

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Study on Synthesis and Liquid Crystalline Properties of Alkoxy Viologen Polymers

Minhui Feng^a; Guimei Wu^a; Yi He^a; Zhaoxi Liang^a

^a (Institute of Polymer Science, Zhongshan University, Guangzhou, P. R. China)

To cite this Article Feng, Minhui , Wu, Guimei , He, Yi and Liang, Zhaoxi(1995) 'Study on Synthesis and Liquid Crystalline Properties of Alkoxy Viologen Polymers', Journal of Macromolecular Science, Part A, 32: 1, 1271 – 1277

To link to this Article: DOI: 10.1080/10601329508020349

URL: <http://dx.doi.org/10.1080/10601329508020349>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

STUDY ON SYNTHESIS AND LIQUID CRYSTALLINE PROPERTIES OF ALKOXYL VIOLOGEN POLYMERS

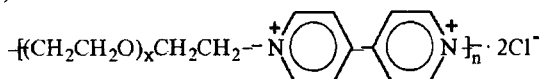
Minhui FENG, Guimei WU, Yi HE and Zhaoxi LIANG
(*Institute of Polymer Science, Zhongshan University,
Guangzhou, 510275, P. R. China*)

Abstract

A series of alkoxy viologen polymers containing the different alkoxy chain length have been synthesized and were identified by elemental analysis, IR, ^1H NMR, UV and laser light scattering. The liquid crystalline properties, texture structure and phase transition have been investigated by using polarizing optical microscope, DSC and X-ray diffraction, the results show that poly(3,6,9-trioxaundecyl viologen) dichloride (PTUV) exhibits a birefringent schlieren texture that indicates its nematic phase structure and monotropic characteristics.

Keywords: Photoresponsive polymer liquid crystal, Viologen polymer, Monotropic nematic liquid crystal

One part of the vast field of functional materials that has received quite a lot of attention are photoresponsive polymer liquid crystal performed both the properties of photoresponse and liquid crystal. Several interesting applications of photoresponsive polymer liquid crystal, such as the polymers containing azobenzene or spiropyran in main chain or side chain, are described in the fields of optical recording, optical storage, optical display and nonlinear optics^[1-4]. The N, N'-disubstituted 4, 4'-dipyridinium compound known as viologens is a kind of redox compound that can undergo two-step reduction accompanied with obvious color changes by chemical, electrochemical or photochemical methods^[5-6]. In alkoxy viologen polymers, dipyridinium unit or *trans*-1,2-bis(4-pyridyl)ethylene unit used as the mesogenic unit as well as photoresponsive unit and alkoxy unit used as the flexible chain segment, thus a new kind of photoresponsive polymer liquid crystal can be synthesized. In this paper, some alkoxy viologen polymers containing the different alkoxy chain length have been synthesized with main chain structure as PAoV ($y=0$; $x=0, 1, 2$ abbreviated as POPV, PDOV, PTUV) and as PAoE ($y=1$; $x=0, 1, 2$ abbreviated as POPE, PDOE, PTUE):



The liquid crystalline properties, texture structure and phase transition have been investigated by using polarizing optical microscope, differential scanning calorimetry(DSC) and X-ray diffraction, the results show that PTUV exhibits a birefringent schlieren texture indicating its nematic phase structure and monotropic characteristics.

Experimental

Materials

4,4'-bipyridine(BPy), *trans*-1,2-bis(4-pyridyl)ethylene(*t*-BPyE) were obtained from Tokyo Kasei Kogyo Co., Ltd. Benzyltriethylammonium chloride(BTEAC), absolute ethanol, ethyl acetate, methanol and isopropanol were A.R. without purification before use. Diethylene glycol, triethylene glycol and tetraethylene glycol were dried over 24 hours by anhydrous sodium sulfate and purified by reduced pressure distillation. Thionyl chloride(TC) was refluxed 2~3 hours with triphenyl phosphite and then purified by distillation. Acetonitrile(AN), dimethyl sulfoxide(DMSO) and *N,N'*-dimethylformamide(DMF) were dried over 24 hours separately by anhydrous calcium chloride, sodium hydroxide and anhydrous sodium sulfate and then purified by distillation or reduced pressure distillation.

Synthesis of α,ω -dichloroglycol ethers(DCG), PAoV and PAoE

DCG was prepared by reacting the corresponding glycol diol with TC in the existence of BTEAC under stirring at 60~65°C as described in previous paper^[7]. The products were purified by reduced pressure distillation to obtain dichloroethyl ether(DCEE) (90~92°C/7~8mmHg), dichlorotriglycol ether(DCTrE) (142~144°C/7~8mmHg) and dichlorotetraglycol ether(DCTeE) (160~162°C/4~5mmHg), respectively. PAoV and PAoE were synthesized by Menschutkin reaction of BPy and *t*-BPyE with the appropriate alkoxy ether dichlorides under stirring in AN, DMSO or DMF at 70~90°C for 48~144 hours. During the reaction, the polymers precipitated out as a brown or light red solid. They were filtered, dissolved in absolute ethanol and reprecipitated twice with ethyl acetate, then dried in vacuum. The yields of PAoV and PAoE were approximately 50%.

