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2 **Thermotropic liquid crystalline properties of (hydroxypropyl)cellulose derivatives with**
3 **butyryl and heptafluorobutyryl substituents**

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14

15 **Abstract:** (Hydroxypropyl)cellulose (HPC) derivatives with butyryl (Bu) and
16 heptafluorobutyryl (7FBu) substituents were prepared in various proportions of the Bu/7FBu
17 groups and at a fixed total DS ($DS_{\text{Bu}} + DS_{7\text{FBu}}$) of 3.0. Thermotropic liquid crystallinity of
18 the derivatives (Bu7FBu-HPC) was investigated to specify the effect of the fluoroacylation on
19 the mesophase behavior. Thermal transition data were collected using differential scanning
20 calorimetry and polarized light microscopy. The Bu7FBu-HPC samples formed a chiral
21 nematic phase between their glass transition and isotropization temperatures, T_g and T_{i-a} ,
22 respectively; these transition temperatures rose moderately as the 7FBu proportion increased
23 ($T_g = -44$ – -27 °C and $T_{i-a} = 158$ – 190 °C for $DS_{7\text{FBu}} = 0.04$ – 1.60). The structural property of
24 the mesophase was examined at 70 °C by circular dichroism and other optical measurements.
25 The chiral nematic pitch (P) sensitively increased with increasing 7FBu proportion, while the
26 supramolecular helical arrangement remained right-handed. Selective light-reflection colors
27 were observed for the samples of $DS_{7\text{FBu}} = 0.04$ – 0.8 , covering an entire spectrum range from
28 violet to red. Temperature dependence of P was also examined for selected samples below
29 T_{i-a} , and it was found to increase with increasing temperature; however, there was no
30 indication of inversion in the handedness of the helical structure. Wide-angle X-ray
31 diffractometry revealed that the increases of P responding to the increases in $DS_{7\text{FBu}}$ and
32 temperature were attributable to the decrease of the twist angle between adjacent thin nematic
33 layers.

34

35

36 **Keywords:** (Hydroxypropyl)cellulose (HPC); HPC ester; Fluoroacylation; Thermotropic
37 liquid crystal; Chiral nematic structure

38

39 **Introduction**

40

41 Cellulosic polymers can form a liquid crystalline phase in a condensed fluid state
42 because of the inherent semirigidity in the carbohydrate backbone (Fukuda et al. 1994;
43 Fukuda et al. 1995; Gray 1994; Gray and Harkness 1994; Guo and Gray 1994; Nishio et al.
44 2016; Zugenmaier 1994; Zugenmaier 1998). The supramolecular arrangement in the
45 mesophase is mostly chiral nematic (synonymous with cholesteric), probably originating from
46 a chiral nature (asymmetry) in the molecular structure. (Hydroxypropyl)cellulose (HPC) is a
47 familiar liquid-crystalline cellulose derivative and offers the chiral nematics in a variety of
48 common solvents (Gilbert and Patton 1983; Gray 1983, 1985, 1994; Guo and Gray 1994;
49 Nishio 2006; Nishio et al. 2016; Zugenmaier 1998). This type of mesophase often imparts a
50 vivid color due to selective light reflection, when the supramolecular helical periodicity (i.e.,
51 pitch P) is comparable to wavelengths of visible light. For instance, HPC solutions in water
52 exhibit such a typical optical character at polymer concentrations of ca. 50–70 wt%
53 (Werbowyj and Gray 1976, 1980). With regard to thermotropic liquid crystals realized in
54 melt without any solvents, several derivatives of HPC obtained by esterifying or etherifying
55 the hydroxyl groups of HPC were reported to form stable chiral nematic phases that displayed
56 iridescent colors over a range of temperatures (Guittard et al. 1994; Hou et al. 2000; Huang et
57 al. 2007; Ishizaki et al. 2015; Kosho et al. 1999; Ohlendorf and Greiner 2015; Ritcey and
58 Gray 1988; Tseng et al. 1981; Yamagishi et al. 1994; Yamagishi et al. 2006). Those HPC
59 ester/ether series can serve as media for a thermal sensor, or a display or light reflection
60 device adaptable to various temperature conditions.

61 For the thermotropics of alkyl esters (normal acylates) of HPC (Hou et al. 2000; Huang
62 et al. 2007; Kosho et al. 1999; Yamagishi et al. 1994), we find the following general
63 tendencies regarding the chiral nematic pitch P : (1) As the alkyl chain-length increases, the
64 thermal range involving mesophase formation shifts downwards and the pitch P increases at a

65 constant temperature; (2) P decreases with increasing degree of substitution (DS) for the acyl
66 group; (3) the handedness of the supramolecular helical arrangement is always right-handed.
67 Concerning the temperature dependence of P , it appears certain that P increases with
68 temperature unless the carbon number (n) of the introduced acyl group exceeds at least 5
69 (Kosho et al. 1999; Yamagishi et al. 1994); however, there is a claim to have discovered the
70 negative dependence of P on temperature for the HPC esters with $n = 7-9$ (Kosho et al. 1999).

71 A few reports dealt with thermotropic behavior of HPC esters containing fluorocarbon
72 components, such as a fully substituted perfluorooctanoate of HPC (Guittard et al. 1994;
73 Yamagishi et al. 1994). For example, it was inferred that the reverse pitch (P^{-1}) of the
74 fluoroacylated derivatives would be larger (i.e., the P would be smaller) than that of HPC
75 esters with the corresponding hydrocarbon substituents, when compared at the same
76 temperature (Yamagishi et al. 1994). However, the actual comparison was not made based
77 on quantitative P data between the two sorts of HPC derivatives having the same number of
78 carbons in the substituents, and therefore that conclusion seems to be rough-and-ready.

79 In the present study, we prepared a kind of mixed ester of HPC with two different acyl
80 substituents of $n = 4$, butyryl (Bu) and heptafluorobutyryl (7FBu) substituents, at the total DS
81 = 3 and in various proportions of the 7FBu to Bu groups. The reason for the selection of the
82 carbon number $n = 4$ was that butyrylated HPC (Bu-HPC) had been well characterized for the
83 thermotropicity and reported to exhibit reflective colorations in a wide temperature range of
84 ca. 20–90 °C (Hou et al. 2000; Huang et al. 2007; Yamagishi et al. 1994); the range is
85 convenient in practice. The objective of this paper is to clarify the effect of fluoroacylation
86 on the chiral nematic properties of the thermotropic HPC derivative (termed Bu7FBu-HPC).
87 It is shown that the 7FBu introduction, even at quite a low DS_{7FBu} of <0.15 , drastically
88 "increases" the chiral nematic pitch.

89
90

91 **Experimental**

92

93 **Materials**

94

95 The HPC used was a commercially available powder sample (Scientific Polymer
96 Products, Inc., lot no. 491018005); the nominal molecular weight was 60,000. On the basis
97 of GPC measurements (see below), the number-average and weight-average molecular
98 weights of this HPC were estimated as $M_n = 2.02 \times 10^4$ and $M_w = 7.29 \times 10^4$, respectively.
99 The degree of side-group substitution was evaluated as $DS_{pr} = 2.93$ and $MS_{pr} = 4.87$ from 1H
100 and ^{13}C NMR measurements (Ho et al. 1972; Lee and Perlin 1982), where DS_{pr} and MS_{pr}
101 denote an average number of substituted hydroxyls and that of introduced hydroxypropyl
102 groups, respectively, per anhydroglucose unit (AGU).

103 Butyryl chloride (BuCl), pyridine (dehydrated), and tetrahydrofuran (THF; containing no
104 stabilizer) were purchased from Wako Pure Chemical Industries. Heptafluorobutyric acid
105 anhydride (7FBuA) was purchased from Sigma-Aldrich, and acetone and other reagents were
106 products of Nacalai Tesque, Inc. All the chemicals were guaranteed reagent-grade and used
107 as received.

