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Chain Alignment of a Rigid Ring Polymer in the Lyotropic Liquid Crystal Phase: Cyclic Amylose Tris(*n*-butylcarbamate) in Tetrahydrofuran and Ethyl Lactate

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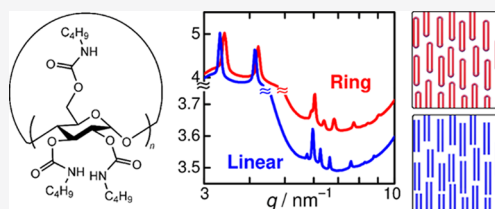
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ABSTRACT: Concentrated solutions of a rigid ring polymer, cyclic amylose tris(*n*-butylcarbamate) (cATBC), have lyotropic liquid crystallinity. Phase boundary concentrations of cATBC in tetrahydrofuran (THF) and *L*-ethyl lactate (EL) were almost identical to those for the linear polymer (ATBC) with the same molar mass. X-ray diffraction for the concentrated cATBC solutions revealed that nematic phases were found for cATBC in the two solvents, while the cholesteric structure was observed for the cATBC–EL system. Several peaks were found in the high q range between 3 and 10 nm^{−1} with q being the magnitude of the scattering vector. The obtained patterns were almost the same as that for an ATBC sample in the corresponding solvent, indicating that the local alignment of the polymer chains is similar between the ring and linear polymers. This result strongly suggests that cATBC chains in concentrated solutions form a pseudo-rodlike conformation with two kinks, whereas cATBC chains behave as semirigid rings in dilute solution. The phase diagram can be also explained in terms of the known theory for the wormlike cylinder, assuming the pseudo-rodlike conformation.

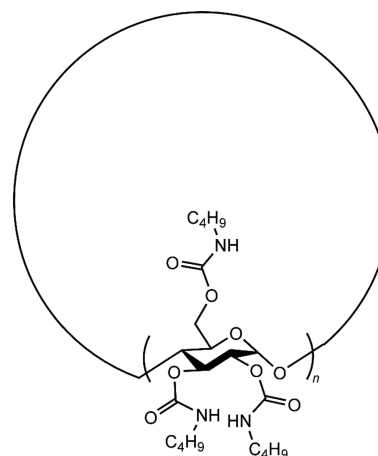


INTRODUCTION

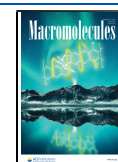
Lyotropic liquid crystallinity is a characteristic feature of rigid rodlike polymers in concentrated solution. Various shaped small molecules have liquid crystallinity¹ and they are actively investigated for diverse applications of the functional material science.² Previous research studies for the lyotropic liquid crystallinity of polymers are, however, almost limited to rigid linear chains except for liquid crystalline (LC) polymers with relatively short mesogens,^{3–5} while some nonlinear polymers, namely, supercoiled cyclic DNA,⁶ highly branched comb polymers,^{7–9} and three-arm star chains,^{10,11} can form a lyotropic liquid crystal phase. Recently, Avendaño et al.^{12–14} theoretically predicted that the LC phase can be found for rigid nanorings even at very low concentrations despite substantially no experimental work for rigid ring polymers. On the contrary, we found that cyclic amylose tris(*n*-octadecylcarbamate) (cATODC) in organic solvents, tetrahydrofuran (THF) and 2-octanone, has a higher phase boundary concentration than the linear analog with the same molar mass and the solvent.¹⁵ The modified scaled particle theory¹¹ (SPT) considering that the cyclic polymer chains form a pseudo-rodlike conformation in the LC phase could explain the phase diagram,¹⁵ while cATODC behaves as a semirigid ring polymer in dilute solution.¹⁶ cATODC may not, however, be suitable to confirm the specific conformation in the LC phase, because no significant information can be obtained from X-ray diffraction. If we consider that quite sharp X-ray diffractions were observed for concentrated ethyl lactate solutions of linear amylose tris(*n*-butylcarbamate) (ATBC),¹⁷ cyclic ATBC (cATBC, Chart 1) is a

good candidate to determine the orientational structure of the semirigid ring polymers in concentrated solution.

