ARTICLE

OBC
www.rsc.org/obc

Thermotropic liquid–crystalline peptide derivatives: oligo(glutamic acid)s forming hydrogen-bonded columns

Masayuki Nishii, Toru Matsuoka, Yuko Kamikawa and Takashi Kato*

Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. E-mail: kato@chiral.t.u-tokyo.ac.jp; Fax: (+81) 3-5841-8661

Received 29th October 2004, Accepted 10th January 2005
First published as an Advance Article on the web 2nd February 2005

We report on new thermotropic liquid–crystalline oligo(amino acid) derivatives forming columnar structures. These are based on branched oligo(glutamic acid)s and 2-(3,4-dialkyloxyphenyl)ethyl moieties. An oligo(glutamic acid) derivative, α,γ-bis(L-glutamoyl) L-glutamic acid tetra[2-(3,4-dioctadecyloxyphenyl)ethyl]ester, shows a hexagonal columnar phase, whilst a glutamic acid derivative, α,γ-bis[2-(3,4-dioctadecyloxyphenyl)ethyl] L-glutamate, does not show a mesophase. Hydrogen bonds formed by the oligo(glutamic acid) moieties should contribute to the induction of the columnar liquid–crystalline properties. In addition, we have examined the effects of the molecular chirality of the oligo(glutamic acid) parts and the functionalisation at the focal position of the taper shaped molecules on the liquid–crystalline properties of the compounds.

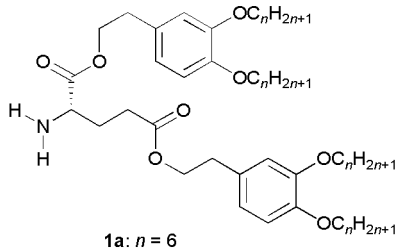
Introduction

Intensive work has focused on molecular self-assembled materials that can be used for nanoscience and advanced technologies.[1,2] Amino acids have been used as building blocks for self-assembled materials such as liquid crystals,[3–8] fibres,[9] micelles[10] and tubes.[11] For thermotropic liquid crystals, poly(amino acids)s such as poly(γ-benzyl L-glutamate)[5] and poly(γ-alkyl L-glutamate)s[6] have been shown to exhibit liquid–crystalline properties. Liquid–crystalline peptides bearing mesogens in the side chains were also reported to show mesophases.[7] However, examples of liquid crystals in which the amino acid parts play critical roles for mesomorphism are rare, whilst a large number of sugar derivatives have shown thermotropic and lyotropic liquid–crystalline properties.[12]

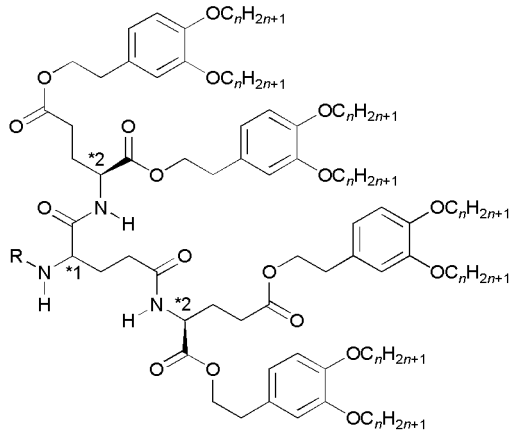
Our intention is to explore new liquid crystals composed of amino acids, forming supramolecular structures. We previously developed liquid–crystalline folic acid derivatives containing oligo(glutamic acid) moieties.[3,4] These folic acid derivatives exhibit thermotropic smectic, columnar and cubic phases. For these materials, the glutamic acid moieties play a critical role in the self-assembly and the induction of supramolecular chirality. Glutamic acid has two carboxylic acids and one amino group. We consider that this molecular structure can function as a new useful component for the molecular design of liquid crystals.

A number of dendritic and taper shaped liquid crystals having no rod-like mesogens have been designed and synthesised,[3,4,13] whilst a large number of dendrimers[14] and the dendrimers having rod-like mesogens[15] have been reported. Tschierske *et al.*[13a–c] showed gluconamide derivatives with di- or trialkyloxybenzoyl groups exhibit columnar and cubic phases. Percec and coworkers[13d,e] developed a series of aromatic taper shaped dendrons having alkyl chains that exhibit thermotropic liquid–crystalline properties. Recently, Stupp *et al.*[13f] have reported liquid crystals with rod-dendron block molecular structures of biphenyl-based segments and polyether dendrons. The liquid–crystalline properties of these materials are induced by nanoscale segregation and specific molecular interactions as well as by specific molecular shape.[1d,e,2–4,13,15]

Here we report on new thermotropic liquid–crystalline compounds consisting of oligo(amino acid)s as shown in Fig. 1. We focus on glutamic acid as a building block for thermotropic liquid crystals. We have designed taper shaped molecular structures based on glutamic acid. Oligo(glutamic acid) derivatives **1–4** were prepared and their liquid–crystalline properties were examined. Compounds **1–4** are made up of two molecular components, the oligo(glutamic acid) parts capable of hydrogen bonding and the lipophilic alkyl chains. Compounds **4** have a benzoyl group (**4a**) and alkanoyl groups (**4b**, **4c**) attached to the inner amino groups.



