Confirmation of Crystal Structure of Poly(vinylidene fluoride) through the Detailed Structure Analysis of Vinylidene Fluoride Oligomers Separated by Supercritical Fluid Chromatography

Kohji Tashiro* and Makoto Hanesaka

Department of Macromolecular Science, Graduate School of Science, Osaka University,
Toyonaka, Osaka 560-0043, Japan

Received July 27, 2001; Revised Manuscript Received October 18, 2001

ABSTRACT: Vinylidene fluoride (VDF) oligomers with uniform molecular weights were separated successfully by using supercritical fluid chromatography, and the crystal structures were determined by X-ray analysis of the single crystals. Although the chemical formulas of these oligomer components had not been known clearly, the X-ray structure analysis gave us the following results: $CF(CF_3)_2-(CH_2\text{-}CF_2)_n-I$ with $n = 6-12$. The oligomer chains were found to form a layer structure, in which the chains are tilted slightly from the normal to the layer plane. The chain conformation of the oligomers, when crystallized from ethanol solutions, was a repetition of $TGT\bar{G}$, essentially the same with that of poly(vinylidene fluoride) crystal form II. The packing structure of central VDF sequence parts was also found to be the same with that of form II: the chains are packed in an antiparallel mode with respect to the chain direction as well as the direction of CF_2 dipoles. A series of oligomers were found to show a variety of crystal modifications depending on the sample preparation conditions, as seen from the infrared spectral patterns.

Introduction

In general, polymer substance is a mixture of molecules with different molecular weights or different number of monomeric units. Because of this molecular weight distribution, polymers cannot be grown to single crystals of large size but give quite small crystallites of low quality in general. Therefore, it is difficult to carry out the precise crystal structure analysis, forcing us to make only ambiguous discussion about the structure−property relationship. To get any useful information about the crystal structure of polymer, model compounds are sometimes used as references for the corresponding polymer. For example, *n*-alkanes $CH_3-(CH_2)_n-CH_3$ and perfluoroalkanes $CF_3-(CF_2)_n-CF_3$ are good model compounds for polyethylene and poly(tetrafluoroethylene), respectively. These model compounds must be long enough to simulate the structure of the parent polymer. In the present study we will treat vinylidene fluoride (VDF) oligomers. The structure information obtained from these VDF oligomers will be quite useful for the establishment of the crystal structures proposed so far for the several crystal modifications of poly(vinylidene fluoride) (PVDF) itself.

The VDF oligomers used in the present study were presumed to have the chemical formula of $X-(CH_2\text{-}CF_2)_n-Y$ but the end groups X and Y had not been identified. Besides, the sample was a mixture of the components with various monomeric unit number *n*. We needed to separate them to each component by any method in order to prepare the single crystals and to obtain the detailed information on the crystal structure through the X-ray analysis. As for the separation of a mixture into components, the various types of methods have been reported, among which a supercritical fluid chromatography (SFC) is now becoming a quite useful method.[1−10] In many cases carbon dioxide is used as a development fluid for chromatography. When the temperature and pressure of carbon dioxide gas are increased above the critical temperature (31.3 °C) and critical pressure (72.9 atm), the gas changes into the so-called supercritical fluid state. The critical density is 0.488 g/cm^3. The viscosity of this supercritical fluid state is two digits lower, and the diffusion coefficient is about two digits higher than that of the normal liquids. The solubility of a material into carbon dioxide is also high. Utilizing these characteristic features of supercritical fluid state of carbon dioxide, the SFC has been used widely for the separation of a mixture at higher efficiency than the conventional chromatographic methods. In the field of polymer substances, various kinds of oligomers were separated into individual components, and the crystal structure analysis was made successfully for the single crystals prepared for the thus-separated components.[11−14] These structure information are important in confirmation of the crystal structure of the corresponding polymer substances. The purified oligomer components are useful also for the investigation of the phase transition behavior of the parent polymer because the oligomer exhibits the sharp and clear phase transition, different from the diffuse transition in the polymer.

In the present study we have applied this SFC technique to separate the above-mentioned mixture of VDF oligomers. PVDF is an electrically interesting polymer material and has been extensively investigated from the viewpoint of piezo-, pyro-, and ferroelectricity.[15] This polymer shows at least four kinds of crystalline modifications depending on the sample preparation conditions.[16,17] The crystal form I has a polar structure, in which the essentially planar-zigzag chains are packed in the unit cell with the CF_2 dipoles parallel along the *b* axis.[18,19] In the crystal form II, the chains take the conformation of $TGT\bar{G}$ (T = trans, G = gauche), and these chains are packed in the unit cell in an antiparallel mode by a point of symmetry.[19−21] That is to say, form II is a nonpolar crystal. When this nonpolar form II is subjected to a high electric field, it changes to the

10.1021/ma011339o CCC: $22.00 © 2002 American Chemical Society
Published on Web 12/20/2001

polar structure in which the TGT$\bar{G}$ chains are packed in parallel mode. This crystal form is called the polar form II (II_p or IV).[22] PVDF has another crystal modification, form III, which is obtained by casting from the polar solvent such as dimethylacetamide and dimethylforamide or by heat treatment of the crystal form II or II_p at high temperature.[16,17] The form III takes the TTTGTTT$\bar{G}$ conformation, and the chains are packed in the polar unit cell.[23-25] The crystal structures of these modifications of PVDF were determined by X-ray diffraction, infrared/Raman spectroscopy, and so forth but still have various points to be solved. A utilization of the oligomeric substances might help us to solve these problems clearly.

As for the VDF oligomers, there have been reported several papers on the structure and phase transitional behavior. For example, Herman et al. separated a mixture of VDF oligomers with the formula $Cl-(CH_2CF_2)_n-CCl_3$ by the conventional chromatographic method and measured the X-ray diffraction profile and infrared spectra of the powder samples.[26] They also obtained the oligomers with the formula $I-(CH_2CF_2)_n-H$ from the parent PVDF sample by the vacuum evaporation technique.[27] Yoshida et al. investigated the orientation of the epitaxially grown oligomer $CF(CF_3)_2-(CH_2CF_2)_{20}-I$ on the surface of KCl single crystal by the vacuum evaporation method.[28] These studies clarified many important features of VDF oligomers and gave us information useful for the discussion of phase transition behavior of the parent PVDF. Unfortunately, however, the details of the crystal structure have not yet been analyzed by using the single crystals of these oligomers. The precise and reliable structure analysis will give us quite useful information for the quantitative interpretation of the relationship between structure and physical properties of PVDF. This is the first report about the crystal structure of the oligomer components which could be separated successfully by an SFC technique.