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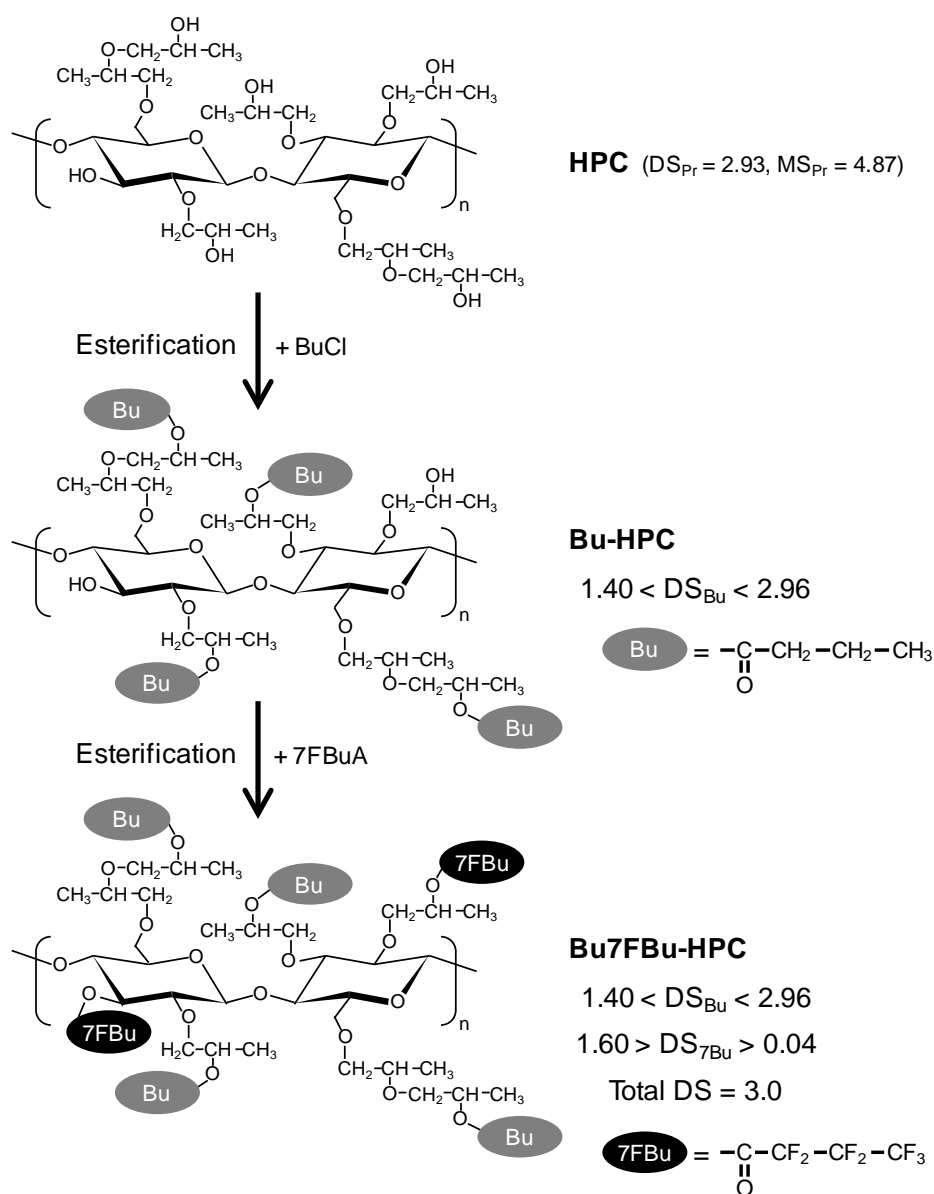
109 **Synthesis of Bu7FBu-HPC**

110

111 Synthesis of the objective derivative Bu7FBu-HPC was conducted via a two-step
112 pathway of reaction (Scheme 1); HPC was first butyrylated with BuCl and then the residual
113 OH groups of the product Bu-HPC were esterified with 7FBuA. In the first step, typically
114 5.0-g HPC (dried powder) was completely dissolved in 70-mL THF at room temperature
115 (20 °C) and the prescribed amount of pyridine (4.0–18 eq/AGU) as a basic catalyst was added
116 into the solution. After heating the solution to 40 °C, BuCl was added thereto. The

117 butyrylation of HPC with BuCl was carried out in various conditions of the attacking reagent
 118 amount and reaction time, as shown in Table 1, but at a constant temperature of 40 °C under a
 119 nitrogen atmosphere. In the termination of the reaction, the solution was poured into an
 120 excess amount of distilled water and the precipitate Bu-HPC was collected by filtration. The
 121 crude Bu-HPC was purified by dissolution–reprecipitation with acetone and distilled water.
 122 The purified Bu-HPC was dried under vacuum at 40 °C for 24 h. We prepared ten Bu-HPC
 123 samples listed in Table 1.

124



125

126 **Scheme 1** Synthetic pathway to Bu7FBu-HPC from HPC

127

128 **Table 1** Reaction conditions for preparation of Bu-HPC (at 40 °C)

Sample code	HPC (g)	THF (mL)	Time (h)	Pyridine in feed*	BuCl in feed*
Bu _{2.96} -HPC	3.0	40	5.0	18	9.0
Bu _{2.95} -HPC	3.0	40	2.5	18	9.0
Bu _{2.92} -HPC	5.0	70	1.0	18	9.0
Bu _{2.87} -HPC	5.0	70	0.50	18	9.0
Bu _{2.86} -HPC	5.0	70	0.25	18	9.0
Bu _{2.67} -HPC	5.0	70	0.50	9.0	4.5
Bu _{2.56} -HPC	5.0	70	0.50	7.5	3.8
Bu _{2.23} -HPC	5.0	70	0.50	6.8	3.4
Bu _{2.11} -HPC	5.0	70	0.50	6.0	3.0
Bu _{1.40} -HPC	5.0	70	0.50	4.0	2.0

* Represented by the molar ratio to an AGU of HPC.

129

130 Next, the Bu-HPC samples were each further esterified with 7FBuA in a similar
 131 procedure, but using the same reaction conditions: Bu-HPC reactant, 1.5 g; THF solvent, 25
 132 mL; pyridine, 18 eq/AGU; 7FBuA, 9.0 eq/AGU; reaction time, 24 h; reaction temperature,
 133 40 °C. Each purified product is encoded as Bu_x7FBu_y-HPC (see Table 2), where $x = DS_{Bu}$
 134 and $y = DS_{7FBu}$, i.e., DSs for the two substituents, and actually it was derived from Bu_x-HPC
 135 of the corresponding sample code in Table 1.

136

137 **Measurements**

138

139 ¹H NMR spectra were acquired using a Varian NMR system 500 MHz with an oneNMR
 140 5MM probe in the following conditions: solvent, CDCl₃; temperature, 23 °C; solute
 141 concentration, 10 mg/0.7 mL; internal standard, tetramethylsilane (TMS); recycle time, 8.5 s;
 142 number of scan, 32. FT-IR spectra were acquired using a Shimadzu IRPrestige-21
 143 spectrometer. A pellet of pristine KBr was first made and then a few drops of polymer

144 solution (1 wt% Bu7FBu-HPC in chloroform) were dropped onto the pellet. The wet pellet
145 was vacuum dried at 40 °C for more than 24 h and employed for the IR measurement over a
146 wavenumber range 400–4,000 cm^{-1} with a resolution of 4 cm^{-1} via accumulation of 32 scans.

147 Elemental analysis was made with a Yanaco CHN Corder MT series (for C and H
148 quantifications) and a combustion ion chromatography system XS-100 constituted of an ion
149 chromatograph pre-treatment unit AQF-100 (Mitsubishi Chemical Analytech, Co., Ltd.) and
150 an ion chromatograph ICS-1500 (Dionex Corp.) (for F quantification).

151 Gel permeation chromatography (GPC) was carried out with a Tosoh HLC-8220 GPC
152 apparatus. The measuring conditions were as follows: column, two Tosoh TSK Super
153 HZM-H columns connected with each other; flow rate, 0.25 mL min^{-1} ; temperature, 40 °C;
154 eluent, THF; standard, monodispersed polystyrene.

