

SYNTHESIS AND CHARACTERIZATION OF SOME THERMOTROPIC LIQUID CRYSTALLINE POLYAMIDES*

ZHOU Deliang (周德亮) ZHANG Dong (张 东) Samuel K.L. TAN

and ZHOU Qifeng (周其凤)**

(*Department of Polymer Science & Engineering, College of Chemistry,
Peking University, Beijing 100871, China*)

ABSTRACT

A series of novel mesogenic polyamides containing a flexible pendent side group was synthesized by solution condensation polymerization. The new monomers, diacids and diamines containing flexible elements of different lengths, were also synthesized and characterized by ^1H NMR, mass spectroscopy and elemental analysis. The polymers were characterized by viscosity measurements, differential scanning calorimetry (DSC), X-ray diffraction and polarizing optical microscopy. These studies revealed that polyamides containing flexible elements of a sufficient length exhibited thermotropic liquid crystalline (LC) properties. The melting temperatures of this series of polymers were particularly sensitive to the length of the flexible segment on the main chain and that of the flexible pendent ester side chain. Lyotropic LC behaviours were also observed in solution.

INTRODUCTION

Aromatic polyamides in general are known to be high-modulus and high-temperature-resistant industrial polymers. Their melting transitions are usually above their decomposition temperatures, which thus prevents the proper characterization of the mesophase. A study by Aharoni^[1] showed that a series of polyamides containing strictly alternating rigid and flexible elements exhibited lyotropic liquid crystallinity. However, thermotropic liquid crystalline (LC) properties could not be observed upon heating as these polymers decomposed without melting.

The authors would like to dedicate the paper to professor Qian Renyuan's 80th birthday

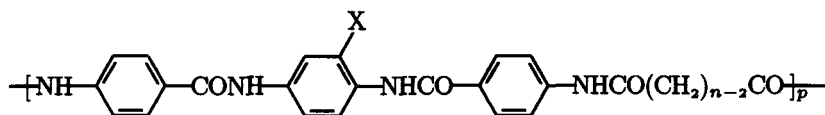
* This work is supported by the National Natural Science Foundation of China

** Author for correspondence

Received April 2, 1997

The incorporation of suitable substituents onto the mesogenic aromatic rings on these polyamides may reduce their melting points sufficiently to allow the thermotropic LC properties to be observed. The presence of pendent substituents reduces the symmetry of the polymer chains and increases their intermolecular distances, thus reducing the intermolecular hydrogen bonding between the polyamide chains.

The present paper is concerned with the design, synthesis and characterization of LC polyamides with the following chemical structure:



where $X = C_2H_5$ or $COO(CH_2)_mH$

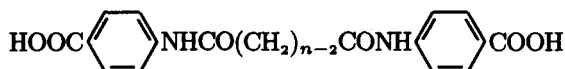
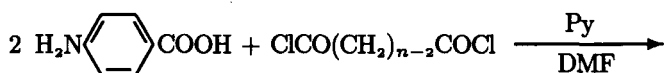
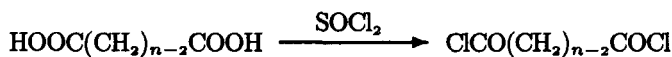
$m = 12, 14, 16, 18$ and $n = 4, 5, 6, 8, 10, 12, 14$

EXPERIMENTAL

Proton NMR spectra were recorded on a Bruker ARX400 NMR spectrometer. Elemental analyses were carried out on ST-02, Heraeus or Carlo Erba 1106 instrument. Mass spectra were recorded on a VG-ZAB-HS mass spectrometer. The inherent viscosities of the polymers were measured at 20°C for solutions in 5% LiCl/DMAc using an Ubbelohde viscometer. Differential scanning calorimetry (DSC) curves were recorded on a Shimadzu DSC-50 instrument under a nitrogen flow, with heating and cooling rates of 10°C/min. X-ray diffraction patterns were obtained with a Rigaku Dmax2400 diffractometer, using copper K_α radiation. Photomicrographs were taken with a WILD MPS 12 camera mounted on a Leitz Laborlux 12 Pol polarizing optical microscope, equipped with crossed polarizers and a Leitz 350 hot stage. Thermogravimetric analysis (TGA) curves were recorded at a heating rate of 10°C/min in a nitrogen atmosphere.