Experimental Section

Samples. The VDF oligomers were supplied by Daikin Kogyo Co. Ltd., Japan. Unfortunately, the sample was a mixture of oligomer components without almost any information on the chemical formula.

Separation. Separation of oligomers was made by using a Japan Spectroscopic Company (JASCO) Super-201 SFE/SFC system. The multichannel detector MD-910 was used for the measurement of visible−ultraviolet (vis−UV) spectra of the components. This vis−UV detector was useful for monitoring the VDF oligomers. (For more general purposes, however, vis−UV spectroscopy is not necessarily almighty for detecting the oligomer components. For many polymers, a Fourier transform infrared spectrometer is more useful as a detector for the SFC system. Refer to ref 29.) A silica gel column of JASCO Superpack SIL with 4.6 mm radius × 250 mm length was used for the component separation. A modifier or a solvent increasing the solubility for CO_2 was ethanol. The pressure was 130 kg/cm^2, and the rate of fluid was 3.00 mL CO_2/min and 0.05 mL ethanol/min. The starting temperature of the column was 90 °C and decreased to room temperature at a rate of 3 °C/min. Each component was collected at an exit with a test tube at every timing of detecting the vis−UV absorption peak.

Infrared Spectral Measurement. Infrared spectra were taken for KBr disks of the separated components by using a JASCO FT/IR 510 spectrometer at a resolution power 2 cm^{-1}.

MAS Measurement. FAB MAS spectra were measured for the separated oligomers. The sample was dissolved in CH_2Cl_2 solvent. As a standard sample for molecular weight calibration, NBA (3-nitrobenzyl alcohol) with a molecular weight of 307.0 g/mol was used.

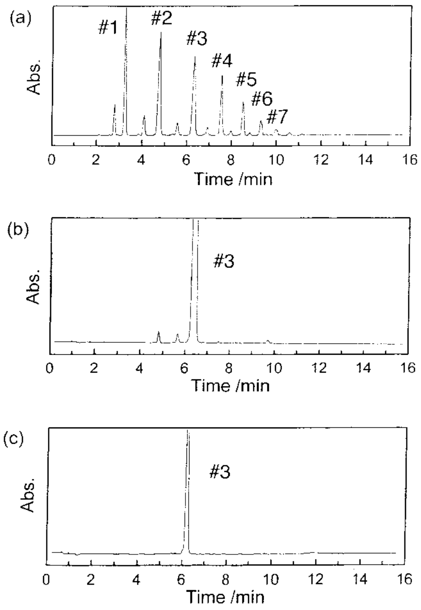


Figure 1. Chromatographs of vinylidene fluoride oligomers developed by a supercritical fluid chromatographic technique: (a) the original mixture, (b) separated component 3 with a small amount of other components, and (c) furthermore purified component 3.

X-ray Structure Analysis. Single crystals of the separated components were grown from the ethanol solutions at room temperature. 2-Dimensional X-ray diffraction images were measured at room temperature by using a MAC Science DIP 3000 diffractometer system with a pair of cylindrical imaging plate cameras. The incident X-ray beam was a graphite-monochromatized Mo Kα line ($\lambda = 0.710\ 73$ Å) from the X-ray generator (MAC Science SRA18X; 50 kV and 200 mA). The oscillation amplitude was $\Delta\phi = 5°$ in the full range of $\phi = 0-120°$. Twenty-four frames in total were collected in 4 h, including the reading-out time of the data. Indexing of the observed reflections, estimation of the unit cell parameters, and integration of the reflection intensities were made by using the software DENZO.[30] The scaling of the thus evaluated reflection intensities and the further refinement of the unit cell parameters were made by the software SCALEPACK. The structure analysis was made by using a kit of software (CrystanGM by MAC Science, Japan). The initial structure was obtained by a direct method (SIR[31]) and refined by a least-squares method with a weight of $w = \exp[\mathrm{FA}\cdot\sin^2\theta/\lambda]/[\sigma^2(F_o) + \mathrm{FB}\cdot F_o^2]$, where $\sigma(F_o)$ was the square of the standard deviation of the observed structure factor and the coefficients FA and FB were set to the values 0.00 and 0.03, respectively. The reliability of the structure analysis was measured by the reliability factors defined in the following equations:

$$R = \sum ||F_o^2| - |F_c^2|| / \sum |F_o^2| \quad \text{and}$$

$$R_w = [\sum w(|F_o^2| - |F_c^2|)^2 / \sum w|F_o^2|^2]^{1/2}$$

Results and Discussion

Separation of VDF Oligomers by SFC. Figure 1a shows a chromatograph of the original VDF oligomers monitored by a vis−UV spectrometer of the SFC system. The chromatograph consists of two series of peaks: one peak of a pair is high and another peak is low. The subpeaks of low intensity were skipped in the present study. The main peaks of high intensity were named as 1, 2, and so on as seen in Figure 1a. Separation of these components was made by collecting each component flowing out of the exit during monitoring the change in the vis−UV spectral intensity at a fixed wavelength. Purity of the thus separated components was

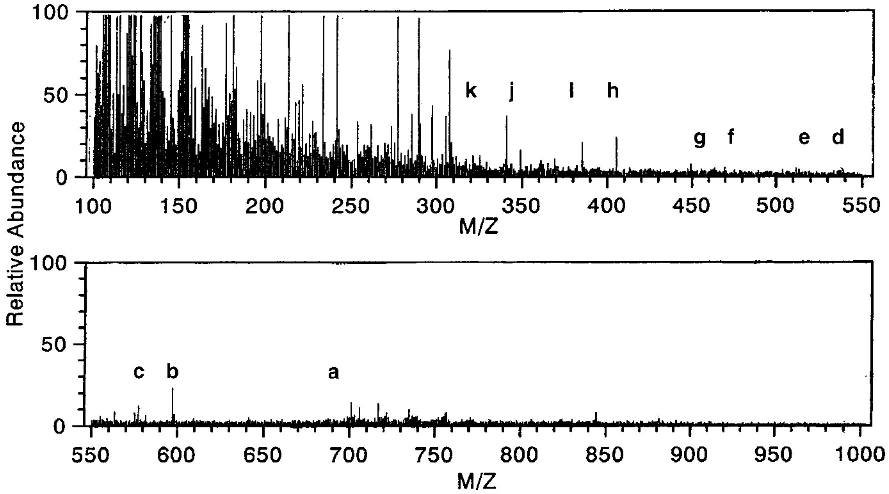


Figure 2. Mass spectrum measured for component 4 separated by a supercritical fluid chromatography. The numberings are referred to Table 2.

