Phase Diagram for Solutions of α-Helical Poly(L-glutamate)s in *m*-Cresol Including Isotropic, Cholesteric, and Columnar Phases

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ABSTRACT: The temperature-concentration phase diagram was constructed for lyotropic solutions of poly(γ-phenylpropyl L-glutamate) in *m*-cresol in the temperature range from 0 to 70 °C and in the concentration range from 0 to 100 vol %. Visual and microscopic observations and the X-ray measurement were employed to determine the phase structures and phase boundaries. The well-known transition from the isotropic phase to the cholesteric phase is observed in the low concentration range of 8 to 14 vol %, as predicted using the Flory lattice theory and reported from experiments. At higher concentrations, however, a novel phase behavior is observed. The cholesteric phase is transformed to the hexagonal columnar phase through the coexistence region. The critical concentration of the columnar phase appearing from the cholesteric one is 49 vol %. The removal of solvents from this columnar solution leads to the solid state structure with the hexagonal packing symmetry. Thus, the phase diagram was well clarified, and found to include three phases: isotropic, cholesteric, and columnar phases. According to this phase diagram, at high temperatures, the isotropic−cholesteric−columnar phase transition takes place upon increasing the concentration, whereas at low temperatures, the isotropic solution directly transforms to the columnar phase. Similar phase diagrams are presumed for other poly(γ-alky L-glutamates) and poly(γ-phenylalky L-glutamates), although the critical concentration of the columnar phase will increase with an increase in side-chain length.

1. Introduction

Liquid-crystalline phases formed by rigid-rod polymers have been studied extensively both theoretically and experimentally. In the initial stage of theoretical work, it was shown that a system of long, rigid molecules can exhibit an orientationally ordered nematic phase in thermotropic[1] and lyotropic systems,[2] if the density and concentration are sufficiently high, respectively. Flory predicted the phase diagram in lyotropic solutions of a rodlike polymer depicted in Figure 1. Isotropic and liquid-crystalline phases coexist over a narrow concentration range in good solvents (at high temperatures), but are widely separated in poor solvents (at low temperatures). These general features have been confirmed in the poly(γ-benzyl L-glutamate)−DMF or −benzyl alcohol system,[3−7] but actual systems may be much more complex, particularly in the high concentration region in which the intermolecular interaction between rigid-rod molecules becomes significant.

Hoshino et al.[8] were the first to predict that a smectic phase, as well as a nematic phase, can be formed in a system of completely aligned, monodisperse cylindrical molecules that interact solely through excluded volume interactions. In their calculations, the nematic to smectic A phase transition for molecules with a sufficiently high axial ratio is a second-order transition whereas that for molecules with the axial ratio of 7 or less is a first-order one. This result renewed the general concept that smectic phases can be formed from only low-molecular-weight molecules as a result of the microsegregation of aromatic mesogenic groups and aliphatic tail groups,[9] and it prompted many further theoretical studies of smectic liquid crystal formation based on simple hard-rod molecules.[10−16] In subsequent simulation studies,[13−16] Frenkel and co-workers presented a complete phase diagram for perfectly aligned monodisperse spherocylinders as functions of the axial ratio of the molecule and molar density. It shows the step-by-step transformation from the nematic phase to the smectic phase and then to the columnar phase with increasing density. In the smectic phases, the molecules are laterally packed with a liquidlike nature as in the nematic phase, but with a one-dimensional positional order along the director. In the columnar phase the lateral positional order appears and then the molecules are packed into two-dimensional hexagonal lattice (refer to

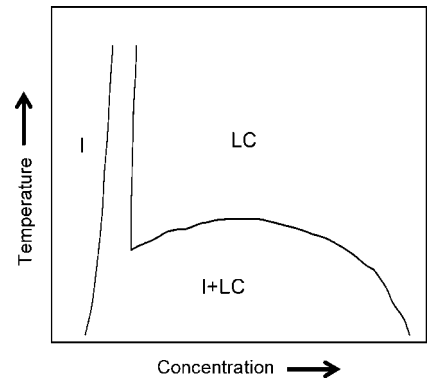

Figure 1. Schematic presentation of phase diagram predicted for lyotropic solutions of rigid-rod molecules by Flory lattice theory.

Table 1. Characterization of Poly-L-glutamates

polymer	inherent viscosity $[\eta]$ (dL g^{-1})	molecular weight $M_w \times 10^{-4}$	density ρ (g L^{-1})
PMLG	0.93	10.4	1.29
PELG	0.84	9.0	1.24
PProLG	1.09	13.0	1.19
PBuLG	1.10	13.2	1.14
PAmyLG	0.90	10.0	1.13
PHexLG	0.85	9.2	1.13
PBLG	2.76	55.4	1.28
PPELG	2.37	46.4	1.23
PPProLG (I)	0.35	5.1	1.19
PPProLG (II)	1.58	29.2	1.19

