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NOTE

Helical Structure of Liquid Crystalline Poly(*N*-((4-*n*-butylphenyl)diphenylmethyl) methacrylamide)

Kanji Nagai,[†,‡,§] Kento Okoshi,*[,‡,∥] Shin-ichiro Sakurai,[‡] Motonori Banno,[†] A. K. M. Fakhrul Azam,[⊥] Masami Kamigaito,[⊥] Yoshio Okamoto,[#,○] and Eiji Yashima*[,†,‡]

[†]*Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan,* [‡]*Yashima Super-structured Helix Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Agency (JST), Japan,* [⊥]*Department of Applied Chemistry, Nagoya University,* [#]*EcoTopia Science Institute, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan, and* [○]*College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, People's Republic of China.* [§]*Present address: Department of Applied Chemistry, Graduate School of Engineering, Nagoya University.* [∥]*Present address: Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8552, Japan.*

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Introduction

Biological polymers, such as proteins and nucleic acids, possess a characteristic single-handed helical structure, which links to their sophisticated functions in living systems.[1] Inspired by biological helices, the synthesis and structures of artificial helical polymers with a controlled helicity have attracted considerable attention. Okamoto et al. prepared the first helical vinyl polymer by polymerization of an achiral bulky methacrylate, i.e., triphenylmethyl methacrylate (TrMA), using chiral anionic initiators, which produced a single-handed, fully isotactic helical polymer with a high optical rotation (PTrMA).[2] Since then, a number of synthetic helical polymers that fold into a one-handed helical conformation has been prepared to develop helical polymers with a controlled helical sense and functions.[3] Later, Okamoto et al. discovered that the one-handed helical PTrMA showed a remarkable chiral recognition for a variety of stereochemically interesting racemic compounds, when the helical PTrMA was used as a chiral stationary phase (CSP) for high-performance liquid chromatography (HPLC),[4] through which many optically active polymers have been prepared and applied to CSPs in HPLC.[3a,d,5] In addition, Reggelin et al. recently found that analogous helical poly(triarylmethyl methacrylate)s bearing pyridyl residues could be used as an efficient polymeric ligand for catalytic asymmetric C−C bond forming reactions.[6]

Although a series of helical poly(triarylmethyl methacrylate)s with optical activity has been prepared in order to use them as CSPs and asymmetric polymeric catalysts, their helical structures have not yet been experimentally elucidated because high-molecular weight polymers suitable for X-ray diffraction (XRD) studies are insoluble in common organic solvents. Computational studies based on molecular mechanics calculations suggested a 3.6 monomer unit per turn (3.6/1) helix with 2.0 Å pitch per monomer unit for an isotactic PTrMA.[7]

Okamoto et al. recently found that the radical polymerization of *n*-butyl-substituted *N*-triphenylmethyl methacrylamides in toluene or tetrahydrofuran (THF) produced high molecular weight polymethacrylamides with a nearly 100% isotacticity being soluble in common organic solvents, such as chloroform. When chiral additives, such as (+)-menthol, were used as a polymerization solvent, the optically active polymers due to a preferred-handed helicity were obtained.[8] Moreover, a few poly(*n*-butyl-substituted *N*-triphenylmethyl methacrylamide)s were found to exhibit a lyotropic liquid crystalline (LC) phase in concentrated chloroform solution,[8c] which enabled us to investigate the helical structure of the polymethacrylamides by XRD measurements of the shear-oriented films prepared from the LC samples. In fact, we recently succeeded in determining the helical structures of LC polyacetylenes and polyisocyanides by the X-ray analyses of the corresponding oriented films.[9] These polymers possess a stiff rodlike helical main-chain with a significant persistence length (q), which is a useful measure to evaluate the stiffness of the rodlike polymers.[10] In this study, we investigated the helical structure of optically active and inactive poly(*N*-((4-*n*-butylphenyl)diphenylmethyl) methacrylamide)s (***h*-poly-1** and poly-**1**, respectively) (Figure 1) by XRD measurements together with high-resolution atomic force microscopy (AFM) observations. The backbone stiffnesses of poly-**1** and ***h*-poly-1** were also estimated by a size exclusion chromatography (SEC) system equipped with multiangle laser light scattering (MALS) and refractive index detectors in conjunction with the wormlike chain model.