checked by flowing the sample again into the SFC system. The result is shown in Figure 1b where component 3 was used as an example. As seen here, a small amount of other components could be still detected as impurities. Then the separation was repeated again, and the pure component 3 could be finally obtained as seen in Figure 1c. The total time needed to collect 10 mg of pure sample was about 120 h from the start of the separation. This long collection time was one of the most serious problems of the SFC method. Of course, the autocollection technique might be used for the collection of a series of components, but it seems a little dangerous to use this technique at the present not-yet-matured stage, because only one mistake of the collection timing of a component might result in the total error. Anyway, the thus purified sample of each component was dissolved in ethanol, and the single crystals were grown at room temperature by the evaporation method.

Characterization of Separated Components. The characterization of the thus separated components was tried by using high-resolution NMR spectroscopy, but the total amount of the sample was too small to detect as an NMR signal. The mass spectra were measured by a FAB MAS technique as shown in Figure 2, where the case of component 4 is given as an example. Unfortunately, however, the spectrum was too complicated to determine the number of monomeric units and the end groups, although an existence of CH_2CF_2 units could be known easily by measuring the difference in mass between a series of adjacent peaks observed at an almost constant separation. Then we tried to know the chemicl formula directly by carrying out the crystal structure analysis of single crystals.

Before carrying out the X-ray structure analysis, we measured the infrared spectra of these components at room temperature. Figure 3 shows the infrared spectra of component 3, as an example, in comparison with those of polymer. Although the spectrum is a little more complicated than that of the parent PVDF itself, the comparison of these two spectra told us immediately that the conformation of the skeletal chain part of the oligomer may take the TGT form.[32] This information will help us to get the initial structure in the X-ray structure analysis. The many additional bands observed for the oligomer are so-called progression bands originating from the different phase relations between the adjacent monomeric units.

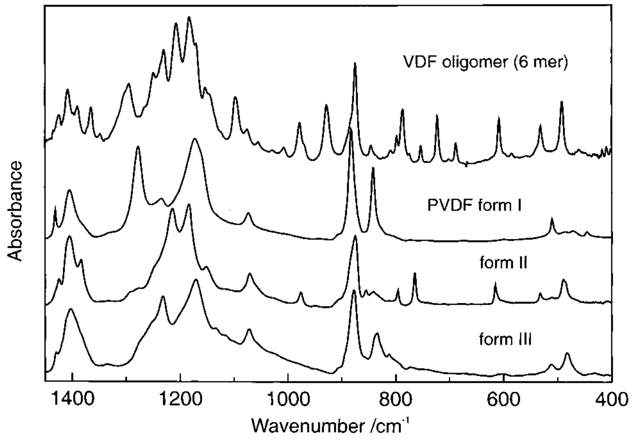


Figure 3. Comparison of infrared spectrum of purified oligomer component 3 with those of various crystal modifications of PVDF.

Table 1. Crystallographic Data of VDF Oligomers

	6-mer	7-mer	8-mer
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$-C_{2h}^5	$P2_1/a$-C_{2h}^5	$P2_1/a$-C_{2h}^5
a/Å	10.927(9)[a]	10.930(10)	10.952
b/Å	9.760(10)	9.717(09)	9.764
c/Å	20.350(10)	22.29(2)	24.39
β/deg	100.51(3)	96.82(3)	96.65
Z	4	4	4
d_{cal}/g/cm^3	2.12	2.10	2.07
no. of total reflections	4193	6541	3212
no. of unique reflections	4024	6230	2380
no. of reflections used in least-squares refine	1763	2980	963
R_{merge}	0.023	0.040	0.099
R	0.042	0.049	0.24
R_w	0.046	0.035	

[a] Parentheses indicates the standard error. For example, 5.432(6) = 5.432 ± 0.006.

X-ray Structure Analysis. Table 1 shows the crystallographic data obtained for the oligomer components 3, 4, and 5 in Figure 1. For components 3 and 4, the structural analysis could be made completely with reliability factors of $R = 4.2$ and 4.9%, respectively. The single crystal of component 5 was of slightly low quality,

Table 2. Assignment of Peaks Detected in the Mass Spectrum of Component 4 (Refer to Figure 2)

peak	(*m*/*z*)	fragment
a	705	$\mathrm{CF(CF_3)_2{-}CH{=}CF{-}(CH_2CF_2)_5{-}I}$
b	597	$\mathrm{CF(CF_3)_2{-}CH{=}CF{-}(CH_2CF_2)_6{}^+}$
c	577	$\mathrm{CF(CF_3)_2{-}CH{=}CF{-}CH{=}CF{-}(CH_2CF_2)_5{}^+}$
d	533	$\mathrm{CF(CF_3)_2{-}CH{=}CF{-}(CH_2CF_2)_5{}^+}$
e	513	$\mathrm{CF(CF_3)_2{-}CH{=}CF{-}CH{=}CF{-}(CH_2CF_2)_4{}^+}$
f	469	$\mathrm{CF(CF_3)_2{-}CH{=}CF{-}(CH_2CF_2)_4{}^+}$
g	449	$\mathrm{CF(CF_3)_2{-}CH{=}CF{-}CH{=}CF{-}(CH_2CF_2)_3{}^+}$
h	405	$\mathrm{CF(CF_3)_2{-}CH{=}CF{-}(CH_2CF_2)_3{}^+}$
i	385	$\mathrm{CF(CF_3)_2{-}CH{=}CF{-}CH{=}CF{-}(CH_2CF_2)_2{}^+}$
j	341	$\mathrm{CF(CF_3)_2{-}CH{=}CF{-}(CH_2CF_2)_2{}^+}$
k	321	$\mathrm{CF(CF_3)_2{-}CH{=}CF{-}CH{=}CF{-}(CH_2CF_2)^+}$

and the structural analysis was still uncompleted, but the structure was believed to be essentially correct when compared with the other members. Therefore, the temporarily obtained structure model of component 5 will be also used for the discussion in this paper. The X-ray structure analysis told us the following chemical formula for the oligomers used in this experiment.