1a: *n* = 6
1b: *n* = 11
1c: *n* = 18



2a: R = H, *n* = 6, *1 = L, *2 = L
2b: R = H, *n* = 11, *1 = L, *2 = L
2c: R = H, *n* = 18, *1 = L, *2 = L
3: R = H, *n* = 6, *1 = D, *2 = L
4a: R = C_6H_5CO, *n* = 11, *1 = L, *2 = L
4b: R = $C_9H_{19}CO$, *n* = 11, *1 = L, *2 = L
4c: R = $C_{18}H_{37}CO$, *n* = 11, *1 = L, *2 = L

Fig. 1 Structures of oligo(glutamic acid) derivatives.

DOI: 10.1039/b416474a

Results and discussion

Synthesis of oligo(glutamic acid) derivatives 1–4

Glutamic acid derivatives **1** and oligo(glutamic acid) derivatives **2–4** were synthesised according to previously reported methods.[3,4] *N*-Fmoc-L-glutamic acid was condensed with 2-(3,4-dialkyloxyphenyl)ethanol. The deprotection of the Fmoc groups by piperidine gave α,γ-bis[2-(3,4-dialkyloxyphenyl)ethyl] L-glutamates **1a–c**. These procedures were repeated for **1a–c** to obtain α,γ-bis(L-glutamoyl) L-glutamic acid tetra[2-(3,4-dialkyloxyphenyl)ethyl]esters **2a–c**. Oligo(glutamic acid) **3** was synthesised from *N*-Fmoc-D-glutamic acid and **1a**. Compound **2b** was further reacted with benzoyl chloride, decanoic acid and nonadecanoic acid to obtain **4a–c**, respectively. The thermal properties and liquid–crystalline behaviour of **1–4** were examined by differential scanning calorimetry (DSC), polarising optical microscopy and X-ray diffraction measurements.

Thermotropic liquid–crystalline behaviour of oligo(glutamic acid) derivatives 1–4

The thermal properties of glutamic acid derivatives **1** and oligo(glutamic acid) derivatives **2–4** are listed in Table 1. For a series of glutamic acid derivatives **1a–c**, only **1b** shows liquid–crystalline behaviour. All of the oligo(glutamic acid) derivatives of **2a–c** however, show thermotropic hexagonal columnar phases. For **2a**, having hexyloxy chains, a columnar phase is seen from 51 to 69 °C. In contrast, **1a** is an isotropic liquid at room temperature. For **1a**, the transition to a glassy state is observed below room temperature upon cooling. Compound **1b**, having undecyloxy chains, shows a hexagonal columnar phase at around room temperature, whilst oligo(glutamic acid) derivative **2b** exhibits a columnar phase from 74 to 88 °C. The isotropisation temperature of **2b** is 51 °C higher than that of **1b**. Fig. 2 shows the DSC thermograms of **1c** and **2c** on the second heating. Compound **1c** melts from the crystalline state to the isotropic liquid state at 65 °C. For **2c**, the endothermic peaks corresponding to crystalline–columnar and columnar–isotropic transitions are seen at 71 and 78 °C, respectively. On cooling from the isotropic liquid state, fan-like textures characteristic of the columnar phases are observed for **2c** under a polarising optical microscope, as shown in Fig. 3.

The hierarchical tuning of molecular chirality is possible for the oligo(glutamic acid) derivatives. Oligo(glutamic acid) derivative **3**, the diastereomer of **2a**, was prepared. Compound **3** shows a monotropic liquid–crystalline columnar phase, whilst the enantiotropic columnar phase is seen for **2a**. Upon heating, compound **3** melts to the isotropic liquid at 90 °C. The melting temperature of **3** is 39 °C higher than that of **2a**. Upon cooling, **2a** shows the columnar phase from 37 to −25 °C. For **3**, the monotropic hexagonal columnar phase is seen from 45 to 34 °C. The isotropic to columnar transition temperature of **3** is 8 °C higher than that of **2a**. The change of the molecular chirality at the inner glutamic acid parts for **2a** and **3** (Fig. 1) induces the stabilisation of the crystalline structures for **3**.

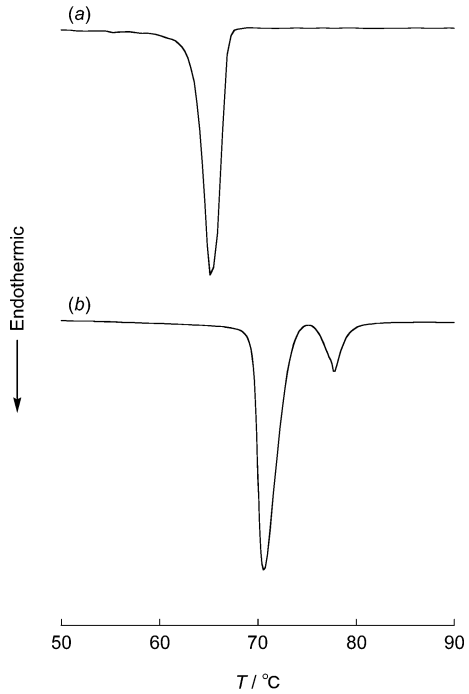


Fig. 2 DSC thermograms of **1c** (*a*) and **2c** (*b*) on the second heating.

