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Synthesis and liquid-crystalline properties of thermotropic polyamides containing flexible rodlike units and aliphatic spacers

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New polyamides with high molecular weights consisting of flexible rod-like mesogenic units (4,4′-diphenyl and 3,4′-diphenyl moieties having bent linkages in the central parts) and aliphatic spacers were synthesized and the thermotropic liquid-crystalline properties were investigated. Differential scanning calorimetry, texture observations by polarizing microscopy, miscibility tests and X-ray analysis suggested that the polymers showed well-defined thermotropic smectic mesophases. The polyamides containing 4,4′-diphenyl moieties had higher transition temperatures and formed more stable liquid-crystalline phases than the polyamide composed of the 3,4′-diphenyl unit with a kinked bond.

In general, it is necessary to introduce rigid, rod-like mesogenic units such as a biphenyl, a stilbene or a terphenyl unit in addition to flexible spacers, substituents and kinked units into the backbone of a polymer to decrease transition temperatures and to form liquid-crystalline mesophases in main chain type polymers like polyesters [1]. Some polyamides showing thermotropic liquid-crystalline phases, which have biphenyl moieties as mesogens in the main chain, have also been reported [2–4].

In recent years, it was found that polyethers composed of flexible rod-like units like diphenyl ether or diphenyl ethane and aliphatic spacers can form thermotropic liquid-crystalline mesophases in spite of having non-traditional, rod-like mesogenic moieties in the main chain [5]. In addition, Matsunaga *et al.* [6–7] pointed out that low molecular weight aromatic amido derivatives of *m*-phenylenediamine and 1,3,5-phenyltriamine exhibit liquid-crystalline mesophases (smectic and/or nematic) owing to molecular interaction through hydrogen bonding although they consist of a benzene ring instead of a biphenyl moiety. These results suggest that the traditional, rigid rod-like mesogens are not always necessary for the formation of the thermotropic liquid-crystalline phases, if there are linkages which represent strong intermolecular interactions like the amido group and flexible rod-like units in the main chain.

Here, the preparation of polyamides consisting of flexible rod-like mesogens (diphenyls with flexible linkages in the central parts such as diphenyl ether and diphenyl ethane) and a long aliphatic chain ($C_{18}H_{36}$) is described and the evaluation of the thermotropic liquid-crystallinity is presented.

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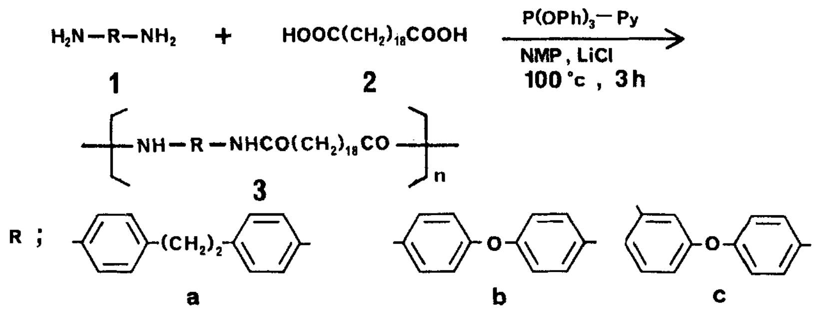


The polyamides (**3a**–**3c**) described here were prepared by direct polycondensation of three aromatic diamines, 1,2-bis(4-aminophenyl)ethane (**1a**), 4,4′-oxydianiline (**1b**) and 3,4′-oxydianiline (**1c**), with an aliphatic dicarboxylic acid, eicosanedioic acid (**2**), in pyridine/*N*-methyl-2-pyrrolidone (NMP) according to the method described by Higashi *et al.* [8] as shown in scheme 1. Into a mixture of NMP (8 ml) and pyridine (2 ml) triphenyl phosphite (4 mmol; 1·24 g) was added. The dicarboxylic acid (**2**) (2 mmol; 0·684 g) and lithium chloride (5 mmol, 0·2 g) were added and the mixture stirred. Then the diamine (2 mmol) was added and the reaction system heated at 100°C for 3 h under nitrogen atmosphere. After the polycondensation, the mixture was poured into a large amount of methanol and the precipitated solid was collected by filtration. The product was purified by reprecipitation from a dichloroacetic acid solution into methanol and washed thoroughly with hot methanol twice. The resulting polymer was dried *in vacuo* at 60°C for 12 h. Yield; 86–95 per cent. The synthetic results are listed in table 1. All the polymers with very high inherent viscosities (0·76–3·35 $dL\,g^{-1}$) were easily obtained in high yields. Analogous polyamides with shorter aliphatic chains have also been reported, but show no liquid-crystalline properties [9].