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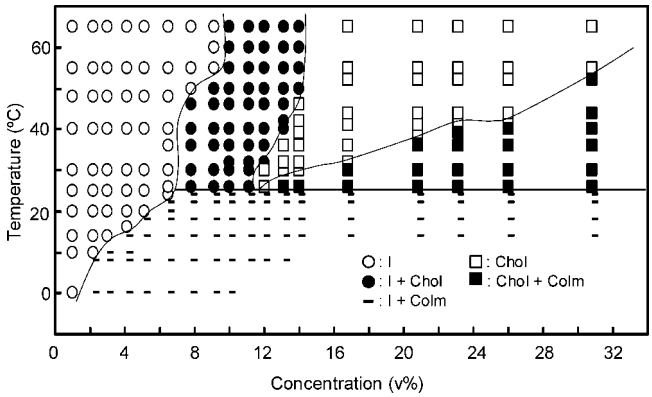

Figure 2. Phase diagram determined from visual and microscopic observations of PPProLG−*m*-cresol solutions in concentration range from 0 to 35 vol %. Here, I, Chol, and Colm indicate the isotropic, cholesteric, and columnar phases, respectively.

Figures 3 and 5 in ref 13). Such step-by-step organization, in fact, has been observed in the thermotropic liquid crystal system of hard-rod polysilines.[17]

To describe the liquid crystalline behavior in more realistic polymer systems, the rigid-rod molecules with polydispersity in their lengths have been theoretically treated by Sluckin,[18] Stroobands,[19] and Bates and Frenkel.[20] According to their results, the phase behavior is essentially unchanged from that observed in a monodisperse system when the polydispersity is small (standard deviation, $s < 0.08$). However, with increasing polydispersity ($0.08 < s < 0.18$), the smectic phase becomes increasingly destabilized in comparison with the nematic and columnar phases, and is eventually depleted at $s = 0.18$, which corresponds to $M_w/M_n = 1.08$. Consequently, for typical hard-rod systems with polydispersity, it is speculated that the nematic liquid crystal directly transforms to the columnar phase upon increasing the concentration in a lyotropic system or decreasing the temperature in a thermotropic system.

In experiments, lyotropic phases have been extensively studied in biological molecular systems, because the liquid crystalline field adds in the self-organization of rodlike biopolymers that may be important for functionality in biological systems. Columnar and smectic liquid crystals have been reported in lyotropic liquid crystals of synthetic polypeptide,[21–25] DNA,[26,27] and tobacco mosaic virus.[28] These new phases can be easily differentiated from the nematic (or cholesteric) phase that has so far been studied well in rodlike polymers; however, there is no report on a temperature-concentration diagram that includes the columnar and smectic phases.

In the present study, we found a clear transition between the cholesteric and columnar phases in addition to the well-known isotropic to cholesteric phase transition in the poly(γ-phenylpropyl L-glutamate)−*m*-cresol system, and constructed the whole phase diagram in the concentration range of 0 to 100 vol % and the temperature range of 0 to 70 °C. The effect of the side chains on phase behavior was also discussed by treating poly(γ-alkyl L-glutamate)s and poly(γ-phenylalkyl L-glutamate)s.

2. Experimental Section

Poly(γ-methyl L-glutamate) (PMLG), poly(γ-benzyl L-glutamate) (PBLG), poly(γ-phenylethyl L-glutamate) (PPELG) and poly(γ-phenylpropyl L-glutamate) (PPProLG) were synthesized by a conventional NCA method. Poly(γ-alkyl L-glutamate)s with ethyl to hexyl side chains, PELG, PProLG, PButLG, PAmLG, and PHexLG, were prepared from poly(γ-methyl L-glutamate) by ester exchange reaction with the corresponding alkyl alcohols. The molecular weights were determined from the intrinsic viscosities

