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On Novel Crystalline Forms of Poly(γ-benzyl L-glutamate)

Previous papers[1-3] have indicated that poly(γ-benzyl L-glutamate) (PBLG) films composed of α-helices exhibit two crystal modifications, denoted forms B and C, when they are cast from solutions in various solvents. Form B, prepared from dimethylformamide, benzyl alcohol, and benzyl propionate, exhibits a well-defined X-ray pattern offering a three-dimensional monoclinic unit cell. In contrast, form C, cast from halogenated hydrocarbons such as chloroform, shows an X-ray pattern with some reflections on the equatorial line and continuous scatterings on other layer lines. Form C is, thus, described by a structure with a poor periodicity in the lateral packing as well as a displacement of mutual levels of α-helices along the axes. The basic structure cannot be altered by heat treatment around 180 °C, showing that these two forms differ from each other not in the side-chain conformation but in the way of disposition of two up and down directed chains.[3] In crystalline form B there is an alternating disposition of two chains while form C is considered to have a random displacement of the chains.[3,4]

Here, we report the structural characteristics of two highly crystalline forms, so-called forms D and E, which are newly prepared from the former kind of solvent. Forms D and E are characterized by extraordinarily large hexagonal unit cells with 7 chains and 19 chains included, respectively, and by having an ordered structure of side chains with restriction of their rotational motion.

PBLG (M_w = 80 000) was synthesized by the conventional NCA method using triethylamine as an initiator. Films of forms D and E were prepared by slow casting solutions in benzyl propionate over 2 weeks at 65 and 80 °C, respectively, where the nonvolatile solvents were evaporated under vacuum. Casting rate as well as temperature is a significant factor in making these forms. Quick casting produces only form B and somewhat prolonged casting over 2–3 days facilitates the coexistence of form B with form D or E, suggesting that both forms have been gradually altered from form B in the casting process. Wide-angle X-ray patterns were recorded with flat-plate and cylindrical cameras, using a Rigaku-Denki X-ray generator with Ni-filtered Cu Kα radiation. Dielectric measurements were conducted with a mutual inductance bridge (TR-1C), a detector (BAD-18), and an oscillator (WBG-3B) manufactured by Ando Electric Co., Ltd., over a frequency range from 30 Hz to 1 MHz.

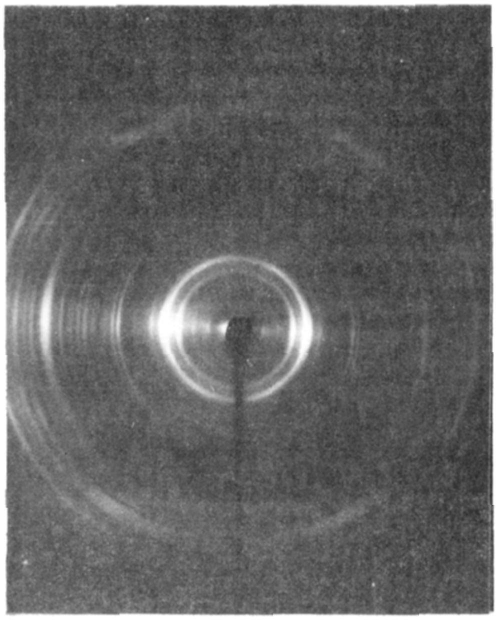

Figure 1. X-ray diffraction pattern of form E film. The X-ray beam was irradiated parallel to the film surface. The film surface is in the vertical direction.

Table I
X-ray Data of PBLG Form E

index[a]	d_{obsd}, Å	d_{calcd},[a] Å	intensity[b]
100		55.74	
110	32.4	32.18	w
200	28.0	27.87	w
210	21.0	21.07	w
300	18.5	18.58	vw
220	16.2	16.09	vvw
310	15.5	15.46	s
400	14.1	13.93	vw
320	12.8	12.79	vs
410	12.1	12.16	m
500	11.2	11.15	vvw
330	10.7	10.73	w
420		10.53	
510	10.1	10.01	vvw
600		9.29	
430		9.16	
520	8.92	8.93	vw
610	8.53	8.50	vvw
440		8.05	
530 700		7.96	
620	7.72	7.73	s
710	7.38	7.38	m

[a] Calculated spacings and indices are based on a hexagonal lattice with an edge of 64.3_6 Å. [b] Code: vs = very strong, s = strong, m = moderate, w = weak, vw = very weak, and vvw = very very weak.