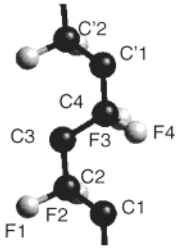
$$\mathrm{CF(CF_3)_2{-}(CH_2CF_2)_{\mathit{n}}{-}I}$$

where $n = 6$ for component 3, $n = 7$ for component 4, and $n = 8$ for component 5. In this way, the X-ray structure analysis was found to be quite useful as a tool for the elementary analysis of the unidentified substance.

At this stage we can interpret reasonably the mass spectra measured before the X-ray structure analysis. The peaks detected in the mass spectrum shown in Figure 2 can be assigned to the chemical fragments listed in Table 2.

Molecular and Crystal Structures. Figure 4 shows the packing structure of the oligomer molecules viewed along the *b* axis for the components of 6–8-mers. All of them show the layer structure of the chains stacked along the *c* axis. The tilt angle of the chain from the normal to the layer plane is about 24° for 6- and 8-mers and about 24° but in the inversed direction for 7-mer. As for the stacking mode of layers, there seems to be an odd–even effect among these oligomers. Figure 5 shows the molecular chains of these oligomers in comparison with the chain conformation of PVDF form II. They take approximately the glide-type symmetry, and the torsional angles of the skeletal chain segments are about 180°, 60°, 180°, and −60°, i.e., TGT$\bar{\mathrm{G}}$. The conformation is essentially the same with that of crystal form II, although the torsional angles of the bonds near the end parts are slightly deviated from the standard gauche values. The X-ray structure analysis could confirm the prediction of chain conformation made from the infrared spectral data (Figure 3). Table 3 lists up the details of the molecular parameters such as bond lengths, bond angles, etc. Fractional atomic coordinates are listed in Tables 4 and 5 for the 6- and 7-mers, respectively.

Table 3. Molecular Parameters of PVDF Form and VDF Oligomers (6-mer and 7-mer)



	polymer[a]	6-mer	7-mer
bond length (Å)			
C1−C2−C3−C4	1.54	1.52	1.51
C2−F1−C2−F2	1.34	1.37	1.36
bond angle (deg)			
C1−C2−C3	112.0	117.1	117.2
C2−C3−C4	117.5	117.6	117.8
F1−C−F2	106.3	104.3	104.2
internal rotation angle (deg)			
C1−C2−C3−C4	176.2	177.1	177.6
C4−C1−C2−C3	65.0	60.7	60.9

[a] Reference 21.

The packing mode of the central VDF sequential parts of the oligomers is compared with that of PVDF form II in Figures 6 and 7. Here we introduced the so-called subcell into the central parts of the chains and compared the thus approximately created cell structure with the unit cell of PVDF form II. The cell parameters a_s, b_s, and c_s in Figures 6 and 7 are those of the subcell structure. The lattice parameters of these subcell structures are almost common to the oligomers and polymer. For all the oligomers of 6–8-mers, the two chains in the subcell are connected by the point of symmetry. The direction of the two chains in the subcell is antiparallel

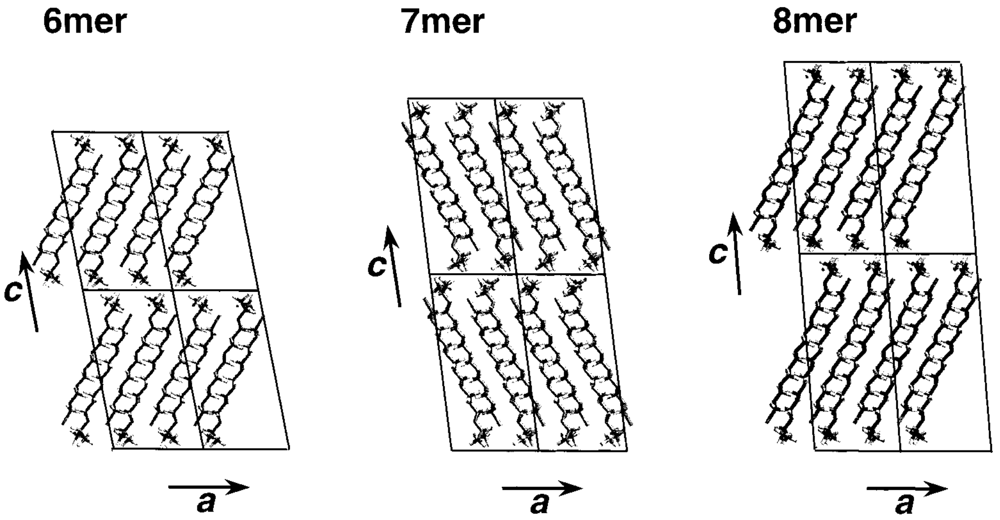


Figure 4. Crystal structure of vinylidene fluoride oligomers with 6, 7, and 8 monomeric units.

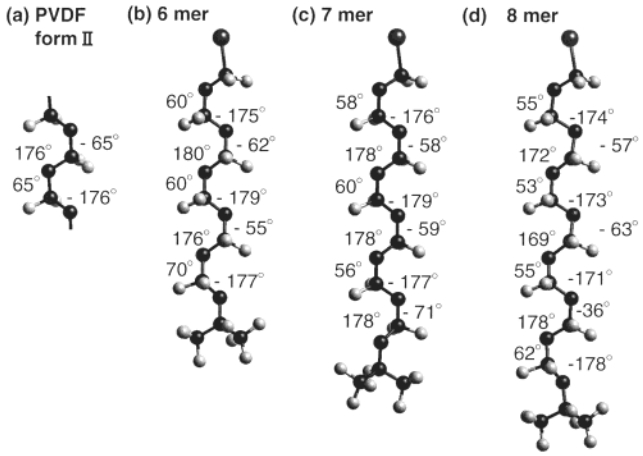


Figure 5. Comparison in molecular conformation between vinylidene fluoride oligomers and PVDF form II: (a) PVDF, (b) 6-mer, (c) 7-mer, and (d) 8-mer. The angles shown in these structures are the torsional angles of the skeletal chains.