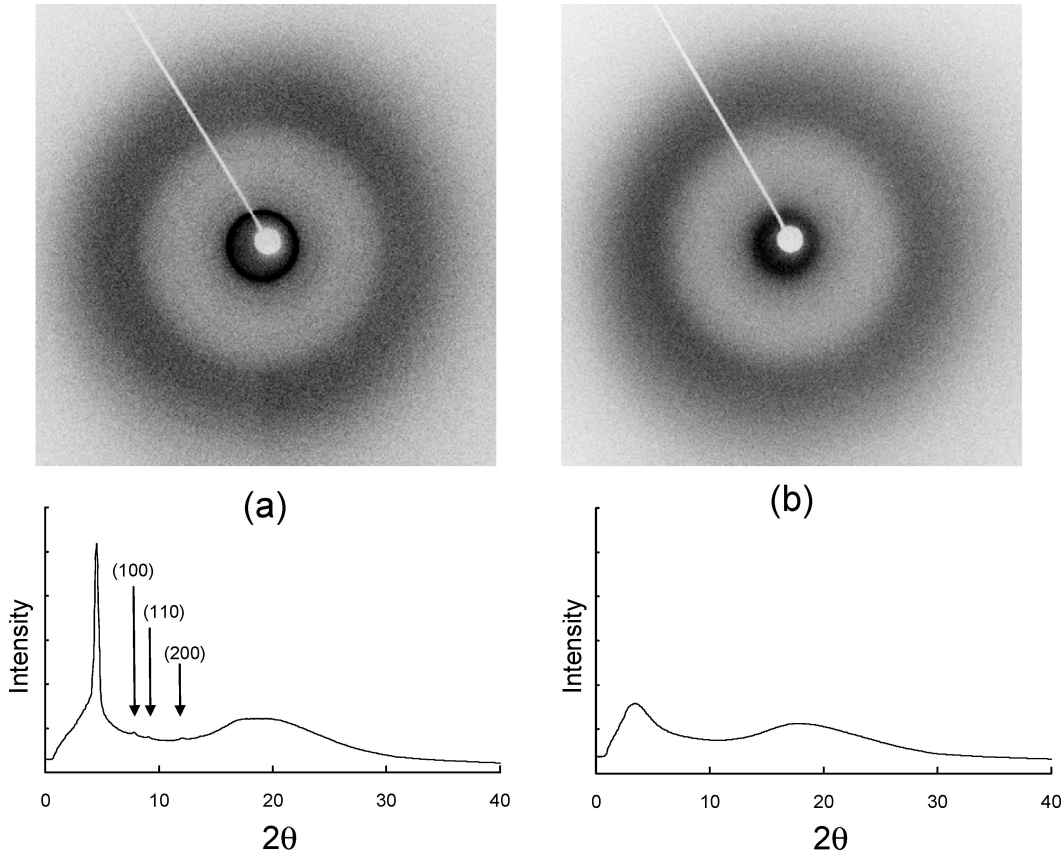

Figure 3. Typical X-ray patterns of (a) the columnar phase observed for solution with concentration of 29.2 vol % at 20 °C and (b) the cholesteric phase at 50 °C. Corresponding 2θ-intensity profiles are given below the photographs.

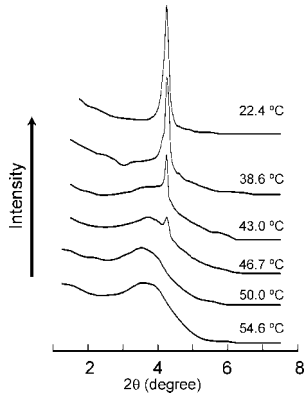

Figure 4. Variation of X-ray diffraction profile observed for solution with concentration of 29.2 vol % when temperature increases from 20 to 60 °C. In the 2θ region of 2−8°, the sharp (100) reflection of the columnar phase and the broad reflection of the cholesteric phase are observed.

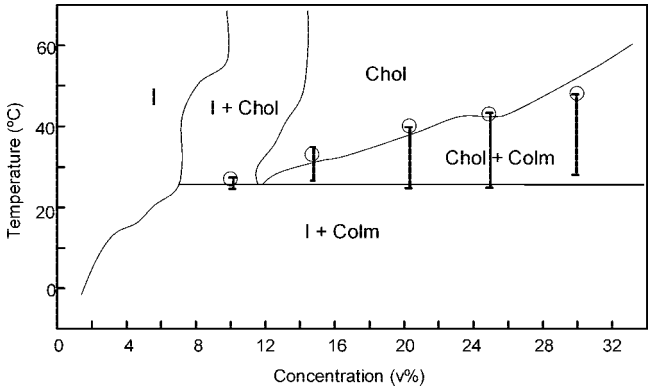

Figure 5. Plot of characteristic temperatures at which columnar phase disappears, against concentration. The data of open circles were collected from the X-ray diffraction profile. The bars show the temperature span of the DSC peak due to the columnar-cholesteric phase transition (see later Figure 6). The phase boundaries are the same as those determined in Figure 2.

in dichloroacetic acid at 25 °C using the relation given by Doty et al.[29] and are listed in Table 1.

m-Cresol solvent for solutions was supplied from Aldrich Co., Ltd., and then used after distillation with a vacuum to avoid moisture and oxygen. Solutions were prepared by weight and homogenized in capped vials containing magnetic stirrers, on a stirring hotplate. The temperature required for dissolution was increased with increasing concentration. When necessary, the temperature was increased to as high as 70−80 °C to ensure homogeneous samples. Such a preparation was used to make the solutions with concentrations below 40 vol %. The higher concentration samples were prepared by keeping both the solid film and solvent inside a sealed tube and annealing it for a prolonged time at 100 °C. The conversion of the weight fraction to the volume fraction (vol %) was calculated based on the additive average of the densities of polymer (listed in Table 1) and *m*-cresol (1.03 g/cm^3).

For the measurement of wide-angle X-ray diffraction (WAXD), an X-ray generator (Rigaku-Denki) with Ni-filter Cu Kα radiation was used. All the X-ray studies were performed in 1.5-mm diameter glass capillaries; the sample was transferred into the capillary, which was then flame-sealed. A good seal was ensured by weighing over a period of several days to check for leaks. Solid films were prepared by casting LC solutions in *m*-cresol at 100−120 °C in a shaded chamber under flowing nitrogen atmosphere. A magnetic field at 5 T was applied to get the oriented film. Interplanar diffraction spacing was calculated and calibrated from the reflection of (111) from the silicon powder sprinkled over the capillary tube.