155 Differential scanning calorimetry (DSC) analysis was performed on a Seiko DSC
156 6200/EXSTAR 6000 apparatus. Both the temperature and enthalpy readings were calibrated
157 with an indium standard. The measurements were conducted on ca. 5.5-mg samples, each
158 packed in an aluminum pan, under a nitrogen atmosphere. Each sample was first heated
159 from ambient temperature (~ 25 °C) to 200 °C at a scanning rate of 15 °C min^{-1} , and then
160 immediately cooled to -90 °C at a rate of 10 °C min^{-1} . Following this, the second heating
161 scan was run from -90 to 200 °C at a rate of 10 °C min^{-1} . The glass transition temperature
162 (T_g) and the mesophase–isotropic phase transition temperature (T_{i-a}) and enthalpy (ΔH_{i-a}) were
163 estimated from thermograms obtained in the second heating scan. The T_g here was taken as
164 a temperature at the midpoint of a baseline shift in heat flow characterizing the glass
165 transition, and the T_{i-a} and ΔH_{i-a} were determined from the peak position and peak area of the
166 relevant endothermic signal appearing in the thermogram.

167 Polarized optical microscopy (POM) was conducted by using an Olympus microscope
168 BX60F5 equipped with a Mettler FP82HT/FP90 hot stage. Samples (~ 20 mg) were
169 sandwiched between a slide and cover glass.

170 Circular dichroism (CD) and optical rotatory dispersion (ORD) spectra were recorded on
171 a Jasco J-820DH spectropolarimeter equipped with a Peltier-type temperature controller
172 PTC-423L. Samples (~15 mg) were sandwiched between two glass plates, to expand into a
173 liquid layer of thickness ~100 μm at the measurement temperature (typically 70 $^{\circ}\text{C}$). Prior
174 to the actual measurement, each sample was allowed to stand for >12 h at the temperature in
175 order to relax possible shear stresses. Refractive index measurements were carried out using
176 an Abbé refractometer (Atago Co., Ltd., Type 2T) equipped with a thermoregulated stage and
177 polarizer rotatable over the eyepiece. For anisotropic samples, the principal refractive
178 indices parallel (n_{\parallel}) and perpendicular (n_{\perp}) to the plane of the prism surfaces were read off.
179 An average refractive index (\tilde{n}) of the mesomorphic medium was evaluated using the formula
180 $\tilde{n} = (2n_{\parallel} + n_{\perp})/3$ in this study.

181 Wide-angle X-ray diffraction (WAXD) measurements were made on a Rigaku Ultima-IV
182 diffractometer in a reflection mode. Nickel-filtered $\text{CuK}\alpha$ (0.1542 nm) radiation was used at
183 40 kV and 40 mA. Fluid samples were relaxed for 12 h in a copper sample holder of 0.50
184 mm height at the prescribed temperature (usually 70 $^{\circ}\text{C}$), and diffraction intensity profiles
185 were collected in the range of $2\theta = 2\text{--}40^{\circ}$. Concerning a sequence of WAXD measurements
186 for a selected sample at different temperatures (30–200 $^{\circ}\text{C}$), each measurement was made
187 after the sample (once annealed) was held at a set temperature for ~35 min. The set
188 temperature was varied by heating at a rate of 10 $^{\circ}\text{C min}^{-1}$.

189

190

191 **Results and discussion**

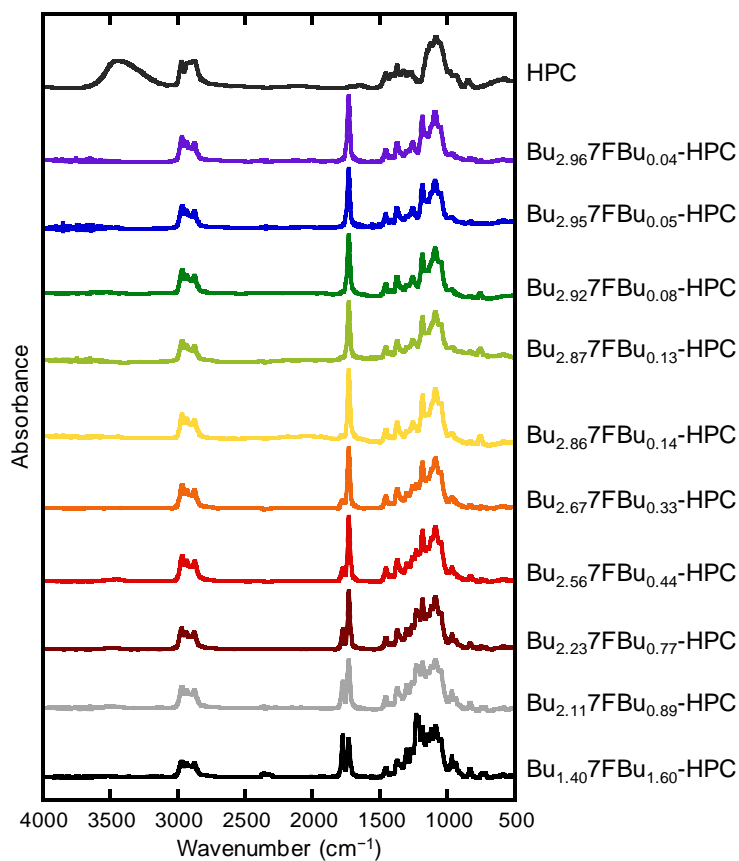
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193 Structure determination of Bu7FBu-HPC products

194

195 The successful preparation of Bu7FBu-HPC products was confirmed by FT-IR and ^1H
196 NMR measurements and elemental analysis. Figure 1 compiles FT-IR spectra obtained for
197 the ten products and the original HPC. The specific OH stretching band ($3,200\text{--}3,600\text{ cm}^{-1}$)
198 appearing in the HPC spectrum completely vanished after the butyrylation and subsequent
199 heptafluorobutyrylation. Instead, an absorption peak located at $1,736\text{ cm}^{-1}$ and another one
200 at $1,780\text{ cm}^{-1}$, derived from C=O stretching vibrations of the Bu and 7FBu groups,
201 respectively, were observed in the spectra of the Bu7FBu-HPC products; the variation in
202 relative intensity of the two IR signals reflects the proportion of the heptafluorobutyryl
203 (7FBu) to butyryl (Bu) substituents, as supported by elemental analysis data (see Table 2).
204 ^1H NMR spectra of the HPC derivatives are exemplified in Fig. S1 and S2 (see Supporting
205 Information). Besides identification of the products, a possible ester-exchange in the
206 heptafluorobutyrylation of Bu-HPC was found to be essentially negligible.

207



208

209 **Fig. 1** FT-IR spectra of HPC and Bu7FBu-HPCs

210

211 The structural parameters DS_{Bu} and DS_{7FBu} were calculated on the basis of the result of
 212 the elemental analysis and by using a few additional predetermined data. The carbons
 213 constituting a Bu7FBu-HPC product include 6 carbons in the AGU, $3 \times MS_{pr}$ carbons in the
 214 oxypropylene sequence, $4 \times DS_{Bu}$ carbons in the butyryl side-chain, and $4 \times DS_{7FBu}$ carbons in
 215 the heptafluorobutyryl side-chain. The number of fluorine in the product is $7 \times DS_{7FBu}$.
 216 Therefore, the following equation holds:

$$217 \quad ([C]/12.01)/([F]/19.00) = (6 + 3 \times MS_{pr} + 4 \times DS_{Bu} + 4 \times DS_{7FBu}) / (7 \times DS_{7FBu}) \quad (1)$$

218 where [C] and [F] are the weight fractions of C and F, respectively, obtained by the elemental
 219 analysis. Using a relation, $DS_{Bu} + DS_{7FBu} = 3$, for the full-substituted product (assured by
 220 FT-IR measurements) and $MS_{pr} = 4.87$ for the HPC material, we can determine DS_{7FBu} and
 221 DS_{Bu} values. Table 2 summarizes the result of the calculations for all the Bu7FBu-HPC
 222 products. The DS_{7FBu} values ranged from 0.04 to 1.60.

223 In an alternative method, DS_{Bu} evaluation was first made using a 1H NMR spectrum of
 224 each Bu7FBu-HPC, and then DS_{7FBu} was quantified using the DS_{Bu} value and the elemental
 225 analysis data (see examples in Supporting Information). The DS_{7FBu} values thus obtained
 226 were in good agreement with the corresponding ones given in Table 2, although there
 227 occurred a small difference ($< \sim 0.1$) between the two compared DS_{Bu} values.

