Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Thermotropic cellulose derivatives with flexible substituents. III. Temperature dependence of cholesteric pitches exhibiting a cholesteric sense inversion

Tadaaki Yamagishi[a]; Takeshi Fukuda[a]; Takeaki Miyamoto[a]; Toshihiro Ichizuka[b]; Junji Watanabe[b]
[a] Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan [b] Department of Polymer Chemistry, Tokyo Institute of Technology, Tokyo, Japan

To cite this Article Yamagishi, Tadaaki , Fukuda, Takeshi , Miyamoto, Takeaki , Ichizuka, Toshihiro and Watanabe, Junji(1990) 'Thermotropic cellulose derivatives with flexible substituents. III. Temperature dependence of cholesteric pitches exhibiting a cholesteric sense inversion', Liquid Crystals, 7: 2, 155 — 161

To link to this Article: DOI: 10.1080/02678299008029204

URL: http://dx.doi.org/10.1080/02678299008029204

LIQUID CRYSTALS, 1990, VOL. 7, NO. 2, 155–161

Thermotropic cellulose derivatives with flexible substituents

III. Temperature dependence of cholesteric pitches exhibiting a cholesteric sense inversion

by TADAAKI YAMAGISHI, TAKESHI FUKUDA
and TAKEAKI MIYAMOTO
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan
and TOSHIHIRO ICHIZUKA and JUNJI WATANABE†
Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama,
Meguroku, Tokyo 152, Japan

(*Received 9 January 1989; accepted 22 March 1989*)

For the thermotropic cholesteric mesophase of tri-*o*-(β-methoxyethoxy)ethyl cellulose (DP = 11), cholesteric pitches larger than 2 μm were precisely determined by microscopic observation and their temperature dependence was examined in the temperature range from 80°C to 140°C. In the initial temperature region of 80°C to 106°C, the pitch increases with increasing temperature. After the pitch diverges at 106°C, it decreases as temperature is raised further. This anomalous temperature dependence of pitch was associated with a thermally-induced inversion from right- to left-handed helicoidal structure which was first observed in this kind of cellulose derivatives.

1. Introduction

A number of the cellulose derivatives (based on D-glucose) have been prepared and found to form thermotropic cholesteric liquid crystals [1–8]. Some of the properties of cholesteric mesophases have been discussed in relation to the chemical structure of the substituents attached to the cellulose backbone. To understand the cholesteric properties of cellulosic mesophases, it is very important to clarify how the pitch of the helicoidal configuration is affected by the temperature, the molecular weight, and the kind of substituents. Above all, the temperature dependence of the cholesteric pitch should be first established since no other effects can be understood without detailed information on the temperature dependence. For this reason, many researchers have examined this problem by treating both of thermotropic and lyotropic cholesteric mesophases. As a general trend, a positive temperature dependence of the pitch ($dP/dT > 0$) has been observed for the right-handed helical cholesteric configuration [2, 3, 6, 9–12], although only one example of negative temperature dependence ($dP/dT < 0$) has been reported for a left-handed helix [12].

A recent study on thermotropic cholesteric polypeptides by Watanabe and Nagase [13] is helpful for understanding the temperature dependence of pitch in the cholesteric cellulose system. In that study, an anomalous variation of pitch with temperature was observed; the pitch initially increases with temperature, then diverges after which the helicity reverses, and decreases as temperature is raised further. This anomalous

---

† Corresponding author.

temperature dependence is exceptional, and may be attributed to the characteristic structure of the constituent polypeptide molecule which consists of rigid α-helical main chain and the surrounding flexible side chains.

Cellulose derivatives also have a similar complexity in chemical structure (although the cellulose skeleton is not as rigid as the polypeptide α-helix). Hence, a similar temperature dependence of pitch may be expected for the thermotropic cellulose derivatives as for the thermotropic polypeptides.

As part of a series treating the thermotropic liquid crystals of fully substituted cellulose derivatives [7, 8], we found that tri-*o*-(β-methoxyethoxy)ethyl cellulose with a degree of polymerization (DP) of 11 displayed the anomalous temperature dependence of pitch described above. A cholesteric mesophase for this material is observed from room temperature to 152°C, and a clear sense inversion of the cholesteric helix can be detected at 106°C. The details of the temperature dependence of pitch are reported here.