Monomer synthesis

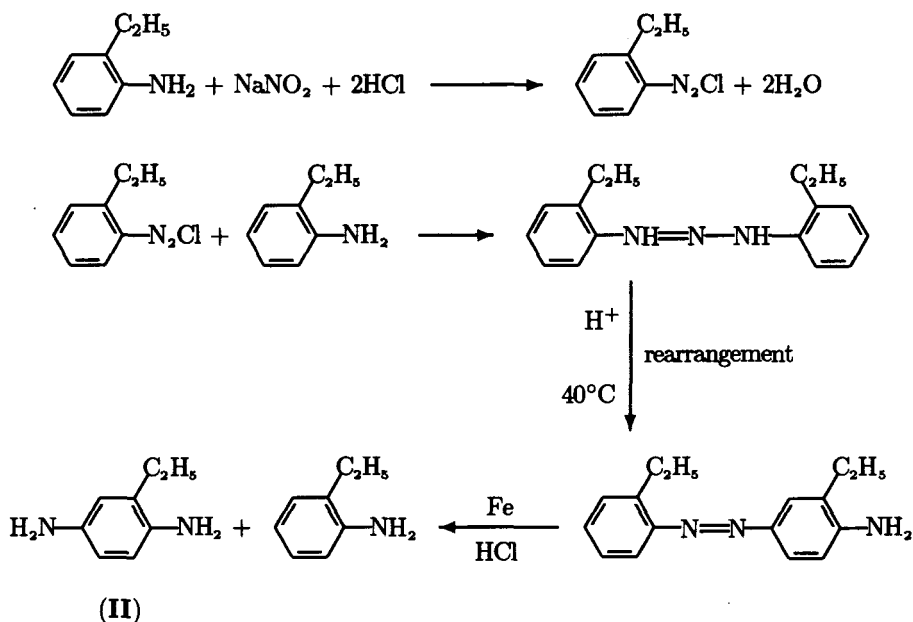
The diacid monomers (I) were synthesized via a Schotten-Baumann type procedure: Pyridine was used as a scavenger for HCl and DMF as the solvent. The monomers were recrystallized from DMF and water. The purity of the monomers was confirmed by proton NMR, mass spectroscopy and elemental analysis.



(I)

where $n = 4, 5, 6, 8, 10, 12, 14$

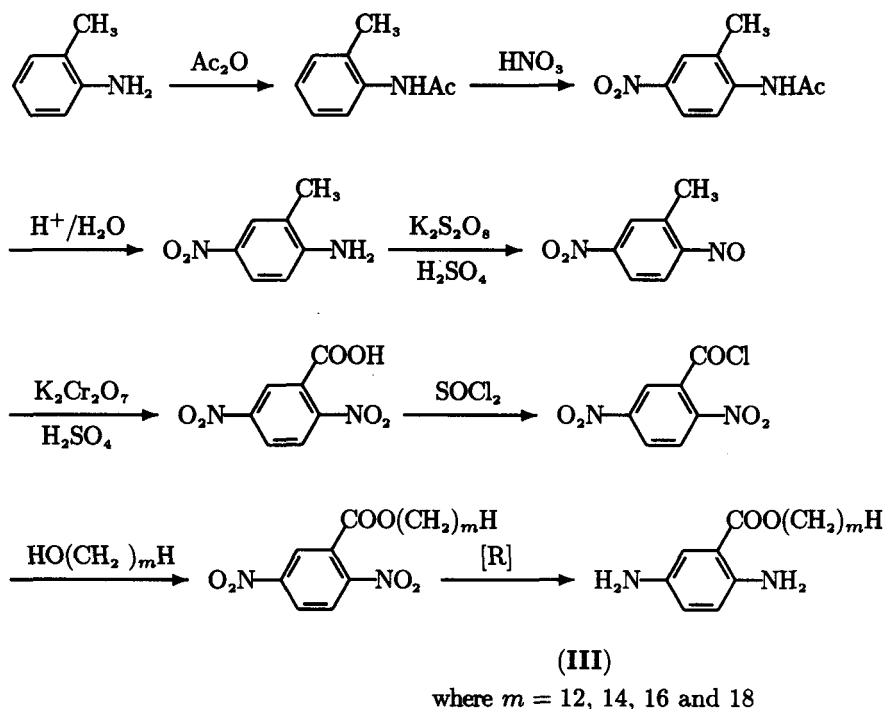
2, 5-Diamino-ethylbenzene, monomer (II), was synthesized as described by Chen et al.[2]:



The product was repeatedly extracted with diethyl ether, followed by fractional distillation after the removal of diethyl ether. The purity of the monomer was confirmed by proton NMR.