228

229 **Table 2** Data of wt% element, degree of substitution, and molecular weight for
 230 Bu7FBu-HPC products

Sample code	Element (wt%)			DS		Molecular weight		
	H	C	F	DS_{Bu}	DS_{7FBu}	$M_n/10^4$	$M_w/10^4$	M_w/M_n
Bu _{2.96} 7FBu _{0.04} -HPC	8.57	58.94	0.74	2.96	0.04	1.97	6.62	3.36
Bu _{2.95} 7FBu _{0.05} -HPC	8.29	58.77	1.00	2.95	0.05	1.89	7.33	3.89
Bu _{2.92} 7FBu _{0.08} -HPC	8.45	58.29	1.64	2.92	0.08	1.95	7.92	4.06
Bu _{2.87} 7FBu _{0.13} -HPC	8.44	57.56	2.56	2.87	0.13	1.91	7.60	3.99

Bu _{2.86} 7FBu _{0.14} -HPC	8.39	58.17	2.72	2.86	0.14	1.85	7.36	3.98
Bu _{2.67} 7FBu _{0.33} -HPC	7.83	55.83	6.35	2.67	0.33	1.85	7.62	4.13
Bu _{2.56} 7FBu _{0.44} -HPC	7.46	54.29	8.17	2.56	0.44	1.74	7.53	4.32
Bu _{2.23} 7FBu _{0.77} -HPC	6.93	51.68	13.61	2.23	0.77	1.90	8.82	4.65
Bu _{2.11} 7FBu _{0.89} -HPC	6.58	50.37	15.20	2.11	0.89	1.99	7.25	3.64
Bu _{1.40} 7FBu _{1.60} -HPC	5.42	45.62	24.84	1.40	1.60	2.07	9.00	4.34

231

232 Table 2 also compiles data of the molecular weights for the ten Bu7FBu-HPC products.

233 The observed data, $M_n = \sim 19,000$ and $M_w = 66,000\text{--}90,000$, were comparable to $M_n = 2.02 \times$
 234 10^4 and $M_w = 7.29 \times 10^4$ of the original HPC, and reasonably it can be assumed that there was
 235 no noticeable degradation of the main chain during the acylation reactions.

236 As shown in the Experimental Part, the products listed in Table 2 were all readily soluble
 237 in THF, acetone, and chloroform, while being insoluble in water. Using three representative
 238 Bu7FBu-HPC samples of $DS_{7\text{FBu}} = 0.04, 0.33,$ and 1.60 , we further examined the solubility in
 239 conventional solvents such as ethanol, *N,N*-dimethylformamide (DMF), and dimethyl
 240 sulfoxide (DMSO). The test was made by visual observation at room temperature (~ 20 °C)
 241 for each polymer/solvent mixture at a concentration of 1–1.5 wt%. As a result, the samples
 242 of $DS_{7\text{FBu}} = 0.04$ and 0.33 dissolved in ethanol and DMF, but the one of $DS_{7\text{FBu}} = 1.60$ was
 243 insoluble (only swelled) in both the solvents. In the employment of DMSO, none of the
 244 samples dissolved in this solvent, although the two sample of $DS_{7\text{FBu}} = 0.04$ and 0.33 swelled
 245 slightly. Therefore, at least, we can deduce that the solubility of the derivative Bu7FBu-HPC
 246 in polar solvents becomes worse as the proportion of the fluoroacyl substitution increases.

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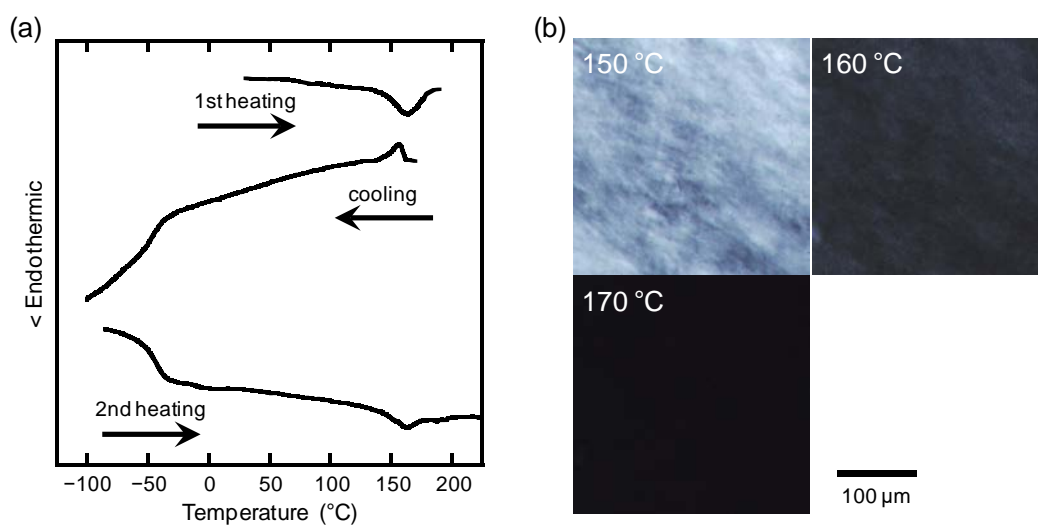
248 Thermal transition behavior of Bu7FBu-HPCs

249

250 As-prepared products of Bu7FBu-HPC were generally in a highly viscous semi-fluid
 251 state at room temperature. Their thermal transition behavior was examined by DSC analysis

252 and POM observations. Figure 2 illustrates DSC thermograms (part a) and POM
253 photographs (part b) measured for Bu_{2.87}FBu_{0.13}-HPC. In the first heating scan of the DSC,
254 this sample gave an endothermic peak at 164.7 °C, and, in the following cooling scan, it
255 provided an exothermic peak at 156.4 °C and a large shift in the baseline below -40 °C; this
256 baseline shift is definitely derived from the glass transition. In the second heating scan, the
257 sample showed a T_g signal at -44.2 °C (midpoint) and an endothermic peak at 162.9 °C with
258 the transition enthalpy of $\sim 2.5 \text{ J g}^{-1}$. In the POM observations for the same sample, the field
259 of view was bright at temperatures lower than 150 °C but became dark in the range of
260 155–165 °C (see Fig. 2b). From these observations, it is evident that the DSC exo- and
261 endo-therms signaled a phase transition between an isotropic liquid (I) and an anisotropic
262 mesophase (M). It should also be noted that, upon cooling, the mesomorphic anisotropy was
263 frozen into the glassy state (G) of the sample that showed no regular crystallinity. In the
264 additional cycles of heating and cooling, the Bu₇FBu-HPC product showed the same
265 enantiotropic phase behavior of $G \leftrightarrow M \leftrightarrow I$.

266



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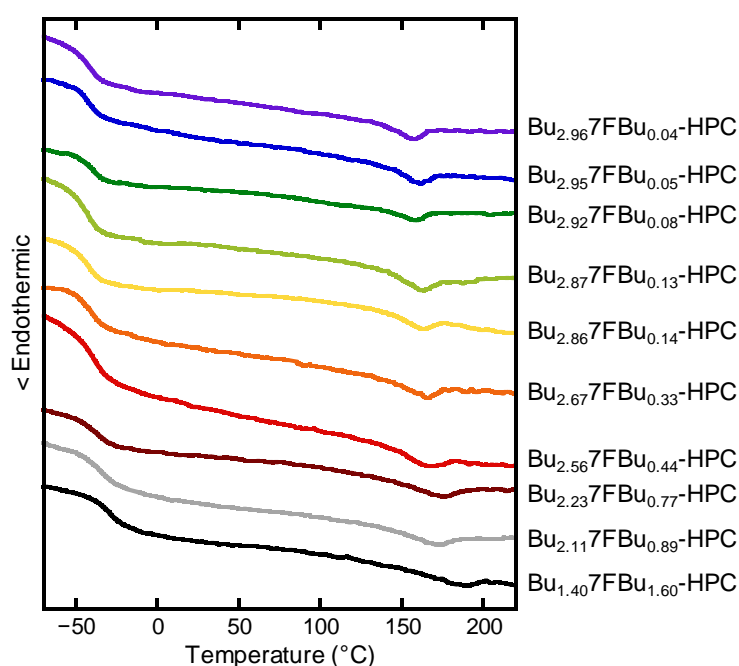
268 **Fig. 2** (a) DSC thermograms and (b) POM images for Bu_{2.87}FBu_{0.13}-HPC. The POM data