Figure 1 shows the X-ray diffraction pattern of form E film where the X-ray beam was aimed parallel to the film surface. From the numerous reflections, one can easily see that this form is a highly crystalline form, which so far has not been observed in this kind of synthetic polypeptide. The spacings of reflections on the equatorial line, ranging from 40 to 7 Å, are well elucidated and are listed in Table I. For the reflections on other layer lines, however, no estimation of spacings was possible because of overlapping of the reflections due to poor orientation. The intense "turn" layer line, associated with the pitch length of the α-helix,[5] appears at 5.25 Å from the equator, as can be seen from Figure 1. We further find another layer line at 10.5 Å. The tilted pattern represents the 1.5-Å meridional reflection. A set of layer lines, hence, are equally spaced about 1/10.5 Å^{-1} apart, indicating that the helical conformation is not of the 18-residue, 5-turn type but of the 7-residue, 2-turn type.[6,7] Turning to the equatorial pattern, it is surprising that the spacing of the first reflection is 32.4 Å, which is remarkably larger than the diameter (=15 Å) of the molecule. This demands an extraordinarily large unit cell in the lateral packing structure. In fact, 16

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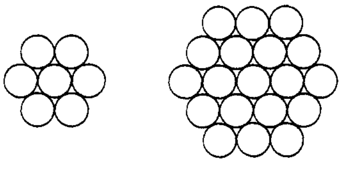

(a) Form D (b) Form E

Figure 2. Close-packed cylindrical rods composed of (a) 7 and (b) 19 α-helices.

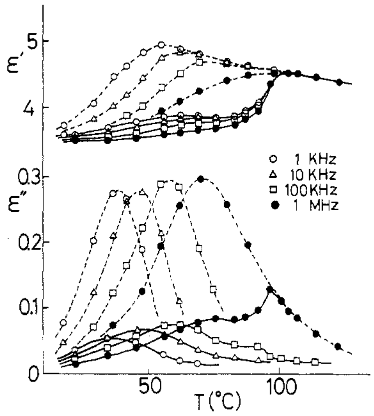

Figure 3. Temperature dependence of ϵ' and ϵ'' measured at a constant frequency for form E. The solid and dashed curves indicate the first and second heating data, respectively (see text).

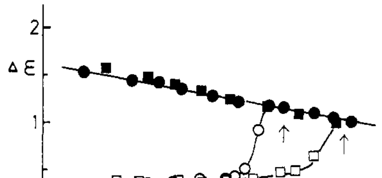

Figure 4. Temperature dependence of dielectric strength, $\Delta\epsilon$, for form D (○) and form E (□). The closed symbols indicate the $\Delta\epsilon$ for form B, which was prepared by heating form D or E above the DSC first-order transition temperature represented by the arrow.

equatorial reflections are well satisfied by a two-dimensional hexagonal lattice with a large edge of 64.3_6 Å, as noted in Table I. Correspondence of the calculated density with the observed one (1.28 g/mL) requires that 19 α-helices are located in this large hexagonal lattice. For form D, the X-ray pattern was observed with similar characteristics except that 7 chains pass through the hexagonal lattice with an edge of 39.0_5 Å.[8]

It is significant that evidence for 7 chains and 19 chains in the unit cells appears in the equatorial reflections. This means that these chains are not crystallographically equivalent to each other when viewed in projection along the axes. The packing structure can most easily occur by the close association of 7 chains or 19 chains. In this aspect, the numbers of 7 and 19 are meaningful since chains in these numbers produce close-packed cylindrical rods, as illustrated in Figure 2, the centers of which can form a large two-dimensional hexagonal lattice.[9]

In DSC thermograms, forms D and E display irreversible first-order transitions with enthalpy changes of 3.4 and 3.5 cal/g at 84 and 100 °C, respectively. On these transitions, the characteristic X-ray patterns mentioned above disappear and are altered to the simple pattern of form B.[3] This signifies that these forms have been induced on form B as suggested above.