n-Alkyl 2, 5-diaminobenzoate, monomer (III), was synthesized according to the following scheme: The amino group of the starting material, 2-methylaniline, was first protected by acetylation using acetic anhydride prior to the nitration step. The nitration of the aceto-o-toluidide was carried out using a procedure described by Page and Heasman^[3]. Hydrolysis of the nitrated product yielded 2-methyl-4-nitroaniline. The next step in this synthesis was the production of 2, 5-dinitrobenzoic acid via the

2-nitroso compound. This involved the use of a procedure described by Langley^[4]. The aromatic acid was converted to its acid chloride, which was then reacted with the appropriate alcohols, $\text{HO}(\text{CH}_2)_m\text{H}$, to produce the *n*-alkyl dinitrobenzoate. Reduction of these esters employing stannous chloride and concentrated hydrochloric acid yielded the corresponding *n*-alkyl 2, 5-diaminobenzoate monomers. The purity of these monomers was confirmed by proton NMR, elemental analysis and mass spectroscopy.

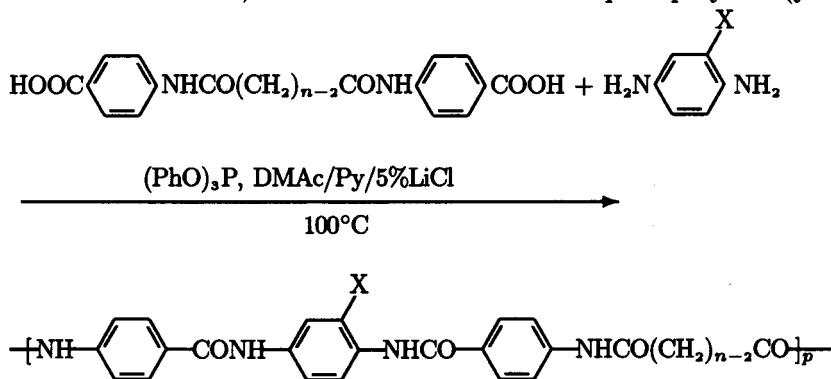


Polymer Synthesis

The polyamides (IV) were synthesized using a procedure described by Yamazaki et al.^[5]:

A detailed procedure illustrating the preparation of a polyamide with $\text{X}=\text{C}_2\text{H}_5$ and $n = 10$ is described below: To a 50 ml three-necked flask was added 2, 5-diaminoethylbenzene (1.25 mmol, 0.1702 g), *N,N'*-bis(4-carboxylphenyl) sebacamide (1.25 mmol, 0.5506 g), triphenyl phosphite (1.25 mmol, 0.33 ml), 6.0 ml dimethylacetamide, 1.5 ml pyridine and 0.38 g anhydrous lithium chloride. Simultaneous evacuation of air and introduction of nitrogen into the flask were carried out, while the contents of the flask were heated to 100°C with stirring for 3–4 h. The reaction mixture gradually thickened and turned cloudy. At the conclusion of the reaction

period, the mixture was cooled to room temperature. This was followed by a drop-wise introduction of methanol with stirring to effect phase separation. The solid was filtered and immersed in methanol for a day. It was re-filtered, washed repeatedly with methanol and acetone, and air-dried to obtain the pure polymer (yield 89%).



where $\text{X}=\text{C}_2\text{H}_5$, $\text{COO}(\text{CH}_2)_m\text{H}$

(IV)

$m = 12, 14, 16, 18$; $n = 4, 5, 6, 8, 10, 12, 14$

RESULTS AND DISCUSSION

Twenty-nine polyamides containing flexible segments were synthesized and characterized. The inherent viscosities of the polymers are listed in Table 1. For reasons of brevity, these polymers are represented in this paper as PEtAn and PEmAn, where Et= C_2H_5 -, Em represents the diamine moieties with pendent group $\text{X}=\text{COO}(\text{CH}_2)_m\text{H}$, and An represents the diacid moieties; m and n are the respective lengths of the $\text{---CH}_2\text{---}$ groups in the flexible segments. For $m = 12, 14$ and 16 , thermotropic liquid crystalline (LC) properties were observed when $n \geq 10$. As the length of the pendent group is increased, e.g. $m = 18$, thermotropic LC properties were exhibited by polymers containing a shorter flexible segment in the main chain (i.e. $n = 8$).

For PEtA10, phase transitions could not be observed because the pendent ethyl group was too short to reduce the transition temperatures of this polymer sufficiently to below its decomposition temperature.