Measurements

Infrared spectra(KBr) were recorded on a Nicolet 205 FTIR spectrophotometer. Elemental analysis was recorded on Perkin-Elmer 240C Elemental Analyzer. ¹HMR spectra were measured by JEOL FX-90Q spectrometer. UV-absorption spectra of polymer solutions in ethanol were obtained on a Shimadzu UV-240 UV-visible recording spectrophotometer. Polarizing optical microscope was performed using a polarizing microscopy equipped with heating stage. Thermal analysis was carried out with a CDR-1 differential scanning calorimeter. X-ray diffraction measurements were made by a D/max-3A X-ray diffractometer using Cu K α radiation. The samples were prepared by quenching the polymers in ice-water melted at above melting point for 3 hours.

Laser light scattering measurements were performed on polymer samples dissolved in 0.1mol/L KBr aqueous solution using a CDC/Milton KMX-6 laser photometer at 30°C(see Table 1).

Table 1 Molecular weight of PAoV and PAoE

Compounds	M_w (g·mol ⁻¹)	A_2 (mL·mol·g ⁻²)
POPV	2.39×10^3	-1.25×10^{-3}
PDOV	2.41×10^3	1.49×10^{-2}
PTUV	5.15×10^3	2.38×10^{-5}
POPE	5.26×10^3	7.17×10^{-3}
PDOE	2.44×10^4	-1.83×10^{-3}

$d_n/d_c = 0.2$

Table 2 Characterization of DCG

Compounds	Empirical formula	C%		H%		Wave numbers (cm ⁻¹)	Group δ (ppm)	Group
		Calc.	Found	Calc.	Found			
DCEE	C ₄ H ₈ OCl ₂	33.53	32.41	5.59	5.56	2870 or so 1120 or so	ν_{C-H} ν_{C-O-C}	3.3 2×2H, -CH ₂ Cl 4.2 2×2H, -CH ₂ O
DCTrE	C ₆ H ₁₂ O ₂ Cl ₂	38.50	38.22	6.42	6.57	746; 747	ν_{C-Cl}	3.1 2×2H, -CH ₂ Cl 3.7 2×2H, -CH ₂ CH ₂ Cl 4.3 2×2H, -CH ₂ OC ₂ H ₄ Cl
DCTeE	C ₈ H ₁₆ O ₃ Cl ₂	41.52	40.92	6.92	7.00			3.2 2×2H, -CH ₂ Cl 3.7 2×2H, -CH ₂ CH ₂ Cl 4.0 2×2H, -CH ₂ OC ₂ H ₄ Cl 4.1 2×2H, -CH ₂ CH ₂ ORCl

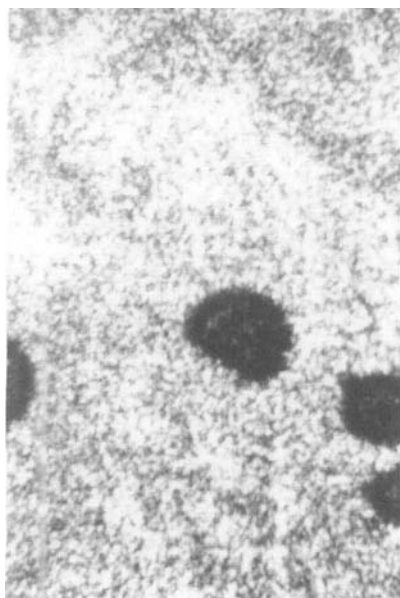
Table 3 Characterization of PAoV

Compounds	C%		H%		N%		λ_{max} (nm)	$\epsilon_{max} \times 10^{-4}$ (mol ⁻¹ ·L·cm ⁻¹)	δ (ppm)	Group
	Calc.	Found	Calc.	Found	Calc.	Found				
POPV	56.10	48.68	5.34	5.49	9.53	8.13	257	1.83	4.1 2×2H, -CH ₂ O 4.9 2×2H, -CH ₂ - 8.4 2×2H, -a-H 8.9 2×2H, -b-H	
PDOV	55.94	50.99	5.83	6.00	8.16	7.53	262	1.80	3.8 2×2H, -OCH ₂ CH ₂ O- 4.0 2×2H, -CH ₂ CH ₂ -Py 4.8 2×2H, -CH ₂ -Py 8.5 2×2H, -a-H 8.9 2×2H, -b-H	
PTUV	55.76	52.90	6.20	6.51	7.23	7.59	261	2.05	3.7 2×2H, -OCH ₂ CH ₂ O- 4.1 2×2H, -CH ₂ CH ₂ -Py 4.8 2×2H, -CH ₂ -Py 8.6 2×2H, -a-H 9.1 2×2H, -b-H	