269 were taken in the second heating process from 10 °C

270

271 A similar transition pattern was confirmed for the other Bu7FBu-HPCs. Figure 3
 272 exemplifies DSC thermograms obtained in the second heating scan for all the products,
 273 indicating the same transformation of G \rightarrow M \rightarrow I. Table 3 summarizes data of the phase
 274 transition temperature (T_{i-a}) and enthalpy (ΔH_{i-a}), T_g , and $\Delta T_M (= T_{i-a} - T_g)$ determined from
 275 the thermograms. The transition entropy ΔS_{i-a} was calculated from $\Delta S_{i-a} = \Delta H_{i-a}/T_{i-a}$ by
 276 assuming an equilibrium at T_{i-a} . As can be seen from the table, T_g and T_{i-a} did not so greatly
 277 vary with the proportion of the introduced 7FBu substituent; however, the temperatures were
 278 comparatively higher for the Bu7FBu-HPCs of $DS_{7FBu} > 0.44$ and tended to gradually rise
 279 with increasing DS_{7FBu} . The DS dependence of ΔH_{i-a} and ΔS_{i-a} was also generally moderate,
 280 but the values systematically decreased with increasing DS_{7FBu} when this parameter exceeded
 281 0.4; thus the order of molecular arrangement in the mesophase seems to become slightly
 282 lowered with increasing prominence of the dual esterification. An observation worthy of
 283 note is that all the Bu7FBu-HPC products were liquid-crystalline in a wide temperature range
 284 ($\Delta T_M \geq 200$ °C) of practical use (ca. -30 – 160 °C).

285



286

287 **Fig. 3** DSC thermograms of Bu7FBu-HPCs, obtained in the second heating scan

288

289 **Table 3** Thermal transition temperatures, enthalpy, and entropy of Bu7FBu-HPCs measured
 290 by DSC

Sample code	T_g (°C)	T_{i-a} (°C)	ΔT_M (°C)	ΔH_{i-a} (J g ⁻¹)	ΔS_{i-a} (mJ K ⁻¹ g ⁻¹)
Bu _{2.96} 7FBu _{0.04} -HPC	-43.6	158.1	201.7	2.25	5.22
Bu _{2.95} 7FBu _{0.05} -HPC	-41.3	161.8	203.1	2.31	5.31
Bu _{2.92} 7FBu _{0.08} -HPC	-38.9	158.6	197.5	1.59	3.68
Bu _{2.87} 7FBu _{0.13} -HPC	-44.2	162.9	207.1	2.54	5.83
Bu _{2.86} 7FBu _{0.14} -HPC	-43.3	162.7	206.0	1.51	3.46
Bu _{2.67} 7FBu _{0.33} -HPC	-41.3	165.1	206.4	2.22	5.07
Bu _{2.56} 7FBu _{0.44} -HPC	-39.5	168.3	207.8	1.87	4.24
Bu _{2.23} 7FBu _{0.77} -HPC	-38.2	175.3	213.5	1.63	3.63
Bu _{2.11} 7FBu _{0.89} -HPC	-35.0	173.2	208.2	1.25	2.80
Bu _{1.40} 7FBu _{1.60} -HPC	-27.2	190.6	217.8	1.09	2.35

291

292

293 Chiral nematic structure and optical properties of Bu7FBu-HPC thermotropics

294

295 *DS_{7FBu} dependence*

296

297 All of the mesophases formed by the Bu7FBu-HPC samples were of chiral nematic type,
 298 as proved by the optical evidences shown below.

299 Figure 4 displays CD spectra measured for a series of Bu7FBu-HPC samples at 70 °C, a
 300 temperature intermediate between T_g and T_{i-a} for any sample. The CD peaks observed here
 301 signalize the selective light-reflection originating from the supramolecular helical periodicity
 302 in the chiral nematic structure. As can be seen in the figure, the position (λ_M) giving a peak
 303 maximum shifted systematically to longer wavelengths as the DS_{7FBu} of the used sample
 304 increased. Plainly this DS_{7FBu} dependence is quite sharp, differing from that of the thermal

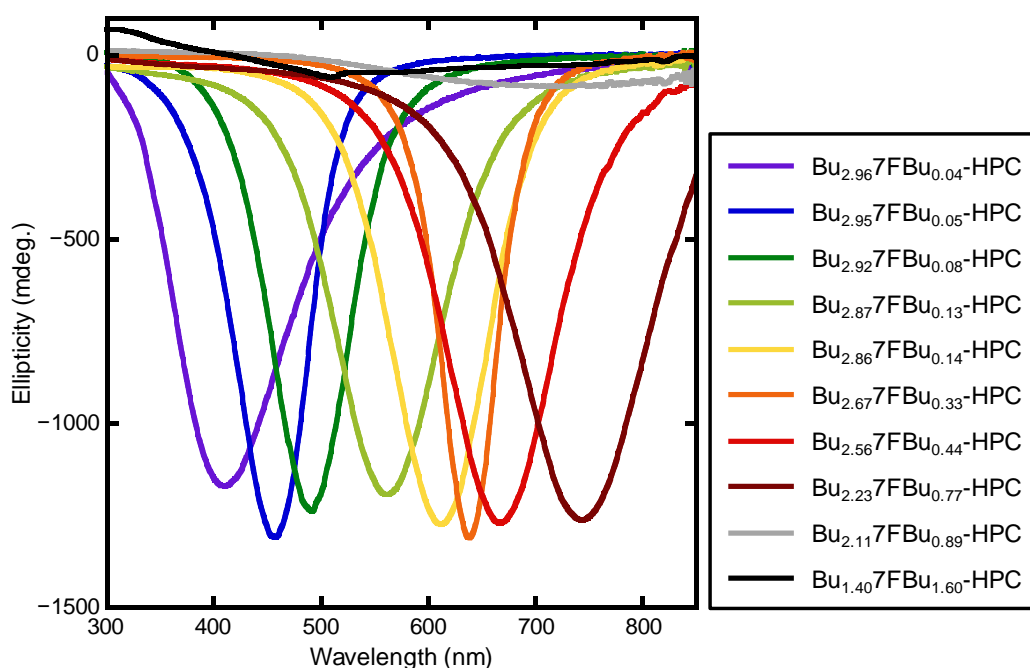
305 transition behavior (Fig. 3). The reflection spectra of eight samples with various $DS_{7\text{FBu}}$'s
 306 ranging from 0.04 to 0.77 covered an entire spectral range from violet to red. This shift in
 307 λ_M to the red side was qualitatively confirmed by visual observations of the reflective colors
 308 of the thermotropic samples. Two samples of $DS_{7\text{FBu}} = 0.89$ and 1.60 were visually colorless
 309 and gave no explicit reflection band in the ordinary range (280–880 nm) of the CD
 310 measurement.

311 The specific wavelength λ_M defined above can be related to the chiral nematic pitch P by
 312 the de Vries equation (de Vries 1951):

$$313 \quad \lambda_M = \tilde{n} P \quad (2)$$

314 where \tilde{n} is an average refractive index of the mesophase. Using data of λ_M and \tilde{n} , P was
 315 calculated for the eight Bu7FBu-HPC samples of $DS_{7\text{FBu}} = 0.04$ – 0.77 ; roughly, the pitch
 316 moved from 280 to 525 nm (see Table S1). Concerning the rotatory sense (handedness) in
 317 the chiral nematic structure, it is taken as right-handed for all these thermotropics; this
 318 decision is based on the negative sign in ellipticity of the CD peaks.