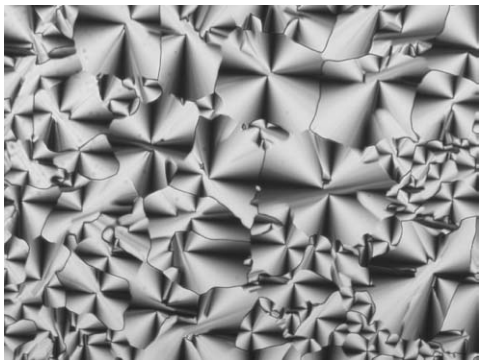


Fig. 3 A polarised optical photomicrograph of **2c** at 75 °C (Col_h).

The oligo(glutamic acid) derivatives of **2** can be further functionalised by introducing various functional moieties at the free amino groups. In the present study, a benzoyl group (**4a**) and alkanoyl moieties (**4b,4c**) have been introduced. The functionalisation of the oligo(glutamic acid)s at the focal position

Table 1 Thermal properties and X-ray results of oligo(glutamic acid) derivatives **1–4**

						X-Ray results	
Compounds	Phase transition behaviour[a]					*T*/°C	Intercolumnar distances/Å
1a			G	−49	Iso		
1b	Cr	26 (63)	Col_h	37 (2.8)	Iso	30	46.8
1c			Cr	65 (119)	Iso		
2a	Cr	51 (26)	Col_h	69 (4.5)	Iso	60	37.5
2b	Cr	74 (97)	Col_h	88 (26)	Iso	80	42.8
2c	Cr	71 (172)	Col_h	78 (26)	Iso	75	50.5
3	Cr_1	75 (16)	Cr_2	90 (62)	Iso	40[b]	37.2
4a			Cr	91 (129)	Iso		
4b	Cr	78 (68)	Col_h	88 (16)	Iso	80	36.7
4c	Cr	71 (20)	Col_h	83 (27)	Iso	80	37.7

[a] Transition temperatures (°C) and enthalpy changes (kJ mol^{-1} in parentheses) were determined by DSC on the second heating. G: glassy; Cr: crystalline; Col_h: hexagonal columnar; Iso: isotropic. [b] A monotropic hexagonal columnar phase is seen from 45 to 34 °C.

has affected their liquid–crystalline properties. Compound **4a** melts at 91 °C to the isotropic liquid state. The introduction of the benzoyl group to **2b** results in the disappearance of the liquid crystallinity. Compounds **4b** and **4c**, bearing flexible alkyl chains at the core, show thermotropic columnar phases, as in the case of **2b**, and the thermal stability of the columnar phases of **4b** and **4c** is almost the same as that of **2b**.

The FT–IR spectra for the oligo(glutamic acid) derivatives were measured to examine the formation of the hydrogen bonds, as shown in Fig. 4 and Table 2. The curve fitting was performed for the IR bands of the amide groups (Amide I) of **2b** upon heating. The absorption band of the carbonyl groups of the oligo(glutamic acid) parts is seen around 1642 cm^{-1} in the crystalline state at 60 °C, which indicates that they form hydrogen bonds. After the transition to the columnar liquid–crystalline phase, the intensities of the absorption bands at 1678 and 1655 cm^{-1} increase (80 °C, Fig. 4). The absorption band centred at 1678 cm^{-1} is ascribed to the free amide groups. The band at 1655 cm^{-1} is due to the formation of weaker hydrogen bonds. In the columnar liquid–crystalline state at 80 °C, about 80% of the amide groups form hydrogen bonds (Table 2). In the isotropic state at 100 °C, the IR band around 1640 cm^{-1} is not seen. More than half of the amide groups do not form hydrogen bonds in the isotropic state. The formation of the hydrogen bonds at the oligo(glutamic acid) moieties should contribute to the induction of the columnar liquid–crystalline properties. Hydrogen bonding has been known to play a critical role in the induction of liquid–crystalline phases.[2a,b,16] However, the compounds reported here are a new series of hydrogen-bonded liquid crystals.

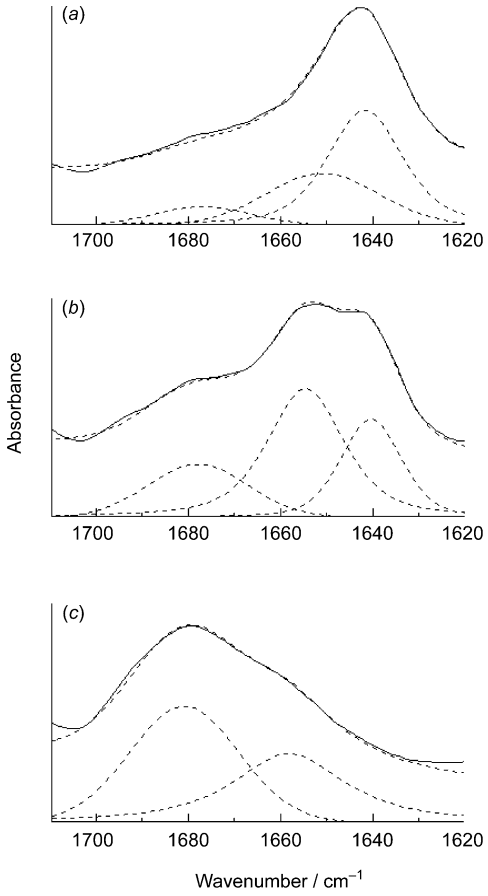


Fig. 4 Curve fitting results for IR bands of Amide I of **2b** at 60 (*a*), 80 (*b*) and 100 °C (*c*).