The polyamide (**3c**) shows good solubility not only in polar aprotic solvents such as NMP and *N*,*N*-dimethylformamide (DMF) on heating or at room temperature but also in acidic solvents like dichloroacetic acid (DCAA) and sulphuric acid. The other polymers (**3a** and **3b**) are soluble only in acidic solvents. The polymers (**3a**–**3c**) are partially soluble or insoluble in dimethysulphoxide (DMSO), tetrahydrofuran (THF) and chloroform.

Table 1. Synthetic results for polyamides (**3a**–**3c**).

			Solubility†				
Polymer	Yield%	η_{inh} $dL\,g^{-1}$	NMP	DMF	DCAA	THF	$CHCl_3$
3a	95	3·36‡	±	±	+	±	−
3b	94	2·26§	±	±	+	±	−
3c	86	0·73‖	+ +	+	+	−	−

† + +, soluble at room temperature; +, soluble on heating; ±, partially soluble; −, insoluble.

‡ Measured in NMP including lithium chloride (2 wt%) at 30°C (a concentration of 0·2 $dL\,g^{-1}$).

§ In DCAA including lithium chloride (2 wt%).

‖ In NMP.

The polyamides (**3a**–**3c**) show characteristic IR absorptions (obtained on a Jasco FT/IR 5300 spectrometer using the KBr disc method) at 1657 cm^{-1} (amide I) and 1524–1545 cm^{-1} (amide II) in addition to NH streching of the amido linkage at 3289–3304 cm^{-1} and CH stretching of alkylenes at 2851–2924 cm^{-1}. In the IR spectra of **3b** and **3c**, absorptions of C–O–C were also observed at 1215–1225 cm^{-1}. Elemental analysis data are in good agreement with the calculated values. Polymer (**3b**): $[C_{32}H_{46}N_2O_3]_n$; (510·0)*n*, Calculated for C; 75·35 per cent, H; 9·74 per cent, N; 5·49 per cent. Found for C; 75·50 per cent, H; 9·23 per cent, N; 5·26 per cent. These data support the structure of these polyamides.

The polyamides (**3a**–**3c**) were subjected to differential scanning calorimetry (DSC) measurement (Shimadzu DSC-50 calorimeter) with heating or cooling rates of 10°C min^{-1} under nitrogen in order to evaluate their thermotropic liquid-crystalline properties (see figure 1). Peak maxima were taken as phase transition temperatures. The mesophases were observed by polarizing microscopy (Olympus Model POM) equipped with a hot stage (magnification ×400) and were determined by miscibility tests with terephthal-bis(4-butylaniline) (TBBA) as a reference compound. The DSC