The phase transition temperatures for the 13 polymers which exhibit thermotropic LC properties are also listed in Table 1. Using polymer PE14A14 as a representative example, birefringence was observed under the polarizing optical microscope when this polymer was heated to around 240°C . Birefringence increased while the temper-

ature was increasing. When the temperature reached 255°C, the polymer began to

Table 1 Inherent viscosities and phase transition tempratures of the polymers

Polymers	Inherent viscosities (dl g ⁻¹)	Phase transitions from polarizing optical microscope (°C)	Phase transitions from DSC (°C)
PEtA10	0.40		
PE12A4	1.12		
PE12A5	0.95		
PE12A6	0.64		
PE12A8	0.93		
PE12A10	0.84	G300LC320I	G157LC298.6I
PE12A12	0.73	G260LC285I	G151LC278I
PE12A14	0.88	G255LC290I	G144LC268.6I
PE14A4	0.32		
PE14A5	0.34		
PE14A6	0.51		
PE14A8	0.35		
PE14A10	0.51	G290LC325I	G160LC295.2I
PE14A12	0.69	G250LC280I	G149LC275.4I
PE14A14	0.30	G240LC260I	G169LC259I
PE16A4	0.46		
PE16A5	1.07		
PE16A6	0.57		
PE16A8	0.75		
PE16A10	0.87	G280LC310I	G160LC293.1I
PE16A12	0.63	G245LC275I	G154LC275.8I
PE16A14	0.73	G250LC260I	
PE18A4	0.56		
PE18A5	0.64		
PE18A6	0.51		
PE18A8	0.52	G305LC325I	
PE18A10	0.52	G280LC300I	
PE18A12	0.23	G240LC255I	G153LC236I
PE18A14	0.63	G235LC260I	G147LC254.6I

soften and the birefringence started to weaken. At 260°C, the polymer melted completely into an isotropic liquid. Upon gentle cooling of this isotropic mass to around 240°C, the birefringent pattern reappeared, along with the Schlieren texture, as shown in Fig.1a. Other polymers were found to behave in a similar manner under

polarizing optical microscope.

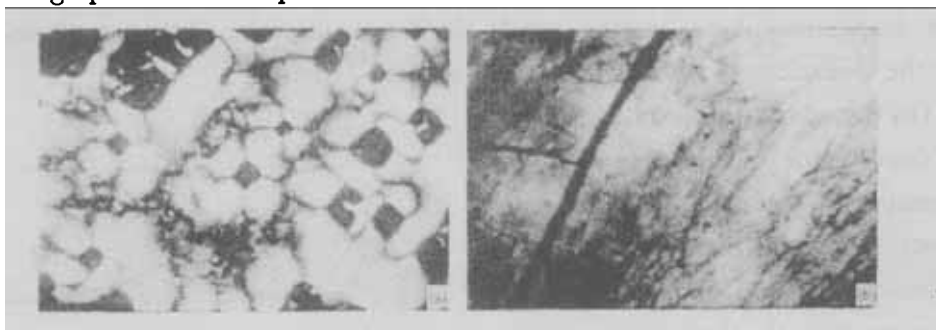


Fig.1 Polarized microscopic textures of PE14A14
 (a) at 240°C, cooling from isotropic phase, magnification 100X;
 (b) at room temperature in NMP solution, magnification 320X

Fig.2 shows the DSC heating curve of PE14A14. The transition at around 170°C corresponds to that of the glassy state towards the LC phase. The peak was observed at 258.6°C, corresponding to the transition of an anisotropic LC phase to