The X-ray diffraction profile for the columnar phase of oligo(glutamic acid) derivative **2b** is shown in Fig. 5. In the wide angle region, the diffused halo of around 4.5 Å is due to the disorder of the terminal alkyl chains. In the small angle region, the sharp reflection of 37.1 Å (100) and the smaller peaks of 21.6 Å (110), 18.4 Å (200) and 13.9 Å (210) are characteristic of the hexagonal structure. The intercolumnar distance is 42.8 Å. We suggest that the columnar structures of **2b** are composed of disk-like aggregates of the compounds. A molecular model of a dimer of **2b** arranged side by side is shown in Fig. 6. The size of the molecular model agrees with the X-ray results. Nanoscale segregation between the hydrogen-bonded oligo(glutamic acid) parts and lipophilic alkyl chains leads to the formation of the self-assembled columnar aggregates. The diameters of the columns for the columnar liquid–crystalline phases of **1–4** are listed in Table 1. The increase in the number of amino acids in compound **1b** results in a decrease in the intercolumnar spacing, from 46.8 Å for **1b** to 42.8 Å for **2b**. The diameters of the columns of **4b** and **4c** are 36.7 and 37.7 Å, respectively, which are shorter than that of **2b**. One possible explanation is that the introduction of the bulky groups at the focal point disturbs a dimerisation in the column, which leads to the decrease of the column diameter. However the FT–IR spectra of **2b** and **4b** show that hydrogen-bonded properties of these compounds are almost the same, which may result in the similar liquid–crystalline behaviour. The column diameters increase with increasing length of the terminal alkyl chains for **2a–c**.

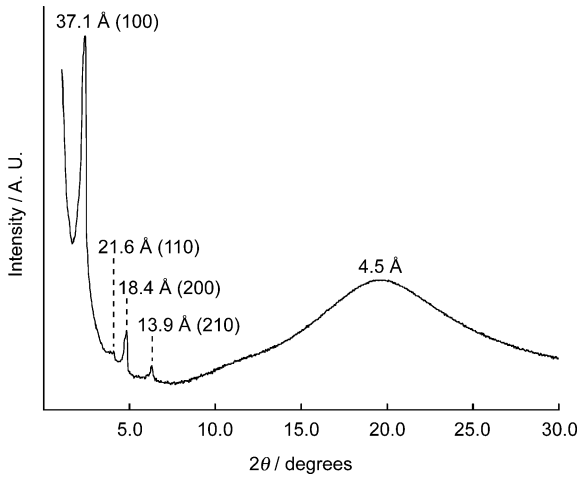


Fig. 5 X-Ray diffraction profile of **2b** at 80 °C.

Table 2 Curve fitting results for IR bands of Amide I of oligo(glutamic acid) **2b**

	H-Bonded C=O bands of Amide I		Free C=O bands of Amide I	
Phase	Wavenumber/cm^{-1}	Fraction of area	Wavenumber/cm^{-1}	Fraction of area
Crystalline (60 °C)	1642	0.58	1677	0.10
	1651	0.32		
Columnar (80 °C)	1640	0.28	1678	0.21
	1655	0.51		
Isotropic (100 °C)	—	—	1681	0.54
	1658	0.46		

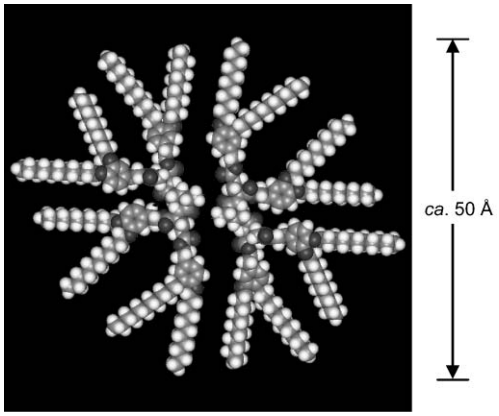


Fig. 6 Molecular model of a dimer of **2b**.

We reported on the self-assembled behaviour of folic acid derivatives **5**[4] and **6**[3] containing the oligo(glutamic acid)s of **1b** and **2b**, respectively (Fig. 7). The folic acid derivatives of **5** and **6** show thermally stable liquid–crystalline properties through the combination of the cyclic hydrogen bonds of the pterin rings and the amide hydrogen bonds of the oligo(glutamic acid) parts. For example, the isotropisation temperature of the liquid–crystalline phase of folic acid **6** is 99 °C higher than that of the oligo(glutamic acid) of **2b**. The oligo(glutamic acid) derivatives shown in the present study are considered to have potential as the building blocks for various molecular self-assembled materials.[3,4,17]

Conclusion

The oligo(glutamic acid)s of **1–4** are the first examples of liquid crystals in which the components of amino acids substantially function to induce thermotropic liquid–crystalline properties. These taper shaped molecules show thermotropic columnar phases through the formation of hydrogen bonds and nanoscale segregation. The liquid–crystalline properties and self-assembled structures of these materials have been tuned by the molecular structures of the compounds, such as the number of amino acids, chirality and focal functionality. Such liquid crystals based on amino acids may be useful for new functional liquid–crystalline materials in bio-related fields.