2. Experimental

2.1. *Material*

An oligomer of cellulose triacetate (CTA) was obtained by depolymerizing a CTA with a DP of about 210 in a H_2SO_4–H_2O/CH_3COOH system, which gives a homogeneous reaction medium [14]. After its lower-molecular weight portion was removed, the oligo-CTA was subjected to vapour-pressure osmometry (VPO, CORONA Model 117) in chloroform solution at 30°C, and found to have a DP of about 11. An approximate GPC analysis indicated that it has a polydispersity index M_w/M_n around 1.5. The oligo-CTA was treated with 14 per cent aqueous ammonia to give a regenerated oligo-cellulose (oligo-cell).

Full etherification of oligo-cell was performed via the two-step procedure described previously [7]. In the first step, an ether derivative having a DS value of about 2·5 was prepared by the use of a SO_2-diethylamine-dimethylsulfoxide(DMSO)/powdered NaOH system [15] and 2-(β-methoxyethoxy)ethyl iodide. In the second step, the product derivative was further treated with 2-(β-methoxyethoxy)ethyl iodide and methylsulphinyl anion in a DMSO–NaH system [16] to have a fully substituted derivative, oligo-tri-*o*-(β-methoxyethoxy)ethyl cellulose.

Complete etherification was confirmed by both proton–N.M.R. and I.R. spectroscopies [7]. A VPO analysis of the final product showed that no significant degradation had occurred at any stage.

2.2. *Methods*

D.S.C. measurements were performed with a Perkin–Elmer D.S.C.-II calorimeter at a scanning rate of 10°C/min. The cholesteric pitches larger than 2 μm were determined by observation of the striation lines with an Olympus BH-2 polarizing microscope. Since the striation lines can be most clearly observed by viewing perpendicular to the helical axis, the mesophase samples were prepared so as to have the polydomain structure, which preferentially arises for samples with a thickness of more than 0·5 mm. The half-pitch was estimated as the spacing between the lines. The helical sense of cholesterics was clarified from the sign of the optical rotational dispersion curves measured with a JASCO automatic recording spectrometer. In order to ensure the equilibrium cholesteric configuration, all the measurements were performed on mesophase samples which were kept at the respective temperature for more than 1 hour on a hot stage (Mettler FP 80).

3. Results

In a first paper of this series [7], we reported the thermotropic mesophase properties of the same cellulose derivatives with a high DP of 210. For this high-molecular-weight derivative, the mesophase has been observed in a wide temperature range from room temperature to the isotropization temperature (T_i) of 183°C. In the material prepared here, the DP value was drastically reduced to be 11, but the thermal behaviour was not essentially altered from that of high-molecular-weight material, as illustrated in the D.S.C thermogram of figure 1. Only a slight decrease of T_i can be seen in a comparison with the high-molecular-weight material and so the stability of mesophase was maintained still in a wide temperature range from room temperature to T_i = 152°C.

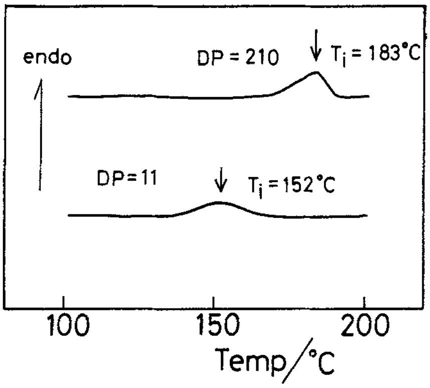
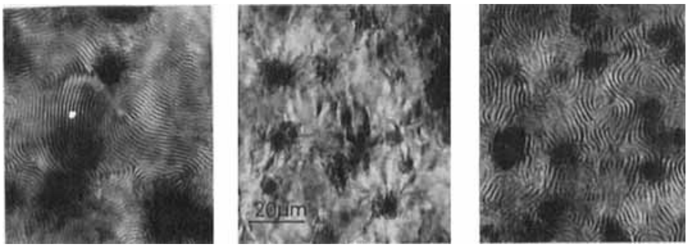


Figure 1. D.S.C thermograms of tri-*o*-(*β*-methoxyethoxy)ethyl celluloses with DP = 210 and 11. The peak observed indicates the mesophase-isotropic phase transition.

The cholesteric character of the mesophase can be directly confirmed by microscopic observation of the striation lines attributable to the cholesteric helical repeat. Here, the viscosity of mesophase is relatively low so that 1 hour is enough for the equilibrium formation of cholesteric twisted configuration at a given temperature. The typical microscopic photographs of cholesteric polydomain texture are shown in figures 2 (*a*), (*b*) and (*c*). The fine striation lines with a long correlation length exhibit the easy formation of cholesteric helical structure.