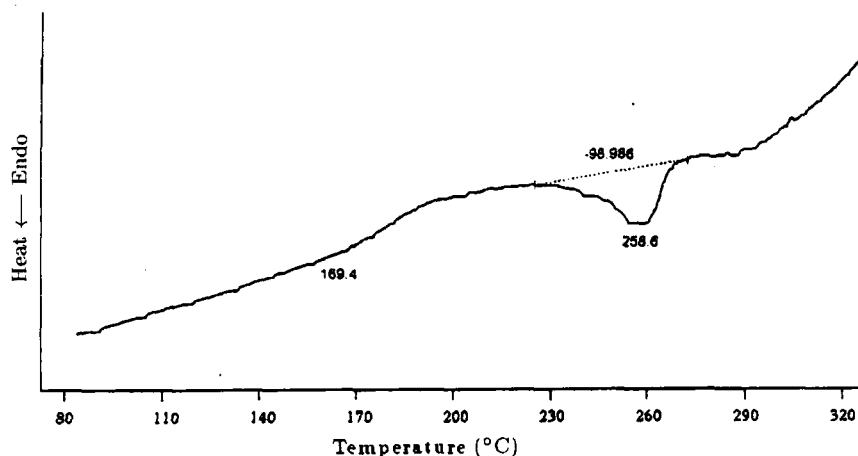


Fig.2 DSC heating curve for PE14A14

an isotropic liquid. Fig.3 show the X-ray diffraction patterns of this polymer before and after heat treatment (see curves a and b). The intensity of diffraction at $2\theta = 3.020^\circ$ was enhanced after heat treatment at 240°C for 10 min. The diffuse peak at 21° suggests that no crystal is developed in the polymer sample even a prolonged annealing at 240°C is carried out. The birefringence given by the sample is therefore not a result of any crystallinity but a result of the mesomorphic ordering. This mesomorphic ordering may be enhanced by annealing as shown by the increased

intensity of diffraction at lower angles (Fig.3), but will never reach the order beyond what of a nematic phase. In other words, the X-ray diffraction of the sample suggests only the nematic type of ordering and no smectic ordering.

On the whole, the results indicate the dependence of the thermotropic LC properties on the flexible elements present in both the main chain and the pendent side group for this series of polymers. Both the thermal transitions to LC phase and the clearing temperatures decreased with the increase in the length of the flexible elements. For instance, when the alkyl group of the ester side chain contained 18 carbon atoms (i.e. $m = 18$), thermotropic LC behaviour could be observed when $n = 8$. This may be compared with Aharoni's study on the strictly alternating polyamides and poly-p-benzamide of similar structures^[1]. In the

absence of a pendent side chain, the polymers ($n = 10$ and 12) decomposed without melting. However, these polymers showed lyotropic LC properties in the concentration range 25–40%. The introduction of the flexible pendent side chain lowered the melting points to below decomposition temperatures of these polymers, thus enabling the LC phase to be observed upon heating. These thermotropic LC polymers also exhibited lyotropic LC properties in solutions of N-methylpyrrolidone (NMP). Figure 1b is the texture of PE14A14 in NMP solution. Thermogravimetric analysis (TGA) of the LC polymers showed that the 5% weight loss occurred in the region of 280°C, while the peak maxima appeared at temperatures between 320–340°C.

CONCLUSIONS

A series of mesogenic diacid and diamine monomers with flexible segments of various length was synthesized and characterized by proton NMR, mass spectroscopy and elemental analysis. Solution condensation polymerization of these monomers led to a series of thermotropic LC polyamides represented by PEmAn. Thermotropic LC behaviour was observed for polyamides containing flexible segments of a suitable length. The introduction of a flexible pendent side chain into the polyamides

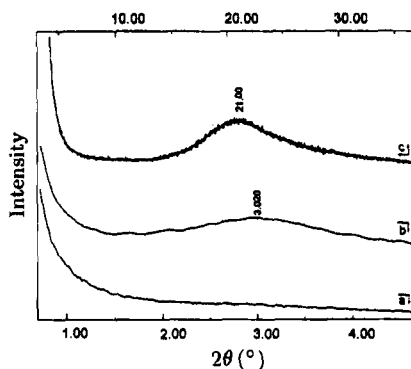


Fig.3 X-ray powder diffraction pattern for PE14A14

(a) at room temperature; (b),(c) after heat treatment at 240°C

Note: Curves (a) and (b) refer to the bottom ordinate and Curve (c) refers to the top ordinate

lowered the melting transition and allowed the mesophase of these polymers to be characterized.

Keywords:

Thermotropic liquid crystals; Mesogenic polyamides; Nematic mesophase

REFERENCES

- [1] Aharoni, S.M., *J. Polym. Sci., Polymer Phys. Ed.*, **1981**, *19*: 281.
- [2] Chen, M.Y. and Liao, W.Z., *Chem. Reag.* (in Chinese), **1986**, *8*(3): 165.
- [3] Page, H.J. and Heasman, B.R., *J. Chem. Soc.*, **1923**, *123*: 3235.
- [4] Langley, W.D., in "Organic Syntheses", Collective Volume 3, Ed. Horning, E.C., John Wiley & Sons, New York, **1995**, p.334.
- [5] Yamazaki, N., Matsumoto, M., and Higashi, F., *J. Polym. Sci., Polym. Chem. Ed.*, **1975**, *13*: 1373.