Experimental

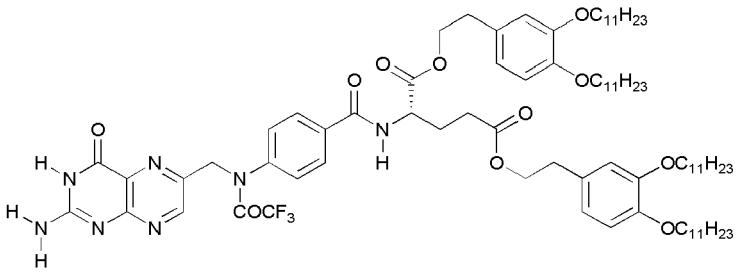
General methods and materials

All reagents and solvents were purchased from Aldrich Chemical, Tokyo Kasei, and Wako Pure Chemicals and were used as received. Analytical thin layer chromatography (TLC) was performed on silica gel plates from E. Merck (silica gel F_{254}). Silica gel column chromatography was carried out with silica gel 60 from Kanto Chemicals (silica gel 60, spherical 40–50 μm). Elemental analyses were carried out on a Perkin-Elmer CHNS/O 2400 apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400. Chemical shifts of ^{1}H and ^{13}C NMR signals are expressed in parts per million (δ) using internal standards Me_4Si ($\delta = 0.00$) and $CDCl_3$ ($\delta = 77.00$), respectively. Mass spectra (MALDI) were recorded on a PerSeptive Biosystems Voyager-DE STR spectrometer. Synthesis and spectroscopic data of compounds **1–3** have been reported in our previous papers.[3,4]

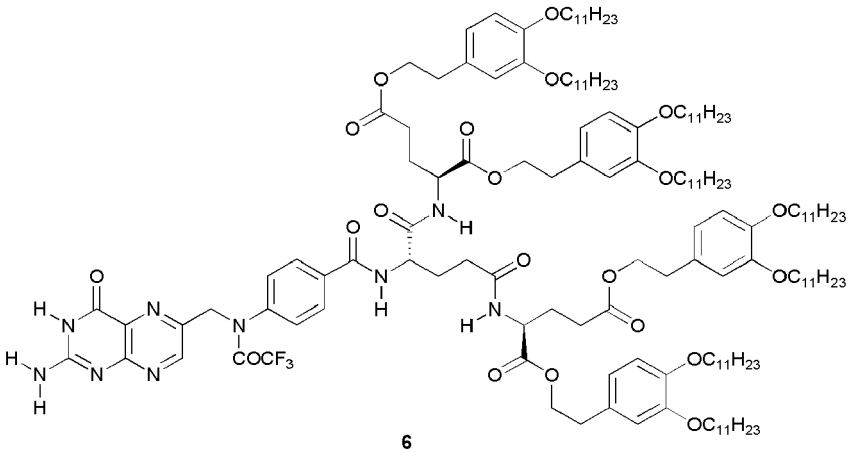
DSC measurements were performed on a Mettler DSC 30 (scanning rate: 5 °C min^{-1}). Transition temperatures were taken at the maximum of transition peaks. A polarising optical microscope Olympus BH-2 equipped with a Mettler FP82HT hot stage was used for visual observation. IR measurements were conducted on a JASCO FT/IR-660 Plus on KBr plates. X-Ray diffraction measurements were carried out on a Rigaku RINT 2100 diffractometer with a heating stage using Ni-filtered CuKα radiation.

Synthesis

***N*-Benzoyl-α,γ-bis(L-glutamoyl) L-glutamic acid tetra[2-(3,4-diundecyloxyphenyl)ethyl]ester (4a).** To a solution of **2b**



5



6

Fig. 7 Structures of folic acid derivatives.[3,4]