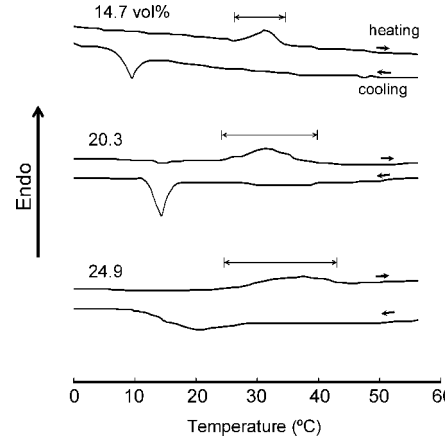

Figure 6. DSC thermogram observed for solutions with concentrations of 14−30 vol %, showing transition from columnar phase to cholesteric phase. Scanning rate is 5 °C/min. The bars indicate the temperature span of the DSC peak.

DSC measurement was taken on Perkin-Elmer DSC2. Ten milligrams of sample was placed onto weighed aluminum pans. The pans were then sealed by crimping. The pans were weighed to check for the leakage of solvent before measurement, and defective samples were discarded.

3. Results and Discussion

3.1. Visual and Microscopic Observations of Phase Behavior in PPProLG−*m*-Cresol. The PPProLG−*m*-cresol solutions with various concentrations from 0 to 35 vol % were contained in a sealed glass tube with a diameter of 3 mm. Here, the molecular weight of used PPProLG is 292000 (refer to Table 1). The concentrations were limited to below 35 vol % because higher concentration solutions are difficult to prepare as a uniform fluid. Three phases, isotropic, cholesteric, and columnar phases, could be recognized in this concentration range by visually observing the solutions. The formation of cholesteric liquid crystal from the isotropic solution can be detected from its strong birefringence, and the whitish and opaque (turbid or cloudy) columnar phase can easily be distinguished from the two other transparent phases. The cholesteric phase is distinguished from the two other phases by the microscopic observation of the fingerprint texture characteristic of its macroscopic helical structure.

The observed phase behavior, which covers the concentration range from 0 to 35 vol % and the temperature range from 0 to 70 °C, is shown in Figure 2. Two features can be observed here. The first is the conventional feature predicted on the basis of the Flory theory.[2] As the concentration increases, the isotropic phase transforms to the cholesteric phase through the chimney zone in the range from 8 to 14 vol % where the two phases coexist in equilibrium. The second feature is observed in the higher concentration range. The columnar phase appears from the cholesteric phase with further increase in concentration, resulting in a coexistence zone of cholesteric and columnar phases. The boundary between the uniform cholesteric zone and the coexistence zone moves to a higher temperature with the increase of concentration. Furthermore, when the temperature decreases to below 25 °C, the cholesteric phase disappears and the columnar phase directly appears from the isotropic solution, resulting in a wide coexistence zone of the columnar and isotropic phases.

3.2. Confirmation of Columnar Phase by X-ray Observation. The columnar phase has a two-dimensional hexagonal packing order that can be identified from the X-ray pattern.[24] The typical X-ray pattern as observed for the solution with the

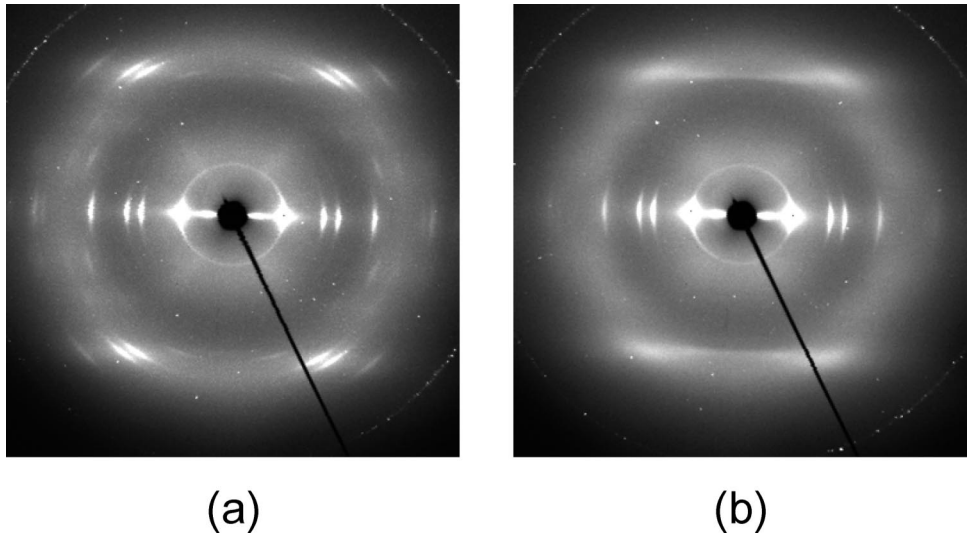

Figure 7. X-ray patterns of solid PPProLG film cast from the *m*-cresol solution (a) at room temperature and (b) at 150 °C. The high degree of orientation is obtained using a magnetic field.