By measuring the spacings between lines in these photomicrographs, the pitches were determined in the temperature range from 80°C to 140°C and are plotted against the temperature in figure 3. The temperature dependence of pitch is anomalous; the



(a) 90°C (b) 106°C (c) 130°C

Figure 2. Optical photomicrographs of cholesteric polydomain texture for the mesophases at (*a*) 90°C, (*b*) 106°C and (*c*) 130°C.

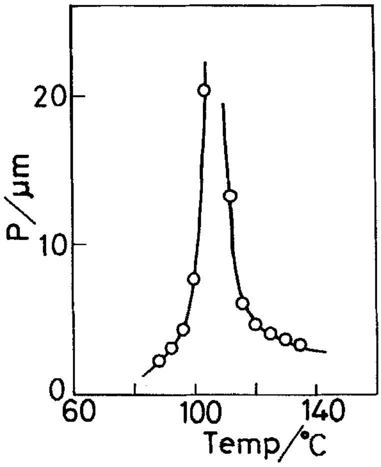


Figure 3. Temperature dependence of cholesteric pitch, P.

pitch increases substantially with the increase of temperature from 80°C to 106°C, diverges at around 106°C, and then decreases as the temperature is further raised to the isotropization temperature, T_i. This trend can be seen from the photomicrographs of figures 2 taken at different temperatures; the fine striation lines clearly seen at 90°C (figure 2 (*a*)) disappear at 106°C (figure 2 (*b*)) and again appear at 130°C (figure 2 (*c*)).

This anomalous temperature dependence of pitch is similar to that observed for the thermotropic polypeptide system [13] and may be understood to contain the helical sense inversion. To confirm the inversion, the helical sense was determined by measuring the optical rotation. According to the de Vries theory [17], the optical rotation ($d\psi/dz$) of the light with a wavelength λ caused by the cholesteric arrangement of pseudonematic layers with the birefringence $\Delta n = n_\parallel - n_\perp$ is written as

$$d\psi/dz = 2\pi P \Delta n^2/8\lambda^2$$

This equation indicates the linear relationship between optical rotation and $1/\lambda^2$. The sign of the line slope clarifies the sense of the cholesteric helix; a positive slope indicates a right-handed helix whereas a negative slope indicates a left-handed one. The optical rotations were measured for the cholesterics in a temperature range from 80°C to 140°C. The representative results arranged according to the above equation are shown for the cholesteric mesophases at 90°C and 130°C in figure 4. The data satisfy the linearity between $d\psi/dz$ and $1/\lambda^2$ and, as can be recognized from the comparison of data at 90°C and 130°C, the sign of slope changes from positive to negative at 106°C where the helical pitch diverges in figure 3. The result dictates the inversion of cholesteric sense from right- to left-handed helix on heating.

Considering further the helical sense inversion, the reciprocal pitches, which are proportional to the twisting angle between the pseudonematic layers, are plotted against temperature in figure 5. Here, the positive value indicates a right-handed helix and the negative a left-handed one. Overall, data point fall on a smooth curve passing through zero at $T_N = 106$°C, indicating that the twisting angle changes continuously with the temperature. At lower temperatures, a large variation of twisting angle is observed whereas at higher temperatures the curve indicates less variation and seems to approach a constant value. Again, this trend is similar to that observed for the thermotropic polypeptide [13].

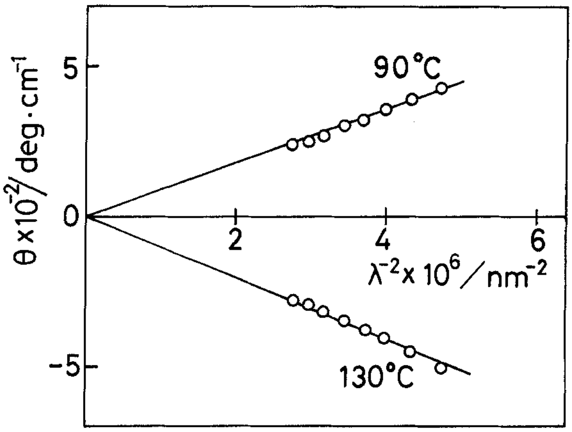


Figure 4. Plots of optical rotation versus $1/\lambda^2$ for the cholesteric mesophases at 90°C and 130°C.