(0.253 g, 0.116 mmol), triethyl amine (0.072 ml, 0.519 mmol) and dry CH_2Cl_2 (30 ml) was added benzoyl chloride (30.5 mg, 0.217 mmol). The solution was stirred under an Ar atmosphere at room temperature for 2 h. To the reaction mixture sat. NH_4Cl aq. was added and extracted three times with $CHCl_3$. The collected organic fractions were washed with sat. NaCl aq., dried over $MgSO_4$ and filtered. The solvent of the filtrate was removed under a reduced pressure. The crude product was purified by flash column chromatography (silica gel, $CHCl_3$–EtOAc, 5 : 2) to give **4a** (0.230 g, 0.101 mmol, 87%) as a colourless solid (found: C, 74.55; H, 10.55; N, 2.12. Calc. for $C_{142}H_{235}N_3O_{19}$: C, 74.53; H, 10.35; N, 1.84%); TLC: $R_f = 0.80$ ($CHCl_3$–EtOAc, 5 : 2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.17$ (d, $J = 8$ Hz, 2H, Ph*H*), 8.05 (d, $J = 8$ Hz, 1H, CON*H*), 7.79 (d, $J = 8$ Hz, 1H, CON*H*), 7.31–7.58 (m, 3H, Ph*H*), 6.96 (d, $J = 7$ Hz, 1H, CON*H*), 6.68–6.81 (m, 12H, Ar*H*), 4.61–4.76 (m, 2H, NHC*H*CH_2), 4.48–4.55 (m, 1H, NHC*H*CH_2), 4.17–4.34 (m, 8H, COOCH_2), 3.91–3.97 (m, 16H, ArOCH_2), 2.86 (t, $J = 7$ Hz, 4H, ArCH_2), 2.81 (t, $J = 7$ Hz, 4H, ArCH_2), 2.36–2.44 (m, 6H, COCH_2), 2.14–2.23 (m, 4H, $COCH_2CH_2$), 1.70–1.94 (m, 16H, $ArOCH_2CH_2$, 2H, $COCH_2CH_2$), 1.27–1.45 (m, 128H, CH_2), 0.88 (t, $J = 7$ Hz, 24H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 173.2$, 173.1, 172.8, 172.4, 171.8, 162.4, 149.4, 147.9, 134.5, 133.6, 131.6, 130.5, 129.7, 128.4, 121.0, 114.6, 113.9, 69.3, 69.2, 66.6, 65.3, 58.2, 52.5, 51.6, 34.4, 31.8, 30.4, 29.5, 29.4, 26.0, 22.6, 18.3, 14.1 and other peaks; MS (MALDI): m/z 2311.35 (calc. $[M + Na]^+ = 2311.38$).

***N*-Decanoyl-α,γ-bis(L-glutamoyl) L-glutamic acid tetra[2-(3,4-diundecyloxyphenyl)ethyl]ester (4b).** To a solution of **2b** (0.416 g, 0.190 mmol) and dry CH_2Cl_2 (50 ml) was added decanoic acid (36.2 mg, 0.210 mmol). To the solution, EDC (44.0 mg, 0.230 mmol) dissolved in dry CH_2Cl_2 (10 ml) was added dropwise and stirred under an Ar atmosphere at room temperature for 24 h. To the reaction mixture sat. NH_4Cl aq. was added and extracted three times with $CHCl_3$. The collected organic fractions were washed with sat. NaCl aq., dried over $MgSO_4$ and filtered. The solvent of the filtrate was removed under a reduced pressure. The crude product was purified by flash column chromatography (silica gel, $CHCl_3$–EtOAc, 5 : 2) to give **4b** (0.260 g, 0.111 mmol, 57%) as a colourless solid (found: C, 74.65; H, 10.59. Calc. for $C_{145}H_{249}N_3O_{19}$: C, 74.47; H, 10.73%); TLC: $R_f = 0.59$ ($CHCl_3$–EtOAc, 5 : 2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 8$ Hz, 1H, CON*H*), 7.57 (d, $J = 8$ Hz, 1H, CON*H*), 6.66–6.81 (m, 12H, Ar*H*), 6.07 (d, $J = 8$ Hz, 1H, CON*H*), 4.59–4.69 (m, 2H, NHC*H*CH_2), 4.15–4.32 (m, 6H, COOCH_2), 3.89–3.94 (m, 16H, ArOCH_2), 2.84 (t, $J = 6$ Hz, 4H, ArCH_2), 2.79 (t, $J = 6$ Hz, 4H, ArCH_2), 2.34–2.40 (m, 8H, COCH_2), 2.12–2.24 (m, 4H, $COCH_2CH_2$), 1.75–1.92 (m, 16H, $ArOCH_2CH_2$, 2H, $COCH_2CH_2$), 1.23–1.42 (m, 144H, CH_2), 0.86 (t, $J = 8$ Hz, 27H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 173.4$, 173.3, 172.7, 172.6, 172.4, 172.3, 172.1, 149.2, 149.1, 148.0, 147.9, 130.0, 129.7, 121.1, 114.7, 114.0, 69.3, 66.7, 65.4, 51.7, 36.4, 34.6, 31.9, 30.5, 30.2, 29.6, 29.5, 29.3, 26.1, 25.5, 22.7, 14.1 and other peaks; MS (MALDI): m/z 2361.65 (calc. $[M + Na]^+ = 2361.54$).