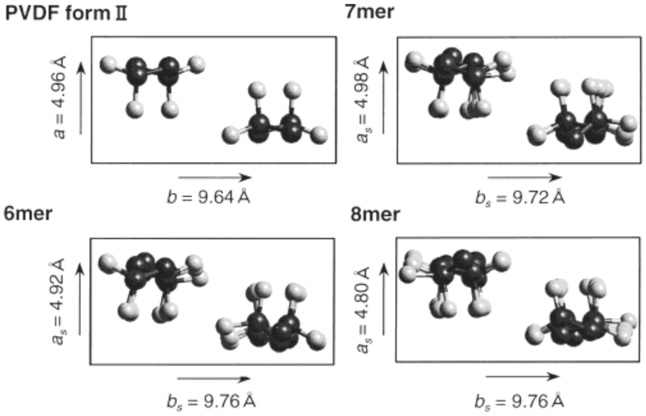


Figure 6. Comparison of crystal structure viewed along the chain axis between PVDF form II and vinylidene fluoride oligomers of 6-mer, 7-mer, and 8-mer. The a_s and b_s are the unit cell axes of the subcell lattice.

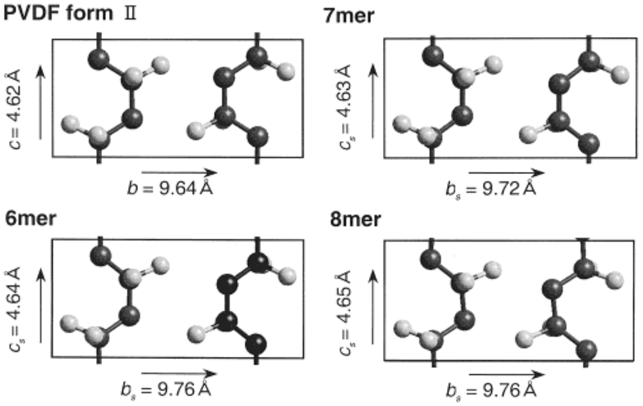
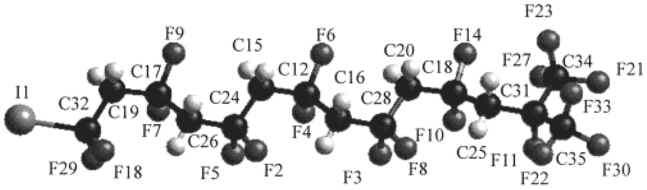


Figure 7. Comparison of crystal structure viewed along the *a* axis between PVDF form II and vinylidene fluoride oligomers of 6-mer, 7-mer, and 8-mer. The b_s and c_s are the unit cell axes of the subcell lattice.

Table 4. Fractional Atomic Coordinates and Equivalent Isothermal Temperature Factors for VDF Oligomer ($n = 6$)



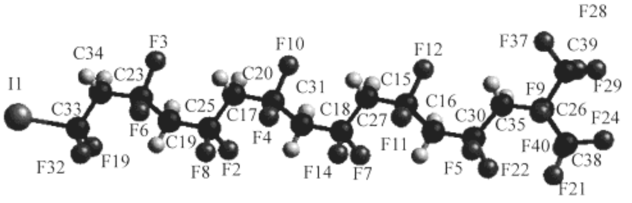
	x/a	y/b	z/c	U_{eq} (Å)[a]
I1	1.00918(9)	0.70847(9)	0.85101(3)	0.0945(5)
F2	0.6676(5)	0.5674(5)	0.5121(2)	0.063(3)
F3	0.3013(5)	0.6639(5)	0.3620(2)	0.062(3)
F4	0.4212(5)	0.8192(5)	0.4673(2)	0.060(3)
F5	0.5464(5)	0.6635(5)	0.5712(2)	0.059(3)
F6	0.5376(5)	0.9293(4)	0.4104(2)	0.061(3)
F7	0.6617(5)	0.8251(5)	0.6737(2)	0.064(3)
F8	0.4199(5)	0.5767(5)	0.2984(2)	0.063(3)
F9	0.7909(5)	0.9254(4)	0.6198(2)	0.066(3)
F10	0.1698(5)	0.7926(7)	0.2540(2)	0.071(3)
F11	0.0819(5)	0.6595(6)	0.1354(3)	0.078(4)
C12	0.5300(8)	0.8062(8)	0.4425(3)	0.041(5)
F13	0.9176(6)	0.5670(5)	0.7292(3)	0.089(4)
F14	0.2720(6)	0.9507(5)	0.2114(2)	0.080(3)
C15	0.6405(8)	0.8057(8)	0.5004(3)	0.042(5)
C16	0.5194(8)	0.6909(8)	0.3932(3)	0.040(4)
C17	0.7717(8)	0.8072(8)	0.6535(4)	0.040(5)
C18	0.2792(8)	0.8163(8)	0.2334(4)	0.045(5)
C19	0.8773(8)	0.8027(9)	0.7134(4)	0.043(5)
C20	0.3846(8)	0.8160(7)	0.2930(4)	0.041(4)
F21	0.0718(7)	0.8350(7)	0.0222(3)	0.122(5)
F22	0.2707(7)	0.5039(7)	0.0933(3)	0.114(5)
F23	0.2360(8)	0.9284(7)	0.0748(3)	0.116(5)
C24	0.6534(8)	0.6849(8)	0.5476(3)	0.041(5)
C25	0.2933(8)	0.7240(10)	0.1752(3)	0.046(5)
C26	0.7635(8)	0.6868(8)	0.6051(4)	0.039(4)
F27	0.0705(7)	0.9197(7)	0.1190(3)	0.101(5)
C28	0.4055(8)	0.6911(8)	0.3369(3)	0.040(5)
F29	0.7711(7)	0.6486(7)	0.7718(3)	0.104(5)
F30	0.1209(7)	0.5746(7)	0.0207(3)	0.106(4)
C31	0.1847(8)	0.7160(10)	0.1155(4)	0.050(5)
C32	0.8830(10)	0.6801(9)	0.7589(4)	0.054(5)
F33	0.2983(8)	0.6710(10)	0.0313(3)	0.131(6)
C34	0.1400(10)	0.8530(10)	0.0823(5)	0.080(8)
C35	0.2200(10)	0.6130(10)	0.0634(5)	0.079(8)
H19A	0.8642	0.8791	0.7411	0.05(3)
H19B	0.9530	0.8163	0.6966	0.05(2)
H20A	0.3710	0.8930	0.3202	0.06(3)
H20B	0.4584	0.8312	0.2746	0.04(2)
H25A	0.3155	0.6329	0.1916	0.12(4)
H25B	0.3614	0.7630	0.1578	0.07(3)
H26A	0.7658	0.6042	0.6309	0.11(4)
H26B	0.8372	0.6928	0.5858	0.04(2)
H15A	0.6320	0.8904	0.5233	0.06(3)
H15B	0.7137	0.8092	0.4807	0.07(3)
H16A	0.5230	0.6081	0.4190	0.06(3)
H16B	0.5922	0.6975	0.3732	0.07(3)