Chart 1. Chemical Structure of cATBC



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We thus investigated both phase boundary concentrations and X-ray diffraction for cATBC in THF and L-ethyl lactate (EL). The obtained phase boundary data were compared to the latest theories. The chain conformations of ATBC^{18,19} in the two solvents and cATBC^{20,21} in dilute THF solution have been revealed as semirigid linear and ring, respectively, from the dimensional and hydrodynamic properties. We therefore made SAXS measurements for cATBC in dilute EL solution to confirm the conformation in the solvent.

EXPERIMENTAL SECTION

Samples. Cyclic amylose (CA) samples were synthesized in the manner reported previously.^{22,23} The residual linear amylose was completely degraded by glucoamylase. Indeed, CA was completely soluble in water, while linear amylose was not soluble. The dried CA sample was dissolved in LiCl solution of *N,N'*-dimethylacetamide and reacted with *n*-butyl isocyanate in the presence of pyridine. The procedures were substantially the same as those in our previous reports for cATBC²⁰ and ATBC.¹⁸ The obtained cATBC samples were further purified by successive fractional precipitation with methanol and water as a solvent and a precipitant, respectively. Seven cATBC samples with the weight-average molar mass M_w ranging from 29 to 122 kg mol⁻¹ were chosen for this study. A linear ATBC sample with M_w of 148 kg mol⁻¹ prepared from an enzymatically synthesized linear amylose sample²⁴ and a previously investigated ATBC sample, ATBC60K,¹⁷ were also used in this study. The chemical structure of all the investigated samples was confirmed by ¹H NMR in CDCl₃, infrared absorption spectra, and elemental analysis. Size-exclusion chromatography measurements with multiangle light scattering and refractive index detectors were made for the samples with THF as an eluent. The evaluated M_w and the dispersity index $\bar{D}$ ($\equiv M_w/M_n$, with M_n being the number-average molar mass) are summarized in Table 1. The linear

Table 1. Molar Masses of the Samples

sample	M_w (kg mol ⁻¹)	$\bar{D}$ (M_w/M_n)
cATBC122K	122	1.17
cATBC110K	110	1.09
cATBC66K	66.1	1.11
cATBC63K	62.8	1.19
cATBC43K	43.3	1.12
cATBC32K	32.0	1.14
cATBC29K	29.1	1.23
ATBC148K (linear)	148	1.14
ATBC60K (linear) ¹⁷	60.3	1.05

ATBC in the cATBC sample may be negligibly few because chain scission of the carbamate reaction of amylose was not observed even for the high molar mass samples ($M_w > 10^6$).¹⁸ Cyclic amylose tris(3,5-dimethylphenylcarbamate) synthesized by almost the same procedure was completely soluble in THF, while the linear analog was not soluble,²⁵ supporting the low linear contaminant. Although we attempted liquid chromatography under critical conditions (LCCC) to analyze the samples, an appropriate combination of columns and eluents was not found because of the insufficient solubility of ATBC and cATBC samples in typical mixed eluents for interaction chromatography. It is indeed well known that almost stiff polymers are only soluble in good solvents.²⁶

Phase Separation Experiments. Two phase boundary concentrations, c_1 and c_A , were determined for cATBC in THF and EL at 25 °C: the former is the phase boundary concentration between isotropic and biphasic regions and the latter is that between biphasic and anisotropic regions. Concentrated solutions were prepared in a conical vial with a screw cap in the manner reported previously.¹⁵ The solvents THF and EL were purchased from Fujifilm Wako Pure Chemical Co. and purified by fractional distillation over CaH₂. The initial concentration c_0 was adjusted to be between c_1 and c_A . The vial was calibrated with water to

determine the relationship between the volume and the meniscus height. The resulting solution was centrifuged with a swing rotor at 25 °C to attain two-phase separation. The meniscus height was determined by using a traveling microscope to estimate the volume fraction Φ_{LC} of the liquid crystal phase at c_0 . Both phases had fluidity, suggesting that gelation maintained by the intermolecular hydrogen bonds did not occur for this system.