Results and Discussion

Poly-**1** and ***h*-poly-1** were prepared according to the previously reported method[8b] by the radical polymerization of the corresponding monomer with α,α′-azobisisobutyronitrile (AIBN) in toluene and (+)-menthol containing a small amount of toluene ((+)-menthol/toluene = 100/1 (v/v), respectively, under UV irradiation at 0 °C. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of poly-**1** and ***h*-poly-1** were $M_n = 3.1 \times 10^5$ and $M_w/M_n = 2.6$ and $M_n = 7.5 \times 10^5$ and $M_w/M_n = 1.8$, respectively, as determined by SEC-MALS measurements using chloroform as the eluent. The ***h*-poly-1** prepared in (+)-menthol/toluene was optically active and its specific rotation ($[\alpha]_{365}{}^{25}$) was −20.0 (*c* 0.1, chloroform); this value is considerably lower than that of a one-handed helical PTrMA prepared by the helix-sense-selective anionic polymerization ($[\alpha]_{365}{}^{25}$ = ca. 1400) (*c* 0.5, THF).[3a,11] The tacticities of the poly-**1**s were nearly 100% isotactic (*mm*) as estimated by their ^{1}H

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*To whom correspondence should be addressed. E-mail: (K.O.) kokoshi@polymer.titech.ac.jp; (E.Y.)yashima@apchem.nagoya-u.ac.jp.

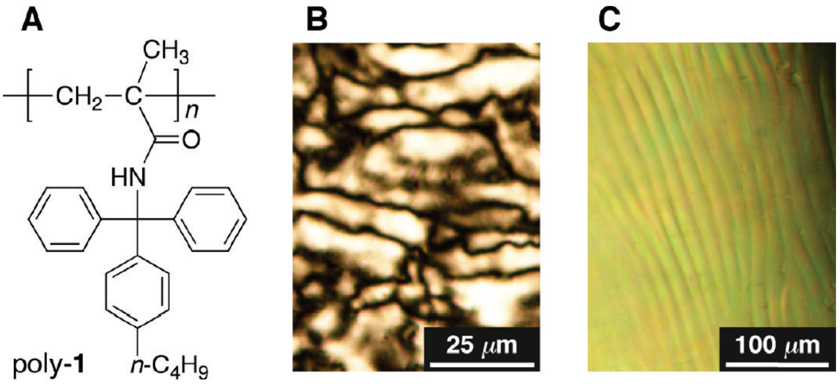

Figure 1. (A) Structure of poly-**1**. (B, C) Polarized optical micrographs of a nematic LC phase of optically inactive poly-**1** in ca. 25 wt % chloroform solution (B) and a cholesteric LC phase of optically active ***h***-poly-**1** in 16 wt % chloroform solution (C) taken at ambient temperature (ca. 25 °C). ***h***-Poly-**1** (M_n = 2.4 × 10^5, M_w/M_n = 3.1, and $[\alpha]_{365}$ = +29.4) prepared in (−)-menthol/toluene was used (C).

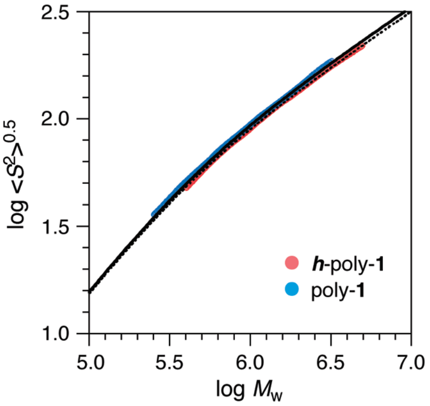

Figure 2. Double-logarithmic plots of the radius of gyration versus the molecular weight of optically inactive poly-**1** (blue dot) and optically active ***h***-poly-**1** (red dot) in chloroform obtained by SEC-MALS measurements at 25 °C. Solid and dotted curves (solid curve for poly-**1** and dotted curve for ***h***-poly-**1**) were obtained on the basis of the wormlike chain theory and fit well with the experimental data. The evaluation parameters are as follows: q = 57.4 nm, M_L = 1678 nm^{-1}, h = 0.23 nm for poly-**1**; q = 52.6 nm, M_L = 1686 nm^{-1}, h = 0.23 nm for ***h***-poly-**1**.