[a] $U_{eq} = (1/3)\sum\sum[U_{ij}a^*(i)a^*(j)a(i)a(j)\cos(\tau_{ij})]$ where U_{ij} is the component of anisotropic thermal parameters tensor. The a^* and a are respectively the unit cell vectors of the reciprocal lattice and the real lattice.

to each other along the *a* and *c* axes. In the crystal lattice of PVDF form II, the upward and downward chains are packed in a statistical way.[21] The chain stems in small domains might be packed in a regular manner with respect to the chain direction, but these domains might be gathered together in a statistically disordered manner. In the crystal lattice of oligomers the chains are packed in a regular manner, not statistically, through the point of symmetry. This difference in chain packing mode between polymer and oligomers might come from the effect of end groups. Such an end group effect can be seen also in the change of shape of the original unit cell. For example, the angle β shown in Table 1 becomes smaller as the VDF sequence is longer. This might also come from the end group effect. To clarify these problems, anyway, we need to investigate the structure of a series of oligomers with longer (or shorter) chain length. As the first approximation, however, we may say that the structure of PVDF form II is realized in the single crystal of the oligomers grown from the ethanol solutions.

Crystal Modifications of Oligomers. In the case of parent PVDF, the various crystal modifications are obtained by changing the preparation conditions such

Table 5. Fractional Atomic Coordinates and Equivalent Isothermal Temperature Factors for VDF Oligomer (n = 7)



	x/a	y/b	z/c	U_{eq} (Å)[a]
I1	0.40495(7)	0.20899(7)	0.36470(2)	0.0911(4)
F2	0.5579(4)	0.0698(3)	0.0587(1)	0.054(2)
F3	0.4937(4)	0.4283(3)	0.1562(2)	0.061(2)
F4	0.7808(3)	0.3245(4)	0.0194(1)	0.053(2)
F5	0.9738(4)	0.2088(5)	−0.2707(2)	0.068(3)
F6	0.6533(4)	0.3282(4)	0.2047(2)	0.056(2)
F7	0.6936(4)	0.0699(3)	−0.1297(1)	0.054(2)
F8	0.7122(3)	0.1671(4)	0.1125(2)	0.051(2)
F9	0.9949(4)	0.3414(5)	−0.3778(2)	0.071(3)
F10	0.6318(4)	0.4324(3)	−0.0336(1)	0.056(2)
F11	0.9044(4)	0.3364(4)	−0.1721(2)	0.057(2)
F12	0.7498(4)	0.4243(3)	−0.2296(2)	0.058(2)
F13	0.4284(5)	0.0670(4)	0.2546(2)	0.084(3)
F14	0.8430(3)	0.1780(4)	−0.0779(1)	0.052(2)
C15	0.7849(6)	0.3098(6)	−0.1951(2)	0.035(3)
C16	0.7794(6)	0.1847(6)	−0.2353(2)	0.036(3)
C17	0.5802(6)	0.3089(6)	0.0481(2)	0.031(3)
C18	0.7204(5)	0.19210(6)	−0.0997(2)	0.031(3)
C19	0.5144(6)	0.1888(5)	0.1427(2)	0.032(3)
C20	0.6599(6)	0.3102(6)	−0.0031(2)	0.034(3)
F21	0.9953(6)	0.0811(6)	−0.3931(2)	0.100(4)
F22	0.8488(5)	0.0511(4)	−0.3091(2)	0.075(3)
C23	0.5315(6)	0.3090(6)	0.1863(2)	0.038(3)
F24	0.9404(6)	0.1660(6)	−0.4803(2)	0.119(4)
C25	0.5912(6)	0.1880(5)	0.0907(2)	0.032(3)
C26	0.8812(6)	0.2850(8)	−0.3952(3)	0.048(4)
C27	0.7039(6)	0.3092(6)	−0.1442(2)	0.035(3)
F28	0.7199(6)	0.3312(8)	−0.4715(2)	0.119(4)
F29	0.8914(6)	0.4275(6)	−0.4813(2)	0.107(4)
C30	0.8534(6)	0.1843(6)	−0.2892(2)	0.040(3)
C31	0.6438(6)	0.1925(6)	−0.0476(2)	0.033(3)
F32	0.5988(5)	0.1486(6)	0.2932(2)	0.094(3)
C33	0.4804(7)	0.1818(7)	0.2814(3)	0.050(4)
C34	0.4587(7)	0.3039(7)	0.2406(3)	0.043(3)
C35	0.8070(6)	0.2775(7)	−0.3414(2)	0.042(3)
F37	0.7829(6)	0.4995(6)	−0.4153(2)	0.108(4)
C38	0.9050(10)	0.1480(10)	−0.4259(3)	0.073(6)
C39	0.8170(10)	0.3890(10)	−0.4422(3)	0.078(6)
F40	0.8048(7)	0.0725(6)	−0.4322(2)	0.113(4)
H34A	0.3737	0.3059	0.2237	0.10(3)
H34B	0.4780	0.3863	0.2636	0.07(2)
H19A	0.4285	0.1890	0.1272	0.03(2)
H19B	0.5325	0.1083	0.1671	0.08(2)
H17A	0.4969	0.3132	0.0288	0.03(2)
H17B	0.5995	0.3923	0.0703	0.04(2)
H31A	0.6641	0.1079	−0.0265	0.04(2)
H31B	0.5597	0.1895	−0.0658	0.03(2)
H27A	0.6206	0.3077	−0.1636	0.05(2)
H27B	0.7192	0.3948	−0.1232	0.05(2)
H16A	0.6930	0.1729	−0.2483	0.03(2)
H16B	0.8081	0.1105	−0.2089	0.04(2)
H35A	0.7240	0.2566	−0.3579	0.06(2)
H35B	0.8110	0.3703	−0.3264	0.05(2)

[a] $U_{eq} = (1/3)\sum\sum[U_{ij}a^*(i)a^*(j)a(i)a(j)\ \cos(\tau_{ij})]$ where U_{ij} is the component of anisotropic thermal parameters tensor. The a^* and a are respectively the unit cell vectors of the reciprocal lattice and the real lattice.