Table 2. X-ray Data for Solid Film of poly(γ-phenylpropyl L-glutamate) Cast from *m*-Cresol

L	d_{obs}/Å	d_{calc}/Å[a]	*hkl*[a]	intensity
0	14.35	14.25	100	VS
	8.21	8.23	110	S
	7.13	7.13	200	MS
	5.42	5.39	210	MS
	4.14	4.12	220	W
	3.98	3.95	310	W
	3.59	3.56	400	VW
	3.28	3.27	320	VW
5	5.09	5.08	105	S
	4.52	4.54	115	S
	4.34	4.32	205	VW
	3.85	3.83	215	W

[a] Based on a hexagonal lattice with $a = b = 16.4^6$ Å and $c = 27.1^8$ Å.

concentration of 29.2 vol % at 20 °C is shown in Figure 3a. The sharp reflections indexed with (100), sometimes followed by weak (110) and (200) reflections, are detected here. This diffraction pattern is markedly different from that of the cholesteric phase observed at 50 °C for the same solution. The cholesteric phase includes only broad reflection near the 2θ position corresponding to the (100) reflection of columnar phase, as shown in Figure 3b. The broadening of the reflection indicates that the long axes of helices are aligned uniaxially, but with some orientational disordering due to the rotational fluctuation around the short axis.

The transformation from the columnar phase to the cholesteric one can therefore be detected by the X-ray method.[30] Figure 4 shows the variation of the X-ray diffraction profile when the temperature increases from 20 to 60 °C. In the higher temperature region of 50−60 °C, only the broad reflection attributable to the cholesteric phase can be seen. On cooling, the sharp (100) reflection of the columnar phase appears at 46 °C. Its relative intensity to that of the broad reflection increases with a decrease in temperature; finally, the broad reflection disappears completely at 35 °C. The spacing of the (100) reflection of the columnar phase remains nearly constant with the change in temperature from 0 to 60 °C. These results indicate that the relative volume fraction of the columnar phase to the cholesteric phase is temperature-dependent but that the concentration of the columnar phase remains constant.

The temperatures at which the columnar phase disappears are collected for the solutions with other concentrations and

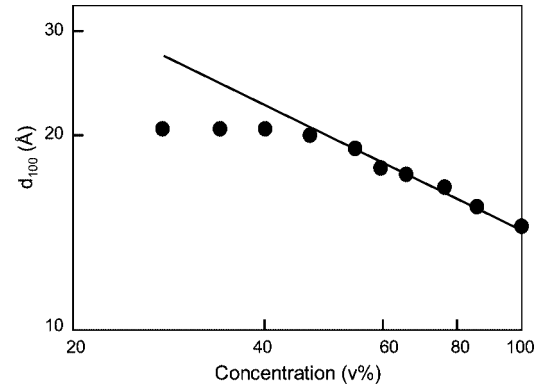

Figure 8. Logarithmic plot of spacing of (100) reflection against concentration. The data were collected for the solutions at 25 °C.

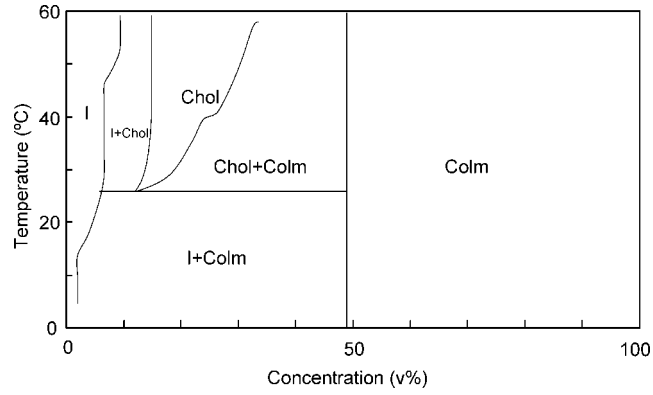

Figure 9. Phase diagram of the PPProLG−*m*-cresol solution system in the whole concentration range.

plotted as open circles in Figure 5. One can see that all these points fall on the boundary between biphasic and cholesteric zones, which was determined from the visual observation of Figure 2. It is interesting that the spacings of the (100) reflection are the same for the coexisting columnar phase in any solution; in other words, it is concentration-invariant as well as temperature-invariant. The spacing of the (100) reflection is 20.2 Å. From this spacing, the concentration of the columnar phase can be calculated as 49 vol %. Thus, the equilibrium line bounding the columnar phase is located at 49 vol % and lies perpendicular