319



320

321 **Fig. 4** CD spectra of Bu7FBu-HPCs, measured at 70 °C

322

323 With regard to the remaining samples, Bu_{2.11}7FBu_{0.89}-HPC and Bu_{1.40}7FBu_{1.60}-HPC, the
324 pitch and handedness of their mesophases were determined by POM and ORD measurements,
325 respectively. The POM observations revealed that both the mesophases (70 °C) were
326 endowed with a well-developed fingerprint texture characteristic of a chiral nematic liquid
327 crystal with comparatively longer helical periodicity. Figure 5a illustrates the optical image
328 for the mesophase of Bu_{2.11}7FBu_{0.89}-HPC. The repeating distance (S) of the so-called
329 retardation lines making up the texture is, ideally, taken as corresponding to $P/2$. From
330 assessment of the average of S , P of the mesophase of Bu_{2.11}7FBu_{0.89}-HPC was estimated at
331 5.37 μm . Similarly $P = 11.1 \mu\text{m}$ was evaluated for the other sample Bu_{1.40}7FBu_{1.60}-HPC.
332 In the meantime, these two samples gave an ORD spectrum that obeyed a positive function
333 increasing monotonically with the decrease of wavelength, as shown in Fig. 5b. In general,
334 wavelength dependence of the optical rotation caused by a chiral nematic mesophase is
335 formulated in the following fashion (de Vries 1951; Guo and Gray 1994).

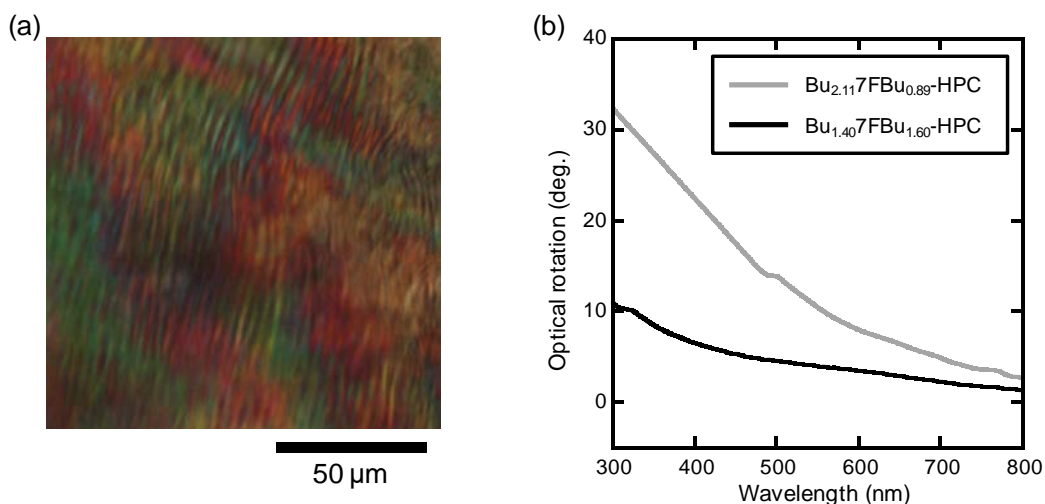
$$336 \quad \alpha = \pi(\Delta n)^2 P / [4\lambda^2 \{1 - (\lambda/\lambda_M)^2\}] \quad (3)$$

337 where α is the optical rotation per unit length for light of wavelength λ , λ_M is the wavelength
338 of selective light reflection, Δn is the birefringence of a nematic layer as structural constituent,
339 and the pitch P here is taken to be a pseudoscalar that is positive for a right-handed helix and
340 negative for a left-handed helix. For the case of $\lambda/\lambda_M \ll 1$, Eq. 3 reduces to

$$341 \quad \alpha \approx \pi(\Delta n)^2 P / 4\lambda^2 \quad (4)$$

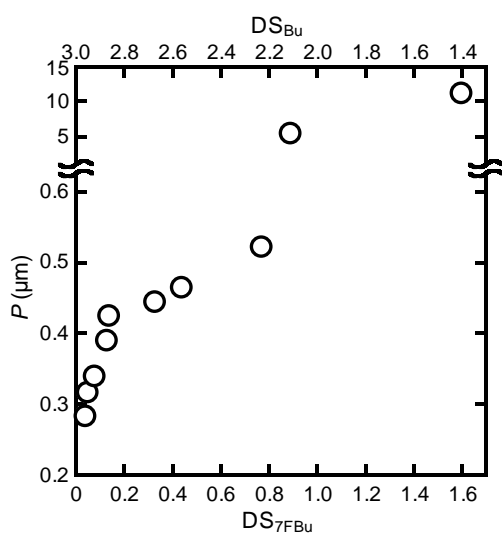
342 Therefore, in the wavelength region of $\lambda \ll \lambda_M$, it follows that α assumes positive or negative
343 values when the chiral nematic phase is right-handed or left-handed, respectively (Guo and
344 Gray 1994). Thus we can deduce that the two samples concerned formed a right-handed
345 chiral nematic arrangement.

346



347
 348 **Fig. 5** (a) POM image of Bu_{2.11}7FBu_{0.89}-HPC and (b) ORD spectra of Bu_{2.11}7FBu_{0.89}-HPC
 349 and Bu_{1.40}7FBu_{1.60}-HPC. All the data were obtained at 70 °C

350
 351 The P data of all the Bu7FBu-HPC thermotropics (70 °C) are plotted in Fig. 6 as a
 352 function of DS_{7FBu} . Broadly, the P vs. DS_{7FBu} plot seems to make upward curvature. The
 353 rise of P at the early stage before DS_{7FBu} reaches ~ 0.3 is particularly steep. There is an
 354 abrupt increase of P with the increase of DS_{7FBu} from 0.77 to 0.89. However, attention
 355 should be paid to an overestimation of P possible in POM observations; because the helical
 356 axis of the chiral nematic structure is not wholly perpendicular to the observation direction.



358
 359 **Fig. 6** Chiral nematic pitch P as a function of DS_{7FBu} for a series of Bu7FBu-HPC