as the solvent for casting, the annealing temperature, the external forces, etc.[16] For the oligomers, also, the change in the preparation condition was found to give the various crystal modifications. For example, Figure 8 shows the infrared spectra taken for a series of oligomers (6−12-mers) crystallized from the ethanol solutions. The oligomers of 6−10-mers show the spectral profile almost similar to that of PVDF form II, where the characteristic bands are detected at 1409, 1385, 1210, 796, 765, 610, and 532 cm^{-1}.[32] Many additional bands are observed in these spectra, which are originated from the end groups as well as the so-called progression bands of VDF segments of finite length. For the oligomers of 11- and 12-mers, the infrared spectra are similar to that of PVDF form III with TTT$\bar{G}$TTT conformation and the characteristic bands are observed at 1234, 835, 810, 512 cm^{-1}, etc.[33,34] When the samples are cooled from the melt to room temperature, all of the oligomer members show an infrared spectral pattern similar to that of PVDF form III, as shown in Figure 9. But, when the sample was embedded into KBr disk and cooled from the melt, these oligomers were found to crystallize into crystal form I with the planar-zigzag conformation, as seen in Figure 10. The crystal form I of PVDF is usually prepared by stretching the unoriented sample at room temperature. In other words, the crystal form I can be prepared by applying the external tensile force along the chain direction, by which the

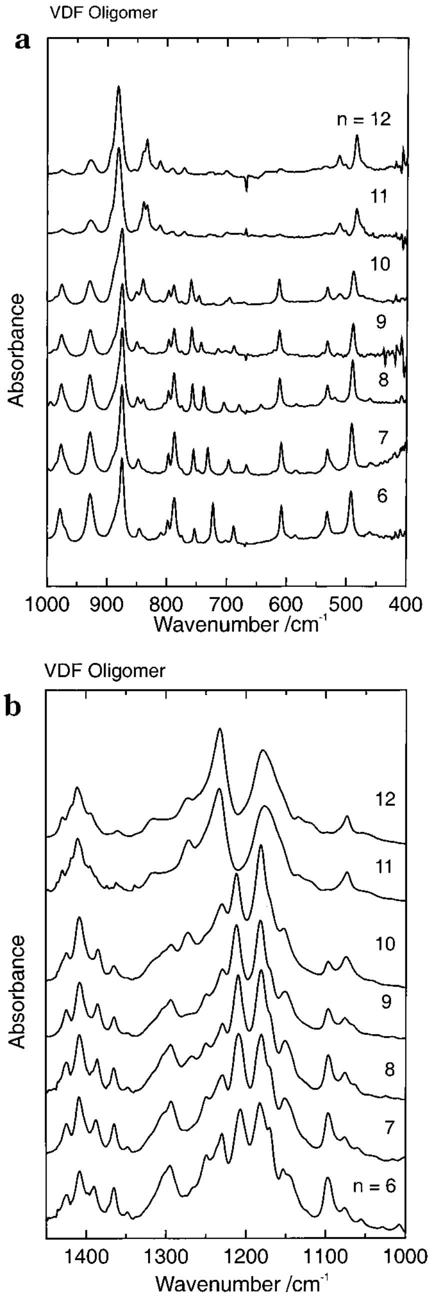


Figure 8. Infrared spectra of a series of VDF oligomers measured at room temperature, where the samples were prepared from ethanol solutions. Frequency region is (a) 400−1000 and (b) 1000−1500 cm^{-1}.

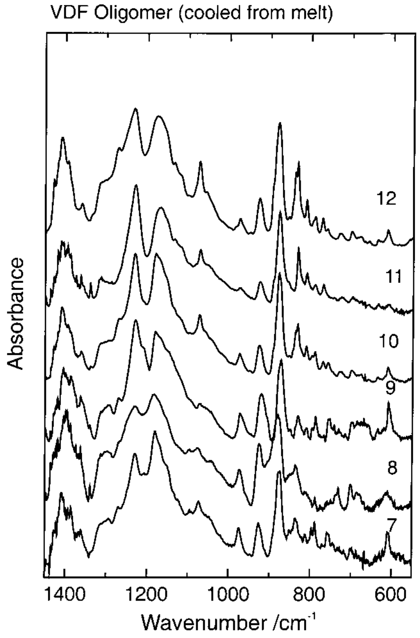


Figure 9. Infrared spectra of a series of VDF oligomers measured at room temperature, where the samples were prepared by cooling slowly from the melt.

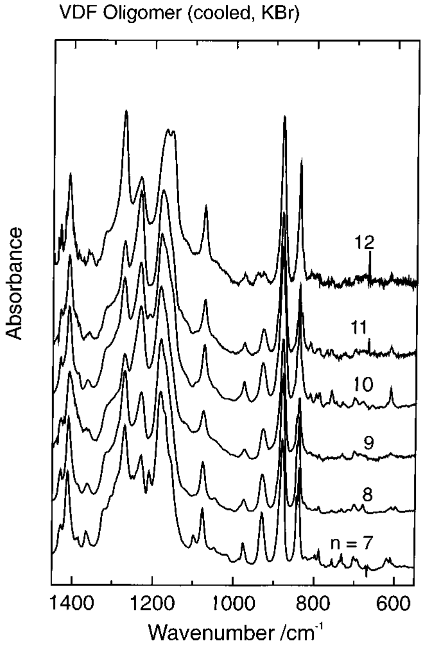


Figure 10. Infrared spectra of a series of VDF oligomers measured at room temperature, where the samples were prepared by slowly cooling the KBr disks from the melting state to room temperature.

gauche bond changes into the trans bond. The KBr disk seems to give a pressure or stress to the oligomer molecules trapped in the KBr powder matrix, resulting in the formation of planar-zigzag conformation. In this way, the oligomers were found to exhibit a variety of crystal modifications depending on the sample preparation conditions, quite similar to the phenomena observed for PVDF parent polymer. They show also various types of phase transitions among these various crystal modifications, the details of which will be reported eslewhere.