Small-Angle X-ray Scattering for Dilute cATBC Solutions. SAXS measurements were made for dilute cATBC solutions at 25 °C at the BL40B2 beamline in SPring-8 (Hyogo, Japan) or at the BL-6A beamline in KEK-PF (Ibaraki, Japan).²⁷ The wavelength λ_0 in a vacuum and the sample-to-detector distance were set to be 0.1 nm and 4.2 m for SPring-8 and 0.15 nm and 2.5 m for KEK-PF, respectively. The solvent and three or four solutions with the polymer mass concentration c ranging between 4 and 50 mg cm⁻³ were measured with a quartz capillary cell (2.0 mm ϕ). Each solution was exposed for 180 s to integrate the scattering intensity with Dectris Pilatus 3S 2 M (SPring-8) or Pilatus 3 1 M (KEK-PF) two-dimensional detectors. The scattering intensity was normalized with the intensity of the direct beam detected at the lower end of the cell to compensate both the intensity of the incident light and the transparency of the solution. The magnitude q of the scattering vector at each pixel on the detector was estimated by using the diffraction from silver behenate. SAngler software²⁸ was utilized to yield the scattering intensity $I(q)$ as a function of q . The excess scattering intensity $\Delta I(q)$ at each q was determined as the $I(q)$ difference between the solution and the solvent in the same cell. The obtained $\Delta I(q)$ data were extrapolated to infinite dilution to estimate $[\Delta I(q)/c]_{c \rightarrow 0}$ (plotted against q in Figure S1), which was further analyzed in terms of the Guinier plot (Figure S2) to determine the radius of gyration R_g and the form factor $P(q)$. The measurements were also examined for the solution diluted from the liquid crystal phase described above for cATBC43K and cATBC63K in EL and cATBC29K, cATBC43K, and cATBC63K in THF. The obtained $[\Delta I(q)/c]_{c \rightarrow 0}$ data were almost fitted by the data for the fresh solution as shown in Figure S1, indicating that no chain scission occurred in the preparation process of the concentrated solutions.

Small-Angle X-ray Scattering for Concentrated cATBC Solutions. Concentrated solutions of cATBC in THF or EL were prepared in Roche 20 μ L Light Cycler glass capillaries (~ 2 mm i.d.). The capillary was centrifuged to obtain a uniform solution and melt-sealed to avoid solvent evaporation. SAXS measurements were made at the BL40B2 beamline in SPring-8 with the incident light of $\lambda_0 = 0.1$ nm. The two sample-to-detector distances of 0.4 and 4.2 m were chosen to cover a wide q range. The detector and used software were the same as those for the dilute solution described above to determine $I(q)$ as a function of q . The solutions installed in a 10 T magnetic field for 70 h and stored at ~ 0 °C (~ 24 h) were also measured. SAXS measurements were also examined for a concentrated ATBC60K solution, which was sandwiched in two thin glass plates (~ 0.1 mm thick): the sample-to-detector distance was 0.5 m and scattered light was acquired with a Rigaku R-Axis VII imaging plate detector.

RESULTS AND DISCUSSION

Conformation of cATBC in Dilute EL. Figure 1 shows the dimensional properties of cATBC in EL. The radius of gyration R_g for cATBC is smaller than that for linear ATBC with the same M_w as shown in Figure 1a. The black solid curve is the theoretical values for the linear wormlike chain model^{29,30} with the parameters of the Kuhn segment length $L_k = 34$ nm (chain stiffness, twice the persistence length) and the helix rise per residue $h = 0.26$ nm:¹⁹ the latter parameter is related to the contour length L as $h = L/DP$, where DP is the weight-average degree of polymerization. The dashed red curve indicates the simulated values for the wormlike ring³¹ with $h = 0.26$ nm and $L_k = 34$ nm. The calculated values represent the experimental data for the highest M_w but deviate downward with lowering M_w . This is most likely because of the extended local helical structure with