NMR spectra of the corresponding polymethacrylamide derived from the poly-**1**s in D_2SO_4.[8b]

Figure 1B shows the polarized optical micrograph of a concentrated chloroform solution of poly-**1**. Poly-**1** formed a lyotropic nematic LC phase as previously observed for the analogous poly(*N*-di(4-*n*-butylphenyl)phenylmethyl methacrylamide),[8c] indicating the rigid rodlike main-chain structure of the polymer. Interestingly, the optically active poly-**1** (***h***-poly-**1**) exhibited a cholesteric LC phase in chloroform due to the preferred-handed helical structure and showed a fingerprint texture (Figure 1C). The spacing of the fringes corresponding to the half-pitch of the cholesteric helical structure was 15.9 μm, suggesting that the ***h***-poly-**1** is a stiff rodlike helical polymer with an excess one-handedness, although its helical sense excess remains unknown.

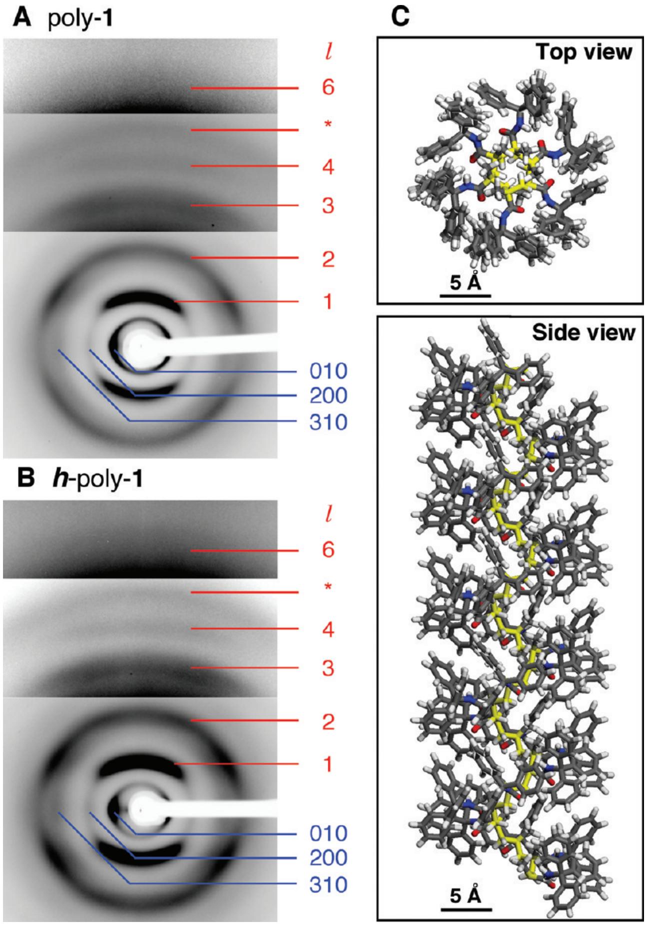

Figure 3. WAXD patterns of oriented optically inactive poly-**1** (A) and optically active ***h***-poly-**1** (B) films with different ranges of sensitivities; the representative layer lines are labeled. The vertical direction is nearly corresponding to the helix axis. The meridian reflections around 2.1 Å indicated by asterisks are probably not attributed to the reflections due to helical structures judging from WAXD data of the same polymer films using a flat imaging plate. The uniaxially oriented films were prepared from concentrated LC chloroform solutions. (C) Top and side view of a possible 6/1 helical structure of isotactic poly-**1** (30-mer) on the basis of the X-ray structural analysis followed by molecular mechanics calculations (see the Supporting Information). The *n*-butyl groups of poly-**1** are replaced by hydrogen atoms for clarity. The main-chain carbon atoms are shown in yellow colors.