The dielectric properties with respect to the side-chain motion differentiate these novel forms from form B. Figure 3 indicates the variation of dielectric constant, ϵ', and loss factor, ϵ'', with temperature measured at a constant frequency for form E film. The solid and dashed curves show the first heating data of form E and the second heating data of form B, respectively; the latter form B was prepared by heating form E above the DSC transition temperature. At a glance of this figure, we notice that the ϵ'' loss peak attributable to the side-chain motion is smaller in form E than that of form B at each frequency and the corresponding dispersion of ϵ' is also negligibly small. Irrespective of this difference, the frequency dependence of the ϵ'' peak temperature is similar for both forms, offering a similar activation energy of around 40 kcal/mol of repeat unit. The dielectric data of Figure 3 are thus realized such that the side chain rotational mode does not essentially differ between forms E and B and that form E, representing the smaller ϵ' and ϵ'', may contain a considerable number of side chains which are not able to move freely and contribute to the dielectric relaxation.

The dielectric strength, $\Delta\epsilon$ ($=\epsilon' - \epsilon''$), evaluated from conventional Cole–Cole plots, allows elucidation of the number of such unmoving side chains according to the equation[10]

$$\Delta\epsilon = 4\pi N\mu^2/3kT \qquad (1)$$

where N is the number of side chains in a unit volume contributing to the dielectric relaxation, μ the dipole moment of the carbonyl group of the side chain, k the Boltzmann constant, and T the temperature in Kelvin. In Figure 4, $\Delta\epsilon$ for forms D and E is plotted against temperature and compared to that of form B. When compared at around 40 °C, $\Delta\epsilon$ of 0.35 for forms D and E is approximately one-quarter of $\Delta\epsilon$ of 1.46 for form B. The latter value is to be expected when all of the side chains contribute to the dielectric relaxation.[7,11] Consequently from inspection of eq 1, there is a motional restriction for three-fourths of the overall side chains in forms D and E and, as found in Figure 4, such a restriction has been imposed until each DSC first-order transition temperature.

A recent paper[12] indicated that in poly(γ-n-alkyl L-glutamates) such a restriction of side-chain motion is imposed by the self-crystallization of the n-alkyl groups of the side chains. It also reported that the crystal formed is similar to an n-alkane crystal and only side chains with n-alkyl groups longer than the decyl group can participate in crystallization. Accordingly, the shorter side chains assume only an amorphous sheath around the main chain and so all of them can contribute to the dielectric and dynamic mechanical relaxations. It should be noted here that the amorphous nature of short side chains does not disappear even in polymers where α-helical rods are packed into a three-dimensional lattice. A representative example can be seen in poly(γ-methyl L-glutamate) (PMLG). PMLG exhibits a well-defined crystal lattice with dimensions of $a = b = 11.96$ Å, $c = 27$ Å, and $\gamma = 120°$,[13,14] although the side chains are in an amorphous-like state exhibiting a glass-like transition around 0 °C.[14,15] Possibly, the side chains are placed at somewhat confined positions around the main chain so as to promote the crystalline arrangement of α-helical rods but still have enough configurational freedom to cause the dielectric and dynamic mechanical losses. The same situation has appeared in PBLG forms B and C[7,15] and one could hardly imagine how the considerably restricted motion arises, especially in the short side chains of forms D and E.

In this particular case of PBLG, however, it is known that the benzene rings at the end of the side chains can organize to form a cooperative stack with a face-to-face arrangement.[7,16,17] This can be seen in the racemic mixture of PBLG and PBDG, in which the cooperative stack is preferentially formed between D and L molecules,[17,18] and its melt appears as a first-order transition at around 100 °C.[19] The dielectric and dynamic mechanical strengths in this film have been reduced,[20,21] as in this study, since relaxation occurs only in side chains free from the stack. We are thus led to the view that similar regular cooperative stacks of benzyl groups between adjacent molecules have been created in the present forms D and E. These stacks might be one of the factors stabilizing the specific association of 7 or 19 chains. Work is in progress to illustrate the packing structure of these novel forms in relation to the side-chain structure.