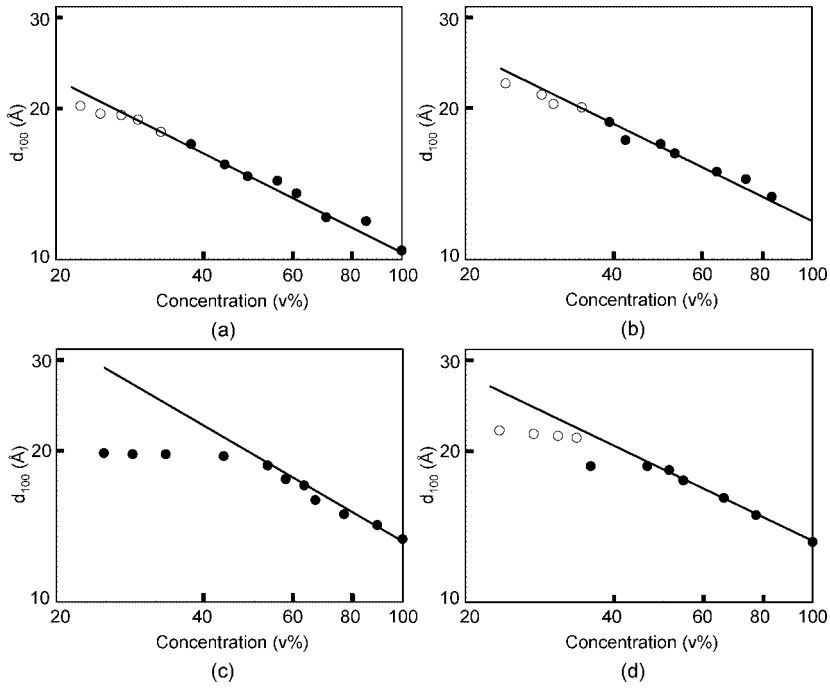

Figure 10. Logarithmic plots of spacing of (100) reflection of columnar phase against the concentration: (a) poly(γ-methyl L-glutamate), (b) poly(γ-propyl L-glutamate), (c) poly(γ-amyl L-glutamate), and (d) poly(γ-benzyl L-glutamate). The closed and open circles are collected for the columnar and cholesteric phases, respectively.

to the concentration axis (see later, Figure 9). Note here that this critical concentration does not depend on molecular weight; PPProLG with molecular weights of 292000 and 51000 show the same critical concentration of 49 vol %. This is in contrast to the fact that the concentration of the isotropic−cholesteric biphasic zone strongly depends on the axial ratio.[2,5] Only the nature of the side chain affects the critical concentration, as discussed below.

3.3. DSC Thermogram for the Columnar to Cholesteric Phase Transition. The transition from the columnar phase to the cholesteric phase can also be detected in the DSC thermogram. A typical example is shown in Figure 6. The endothermic peak is relatively sharp when the concentration is as low as 15 vol %, whereas the peak becomes wide when the concentration is high. This is reasonable because the columnar phase gradually transforms to the cholesteric phase through the biphasic temperature zone, which becomes wider with an increase in concentration (refer to Figure 2). The temperature range of the DSC peak is given by the bars in Figure 5. It clearly corresponds to the temperature region of the biphasic zone of the columnar and cholesteric phases. The total transition enthalpy, 0.1 kcal/mol of repeating unit, is almost constant, which is attributable to the melting of the two-dimensional positional order of the columnar phase.

3.4. Structural Change in the Concentration Region above 49 vol %. The solid film cast from the *m*-cresol solution of PPProLG shows the well-defined packing structure, as shown in the X-ray pattern of Figure 7a. The spacings are listed in Table 2. The helical molecules are packed in a three-dimensional hexagonal lattice with parameters of $a = b = 16.5$ Å and $c = 27.2$ Å. The simple hexagonal lattice is thus similar to that of the columnar phase with a concentration of 49 vol %. However, there is a remarkable difference between them. The lyotropic columnar phase possesses the two-dimensional hexagonal packing order, showing only sharp reflections with indices of (*hk*0). On the other hand, the solid film shows additional sharp reflections on the layer lines such as the second, third, and fifth layer lines, indicating the three-dimensional order.

Table 3. Spacing Reflection (d_{100}) and Polymer Volume Fraction of Columnar Phase at the Critical Concentration

polymer	d_{100}/Å	polymer volume fraction (vol %)	calculated volume fraction (vol %)[a]
PMLG	16.9	37.4	60.0
PELG	17.5	38.9	47.8
PProLG	18.6	40.0	47.2
PBuLG	18.7	44.6	40.3
PAmyLG	19.4	44.7	35.3
PHexLG	20.0	45.2	31.0
PBLG	18.4	48.6	43.0
PPELG	19.4	48.5	40.0
PPProLG (I)	20.2	49.0	35.3
PPProLG (II)	20.2	49.0	35.3

[a] Calculated under the assumption that the solvents are included only within the side chains which are fully extended.

Thus, one may speculate some structural transformation between the lyotropic columnar phase and solid crystalline phase on increasing the concentration. To clarify this, we examined the X-ray pattern in the concentration range from 49 to 100 vol %.

Highly concentrated solutions were prepared as follows. A film sample was first kept inside the capillary tube, and the solvent was added to achieve a certain weight fraction. After the sample was annealed for 24 h at 100 °C, the X-ray pattern was examined. The result simply indicates that the hexagonal packing is maintained, but the spacing of the (100) reflection (d_{100}) continuously increases with a decrease in the concentration from 100 to 49 vol %. Figure 8 shows the variation in d_{100} with the volume fraction of polymer (C) in double logarithmic plots. There is a linear relationship between the spacing and polymer volume fraction in the concentration range from 49 to 100 vol %. The solid line was calculated from using

$$\log d_{100} = -{}^1/_2 \log C + \log d_{100}{}^0$$

under the assumption that the solvents expand only on the lateral side of α-helical molecules. Here, $d_{100}{}^0$ is the spacing of the (100) reflection for the solid film (refer to Table 2). Good correspondence was attained between the observed and calculated results, indicating that the structural change takes place