The q values of poly-**1** and ***h***-poly-**1** were then estimated on the basis of the wormlike chain model,[12] which can be described as an analytical function of the molecular weight (M_w) and the radius of gyration (S) if the q values and the molar mass per unit contour length (M_L), which eventually leads to the monomer unit height (h), are given. The radii of gyration (S) of the poly-**1**s in chloroform were measured as a function of M_w using SEC equipped with MALS and refractive index detectors in series (Figure 2). The solid and dotted curves in the plots were calculated using the parameters determined from the fits of the unperturbed wormlike chain model over the entire M_w studied range, and are represented by the theoretical values of $<S^2>^{0.5}$. The calculated q values of

Table 1. X-ray Diffraction Data of Oriented Optically Inactive Poly-1 and Optically Active *h*-Poly-1 Films Prepared from Concentrated Chloroform Solutions

	optically inactive poly-**1**				optically active ***h***-poly-**1**				
layer line l	d_{obs} (Å)[a]	d_{cal} (Å)[b]	I_{obs}[c]	hk[b]	d_{obs} (Å)[a]	d_{cal} (Å)[d]	I_{obs}[c]	hk[d]	n[e]
0	15.70	15.70	vs	01	15.80	15.80	vs	01	0
	8.68	8.68	w	20	8.80	8.80	w	20	
	~5.5	5.43	w	31	~5.4	5.50	vw	31	
1	8.93	8.86	vs	10	8.84	8.86	vs	10	1
	~5.3	5.07	vw	22	~5.3	5.10	vw	22	
	4.66	4.67	s	03	4.65	4.68	s	03	
2	4.59	4.71	s	11	4.62	4.70	m	11	2
	~3.6	3.67	vw	03	~3.6	3.67	vw	03	
3	~3.0	2.96	w	22	~3.1	2.95	m	22	3
4	~2.5	2.58	vw	streak	~2.5	2.56	m	streak	−2
6	~1.7	1.72	vw	streak	~1.7	1.71	vw	streak	0

[a] Spacings observed in X-ray diffraction patterns. [b] Spacings calculated and indexed on the basis of an orthorhombic unit cell with parameters, a = 17.36, b = 15.70, and c = 10.30 Å. [c] Observed intensities; vs = very strong, s = strong, m = medium, w = weak, and vw = very weak. [d] Spacings calculated and indexed on the basis of an orthorhombic unit cell with parameters, a = 17.60, b = 15.80, and c = 10.25 Å. [e] Bessel function order based on a 6/1 helix. The average intensity of the layer line is stronger with smaller n.