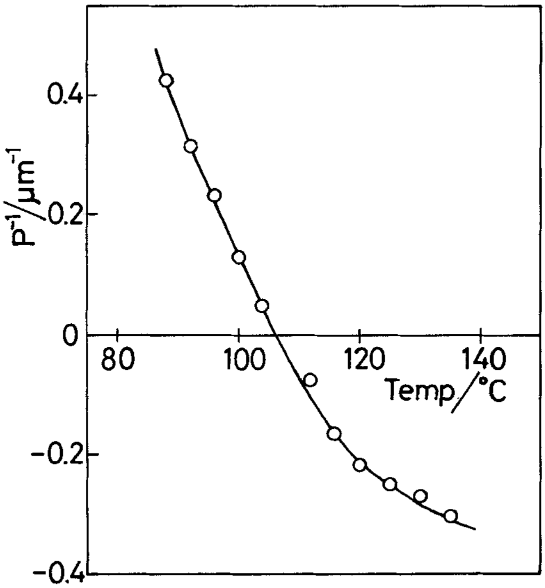


Figure 5. Temperature dependence of the reciprocal pitch, $1/P$. The positive values indicate the right-handed cholesteric helix while the negative the left-handed one.

4. Discussion

4.1. *On sense inversion of cholesteric helix*

The helix inversion caused by the temperature variation is exceptional. So far as we know, only one example has been observed for the polypeptide system.

The sense inversion was initially observed for lyotropic cholesteric mesophases of polypeptides [18, 19]. For this reason, the solvent as a dielectric medium surrounding the polymers had been expected theoretically and experimentally to be a significant factor in the helix inversion [19–22]. More recently, however, Watanabe and Nagase found that the helix inversion also occurs in the thermotropic cholesteric mesophase of polypeptides [13]. This finding leads to the conclusion that the predominant explanation for the thermally-induced helix inversion should be directed to the structural characteristics of polypeptide rather than the properties of solvent.

It is interesting that the thermotropic cholesteric mesophase for a cellulose derivative represents a second example of helix inversion, since the cellulose derivatives have the same structural characteristics as the polypeptides in the two following aspects. First, both have rigid or semi-rigid main chains which contain the asymmetric carbons and so assume the helical conformation. Second, they have flexible side chains protruding from the helical main chain. Although there is no doubt that the cholesteric twist results directly from the asymmetric carbons of the main chain, in these specific systems the twist can be also forced by the averaged side-chain chirality; the side chains would assume the helical arrangement depending on the helical conformation of the main chain and so produce the screw-like van der Waals surface on the exterior of the main-chain core which provides a property of a twisted rod to the polymer molecule. As predicted from the molecular theory of cholesteric twist, the driving force of twist in the former case is the Goossens type dispersion force [23] and in the latter case is mainly the steric hindrance between the twisted rods [24]. Both may independently affect not only the magnitude of the pitch but also the sense of helicity. In such a case, the temperature dependence of the pitch may appear complicated and as one possibility, the thermally-induced sense inversion can be expected if the twists occur with the opposite sense to each other. This has been theoretically predicted by Kimura *et al.* [25]. The several observations of cholesteric polymers exhibiting the sense inversion may confirm this prediction.

4.2. *The effect of a degree of polymerization on cholesteric pitch*

We previously reported the temperature dependence of cholesteric pitch for tri-*o*-(β-methoxyethoxy)ethyl cellulose with a relatively high degree of polymerization (DP = 210) [7]. In this case, the magnitude of the pitch was comparable to the wavelength of visible light in the temperature range of 60°C to 120°C. Hence, the pitch values are smaller than those of the present material of DP = 11, indicating a significant effect of DP on the pitch magnitude. For comparison, the reciprocal pitches for both materials are plotted against temperature in figure 6. Although for the material of DP = 210 the range of reciprocal pitches is somewhat limited, a similar trend in temperature dependence can be seen as in the material of DP = 11.

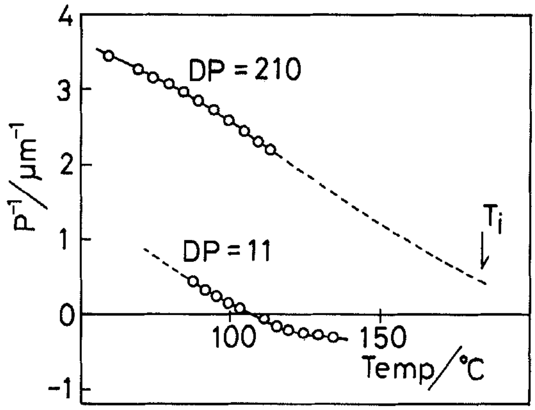


Figure 6. Comparison of the temperature dependence of reciprocal pitch, $1/P$, between two specimens having the different DP of 210 and 11. The dashed curve for the specimen of DP = 210 is the tentative curve drawn under the assumption that the temperature dependence of $1/P$ observed is maintained still in a higher temperature range.