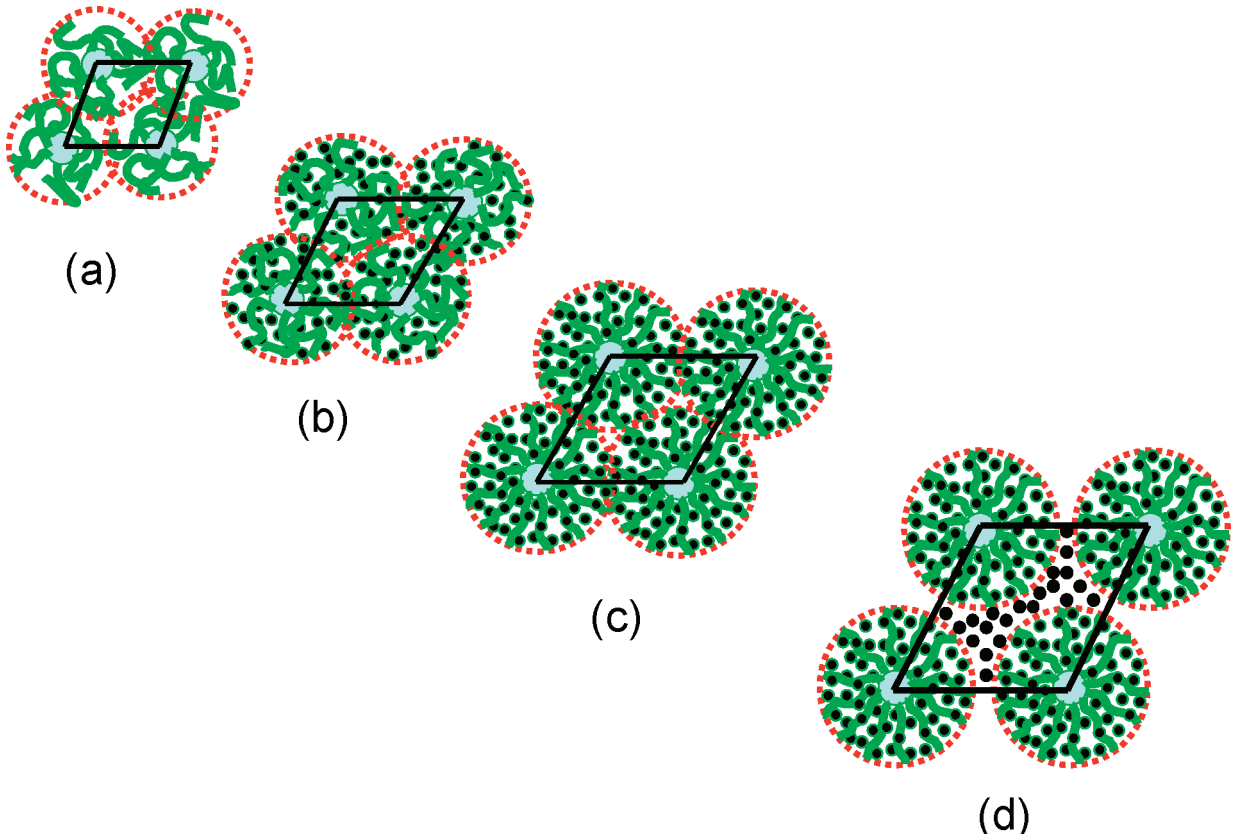

Figure 11. Structural change with swelling of (a) solid state. The solvents (closed circles) enter the side-chain domain in part b and then completely mix with side chains in part c. Additional solvents fill the space between the side-chain domains in part d.

continuously in this concentration range so that the added solvents are accommodated in the space between α- helices, i.e., within the side-chain zone. Figure 8 also shows the significant trend where the spacing becomes constant upon further decreasing the concentration below 49 vol %. This trend is expected since, at 20 °C, the isotropic solution coexists with the columnar phase so that the concentration of the columnar phase is invariant even when the concentration of the solution is varied (refer to Figure 5). In this concentration range below 49 vol %, only the relative volume fraction of the columnar phase to the isotropic phase is changed.

The above results indicate that there is no definite transformation from the lyotropic columnar phase to solid crystalline phase. Yet a remarkable difference between them is observed in the diffraction profile of layer lines as mentioned above; sharp reflections are included on the second, third and fifth layer lines in the solid state whereas broad scattering on the same lines in the lyotropic columnar phase. This difference would not be decisive in distinguishing between these two phases since the reflections on the layer lines in the solid film become broad when heated to a high temperature (Figure 7b). This temperature-induced change takes place gradually, i.e., without a definite transition, and can be explained to result from the activated molecular motion along and around the helical axis.[31] Such a nature is attributed to the nature of side chains. The side chains in the poly-L-glutamates behave like amorphous polymers. They show the glass transition in the DSC thermogram and mechanical loss due to frequent mechanical stressing. For example, the side chains of PPProLG show a T_g of −7 °C in the DSC thermogram. Thus, α-helical rods are surrounded by amorphous-like side chains. In other words, the solid phase is not assigned to the crystalline phase; at lower temperatures, the rods take a crystalline-phase-like position on average, but at higher temperatures, crystalline-like positional order is lost because of the rotational and translational motions of α-helices induced by the activated motion of the side chains. Such a temperature-induced structural change is similar to that observed on decreasing the concentration from 100 to 49 vol %. Thus, whether the system has a two-dimensional or three-dimensional positional order, simply depends on the degree of molecular motion. We believe that the phases with hexagonal symmetry in this concentration region from 49 to 100 vol % can be assigned to the same columnar phase in a thermodynamic sense. Only the degree of molecular motion of α-helices along and around their long axis varies with concentration or temperature.