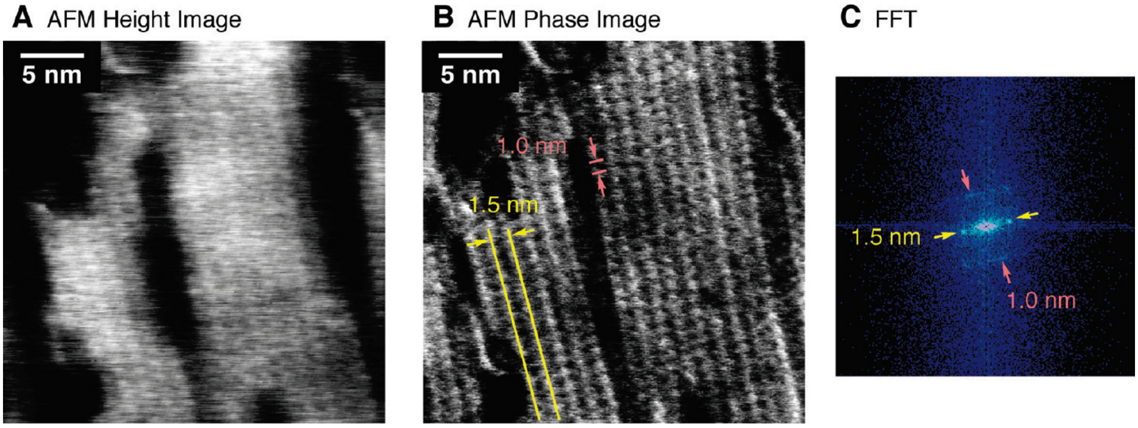

Figure 4. High-resolution AFM height (A) and phase (B) images of 2D self-assembled poly-**1** prepared by casting a dilute chloroform solution (0.01 mg/mL) on HOPG. Yellow lines represent the main-chain axes of poly-**1**; pink lines indicate the helical pitch of poly-**1** helices. Scale 30 × 30 nm. (C) Typical 2D fast Fourier transform (FFT) of the image in part B.

poly-**1** and ***h***-poly-**1** are 57.4 ± 3.8 and 52.6 ± 2.0 nm, respectively.[13] We note that the q values are almost the same for both the optically inactive and active poly-**1**s. The fact that both polymers are highly isotactic and independent of the polymerization solvent, i.e., toluene for poly-**1** and (+)-menthol/toluene for ***h***-poly-**1**, suggests that the difference in the optical activity that corresponds to the difference in their helical sense excess may hardly influence the rigidity of the polymers; kinks due to the helical reversal in the polymer chain are too few to contribute to the chain flexibility. These high q values indicate that both poly-**1**s are rigid and their LC formations are definitely based on their main-chain stiffness. Such stiff helical polymethacrylamides are expected to form a regular helical structure over a long distance, therefore, we anticipated that their helical conformations could be determined from the X-ray analysis.

Parts A and B of Figure 3 show the wide-angle X-ray diffraction (WAXD) patterns of the uniaxially oriented optically inactive poly-**1** and optically active ***h***-poly-**1** films prepared from concentrated LC chloroform solutions, respectively. X-ray photographs were taken from the edge-view position with a beam parallel to the film surface at ambient temperature (20−25 °C). The X-ray diffractions of the oriented poly-**1** and ***h***-poly-**1** films showed essentially the same pattern, exhibiting diffuse, but apparent equatorial and near- and off-meridional reflections. The three equatorial reflections, 15.70, 8.68, and 5.5 Å for poly-**1** and 15.80, 8.80, and 5.4 Å for ***h***-poly-**1**, can be indexed with a two-dimensional orthogonal lattice of a = 17.36 and b = 15.70 Å for poly-**1** and a = 17.60 and b = 15.80 Å for ***h***-poly-**1**, and the observed d-spacings are listed in Table 1. We then determined the fiber periods to be 10.30 Å for poly-**1** and 10.25 Å for ***h***-poly-**1** (= c) from the layer lines, and attempted to index the reflections based on the orthogonal unit cell (Table 1). Although, due to the limited resolution and number of reflections, an unambiguous helical structure of poly-**1**s could not be determined at the present, we assumed that poly-**1**s may have a 6/1 helix on the basis of the reflection on the third layer line (~3.0 Å) and on the fourth layer line (~2.5 Å) combined with the density measurement results.[16]

Figure 3C shows the plausible 6/1 helical structure of the right-handed helical poly-**1** postulated by X-ray structural analyses followed by molecular mechanics calculation (see Supporting Information). The present X-ray results together with the fact that both polymers have almost the same persistence length support the fact that poly-**1** and ***h***-poly-**1** have a stiff 6/1 helical structure independent of their helical sense ratio. However, as mentioned above,[17] the proposed helical structure of the poly-**1**s may need a further revision.