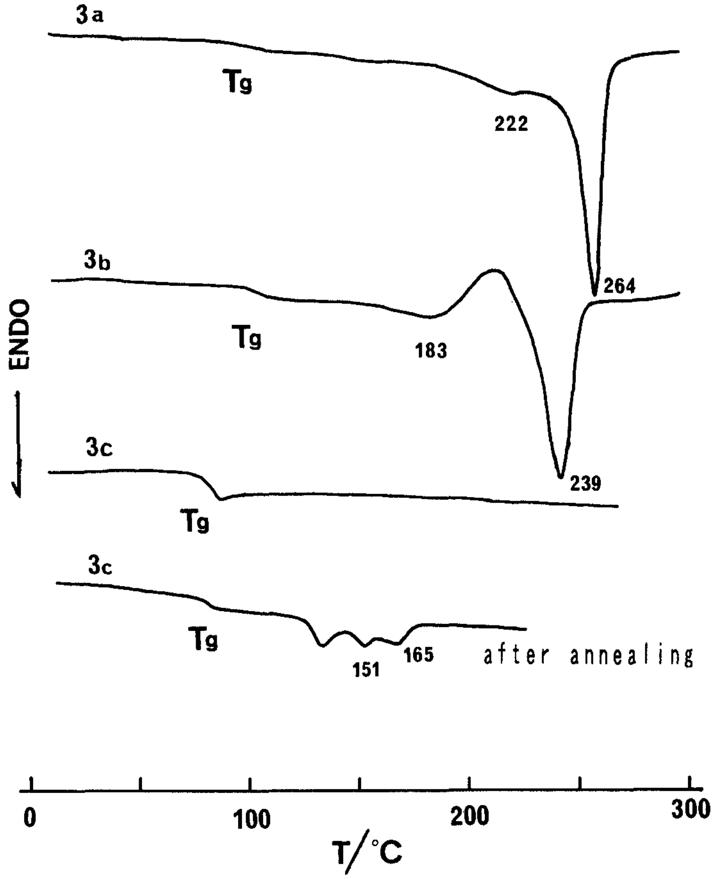


Figure 1. DSC curves for polyamides (**3a**–**3c**) on the second heating and after annealing at 120–130°C for 4 h.

Table 2. Phase transition data for polyamides (**3a**–**3c**)†.

Polymer	T_g°C	T_1°C	T_2°C	T_3°C	ΔT°C‡
3a	97	—	222	264	42
3b	102	—	183	239	56
3c	80	131§	151§	165§	14

† Data on the second heating.
‡ Liquid crystal temperature ranges, $\Delta T = T_3 - T_2$.
§ Data after annealing at 120–130°C for 4 h.

curves of the polymers (**3a**–**3c**) showed on the second heating runs and after annealing, two or three endothermic peaks corresponding to solid–solid (T_1), solid–liquid crystal (T_2) and liquid crystal–isotropic (T_3) transitions before the exotherms due to decomposition. The phase transition data are listed in table 2. The polymers (**3a** and **3b**) have two endotherms at T_2 (222°C and 183°C) and at T_3 (264°C and 239°C), and wide liquid crystal temperature ranges (42°C and 56°C) in addition to glass transition temperatures (T_g) at 97°C and 102°C. The textures observed by polarizing microscopy and miscibility tests indicate that polymers **3a** and **3b** form well-defined smectic mesophases between T_2 and T_3 as shown in figure 2. The textures are retained at room temperature when the polymers are cooled from the isotropic state. The polyamide (**3c**) has only a T_g at 80°C, showing no endotherms on the second heating scan and displays a turbid melt at room temperature on cooling from the isotropic state. This means that the cooling rate of 10°C min^{-1} is sufficient to suppress the crystallization of the polymer (**3c**). So the polyamide sample after the first cooling was annealed at 120–130°C for 4 h before the DSC measurement was conducted. The measurement shows three endothermal peaks in the DSC curve. Polarizing microscopy observations and miscibility tests suggest that the polyamide (**3c**) displays a solid–solid transition at T_1 and a smectic phase between T_2 and T_3. In order to check the liquid-crystalline mesophases for the polyamides (**3a**–**3c**), powder X-ray diffraction measurements were performed using a Rigaku Denki RU-200 X-ray generator equipped with a PTC-10C temperature controller with CuK$_\alpha$ radiation at elevated temperatures. The powder X-ray diffraction patterns for the polyamides (**3a** and **3c**) demonstrate that the polyamides represent sharp reflections at small angles in the liquid-crystalline states ($2\theta = 3{\cdot}0°$ at 252°C for **3a** and $2\theta = 3{\cdot}4°$ at 159°C for **3c**, respectively). In addition, a sharp reflection at $2\theta = 20{\cdot}2°$ together with weaker ones in the range of $2\theta = 16$–$23°$ were observed at the same temperature for the polyamide **3a**. In the polyamide **3c**, a broad reflection was also detectable at around $2\theta = 20{\cdot}0°$. These data suggest that the polyamides show smectic phases. More detailed information on the types of mesophase will be reported in the near future. Polymers **3a** and **3b** exhibit higher liquid crystal transition temperatures and more stable liquid-crystalline phases than **3c** which has a kinked linkage in the flexible rod-like unit as already known for thermotropic liquid-crystalline polyesters with traditional mesogenic units [1]. This might be explained by assuming that in the polyamide (**3c**) the ability to generate a phase is lowered, because the kinked linkage and the presence of conformer (II) in the polymer chain as shown in scheme 2 disturb the molecular alignment of the flexible rod-like unit, whose linearity and planarity are not maintained.