360 thermotropics at 70 °C

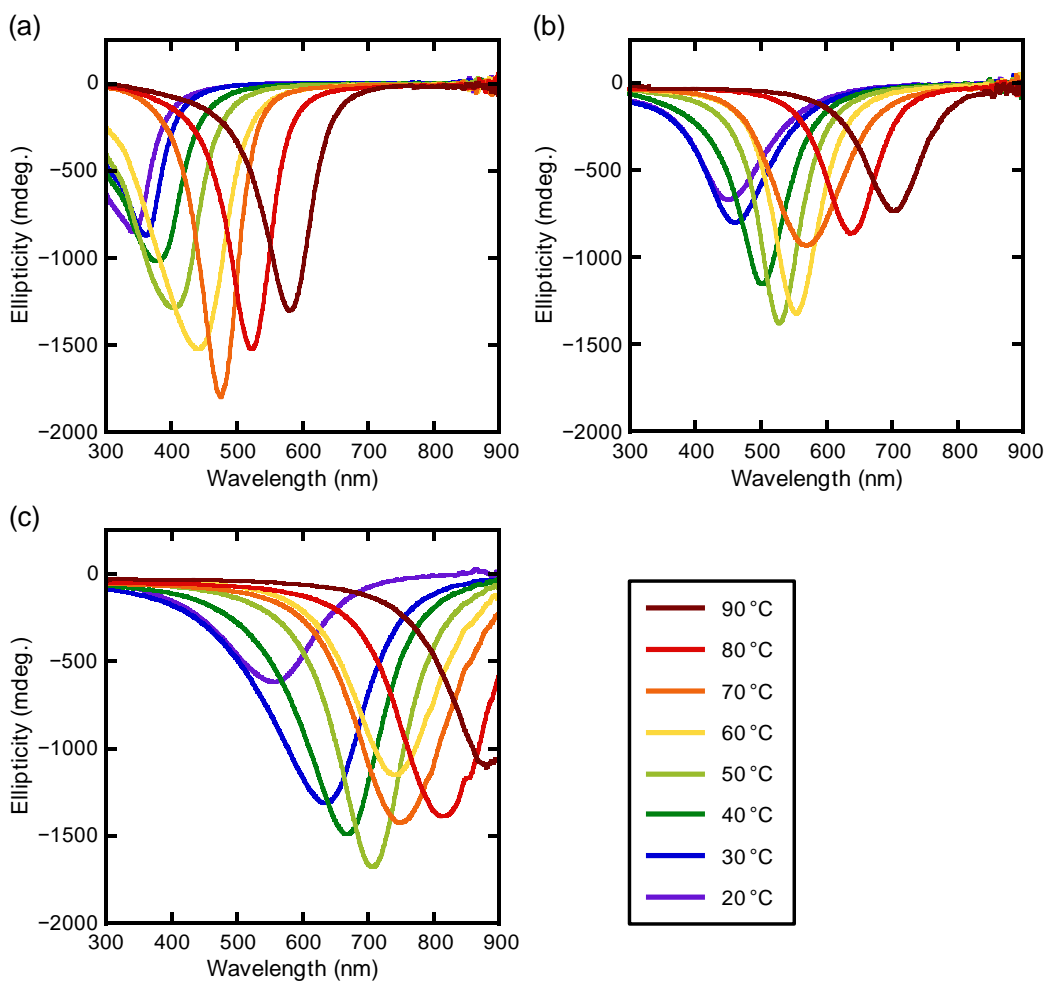
361

362 *Temperature dependence*

363

364 Figure 7 illustrates CD spectra measured at different temperatures of 20–90 °C for three
365 Bu7FBu-HPCs ($DS_{7\text{FBu}} = 0.05, 0.13, \text{ and } 0.77$). Any of the three examples demonstrates a
366 systematic red shift in λ_M of the selective light reflection, with the elevation in temperature.
367 Particularly the Bu_{2.87}7FBu_{0.13}-HPC sample can impart reflective colors covering the whole
368 wavelength region of visible lights in the practical range of temperature. From λ_M data
369 obtained from these CD spectra, the chiral nematic pitch P was calculated by Eq. 2. For the
370 calculation for each sample, the index \tilde{n} at 70 °C (e.g., 1.445 for Bu_{2.87}7FBu_{0.13}-HPC) was
371 adopted, because the temperature variation did not greatly affect the second decimal place of
372 the \tilde{n} data. In Fig. 8, the reciprocal of pitch (P^{-1}) is plotted against temperature for the three
373 Bu7FBu-HPC samples. It is found that P^{-1} decreases almost linearly with elevating
374 temperature and the decreasing rate becomes gradual with increasing in $DS_{7\text{FBu}}$ of the
375 derivative.

376

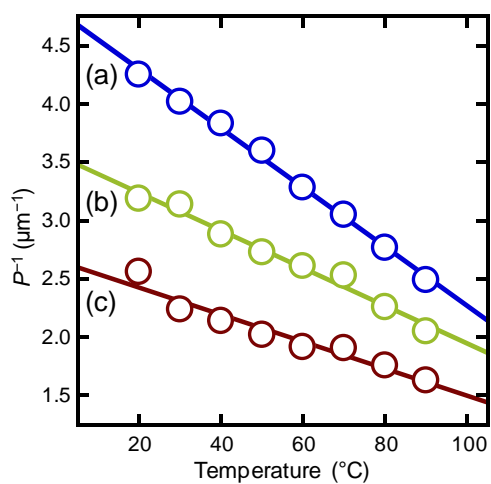


377

378 **Fig. 7** CD spectra of (a) $\text{Bu}_{2.957}\text{FBu}_{0.05}\text{-HPC}$, (b) $\text{Bu}_{2.877}\text{FBu}_{0.13}\text{-HPC}$, and (c)

379 $\text{Bu}_{2.237}\text{FBu}_{0.77}\text{-HPC}$, measured at temperatures ranging from 20 to 90 °C

380



381

382 **Fig. 8** P^{-1} versus temperature plots for (a) $\text{Bu}_{2.957}\text{FBu}_{0.05}\text{-HPC}$, (b) $\text{Bu}_{2.877}\text{FBu}_{0.13}\text{-HPC}$, and

383 (c) $\text{Bu}_{2.237}\text{FBu}_{0.77}\text{-HPC}$

384

385 A similar linearity of P^{-1} versus temperature (T) has been observed for other
386 thermotropic HPC derivatives (Kosho et al. 1999; Laivins and Gray 1985; Ritcey and Gray
387 1988), typically expressed in the following empirical form:

$$388 \quad P^{-1} = a(1 - T/T_n) \quad (5)$$

389 where a is a constant and T_n is a temperature at which the nematic state of $P = \infty$ is attained.
390 According to this relation, when T is elevated to exceed T_n , the handedness of the chiral
391 nematic arrangement should be reversed, for instance, from right ($P > 0$) to left ($P < 0$) in the
392 present thermotropics of Bu7FBu-HPC. In view of this, we extrapolated the linear plots
393 shown in Fig. 8 and estimated the specific temperature T_n to be 195, 220, and 229 °C for
394 Bu_{2.95}7FBu_{0.05}-HPC, Bu_{2.87}7FBu_{0.13}-HPC, and Bu_{2.23}7FBu_{0.77}-HPC, respectively. These T_n
395 values exceed the T_{i-a} 's (see Table 3) determined by DSC for these samples. In actuality,
396 therefore, the thermotropic samples solely showed a transition from the right-handed chiral
397 nematic phase to isotropic melt around 155–170 °C, without taking such a handedness
398 inversion.

399

400 Insight into short-range order in mesophases of Bu7FBu-HPC

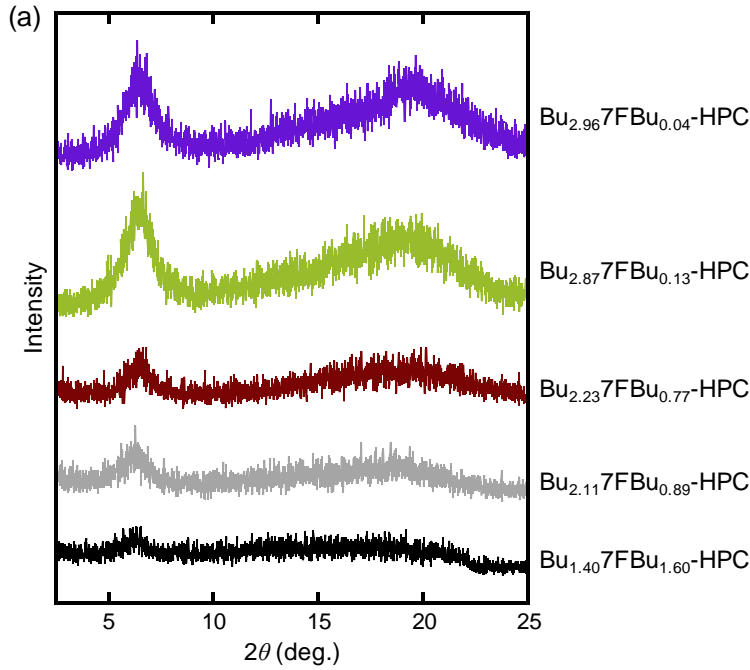
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402 Figure 9a illustrates WAXD intensity profiles measured for selected Bu7FBu-HPC
403 thermotropics at 70 °C. All diffraction intensity curves gave only one significant peak at a
404 lower angular position of $2\theta \approx 6.4^\circ$, except for a diffuse scattering halo centered at $2\theta \approx 19^\circ$.
405 Therefore, the Bu7FBu-HPC thermotropics are found to assume an essentially nematic
406 structure, and the short-range order of less than a few nanometers in the mesophase is
407 analyzable in terms of a pseudo-hexagonal packing of the molecular main chains. The
408 distance (d) between the nematic layers stacking in the mesophase can be directly estimated
409 from the low-angle peak by Bragg's equation ($\lambda = 2d\sin\theta$, $\lambda = 0.1542$ nm). Then, the twist

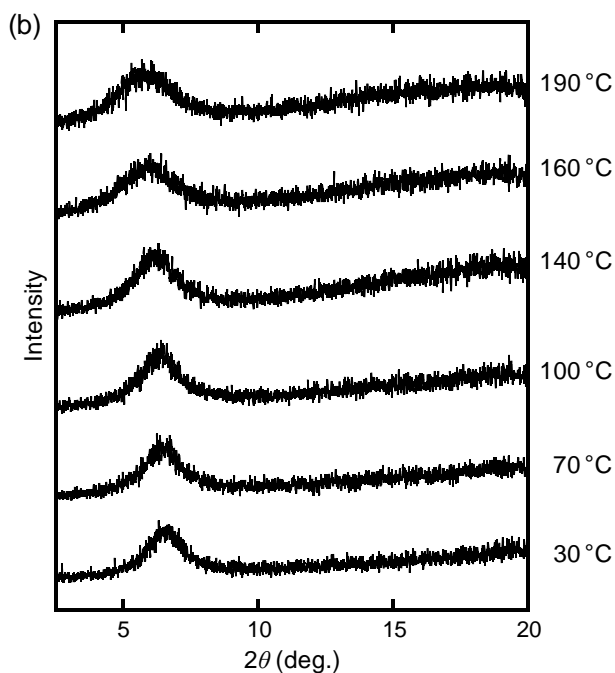
410 angle (φ), defined as an azimuth difference between adjacent nematic thin layers, is calculated
411 from the relation $\varphi = 360^\circ \times d/P$ by use of the chiral nematic pitch data obtained in optical
412 measurements.