The helical structure of the poly-**1**s was further investigated by AFM. Figure 4 shows typical high-resolution AFM height (A) and phase (B) images of poly-**1** deposited from a dilute chloroform solution (0.01 mg/mL) on highly oriented pyrolytic graphite (HOPG) followed by chloroform vapor exposure at ca. 25 °C for 12 h.[18] The poly-**1** self-assembled into well-defined 2D helix-bundles with a constant height of ~1.8 nm (Figure S2 in the Supporting Information). The bundle structures were resolved into individual poly-**1** chains packed parallel to each other with a chain−chain spacing of ca. 1.5 nm. Although a number of periodic oblique stripes with a pitch of ca. 1.0 nm (see also Figure 4C) was observed along the main-chain (yellow lines), which may originate from the helical array of the pendants, it was difficult to identify the helical sense (right- or left-handed helix) because the observed helical pitch is too short to definitely determine the helical sense. However, the helical pitch and the chain−chain distance of poly-**1** by high-resolution AFM images were in good agreement with those observed by X-ray diffraction measurements (1.0 nm and 1.6−1.8 nm, respectively). ***h*****-**Poly-**1** also formed similar 2D helix-bundle structures with a helical pitch of ca. 1.0 nm on HOPG. However, the helical sense of the ***h*****-**poly-**1** with an excess handedness could not be identified by AFM.

In summary, we investigated the helical structure of poly(*N*-((4-*n*-butylphenyl)diphenylmethyl) methacrylamide) (poly-**1**) by X-ray diffraction measurements of the oriented films prepared from the LC state together with high-resolution AFM observations. To the best of our knowledge, this is the first example of the helical structure (6/1 helix) experimentally proposed for poly(triarylmethyl methacrylamide)s based on the X-ray measurements. Moreover, persistence length measurements unambiguously revealed that the poly-**1** chain is a rigid-rod that forms an LC phase due to the main-chain stiffness. We believe that the present results will contribute to a better understanding of the mechanism of the helix-sense-selective polymerization of triarylmethyl methacrylamides and analogous triarylmethyl methacrylates and also help in developing a more efficient CSP and asymmetric polymer catalysts.

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Supporting Information Available: Text giving experimental details in the SEC-MALS, WAXD, and AFM measurements, a chart showing the atomic connectivities and dihedral angles of poly-**1**, a table showing a comparison of 4/1 and 6/1 helical structural data of poly-**1**, and figure showing AFM and structural images. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) In general, the persistence length of common vinyl polymers is small. The reported q values are $\sim$ 1 nm (atactic polystyrene),[14] $\sim$ 2 nm (isotactic poly(methyl methacrylate)),[15] and 2−3 nm (atactic poly(methyl methacrylate)).[15]

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(16) The densities of the poly-**1** films were measured by the standard flotation method in a KBr saturated aqueous solution—water mixture at ambient temperature (20−25 °C).

(17) The observed density of the optically inactive poly-**1** (1.072 g/cm^3) was different from the calculated value (1.362 g/cm^3) for this unit

cell. This may be because the unit cell of poly-**1** was determined on the basis of the strong reflections of 15.70 Å and 8.68 Å, and the observed irregularity of the two-dimensional lattice may influence the lower density of the poly-**1** films. Because we could not completely exclude the possibility that the poly-**1** may have a 4/1 helical structure, a possible 4/1 helical poly-**1** was constructed in the same way for the 6/1 helical poly-**1**. The optimized 4/1 helical structure is shown in Figure S3 in the Supporting Information. We note that the 4/1 helical poly-**1** had a much higher energy than that of the 6/1 helical poly-**1** (Table S1 in the Supporting Information). Although the 6/1 helical poly-**1** was energetically more stable than that of the 4/1 helical poly-**1** based on empirical MM calculations, more detailed analyses are required to unambiguously determine the helical structure of poly-**1**.

(18) This method is very useful for constructing highly ordered two-dimensional (2D) helix-bundles with a controlled helicity for helical polyacetylenes, polyisocyanides, and complementary double-stranded helical polymers on HOPG, and their helical structures were visualized by AFM; see refs 9b−9d. See also: (a) Kajitani, T.; Okoshi, K.; Sakurai, S.-i.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 708–709. (b) Maeda, T.; Furusho, Y.; Sakurai, S.-i.; Kumaki, J.; Okoshi, K.; Yashima, E. *J. Am. Chem. Soc.* **2008**, *130*, 7938–7945. (c) For reviews: Kumaki, J.; Sakurai, S.-i.; Yashima, E. *Chem. Soc. Rev.* **2009**, *38*, 737–746.