***N*-Nonadecanoyl-α,γ-bis(L-glutamoyl) L-glutamic acid tetra[2-(3,4-diundecyloxyphenyl)ethyl]ester (4c).** Yield: 83%; found: C, 74.91; H, 11.18; N, 1.98. Calc. for $C_{154}H_{267}N_3O_{19}$: C, 75.04; H, 10.92; N, 1.70%; TLC: $R_f = 0.61$ ($CHCl_3$–EtOAc, 5 : 2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.96$ (d, $J = 8$ Hz, 1H, CON*H*), 7.58 (d, $J = 8$ Hz, 1H, CON*H*), 6.68–6.81 (m, 12H, Ar*H*), 6.09 (d, $J = 7$ Hz, 1H, CON*H*), 4.63–4.69 (m, 2H, NHC*H*CH_2), 4.17–4.34 (m, 6H, COOCH_2), 3.91–3.97 (m, 16H, ArOCH_2), 2.86 (t, $J = 7$ Hz, 4H, ArCH_2), 2.81 (t, $J = 7$ Hz, 4H, ArCH_2), 2.36–2.44 (m, 8H, COCH_2), 2.14–2.23 (m, 4H, $COCH_2CH_2$), 1.78–1.94 (m, 16H, $ArOCH_2CH_2$, 2H, $COCH_2CH_2$), 1.27–1.45 (m, 162H, CH_2), 0.88 (t, $J = 7$ Hz, 27H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 173.4$, 173.3, 172.6, 172.5, 172.4, 171.9, 149.2, 149.1, 147.9, 147.3, 133.6, 121.1, 114.7, 114.1, 69.3, 66.7, 65.4, 51.7, 36.4, 34.6, 33.8, 30.7, 29.9, 29.5, 26.7, 25.5, 22.7, 14.1 and other peaks; MS (MALDI): m/z 2488.02 (calc. $[M + Na]^+ = 2487.78$).

Acknowledgements

This work was financially supported by a Grant-in-Aid for Scientific Research on Priority Areas of "Dynamic Control of Strongly Correlated Soft Materials" (No. 413/13031009) and a Grant-in-Aid for The 21st Century COE Program for Frontiers in Fundamental Chemistry from the Ministry of Education, Culture, Sports, Science and Technology. Partial financial support of the Sasakawa Scientific Research Grant from the Japan Science Society (MN) is also acknowledged.

References

1 (*a*) *Molecular Self-Assembly, Organic Versus Inorganic Approaches*, ed. M. Fujita, Springer, Berlin, 2000, *Structure & Bonding*, vol. 96; (*b*) J.-M. Lehn, *Science*, 2002, **295**, 2400–2403; (*c*) G. M. Whitesides and B. Grzybowski, *Science*, 2002, **295**, 2418–2421; (*d*) T. Kato, *Science*, 2002, **295**, 2414–2418; (*e*) G. ten Brinke and O. Ikkala, *Chem. Rec.*, 2004, **4**, 219–230; (*f*) G. Gottarelli and G. P. Spada, *Chem. Rec.*, 2004, **4**, 39–49.

2 (*a*) T. Kato, *Struct. Bonding*, 2000, **96**, 95–146; (*b*) T. Kato, N. Mizoshita and K. Kanie, *Macromol. Rapid Commun.*, 2001, **22**, 797–814; (*c*) C. Tschierske, *J. Mater. Chem.*, 2001, **11**, 2647–2671.

3 (*a*) T. Kato, T. Matsuoka, M. Nishii, Y. Kamikawa, K. Kanie, T. Nishimura, E. Yashima and S. Ujiie, *Angew. Chem., Int. Ed.*, 2004, **43**, 1969–1972; (*b*) Y. Kamikawa, M. Nishii and T. Kato, *Chem. Eur. J.*, 2004, **10**, 5942–5951.

4 (*a*) K. Kanie, T. Yasuda, S. Ujiie and T. Kato, *Chem. Commun.*, 2000, 1899–1900; (*b*) K. Kanie, M. Nishii, T. Yasuda, T. Taki, S. Ujiie and T. Kato, *J. Mater. Chem.*, 2001, **11**, 2875–2886; (*c*) K. Kanie, T. Yasuda, M. Nishii, S. Ujiie and T. Kato, *Chem. Lett.*, 2001, 480–481; (*d*) T. Kato and N. Mizoshita, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 579–587.

5 S. M. Yu, V. P. Conticello, G. Zhang, C. Kayser, M. J. Fournier, T. L. Mason and D. A. Tirrell, *Nature*, 1997, **389**, 167–170.

6 (*a*) J. Watanabe, Y. Fukuda, R. Gehani and I. Uematsu, *Macromolecules*, 1984, **17**, 1004–1009; (*b*) J. Watanabe, H. Ono, I. Uematsu and A. Abe, *Macromolecules*, 1985, **18**, 2141–2148; (*c*) J. Watanabe and Y. Takashina, *Macromolecules*, 1991, **24**, 3423–3426.

7 (*a*) P. A. G. Cormack, B. D. Moore and D. C. Sherrington, *Chem. Commun.*, 1996, 353–354; (*b*) C. Guillermain and B. Gallot, *Macromol. Chem. Phys.*, 2002, **203**, 1346–1356.

8 W. Zhou, W. Gu, Y. Xu, C. S. Pecinovsky and D. L. Gin, *Langmuir*, 2003, **19**, 6346–6348.

9 (*a*) A. Aggeli, M. Bell, N. Boden, J. N. Keen, P. F. Knowles, T. C. B. McLeish, M. Pitkeathly and S. E. Radford, *Nature*, 1997, **386**, 259–262; (*b*) K. Hanabusa, J. Tange, Y. Taguchi, T. Koyama and H. Shirai, *J. Chem. Soc., Chem. Commun.*, 1993, 390–392; (*c*) M. Suzuki, M. Yumoto, M. Kimura, H. Shirai and K. Hanabusa, *Chem. Eur. J.*, 2003, **9**, 348–354; (*d*) N. Mizoshita, Y. Suzuki, K. Kishimoto, K. Hanabusa and T. Kato, *J. Mater. Chem.*, 2002, **12**, 2197–2201; (*e*) N. Yamada, K. Ariga, M. Naito, K. Matsubara and E. Koyama, *J. Am. Chem. Soc.*, 1998, **120**, 12192–12199; (*f*) T. Niwa, H. Yokoi, T. Kinoshita and S. Zhang, *Polym. J.*, 2004, **36**, 665–673.