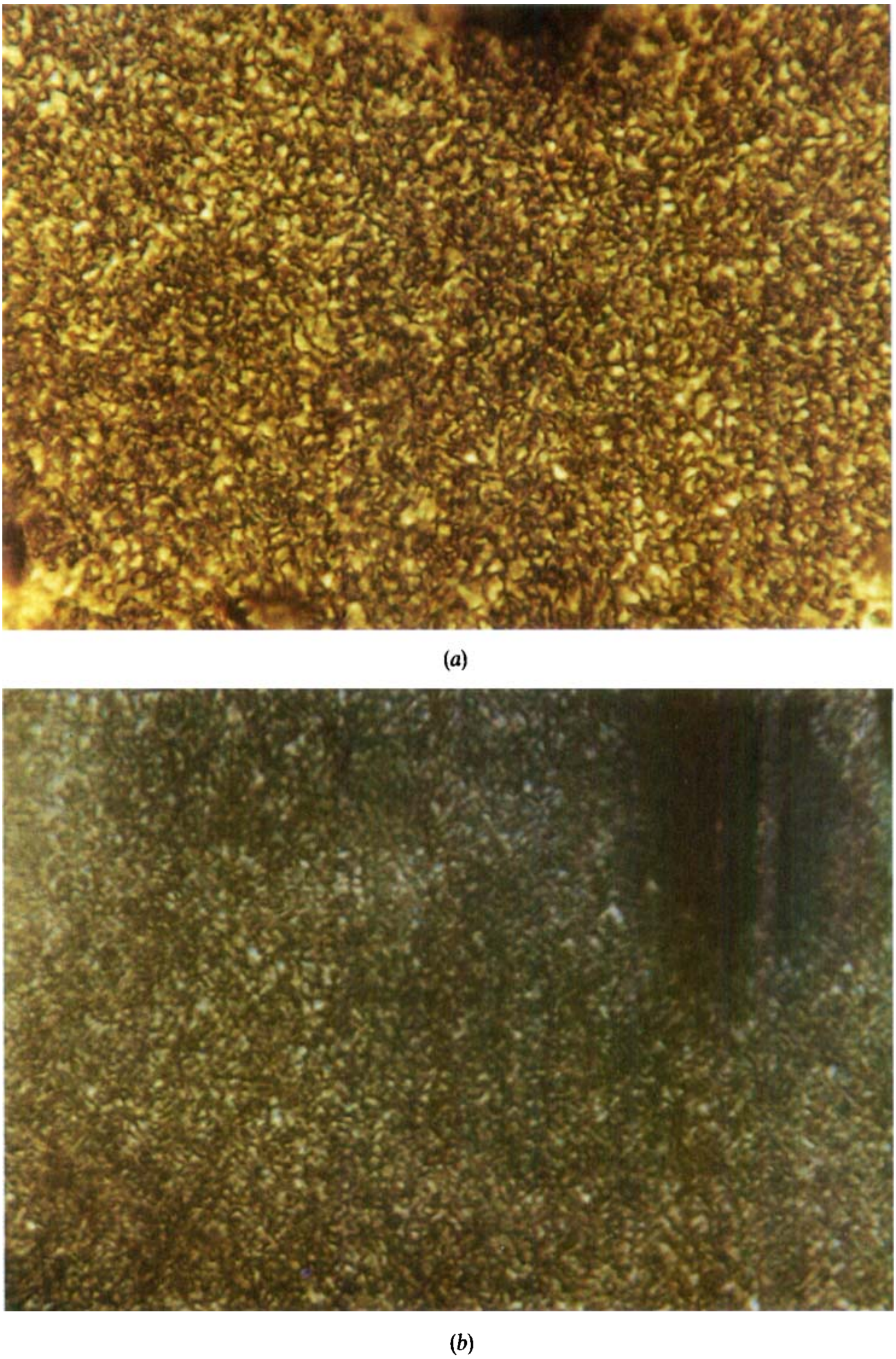
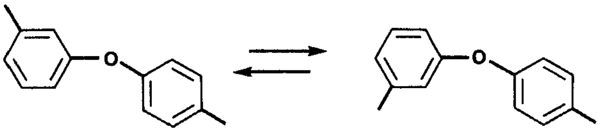


Figure 2. Polarizing microscopy textures for polyamides **3a** and **3c** (magnification ×400). (*a*): **3a** at 110°C on cooling. (*b*): **3c** at 166°C on the second heating after annealing at 146°C for 3 h.



3c(I) **3c(II)**

In conclusion, it was discovered that thermotropic liquid-crystalline polyamides (**3a**–**3c**) containing flexible rod-like diphenyl units and aliphatic spacers in the main chains possessed well-defined thermotropic smectic mesophases in spite of the introduction of non-traditional moieties in the backbones.

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