Referring to the data elucidated above, we illustrate the phase behavior over the whole concentration region in Figure 9.

3.5. Critical Concentration of Columnar Phase in Polymers with Different Side Chains. In the PPProLG−*m*-cresol system, the columnar phase which is segregated from the cholesteric and isotropic phases, possesses the critical concentration of 49 vol %. To consider the nature of the columnar phase, it is important to know how the critical concentration depends on the kind of side chain or the length of side chain. The X-ray observations were thus made for the *m*-cresol solutions of various poly(γ-alkyl L-glutamate)s with the side chains of methyl to hexyl groups, PBLG, and PPELG. The spacings of the (100) reflection of the columnar phase are plotted against the concentration for selected systems in Figure 10a−d, where the data were collected at 20 °C. In Table 3, the critical concentrations are listed. From these data, we can find two significant trends. The first is that all systems have critical concentrations of around 40−50 vol %, but some weak dependence on the side-chain length can be observed; as found in Table 3, the critical concentration increases steadily with an increase in side-chain length. Second, the phase coexisting with the columnar phase at 20 °C depends on the side-chain length; it is the cholesteric phase for the shorter side-chain homologues, and

the isotropic phase for the longer ones. Thus, all of these polymers show the phase diagram similar to that elucidated for the PPProLG−*m*-cresol system, and the χ parameter,[2,4,5] which is dominated by the interaction between the side chain and the solvent, is different between the systems. The longer-side-chain polymer has the larger χ parameter; in other words, *m*-cresol becomes a poorer solvent for longer side-chain homologues.

It is interesting to consider what determines the critical concentration of the columnar phase. The answer may be revealed by considering the swelling of a solid film. As illustrated in Figure 11, the solvents added to a solid film are initially accommodated in the side-chain zone or mixed with amorphous-like side chains. Such a mixing is completed at a certain concentration (Figure 11c), and then, additional solvents are accommodated in the space between the side-chain domains (Figure 11d). Thus, molecules gain some rotational freedom with respect to their short axis and then lose the positional order of lateral packing to induce the columnar-cholesteric phase transition. If this is the case, it is of interest to compare the experimentally determined critical concentration with the concentration that can be calculated under the assumption that the solvents are spaced inside the side-chain domain produced by the most extended side chain. The calculated concentrations are listed and compared with the observed ones in Table 3. The correspondence between calculated and observed concentrations is good in the intermediate side-chain homologues, PProLG, PButLG, and PBLG, suggesting that the critical concentration is the concentration at which the solvents complete to mix with the side chain. The calculated concentration is lower than the observed one for the longer side-chain homologue. This deviation is reasonable because of the unrealistic assumption that long side chains are fully extended.

4. Conclusions

The temperature-concentration phase diagram was determined for the lyotropic solutions of PPProLG in *m*-cresol in the temperature range from 0 to 70 °C and in the concentration range from 0 to 100 vol %. The phase structures and phase boundaries were well elucidated by visual and microscopic observations and X-ray measurement. The well-known phase boundaries between the isotropic and cholesteric phases are observed in the lower concentration range of 8 to 14 vol %, as predicted using the Flory lattice theory and reported from experiments. At higher concentrations, however, a novel phase behavior is observed. The cholesteric phase is transformed to the hexagonal columnar phase through the coexistence region, which is in accordance with the recent simulation results. The critical concentration of the columnar phase appearing from the cholesteric or isotropic phase is 49 vol %. The removal of solvents from this columnar solution leads to the solid state structure without changing the hexagonal packing symmetry so that the highly concentrated phases above 49 vol % are commonly assigned to the columnar phase. Thus, the phase diagram is well illustrated, including isotropic, cholesteric and columnar phases. According to this phase diagram, at higher temperatures, the isotropic-cholesteric-columnar phase transition takes place upon increasing concentration. In other words, the cholesteric helical structure is unwound and transforms to the uniaxially oriented columnar structure. At lower temperatures, on the other hand, the isotropic solution directly transforms to the columnar phase with a concentration of 49 vol % through the wide biphasic zone from 2∼6 to 49 vol %. Similar phase diagrams are presumed for other poly-L-glutamates with different kinds of side chains, although the critical concentration of the columnar phase increases with an increase in side-chain length.

We are now proceeding to construct a phase diagram that includes another interesting smectic A phase in the lyotropic solution of polypeptides with a narrower molecular weight distribution.

References and Notes

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