PDHVT backbones, similar to that of atactic polystyrene (*at*-PS). In a qualitative sense, we have speculated that, when the substituted groups are much larger than the repeating units in the backbone, they may provide steric hindrance by restricting the backbone mobility in the bulk. Therefore, a somewhat extended conformation of the backbones would be expected, and each chain, as a building block, would possess an overall cylindrical symmetry, leading to 2D hexagonal packing.⁴ This self-assembly is similar to that of monodendron-jacketed polymers that possess very bulky side groups.⁵⁻⁹ However, a quantitative understanding of the effect of the side-group size on the phase structures has not yet been achieved. In this communication, we intend to show that, by fine-tuning the size and shape of the side groups within a series of vinyl polymers, a structural evolution between an amorphous and a 2D Φ_H phase can be observed. This serves as an example of alternating the backbone conformation between a random coil and a relatively extended one by controlling the composition of the side groups.

A series of poly[di(alkyl) vinylterephthalates] (PDAVTs) were synthesized with alkyl side groups in the monomers varied from methyl to dodecyl groups. They are abbreviated as P-*m* (*m* is the number of carbons in the alkyl groups). Scheme 1 shows the synthesis of the polymers. An isopropyl group was also substituted in the R position, abbreviated as P-3', to study the effect of the shape of the side group. The synthesis of the precursors of 2-vinylterephthalic acid and monomers was reported elsewhere.^{10,11} The free radical polymerization was carried out in THF at 60°C for 24 h using 0.5% equivalent moles of AIBN as an initiator. The polymer solutions were precipitated in methanol and washed at least

Scheme 1. Chemical Structure and Synthesis of PDAVT^a



^a R = C_mH_{2m+1}, m = 1-6, 8, 10, or 12.

three times, followed by drying in a vacuum over P₂O₅ at 50°C for 24 h before further characterization. The chemical structures of these polymers were confirmed by ¹H NMR, FT-IR, elemental analysis, and mass spectrometry experiments.¹¹ Number average molecular weights (*M_n*) of these samples were measured by GPC using PS standards and ranged from 0.8×10^5 to 2.2×10^5 g/mol, with polydispersities (PDs) of 1.4-1.7. A low-molecular-weight P-3 was also synthesized to investigate the molecular weight (MW) dependence of the LC phase. Detailed information about MWs and PDs is provided in the Supporting Information. One-dimensional (1D) WAXD (Philips X'pert Pro with an X'Celerator detector) was employed to study phase transitions. The 2D WAXD experiments were carried out on a Bruker D8 DISCOVER with a GADDS detector to determine the phase structures of the samples. The X-ray wavelength λ was 0.154 nm.

Figure 1 describes the structurally sensitive 1D WAXD patterns of the P-*m*'s at 250°C . P-1 and P-2 behaved very similarly to *at*-PS, and the two scattering halos appeared in the 2θ region between 2° and 30° . The low-angle scattering centers were shifted to 2θ 's of 7.2° and 6.7° , respectively, compared with that of *at*-PS at $\sim 10^\circ$. For P-3 to P-6, despite the amorphous halos around 20° , the samples exhibited sharp and intense diffractions at low 2θ angles, indicating the existence of ordered structures. However, the intensity of the low-angle diffractions decreased dramatically in P-8 to P-10, and the diffraction peaks coexisted with the scattering halos. In P-12, the sharp diffraction completely disappeared, and no long-range ordered structure was observed, although a much stronger scattering halo was seen compared with those in P-1 and P-2. This reveals

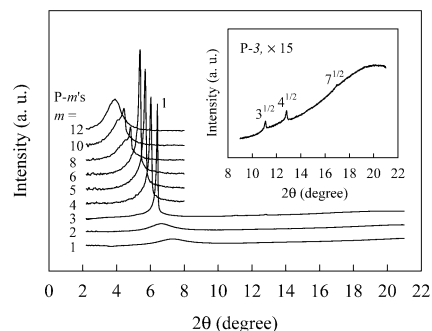


Figure 1. 1D WAXS powder patterns of PDAVTs (P-*m*'s, *m* = 1-12) at 250°C . The inset is the enlarged curve of P-3.