Registry No. PBLG (homopolymer), 25014-27-1; PBLG (SRU), 25038-53-3.

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On the Curie Temperature of Poly(vinylidene fluoride)

The existence and location of a Curie transition in poly(vinylidene fluoride) (PVF$_2$) have been issues of major importance in regard to the ferroelectric nature and the useful piezoelectric and pyroelectric properties of this polymer. While the first of these issues has now been resolved, the second remains controversial. Existence of Curie transitions in PVF$_2$ has been demonstrated primarily through studies of its copolymers with trifluoroethylene (F$_3$E).[1-9] However, trifluoroethylene introduces a new chemical species (–CHF–) that is absent in PVF$_2$, thus altering its chemical structure. It also introduces the possibility of stereoirregular defects (which, of course, does not exist for PVF$_2$); the resulting VF$_2$/F$_3$E copolymers have, in fact, been shown to be atactic.[1,10] We were the first to report on similar Curie transitions in a different copolymer of PVF$_2$, one containing ~19 mol % *tetra*fluoroethylene (F$_4$E).[11,12] This demonstration has been of importance in applying findings of Curie behavior to PVF$_2$ *homo*polymer, because the F$_4$E units introduce neither new chemical species nor tacticity defects but act simply as additional head–head linkages within PVF$_2$ (which typically contains ~3.5–6% of such units).

While the existence of a ferroelectric-to-paraelectric phase transition in PVF$_2$ is thus now generally accepted, its corresponding temperature is still a subject of controversy. The first reported values were given in 1980 by Micheron[13] and Herchenröder et al.[14] Micheron[13] suggested a Curie temperature of ~170 °C by extrapolation of data for the temperature dependence of the dielectric permittivity of PVF$_2$. This temperature lies just below the melting point of the piezoelectric β-phase of PVF$_2$, which is generally in the region ~175–185 °C (depending upon thermal treatment, polarization, orientation, etc.). The temperature proposed by Herchenröder and co-workers[14] is much lower (i.e., ~140 °C) but has been questioned because both piezoelectric constant (d_{31})[15] and remanent polarization[16] persist well above that temperature, and nearly saturated ferroelectric hysteresis loops are still observed at 140 °C.[17]

Further proposals of a Curie temperature for PVF$_2$ were made in 1983 by Tashiro and co-workers[18,19] and Lovinger et al.[7,8] Tashiro et al. showed that very small new peaks in IR absorbance[18] and X-ray diffracted intensity[19] are obtained at 172 °C during heating of β-PVF$_2$. These peaks were associated with adoption of a paraelectric-phase structure containing gauche and gauche$^-$ segments. Because the melting process is already well under way at this temperature, these peaks are very weak: for example, as seen in Figure 3 of ref 19, the (020) X-ray peak for the paraelectric phase appears only after ~80% of the room-temperature intensity of the corresponding (200,110) peak for the ferroelectric phase has been lost and does not rise above ~15% of that initial intensity. The Curie temperature that we proposed in our earlier work[7,8] was ~205 °C, which is significantly higher than any of the others. We obtained this estimate by extrapolating Curie temperatures from X-ray and dielectric data of VF$_2$/F$_3$E copolymers to 100 mol % VF$_2$. Our X-ray scans showed that the Curie transition for each of the copolymers is very broad (as are typically all transitions in polymers) and can thus encompass up to 40 °C from the first appearance of the paraelectric phase to complete disappearance of its ferroelectric counterpart. Accordingly, the Curie temperatures for each copolymer were reported as temperatures of maximal rate of transformation from the X-ray data and as peak maxima from dielectric spectra. As a result, we pointed out[7,8] that, if the Curie transition for PVF$_2$ is indeed centered at ~205 °C, its earliest manifestations should, in fact, be observable just below the melting point. We, therefore, consider the results of Tashiro et al.[18,19] consistent with ours, since their data show clearly that they observed only the *beginnings* of a transition that was in the process of being aborted by ongoing

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