SHORT COMMUNICATIONS

Thermotropic Polypeptides IV.   Thermotropic Cholesteric Mesophase of Copolyglutamates Based on γ-Benzyl L-Glutamate and γ-Alkyl L-Glutamate

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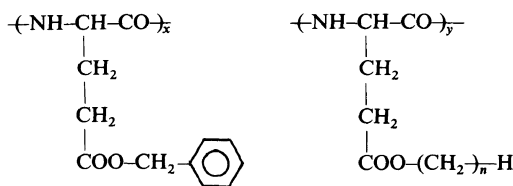Ookayama, Meguro-ku, Tokyo 152, Japan*

Paper I of this series[1] reported the first observation of thermotropic liquid crystals on α-helical poly(γ-methyl D-glutamate-*co*-γ-hexyl D-glutamate)s. In that paper, it was found that the thermotropic liquid crystalline phase arises in copolymers with intermediate hexyl contents of 30—70% and an appreciable difference in side chain length between the monomer components is attributable to the appearance of thermotropic nature in copolymers. In the same vein, thermotropic mesophases were successfully attained in poly(γ-benzyl L-glutamate-*co*-γ-dodecyl L-glutamate)s and the details of their cholesteric mesophase properties were reported in Paper III.[2] On the other hand, paper II[3] indicated that even in homopolymers of L-glutamates, the thermotropic nature can be induced if *n*-alkyl groups longer than decyl are attached to the side chain. Induction of thermotropic phase has been also reported in poly(4-substituted γ-benzyl L-glutamate)s with similar alkyl groups as substituents.[4] In all cases, the long flexible side chains may be responsible for the occurrence of thermotropic liquid crystals where they may play the role of solvent in familiar lyotropic liquid crystals. These novel thermotropic liquid crystalline (TLC) polymers, having a mesogenic α-helical rod surrounded by flexible side chains, should be differentiated from two kinds of TLC polymers—the so called main-chain TLC polymers and the side-chain TLC polymers, and classified into a third kind of TLC polymer.[2] In this work, we prepared several kinds of copolyglutamates composed of two comonomers, a familiar γ-benzyl L-glutamate and γ-alkyl L-glutamates, with the objective of seeking new thermotropic polypeptides. Thermotropic mesophases were easily attained in the copolymers in which the alkyl L-glutamates have the side chains longer than decyl group. In this communication, we report some of their mesogenic properties.

Five series of poly(γ-benzyl L-glutamate-*co*-γ-alkyl L-glutamate)s, were synthesized by ester exchange reactions of poly(γ-benzyl L-glutamate) ($\bar{M}_w = 170,000$) with the respective *n*-alkyl alcohols; octyl ($n=8$), decyl ($n=10$),

$$\begin{array}{cc} -(\text{NH–CH–CO})_x & -(\text{NH–CH–CO})_y- \\ | & | \\ \text{CH}_2 & \text{CH}_2 \\ | & | \\ \text{CH}_2 & \text{CH}_2 \\ | & | \\ \text{COO–CH}_2-\langle\bigcirc\rangle & \text{COO–(CH}_2)_n\text{–H} \end{array}$$

(the carbon number of alkyl group:

$n = 8$, 10, 12, 14 or 16)

dodecyl ($n = 12$), tetradecyl ($n = 14$) and hexa-decyl ($n = 16$) alcohols. The polymers in each series were designated by the letter PBn followed by a number indicating the molar percent of alkyl glutamate. Each reaction was carried out at 60°C in 1,2-dichloroethane containing p-toluene sulfonic acid as a catalyst. After an appropriate reaction time, the polymers were precipitated by pouring the solution into methanol. Then, they were purified twice by fractional-precipitation. The copolymer composition, as determined by ^{1}H NMR spectroscopy, was adjusted by changing the reaction time. Film specimens were cast from chloroform solutions. IR spectra and X-ray diffraction patterns of these films indicated that all polymers assume a right-handed α-helical conformation in the present experimental temperature range of 20°C to 170°C.