413 Figure 10a collects d and φ values obtained for the explored ten Bu7FBu-HPC samples
414 (70 °C), by plotting the data as a function of DS_{7FBu} . The distance d was hardly affected by
415 DS_{7FBu} and almost constant at 1.38 nm. In contrast, the twist angle φ sharply decreased with
416 increasing DS_{7FBu} from 1.76° ($DS_{7FBu} = 0.04$) to $\sim 0.1^\circ$ ($DS_{7FBu} = 0.89$). Thus the distinctive
417 variation of P with DS_{7FBu} shown in Fig. 6 is attributable to the variation of φ .

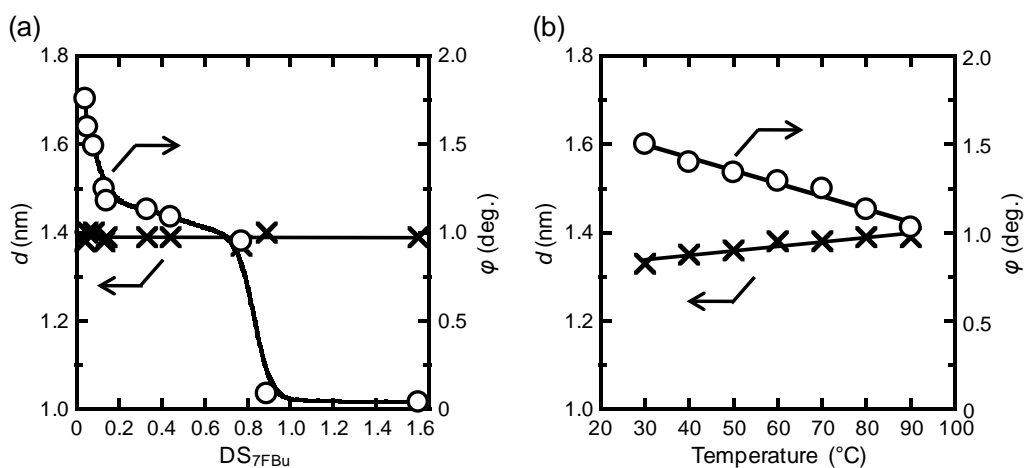
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419



420
 421 **Fig. 9** WAXD intensity profiles obtained for (a) selected Bu7FBu-HPC samples at 70 °C
 422 and (b) Bu_{2.877}FBu_{0.13}-HPC at different temperatures
 423



424
 425 **Fig. 10** Plots of the interlayer distance d (cross symbol) and twist angle φ (open circle): (a)
 426 as a function of DS_{7FBu} of Bu7FBu-HPC; (b) as a function of temperature for
 427 Bu_{2.877}FBu_{0.13}-HPC
 428

429 Figure 9b illustrates temperature dependence of the WAXD profile in the range of $2\theta \leq$
 430 20° for a representative sample of $DS_{7FBu} = 0.13$, Bu_{2.877}FBu_{0.13}-HPC. The maximum

431 position of the low-angle peak was situated at $2\theta \approx 6.55\text{--}6.35^\circ$ at temperatures of $30\text{--}130^\circ\text{C}$.
432 Above 140°C , however, the peak became broader and the maximum position shifted
433 explicitly to lower angles ($2\theta < 6^\circ$ at $T > 150^\circ\text{C}$). Plainly this change can be ascribed to the
434 mesophase to isotropic phase transition which was observed at $150\text{--}170^\circ\text{C}$ for this sample
435 ($T_{i-a} = 162.9^\circ\text{C}$, see Fig. 2a). Somewhat surprisingly, as exemplified in Fig. 9b, the
436 short-range hexagonal structure was still retained even at 190°C to some degree in the
437 optically isotropic melt; probably the high viscosity would prevent a rapid decline of the
438 structure.

439 Figure 10b shows a result of the d and φ quantifications as a function of temperature for
440 the $\text{Bu}_{2.87}\text{7FBu}_{0.13}\text{-HPC}$ sample; the data plotting was made in the range of $30\text{--}90^\circ\text{C}$ where
441 the pitch P of the mesophase was determinable by CD measurements (Fig. 7b). With the
442 increase in temperature from 30 to 90°C , the d value slightly fluctuated from 1.33 to 1.39 nm,
443 whereas the twist angle φ diminished more sensitively from 1.50° to 1.03° . It can therefore
444 be deduced that the increase of P (i.e., the decrease of P^{-1}) with temperature was determined
445 mainly by the variable twist angle.

446 Finally, we add a remark about the effect of the heptafluorobutyryl group; i.e., why did
447 the introduction of such a fluoroacyl group to the HPC ester result in the sharp decrease in φ
448 and ensuing increase in P of the formed chiral nematic mesophase? As is generally known,
449 fluoropolymers having a perfluoroalkyl side chain show unique properties represented by the
450 water- and oil-repellency, low dielectric permittivity, low refractive index, etc. (Hasegawa
451 2017). The perfluoroalkyl (R_f) chains take an attitude of spontaneous aggregation induced
452 by the dipole-dipole interaction, and the above-mentioned bulk properties of fluoropolymers
453 seem to be dominated strongly by the intrinsic interaction between the R_f groups (Hasegawa
454 2015, 2017). By deduction, the 7FBu groups of the cellulose derivative Bu7FBu-HPC
455 would also show such a habit of attractive interaction that becomes noticeable in frequency
456 when the $\text{DS}_{7\text{FBu}}$ is increased. Then, the cellulosic main chains constituting a chiral nematic

457 layer would become arranged to be more parallel to those in the neighboring layers, i.e., the
458 twist angle φ approaches zero, via the increasing 7FBu-attractions between adjacent two
459 layers. This is still a speculative explanation, however.

460

461

462 **Conclusions**

463

464 We successfully prepared a series of fully esterified HPC derivatives, Bu7FBu-HPCs,
465 with various ratios of butyryl (Bu)/heptafluorobutyryl (7FBu) substitutions, $DS_{\text{Bu}}/DS_{7\text{FBu}} =$
466 2.96:0.04–1.40:1.60, and investigated the thermotropic phase behavior.

467 The Bu7FBu-HPC samples formed a chiral nematic mesophase in a wide temperature
468 range between the T_g (≈ -40 – -30 °C) and T_{i-a} (≈ 160 – 190 °C); the transition temperatures
469 elevated gently as the $DS_{7\text{FBu}}$ increased. In contrast to the small diversity in thermal
470 transition behavior between the samples, the mesomorphic property derived from the chiral
471 nematic periodicity was much affected by the varying 7FBu proportion. It was proved that
472 the pitch P of the mesophase sharply increased with increasing $DS_{7\text{FBu}}$ at a constant
473 temperature, differing from the previous inference (Guittard et al. 1994; Yamagishi et al.
474 1994). With a constant $DS_{7\text{FBu}}$, the P increased with elevating temperature, in accordance
475 with the general tendency observed for thermotropic HPC esters (Kosho et al. 1999;
476 Yamagishi et al. 1994). The supramolecular helical arrangement remained right-handed and
477 conversion of the handedness was not observed in the present sampling and surrounding
478 conditions. The increases of P responding to the increases in $DS_{7\text{FBu}}$ and temperature were
479 attributed to the decrease of the twist angle between adjacent nematic layers. This angular
480 decrease might be related to a possible dipolar interaction between the 7FBu side groups
481 distributed in the space between the layers.

482

483

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487

488 **Compliance with ethical standards**

489 **Conflict of interest** The authors declare no conflict of interest.

490

491

492 **References**

493

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567 **Electronic supplementary material** The online version of this article
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569 available to authorized users.

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