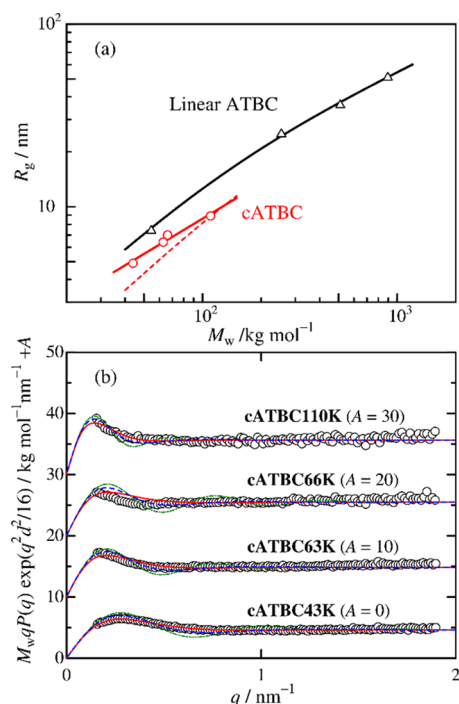


Figure 1. Dimensional properties of cATBC in dilute EL solution at 25 °C. (a) Weight-average molar mass M_w dependence of the radius of gyration R_g with the data for linear ATBC.¹⁹ Black solid and red dashed curves: theoretical values for the linear and cyclic wormlike chains, respectively, with the parameters of $h = 0.26$ nm and $L_k = 34$ nm. Red solid line: eye guide. (b) Reduced Holtzer plots for the indicated cATBC samples. Curves: theoretical values for the wormlike ring with the parameters of $h_{\text{ring}} = 0.26, 0.26, 0.30$, and 0.31 nm and $L_{k,\text{ring}} = 27, (45), 25$, and (20) nm for cATBC110K, cATBC66K, cATBC63K, and cATBC43K, respectively, with $\bar{D} = 1.00$ (dot-dashed green), 1.10 (dashed blue), and 1.30 (solid red). The values in the brackets cannot be determined from the curve fitting (see text).

a larger h value owing to the permanent bending effect of the rigid ring as described below.

The form factor $P(q)$ of the wormlike ring can be numerically evaluated in terms of the simulation method by Tsubouchi et al.³² A curve fitting procedure was examined for the $P(q)$ data in Figure 1b to estimate h and L_k for each sample. The resulting theoretical values follow the experimental data, taking the appropriate molar mass dispersity $\bar{D}$ with log-normal distribution into consideration. Some experimental data are better fitted by the theoretical curves for $\bar{D} = 1.3$, which is slightly larger than those from SEC-MALS. This is likely because of the assumption of the distribution function. It should be noted that L_k was determined only for cATBC110K and cATBC63K because $P(q)$ data for the other samples are not discrete enough from the theoretical values for the rigid ring ($L_k = \infty$). The vertical axis is multiplied by $\exp(q^2 d^2 / 16)$ to compensate the chain thickness effect on $P(q)$. The effective chain diameter d was estimated by the well-known cross-sectional plot (Figure S3), as in the case with the linear ATBC in EL;¹⁹ note that the slight negative d^2 value is owing to the electron density profile around the chain contour including solvent molecules. Similar analysis was also made for cATBC in THF (Figure S4). The evaluated R_g and h_{ring} values were consistent with our previous reports.^{20,21} The obtained helix rise per residue h_{ring} and the Kuhn segment length $L_{k,\text{ring}}$ for the ring chain are plotted against the reduced chain length $(L/L_k)_{\text{linear}}$ for the corresponding linear chain with the

same M_w in Figure 2, in which h_{linear} and $L_{k,\text{linear}}$ denote the literature values for h and L_k for the corresponding linear chain,