Transformation of crystal to liquid crystal was found to be a first-order transition from DSC curves measured by a Perkin-Elmer DSC-II calorimeter. It appeared reversibly on heating and cooling. Transition entropies, which were not significantly changed by a kind of copolymer and copolymer content, ranged from 0.1 to 0.2 cal (mol of residue)$^{-1}$ K^{-1}. These small transition entropies seem to be reasonable on considering that no conformational change of main chain is included in this transformation. The transformation was also followed by X-ray and dynamic mechanical methods. In the X-ray method, a crystal pattern disappeared at the DSC transition temperature, being replaced by a pattern displaying only diffuse halos. This was typically observed on the equatorial diffraction pattern, indicating a disordering in the lateral packing of rodlike macromolecules which is just characteristic of liquid crystals. On the other hand, mechanical method exhibited an abrupt drop of storage modulus from about 10^9 dyn cm^{-2} into the order of 10^6—10^7 dyn cm^{-2}. Thus, the liquid crystalline nature of the material is also apparent in the mech-
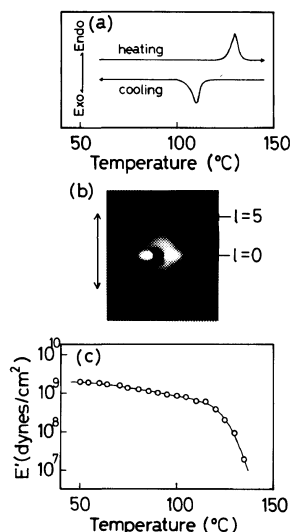
Figure 1. The data clarifying the transformation of crystal to liquid crystal for PB14-35: (3) DSC curves as measured at a rate of 10 K min^{-1}, exhibiting a first-order crystal to liquid crystal transition; (b) X-ray pattern observed for oriented liquid crystal at 160°C where the oriented samples were prepared by melt-spinning from the mesophase at 160°C (the arrow indicates the orientation direction of chain axis and $l = 0$ and 5 indicate the equatorial and 5th (turn) layer lines, respectively); (c) temperature dependence of the storage modulus measured at 110 Hz, exhibiting an abrupt drop on transition.
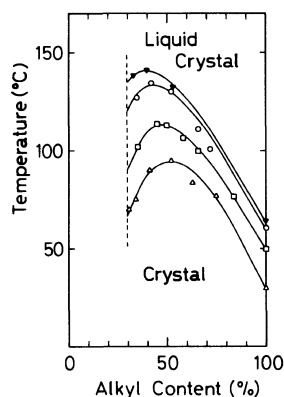
Figure 2. Plots of the crystal to liquid crystal transition temperatures against the content of alkyl glutamate for PB10 ($\triangle$), PB12 ($\square$), PB14 ($\bigcirc$), and PB16 ($\blacktriangledown$) where the transition temperature were measured in DSC heating curves.

anical aspect. In fact, specimens in the liquid crystalline phase easily flowed between glasses under a slight pressure. Figures 1a, 1b, and 1c illustrate the representative data observed for PB14-35.

In Figure 2, the transition temperatures based on DSC heating data are plotted against the content of alkyl L-glutamate. It can be seen that thermotropic liquid crystalline phases appear in copolymers of PB10, PB12, PB14, and PB16 and the alkyl contents more than 30% are necessary for the occurrence of thermotropic nature. In contrast, no thermotropic phase arose in PB8 in the whole range of octyl content. This agrees with the previous conclusion[1,2,5] that an appreciable difference in side chain length is necessary for the induction of a thermotropic liquid crystalline phase of copolypeptide. The dependence of transition temperature T_2[6] on copolymer content appears similar for all series; T_2 increases initially with an increase of alkyl glutamate content from 30%, exhibits a maximum and gradually decreases to the T_2 value of the respective poly(γ-alkyl L-glutamate) homopolymer.[3] When compared at a given copolymer content, T_2 increases with increase in length of alkyl side chain.