In other words, the reciprocal pitches decrease with temperature, leaving the suggestion that the sense inversion is likely to occur beyond T_i.

Different variations of pitches with a degree of polymerization have been so far reported; constant [26], decreasing [27] and increasing [4, 12]. Those, however, are compared at an ambient temperature without detailed information on the temperature dependence. If the helix inversion occurs thermally as in this case, such a simple comparison of the pitch magnitude is meaningless since the situation appears different depending on the given temperature. At least in this specific system, it is clear that the increase of DP increases T_N, and so if the pitch magnitudes are compared for the cholesteric mesophases with the right-handed helical configuration, the increase of DP decreases the pitches.

References

[1] Tseng, S-L., Laivins, G. V., and Gray, D. G., 1982, *Macromolecules*, **15**, 1262.
[2] Bhadani, S. N., and Gray, D. G., 1983, *Molec. Crystals liq. Crystals*, **99**, 29.
[3] Laivins, G. V., and Gray, D. G., 1985, *Polymer*, **26**, 1435.
[4] Pawlowski, W. P., Gilbert, R., Fornes, R. F., and Purrington, S. T., 1987, *J. Polym. Sci.* B, **25**, 2293.
[5] Charlet, G., and Gray, D. G., 1987, *Macromolecules*, **20**, 33.
[6] Ritcey, A. M., and Gray, D. G., 1988, *Macromolecules*, **21**, 1251.
[7] Yamagishi, T., Fukuda, T., Miyamoto, T., and Watanabe, J., 1989, *Molec. Crystals liq. Crystals*, **172**, 17.
[8] Yamagishi, T., Fukuda, T., Miyamoto, T., and Watanabe, J., 1988, *Polym. Bull* (*Berlin*), **20**, 373.
[9] Werbowyj, R. S., and Gray, D. G., 1980, *Macromolecules*, **13**, 69.
[10] Sixou, S., Lematre, J., Bosch, A. T., Gilli, J. M., and Dayan, S., 1983, *Molec. Crystals liq. Crystals*, **91**, 227.
[11] Patel, D. L., and Gilbert, R. D., 1983, *J. Polym. Sci. Polym. Phys. Ed.*, **21**, 1079.
[12] Vogt, V., and Zugenmaier, Z., 1985, *Ber. Bunsenges. Phys. Chem.*, **89**, 1217.
[13] Watanabe, J., and Nagase, T., 1988, *Macromolecules*, **21**, 171.
[14] Steinmann, H. W., 1970, *Polym. Prep.*, **11**, 285.
[15] Isogai, A., Ishizu, A., and Nakano, J., 1984, *J. appl. Polym. Sci.*, **29**, 2097.
[16] Hakomori, S., 1964, *J. biochem.*, **55**, 205.
[17] de Vries, H., 1951, *Acta crystallogr.*, **4**, 219.
[18] Uematsu, I., and Uematsu, Y., 1984, *Adv. Polym. Sci.*, No. **59**, 37.
[19] Toriumi, H., Yahagi, K., Uematsu, I., and Uematsu, Y., 1983, *Molec. Crystals liq. Crystals*, **94**, 267.
[20] Samulski, T. V., and Samulski, E. T., 1977, *J. chem. Phys.*, **67**, 824.
[21] Osipov, M. A., 1985, *Chem. Phys.*, **96**, 259.
[22] Czarniecka, K., and Samulski, E. T., 1981, *Molec. Crystals liq. Crystals*, **63**, 205.
[23] Goossens, W. J. A., 1971, *Molec. Crystals liq. Crystals*, **12**, 237.
[24] Straley, J. P., 1976, *Phys. Rev.* A, **14**, 1835.
[25] Kimura, H., Hoshino, M., and Nakano, H., 1979, *J. Phys., Paris*, **40**, C3-174.
[26] Robinson, C., Ward, J. C., and Beevers, R. B., 1958, *Discuss. Faraday Soc.*, **25**, 29.
[27] Dupre, D. B., and Duke, R. W., 1975, *J. chem. Phys.*, **63**, 143.