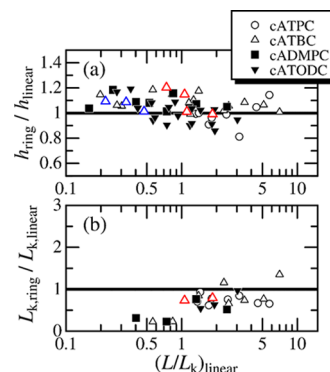


Figure 2. Reduced chain length $(L/L_k)_{\text{linear}}$ dependence of (a) $h_{\text{ring}}/h_{\text{linear}}$ and (b) $L_{k,\text{ring}}/L_{k,\text{linear}}$ for cATBC in EL (red triangles) and THF (blue triangles). Black symbols are the literature values for cATBC (unfilled triangles),²¹ cyclic amylose tris(phenylcarbamate) (cATPC, unfilled circles, in 1,4-dioxane and 2-ethoxyethanol),²¹ cyclic amylose tris(3,5-dimethylphenylcarbamate) (cADMPC, filled squares),²⁵ and cyclic amylose tris(*n*-octadecylcarbamate) (cATODC, inverted filled triangles).¹⁶

respectively. The $h_{\text{ring}}/h_{\text{linear}}$ value tends to increase with lowering $(L/L_k)_{\text{linear}}$ as is the case of the other cyclic amylose derivatives, indicating that the conformational feature of cATBC in dilute EL is similar to the previously investigated cyclic amylose derivatives,^{16,21,25} that is, the local helical structure for the rigid ring polymer for $(L/L_k)_{\text{linear}} < 1$ is somewhat extended, while the extended helical structure cannot retain the high chain stiffness.

Phase Boundary Concentrations. Results from the phase separation experiments are illustrated in Figure 3 in which the

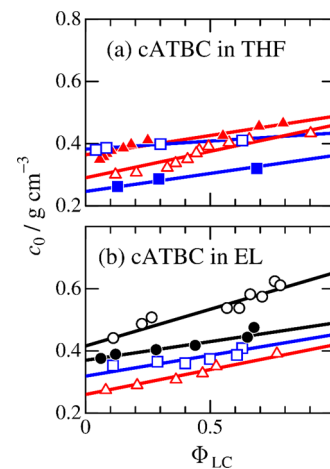


Figure 3. Plots of c_0 versus Φ_{LC} for cATBC in (a) THF and (b) EL at 25 °C. Symbols indicate cATBC32K (unfilled circles), cATBC43K (filled circles), cATBC63K (unfilled triangles), cATBC66K (filled triangles), cATBC110K (unfilled squares), and cATBC122K (filled squares).

initial concentration c_0 is plotted against the volume fraction Φ_{LC} of the liquid crystalline phase. The phase boundary concentrations, c_1 and c_A , were estimated as the extrapolated c_0 values to $\Phi_{\text{LC}} = 0$ and 1 , respectively. Since complete phase separation was not achieved for some samples, c_1 was estimated using the previously reported method.¹⁷ The obtained phase

boundary concentrations shown in Figure 4 are quite close to those for the linear ATBC in the corresponding solvent. In

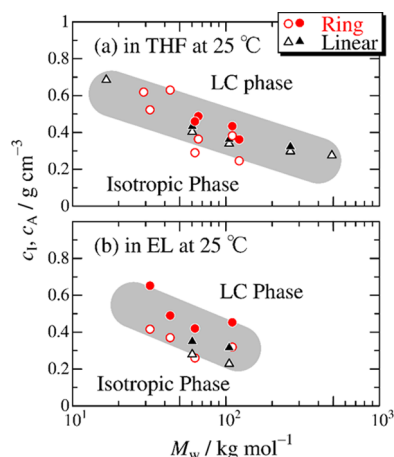


Figure 4. M_w dependence of c_l (unfilled symbols) and c_A (filled symbols) for cATBC (red circles) in (a) THF and (b) EL at 25 °C. Black triangles denote the literature data¹⁷ for linear ATBC.

contrast, the recently reported rigid cyclic polymer (cA-TODC)¹⁵ and rigid star polymer¹¹ had quite higher phase boundary concentrations than the corresponding linear chain.