All these chiral polypeptides formed cholesteric liquid crystals in which there appears a macro-helical structure with a periodic pitch. To characterize the cholesteric structure, helical pitches (P) were measured as a function of temperature or alkyl content and compared among four series of copolypeptides. The pitches in the range of 300 to 700 nm, were determined here from the maximum wavelength, λ_m, of circular dichroism (CD) by using a JASCO automatic recording spectrometer Model J-20. In this measurement, a thin cholesteric film of around 20 μm thickness was prepared by sandwiching the polymers between glass plates and light was aimed perpendicular to the film plane. Since such a thin film takes up a Grandjean-like texture (as clarified by a microscopy) with the molecular axes uniformly distributed in the plane of the film, the pitch is related to λ_m by the equation $\lambda_m = nP$ where n is the refractive index. CD spectra were measured for each specimen after annealing at a given temperature for 2 h, the duration of which is necessary for the well formation of cholesteric helical structure.[2] The CD spectra thus observed were fairly sharp and had half-widths less than 50 nm. In addition, the film showed beautiful colors, which were caused by a selective reflection of light. These exhibit well development of cholesteric structure. Every sample displayed negative CD spectra, offering a right-handed helical sense for the present cholesteric structure.
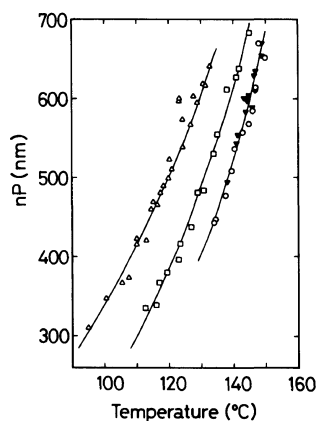

Figure 3. Temperature dependence of the optical pitch, nP, for cholesteric mesophases of PB10-41 ($\triangle$), PB12-43 ($\square$), PB14-42 ($\bigcirc$), and PB16-40 ($\blacktriangledown$).
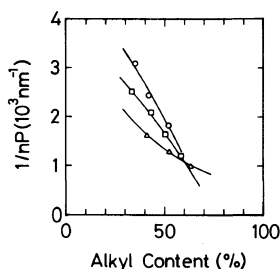

Figure 4. Variation of the inverse optical pitch ($1/nP$) at 130°C with the content of alkyl glutamate: ($\triangle$), PB10 copolymers; ($\square$), PB12 copolymers; ($\bigcirc$), PB14 copolymers.

Figure 3 illustrates the temperature dependence of the optical (nP) for the copolymer series with alkyl content of around 40%. As seen in each sample, the optical pitch increases remarkably with temperature, passing through the visible wavelength region in a temperature span of 40°C. The thermal expansion of pitch (d ln $P/dT = \sim 4 \times 10^{-2}°C^{-1}$) far exceeds that of layer thickness of the order of $10^{-4}°C^{-1}$ and hence, can be attributed mainly to the decrease of twisting angle between neighboring cholesteric layers. For example, the twisting angle for the mesophase of PB14-42 was calculated to change from about 2 to 1 degrees with the increase of 30°C under the assumption that the thickness of individual cholesteric layer is comparable to a diameter of rodlike molecule.

In Figure 4, the inverse optical pitch ($1/nP$) as a measure of the twisting power, is plotted against copolymer composition using the data collected at 130°C. Although the range of composition is limited to 30—60% because of the limited values of optical pitches from 300 to 700 nm, the data in each series fall on a smooth curve with a common trend such that the inverse pitch decreases (or the pitch increases) substantially with alkyl content.

Finally, we note that these cholesteric structures can be easily retained in the solid films by quenching the mesophases into a temperature below T_2. The resultant films, thus, displayed the various brilliant colors, which were arbitrarily changed from blue to red depending on the temperature of prior existing mesophase.

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6. We have used T_2 for the transition temperature of crystal to liquid crystal in our previous paper,[3] in order to differentiate it from T_1 the melting temperature of crystal of alkyl side chain.