10 (*a*) H.-A. Klok, J. J. Hwang, J. D. Hartgerink and S. I. Stupp, *Macromolecules*, 2002, **35**, 6101–6111; (*b*) R. C. Claussen, B. M. Rabatic and S. I. Stupp, *J. Am. Chem. Soc.*, 2003, **125**, 12680–12681.

11 (*a*) M. R. Ghadiri, J. R. Granja, R. A. Milligan, D. E. McRee and N. Khazanovich, *Nature*, 1993, **366**, 324–327; (*b*) N. Nakashima, S. Asakuma and T. Kunitake, *J. Am. Chem. Soc.*, 1985, **107**, 509–510; (*c*) N. Nakashima, S. Asakuma, J.-M. Kim and T. Kunitake, *Chem. Lett.*, 1984, 1709–1712; (*d*) T. Kunitake, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 709–726; (*e*) T. Shimizu, *Polym. J.*, 2003, **35**, 1–22; (*f*) N. Sakai and S. Matile, *Chem. Commun.*, 2003, 2514–2523.

12 (*a*) C. R. Noller and W. C. Rockwell, *J. Am. Chem. Soc.*, 1938, **60**, 2076–2077; (*b*) J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, 1984, **110**, 205–219; (*c*) G. A. Jeffrey, *Acc. Chem. Res.*, 1986, **19**, 168–173; (*d*) F. Dumoulin, D. Lafont, P. Boullanger, G. Mackenzie, G. H. Mehl and J. W. Goodby, *J. Am. Chem. Soc.*, 2002, **124**, 13737–13748; (*e*) V. Vill and R. Hashim, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 395–409.

13 (*a*) K. Borisch, S. Diele, P. Göring and C. Tschierske, *Chem. Commun.*, 1996, 237–238; (*b*) K. Borisch, S. Diele, P. Göring, H. Kresse and C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 529–543; (*c*) C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 1485–1508; (*d*) V. Percec, W.-D. Cho and G. Ungar, *J. Am. Chem. Soc.*, 2000, **122**, 10273–10281;

(*e*) V. Percec, W.-D. Cho, G. Ungar and D. J. P. Yeardley, *J. Am. Chem. Soc.*, 2001, **123**, 1302–1315; (*f*) S. Lecommandoux, H.-A. Klok, M. Sayar and S. I. Stupp, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 3501–3518; (*g*) J. H. Cameron, A. Facher, G. Lattermann and S. Diele, *Adv. Mater.*, 1997, **9**, 398–403; (*h*) M. Yoshio, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2004, **126**, 994–995; (*i*) J. H. K. Ky Hirschberg, R. A. Koevoets, R. P. Sijbesma and E. W. Meijer, *Chem. Eur. J.*, 2003, **9**, 4222–4231; (*j*) Y. Takaguchi, T. Tajima, Y. Yanagimoto, S. Tsuboi, K. Ohta, J. Motoyoshiya and H. Aoyama, *Org. Lett.*, 2003, **5**, 1677–1679.

14 (*a*) J. M. J. Fréchet, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 3713–3725; (*b*) D. A. Tomalia and J. M. J. Fréchet, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 2719–2728.

15 (*a*) B. Dardel, D. Guillon, B. Heinrich and R. Deschenaux, *J. Mater. Chem.*, 2001, **11**, 2814–2831; (*b*) D. Guillon and R. Deschenaux, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 515–525; (*c*) J.-M. Rueff, J. Barberá, B. Donnio, D. Guillon, M. Marcos and J.-L. Serrano, *Macromolecules*, 2003, **36**, 8368–8375; (*d*) I. M. Saez and J. W. Goodby, *Chem. Eur. J.*, 2003, **9**, 4869–4877; (*e*) P. H. J. Kouwer and G. H. Mehl, *Angew. Chem., Int. Ed.*, 2003, **42**, 6015–6018; (*f*) M. W. P. L. Baars, S. H. M. Söntjens, H. M. Fischer, H. W. I. Peerlings and E. W. Meijer, *Chem. Eur. J.*, 1998, **4**, 2456–2466.

16 (*a*) T. Kato and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1989, **111**, 8533–8534; (*b*) T. Kato, M. Nakano, T. Moteki, T. Uryu and S. Ujiie, *Macromolecules*, 1995, **28**, 8875–8876; (*c*) H. Kihara, T. Kato, T. Uryu and J. M. J. Fréchet, *Chem. Mater.*, 1996, **8**, 961–968.

17 Y. Kamikawa, T. Kato, H. Onouchi, D. Kashiwagi, K. Maeda and E. Yashima, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 4580–4586.