X-ray Diffraction from the LC Phase. Figure 5 illustrates the q dependence of the scattering intensity $I(q)$ for concentrated cATBC and ATBC solutions with $c > c_A$. The LC phase for the cATBC–THF system does not have significant diffraction in the low q region ($< 2 \text{ nm}^{-1}$), indicating no smectic structures, which are predicted for nanorings.¹² The peaks for ATBC148K (linear) can be assigned to the cholesteric structure (3rd, 4th, 6th, and 7th peaks) with the cholesteric pitch of 290 nm. This is consistent with the finding that the concentrated THF solutions of linear ATBC show selective reflection in the visible light wavelength range.¹⁷ Sharp peaks are found, on the other hand, for all the cATBC and ATBC samples at the high q region. Interestingly, the diffraction patterns for cATBC110K (ring) and ATBC148K (linear) are quite similar, indicating substantially the same local alignment of the polymer chains. The highest peak at $q_0 \approx 3.5 \text{ nm}^{-1}$ shows a hexagonally packed cylinder since some of the peaks at higher q are found at $\sqrt{3}q_0$, $2q_0$, and $\sqrt{7}q_0$ (unfilled circles in the figure). A weaker peak set with $q_1 \approx 4.3 \text{ nm}^{-1}$ can be assigned as the tetragonal packing (filled squares at q_1 , $\sqrt{2}q_1$, and $2q_1$). Some other small peaks between 6 and 8 nm^{-1} suggest that the other minor alignment in the solution when we consider the THF solution tends to become inhomogeneous owing to the high vapor pressure of THF even in the sealed glass capillary.

To explain substantially the same local alignment of the linear and ring chains, it is proposed that cATBC chains have a pseudo-rodlike conformation with two kinks in the molecule as illustrated in Figure 6b. The costs of this energetically unfavorable conformation may not be high because the chain stiffness of ATBC is mainly supported by the intramolecular hydrogen bonding interactions between C=O and NH groups on the neighboring glucose unit^{18,33} and much smaller chain stiffness ($L_k = 11 \text{ nm}$) was observed in methanol with a few intramolecular hydrogen bonds. Except for the two kinks, the rodlike part should have a more stable conformation compared with the bent part for the rigid ring conformation in Figure 6a. A

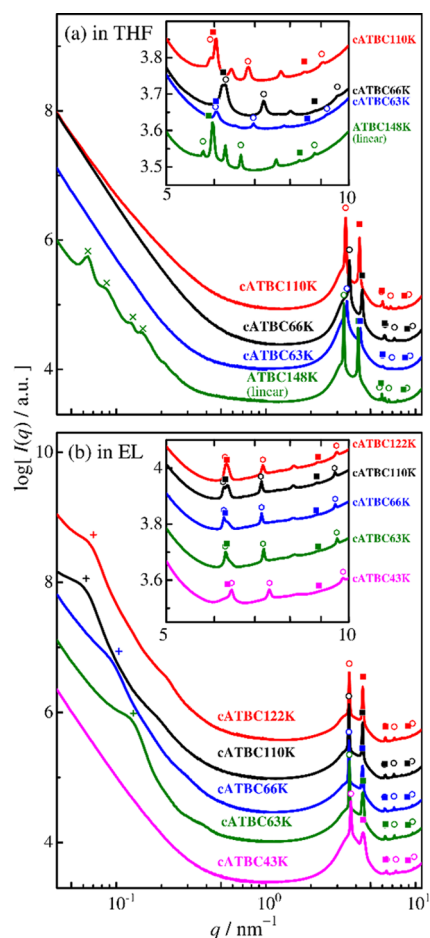


Figure 5. Plots of scattering intensity $I(q)$ versus q for the indicated cATBC and linear ATBC samples. (a) cATBC110K (red, $c = 0.484 \text{ g cm}^{-3}$), cATBC66K (black, $c = 0.475 \text{ g cm}^{-3}$), cATBC63K (blue, $c = 0.476 \text{ g cm}^{-3}$), and ATBC148K (green, $c = 0.494 \text{ g cm}^{-3}$) all in THF at 25 °C. (b) cATBC122K (red, $c = 0.517 \text{ g cm}^{-3}$), cATBC110K (black, $c = 0.528 \text{ g cm}^{-3}$), cATBC66K (blue, $c = 0.527 \text{ g cm}^{-3}$), cATBC63K (green, $c = 0.540 \text{ g cm}^{-3}$), and cATBC43K (magenta, $c = 0.731 \text{ g cm}^{-3}$) all in EL at 25 °C.