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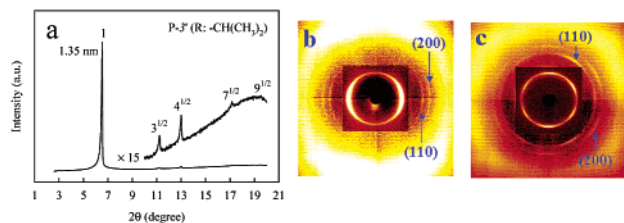


Figure 2. 1D WAXD pattern of P-3' at 200 °C (a) and 2D WAXD patterns obtained with the X-ray beam perpendicular (b) and parallel (c) to the shear direction. The high-order diffractions can also be seen after a prolonged exposure time.

that the low-angle scatterings were associated with the size of the side groups, which substantially affected the phase structure and scattering behavior. This series of P-*m*'s exhibit gradual intensity decreases of the low-angle scatterings with decreasing temperature. P-1, P-2, and P-12 showed no LC phase in the entire temperature range. The low-angle diffractions in P-6, P-8, and P-10 were diminished at low temperatures and reappeared at high temperatures, representing a phase reentry behavior. In other ordered samples, the Φ_H phase remained. Furthermore, a critical M_n was required in forming this ordered structure. For P-3, e.g., a low-MW sample with $M_n = 2.6 \times 10^4$ (g/mol) did not show the ordered structure in the entire temperature range.

The ordered structures of P-3 to P-6 were of particular interest. Higher orders of the diffractions were visible to at least the third order (the enlarged curve of P-3 in Figure 1 is an example). In P-3', diffractions up to fifth order were observed (Figure 2a). For these samples, the scattering vector ratio of the diffractions followed $1:3^{1/2}:4^{1/2}:7^{1/2}:9^{1/2}$, demonstrating a long-range ordered hexagonal lattice. The peaks were indexed as the (100), (110), (200), (210), and (300) diffractions. The hexagonal packing was on a nanometer length scale. The sharpness of these diffractions also revealed substantial lateral order of the hexagonal lattices. The apparent correlation length (based on the Scherrer equation) normal to the [001] direction was estimated to be ~ 120 nm.

To further study structural dimensionality, 2D WAXD experiments on the oriented samples were carried out by aligning the X-ray incident beam along different directions. Figure 2b illustrates a pair of strong (100) diffractions of P-3' when the X-ray beam was perpendicular to the shear direction, which was along the meridian. All the diffractions were on the equator, and the higher order diffractions corresponding to the hexagonal packing could be seen by using a prolonged exposure time. The scattering halo on the meridian of Figure 2b implied that there was no long-range order along the chain direction. Figure 2c presents a six-fold symmetry of the (100) diffractions in the same sample when the X-ray beam was parallel to the shear direction. Note that the columns were aligned along the shear direction. Therefore, the 2D WAXD results confirmed that ordered PDAVTs exhibited a 2D Φ_H phase in which the building blocks involved entire molecules having relatively extended conformations.

To better understand the ordered structure in real space, we used the Fourier transformation to convert the diffraction data in reciprocal space to a Patterson function. However, the imperfect chain orientation did not allow the direct use of the 2D WAXD patterns for this calculation. Using the five indexed diffractions and their intensities of P-3' in Figure 2a, Figure 3a presents a constructed 2D diffraction pattern with the [001] zone. Figure 3b describes the resulting 2D Patterson function that represents an electron density difference between the center and the outside ring of the columns. The center part had an inner diameter of ~ 0.6 nm

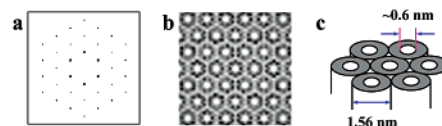


Figure 3. (a) Constructed 2D WAXD pattern based on Figure 2a. (b) 2D Patterson function resulting from the Fourier transformation of (a). (c) Schematic drawing of chain packing; each cylinder represents one chain.

(see the schematic drawing in Figure 3c). From the data, we concluded that the polymer chains adopted a somewhat extended conformation with the cylindrical symmetry. The atomic structure that would cause this electron density difference needs further investigation.

Further size increase in the *n*-alkyl groups of PDAVTs significantly increased the flexibility of the side groups. This could weaken the steric interaction between the side groups and backbones. This effect is evidenced in Figure 1, where P-8 and P-10 only partially developed into the LC phase. Since only a single diffraction peak at the low 2θ 's was observed, this LC phase gradually lost its 2D long-range order. For P-12, the flexibility of the tails seemed to overwhelm the "jacketing" effect of the side groups and hamper the column formation, resulting in a disordered state.

In summary, an effective way of fine-tuning the size and shape of the side groups in this series of PDAVT has been demonstrated. Manipulation of the supramolecular self-assembly has led to control over the formation of a 2D Φ_H phase. To introduce the 2D long-range ordered structure, the size of the ester groups at the 2- and 5-positions of the phenyl ring laterally attached to the backbone should be in the range of propyl/isopropyl to hexyl. The relatively extended backbone conformations observed in these polymers were attributed to steric effects from the side groups. When the *n*-alkyl groups were larger than hexyl, the ability to form the LC phase gradually decreased. A completely disordered phase could be observed by substituting dodecyl groups as side groups. The precise thermodynamics and kinetics of these assembly formations are currently being investigated.

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Supporting Information Available: Molecular characteristics of the PDAVTs studied (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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