Herman et al.[26,27] and Yoshida et al.[28] reported also the formation of many crystal modifications for the VDF oligomers with different end groups. For example, the oligomers with the chemical structure of $CCl_3-(CH_2-CF_2)_n-Cl$ were reported to crystallize into form I (for $n < 10$), form II ($n = 10-16$), and form III ($n > 16$) when they are cooled from the melt. These behaviors are quite different from our cases. In this way, the end groups affect sensitively the crystallization behaviors of the oligomers. To clarify the details of the end group effect from the energetic point of view, we are now trying to analyze the crystal structures by carrying out the packing energy calculation.

Conclusions

In the present study the separation of a series of VDF oligomers could be made successfully at high purity by utilizing the SFC technique. The oligomers with $n = 6$, 7, and 8 VDF units could be grown into single crystals, for which the X-ray structure analyses were made successfully. The molecular conformation and the packing structure in the subcell were found to be essentially the same with those of PVDF form II. In other words, the structural information obtained for the oligomers could allow us to confirm the structural features of PVDF form II, although the effects of end groups cannot be ignored more or less for the strict discussion of the structural similarity between the oligomers and the parent polymer. At the same time, these oligomers were found to exhibit the various types of crystal modifications depending on the preparation conditions of the samples, similarly to that observed for the parent polymer. Depending on the end groups, the different crystal modifications were obtained even when the preparation condition was almost the same, suggesting an important role of the end groups in the structure formation of the oligomers, although the concrete reasons have not yet been clarified from the energetic point of view.

Acknowledgment. The authors thank Daikin Kogyo Co. Ltd., Japan, for kindly supplying oligomer samples.

Supporting Information Available: CIF files (including atomic fractional coordinates, intra- and intermolecular parameters and observed and calculated structure factors) for the structure analysis of VDF oligomers (6-mer and 7-mer). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Morin, P.; Beccard, B.; Caude, M.; Rosset, R. *J. High Resolut. Chromatogr.* **1988**, *11*, 697.
(2) Jenkins, T. J.; Kaplan, M.; Simmonds, M. R.; Davidson, G.; Healy, M. A.; Poliakoff, M. *Analyst* **1991**, *116*, 1305.
(3) Jenkins, T. J.; Kaplan, M.; Davidson, G.; Healy, M. A.; Poliakoff, M. *J. Chromatogr.* **1992**, *53*, 626.
(4) Kirschner, C. H.; Jordan, S. L.; Taylor, L. T.; Seemuth, P. D. *Anal. Chem.* **1994**, *66*, 882.
(5) Jenkins, T. J.; Kaplan, M.; Davidson, G. *J. High Resolut. Chromatogr.* **1994**, *17*, 160.
(6) Gurka, D. F.; Pyle, S.; Titus, R.; Shafter, E. *Anal. Chem.* **1994**, *66*, 2521.
(7) Norton, K. L.; Griffiths, P. R. *J. Chromatogr., A* **1995**, *703*, 503.
(8) Kirschner, C. H.; Taylor, L. T. *J. High Resolut. Chromatogr.* **1994**, *17*, 61.
(9) Smith, S. H.; Jordan, S. L.; Taylor, L. T.; Dwyer, J.; Willis, J. *J. Chromatogr., A* **1997**, *295*, 764.

(10) Liang, S.; Tilotta, D. C. *Anal. Chem.* **1998**, *70*, 616.
(11) Hatada, K.; Ute, K.; Nishimura, T.; Kashiyama, M.; Saito, T.; Takeuchi, M. *Polym. Bull. (Berlin)* **1990**, *23*, 157.
(12) Hatada, K.; Ute, K.; Miyatake, N. *Prog. Polym. Sci.* **1994**, *19*, 1067.
(13) Ute, K.; Yamasaki, Y.; Naito, M.; Miyatake, N.; Hatada, K. *Polym. J.* **1995**, *25*, 1275.
(14) Ute, K.; Takahashi, K.; Matsui, K.; Hatada, K. *Polym. J.* **1995**, *25*, 1275.
(15) *Ferroelectric Polymer*; Nalwa, H. S., Ed.; Marcel Dekker: New York, 1995.
(16) Tashiro, K. Crystal Structure and Phase Transition of PVDF and Related Copolymers. In ref 15, pp 63−181.
(17) Lovinger, A. J. Poly(vinylidene fluoride). In *Developments in Crystalline Polymers-1*; Bassett, D. C., Ed.; Applied Science Publishers: London, 1982; p 195.
(18) Lando, J. B.; Olf, H. G.; Peterlin, A. *J. Polym. Sci., Part A-1* **1966**, *4*, 941.
(19) Hasegawa, R.; Takahashi, Y.; Chatani, Y.; Tadokoro, H. *Polym. J.* **1972**, *3*, 600.
(20) Doll, W. W.; Lando, J. B. *J. Macromol. Sci., Phys.* **1970**, *B4*, 309.
(21) Takahashi, Y.; Matsubara, Y.; Tadokoro, H. *Macromolecules* **1983**, *16*, 1588.
(22) Davis, G. T.; McKinney, J. E.; Broahurst, M. G.; Roth, S. C. *J. Appl. Phys.* **1980**, *51*, 5095.
(23) Weinhold, S.; Litt, M. H.; Lando, J. B. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 585.
(24) Weinhold, S.; Litt, M. H.; Lando, J. B. *Macromolecules* **1980**, *13*, 1178.
(25) Takahashi, Y.; Tadokoro, H. *Macromolecules* **1980**, *13*, 1317.
(26) Herman; Uno, T.; Kubono, A.; Umemoto, S.; Kikutani, T.; Okui, N. *Polymer* **1997**, *38*, 1677.
(27) Herman; Umemoto, S.; Kikutani, T.; Okui, N. *Polym. J.* **1998**, *30*, 659.
(28) Yoshida, Y.; Ishida, K.; Ishizaki, K.; Horiuchi, T.; Matsushige, K. *J. Appl. Phys.* **1997**, *36*, 7389.
(29) Hanesaka, M.; Tashiro, K. *Kobunshi Ronbunshu*, in press.
(30) Otowinowski, Z.; Minor, W. *Macromolecular Crystallography: Part A*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, p 307.
(31) Altmare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.
(32) Kobayashi, M.; Tashiro, K.; Tadokoro, H. *Macromolecules* **1975**, *8*, 158.
(33) Bachmann, M. A.; Gordon, W. L.; Koenig, J. L.; Lando, J. B. *J. Appl. Phys.* **1979**, *50*, 6106.
(34) Tashiro, K.; Kobayashi, K.; Tadokoro, H. *Macromolecules* **1981**, *14*, 1757.

MA011339O