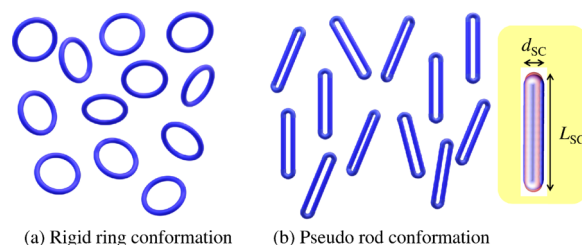


Figure 6. Schematic representation of (a) rigid ring and (b) pseudo-rodlike conformation of cATBC.

similar rodlike conformation with two kinks was observed for cyclic amylose in the crystalline state.³⁴ Furthermore, xanthan, a water-soluble polysaccharide with higher chain stiffness³⁵ than ATBC in methanol, can form a hairpin-like conformation^{36–38} with a kink in aqueous solution,^{39,40} supporting this suggestion. Diffraction peaks for the THF solutions of low M_w cATBC samples, cATBC63K and cATBC66K, are also similar but slightly different from those for the higher M_w samples. This suggests that intermolecular interactions between the kink point and the intermediate chain are quite different from those for the

two linear ATBC chains and the effect becomes more significant with lowering M_w .

Similar peaks are also found for cATBC in EL as shown in Figure S5; see also Figure S5 for a linear ATBC sample. According to Oyamada et al.,¹⁷ only the former hexagonal peaks for linear ATBC in EL were aligned in the magnetic field, and hence, the latter tetragonally packed cylinders may be a minor structure located near the glass capillary. It is noted that no magnetic field alignment was found for the current cATBC samples (Figure S6). These results indicate that cATBC chains form the pseudo-rod conformation in concentrated EL solution as in the case of THF solution described above, suggesting that the pseudo-rod conformation of the cATBC chain is not solvent-specific. Weak shoulders are found in the low q region for cATBC in EL. The d -spacing was calculated to be 91, 101, 62, and 49 nm for cATBC122K, cATBC110K, cATBC66K, and cATBC63K, respectively. Higher-order peaks were not found because of the low regularity of the structure. These are much longer than half of the contour length, that is, $hDP/2$. Consequently, they can be assigned as the cholesteric structure, which is frequently found for helical polymers including ATBC.¹⁷ This contrasts with the smectic structure of EL solutions of linear ATBC.¹⁷ The relatively short cholesteric pitch of the ring polymer compared with the linear chain suggests that the obtained pseudo-rod conformation may have twisted, as is the case with the superhelical structures for ring DNA.

Theoretical Analysis of the Phase Diagram. If rigid cyclic chains behave as a pseudo-rod in concentrated solutions, the phase diagram can be expressed in terms of the scaled particle theory (SPT) for the linear wormlike spherocylinder.^{41–43} According to Sato and Teramoto,^{41–43} the Helmholtz energy is expressed as a function of c with the three parameters, the contour length L_{SC} , the Kuhn segment length $L_{k,SC}$, and the chain diameter d_{SC} of the spherocylinder, which models the pseudo-rod in Figure 6b. The detailed expression can be found in their original paper or in our recent report.¹¹ Thus, the phase boundary concentrations, c_l and c_A , can be calculated from the equation with $L_{k,SC}$ and d_{SC} , assuming that $L_{SC} = hDP/2$. If we assume that $L_{k,SC}$ is the same as that for linear ATBC in dilute solution, that is, 75 and 34 nm in THF¹⁸ and EL,¹⁹ respectively, blue curves in Figure 7 fairly explain the experimental data with $d_{SC} = 2.9$ and 3.4 nm in THF and EL, respectively. The two parallel aligned ATBC chains in the pseudo-rodlike conformation may have higher chain stiffness than linear ATBC chains: If we assume a bending wire model, the chain stiffness of the two ATBC chains can be twice higher than that for the single chain. As a trial, the theoretical black curves calculated with the four times higher chain stiffness ($L_{k,SC} = 300$ and 136 nm) and $d_{SC} = 2.6$ and 3.0 nm in THF and EL, respectively, can also explain the experimental data. It is noted that the phase diagram does not significantly change with increasing chain stiffness because the Kuhn segment numbers ($L_{SC}/L_{k,SC}$) of the highest M_w sample are quite small, that is, 0.23 and 0.46 in THF and EL, respectively, assuming a pseudo-rod conformation with higher chain stiffness. The obtained d_{SC} values of 2.9 or 2.6 nm in THF are reasonably larger than that for linear ATBC (1.47 nm); note that the value for linear ATBC in EL was not decided because it formed a smectic phase in the solvent.¹⁷ The current analysis also speculates that cATBC tends to form the pseudo-rodlike conformation even in the isotropic phase at c_l . This is consistent with the finding that cATBC chains can easily form the pseudo-rod because the high chain stiffness is attained by the intramolecular hydrogen bonds as described above. Another

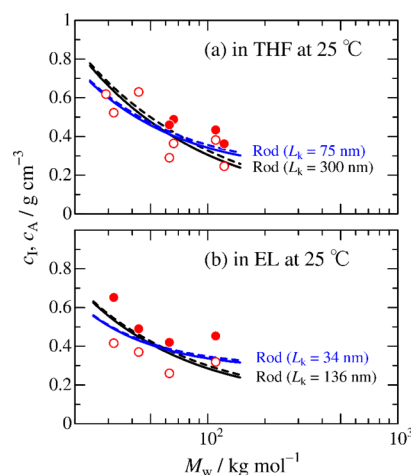


Figure 7. Comparison between experimental c_l (unfilled circles) and c_A (filled circles) for cATBC in (a) THF and (b) EL at 25 °C and the theoretical phase boundaries, c_l (solid curves) and c_A (dashed curves). Blue and black curves: the theoretical curves of the SPT for the pseudo-rodlike conformation with the indicated L_k .

significant feature of the phase diagram is that the molar mass dependence seems more fluctuating than that for the linear chain. Similar trends were also found for cATODC.¹⁵ This is most likely because a slight difference in DP may play an important role for the kink conformation and/or intermolecular interaction of the kink with the other part.

CONCLUSIONS

A rigid cyclic polymer, cATBC, forms a nematic phase in the concentrated THF and EL solutions. The phase boundary concentrations between isotropic and lyotropic phases are substantially identical to that for the linear chain in the corresponding solvent. The local chain alignment evaluated from X-ray diffraction is substantially the same as that for the linear chain, that is, cATBC chains in the nematic phase form a pseudo-rod conformation for which the cylinder length is half the contour length. The obtained phase diagram was explained in terms of the scaled particle theory for the wormlike cylinder, assuming that the polymer chains have a pseudo-rod conformation around the phase boundary concentrations. To attain the ring shape even in the highly concentrated solution and to realize the theoretically predicted smectic phase with nanorings,¹² the Kuhn segment length of 75 nm was not always enough even though the value is generally classified for stiff chains. It is however noticed that the current data set might not be enough to confirm the pseudo-rod conformation of the rigid ring polymers in the lyotropic phase; some other methods such as neutron scattering could be desirable to determine the conformation. Further study for rigid ring polymers with non-intramolecular hydrogen bonding is also desired to clarify whether the currently suggested pseudo-rodlike conformation is general for rigid ring polymers in the liquid crystal phase.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.1c01783>.

Additional figures for the SAXS data for cATBC in dilute solution, diffraction data for linear ATBC in concentrated

EL solution, and 2D diffraction pattern for a cATBC sample (PDF)

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Notes

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