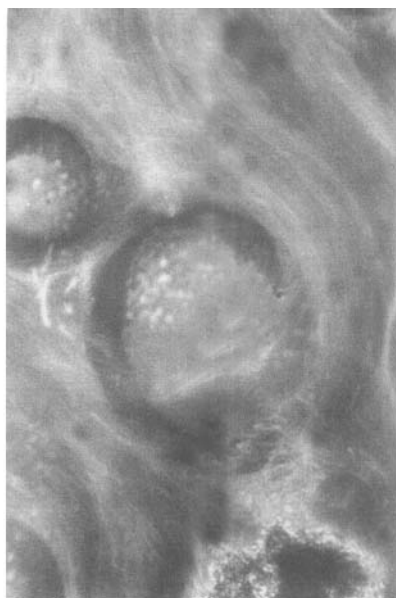


Table 4 Characterization of PAoE

Compounds	C%		H%		N%		λ_{\max} (nm)	$\epsilon_{\max} \times 10^{-4}$ ($\text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$)	δ (ppm)	Group
	Calc.	Found	Calc.	Found	Calc.	Found				
POPE	59.02	53.04	5.53	5.42	8.61	8.15	312	3.14	4.1 2×2H, -CH ₂ O- 4.8 2×2H, -CH ₂ -Py 7.5 2×1H, -CH=CH- 8.1 2×2H, -a-H 8.7 2×2H, -b-H	
PDOE	58.50	55.16	5.96	6.12	7.58	7.36	320	3.01	3.8 2×2H, -OCH ₂ CH ₂ O- 4.1 2×2H, -CH ₂ CH ₂ -Py 4.8 2×2H, -CH ₂ -Py 7.3~8.4 3×2H, -a-H, -CH=CH- 8.9 2×2H, -b-H	
PTUE	58.05	53.02	6.29	6.23	6.78	6.73	320	2.87	3.7 4×2H, -OCH ₂ CH ₂ O- 4.1 2×2H, -CH ₂ CH ₂ -Py 4.8 2×2H, -CH ₂ -Py 7.9 2×2H, -CH=CH- 8.6 2×2H, -a-H 9.1 2×2H, -b-H	



1.



2.

Fig. 1 Texture structure of PTUV
1. at 170°C; 2. at 175°C

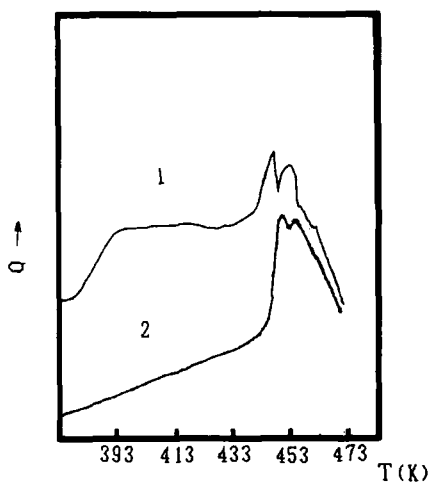


Fig. 2 DSC curves of PTUV
 1. Heat rate: 5°C/min.
 2. Heat rate: 10°C/min.

Table 5 Phase transition temperature of PTUV

Methods	T_m (°C)	T_{Cl} (°C)	ΔT (°C)
Polarizing microscope	170	186	16
DSC, heat rate 5°C/min.	173	180	15
10°C/min.	176	182	16

Results and Discussion

Characterization of DCG, PAoV and PAoE

DCG was synthesized as described in previous paper [7] and characterized by elemental analysis, IR and ^1H NMR, the results were satisfactory (Table 2). In this paper, the DCG products with higher purity have been obtained by using the treatment of alkali solution washing, water washing and reduced pressure distillation.

With the increase of alkoxy chain length, the reactivity of DCG was decreased. In order to obtain the polymer precipitation, the solvent with less polarity such as DMF or AN and higher reaction temperature and accurate stoichiometric ratio of monomers must be used in reaction process. PAoV and PAoE were characterized by elemental analysis, IR, ^1H NMR, UV and laser light scattering method (Table 3, 4).

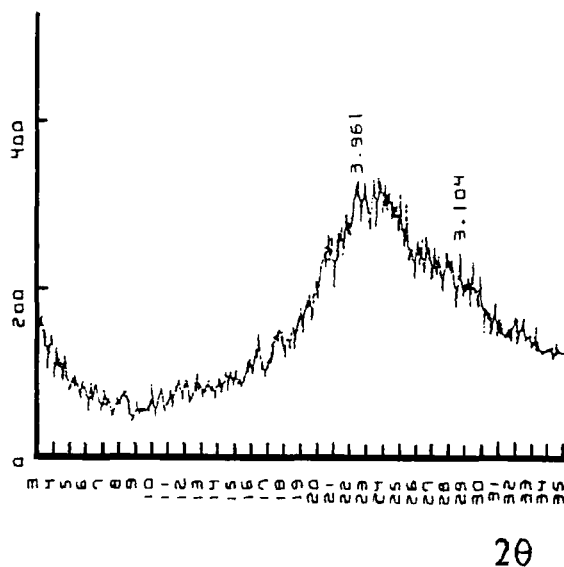


Fig. 3 WAXD analysis of PTUV

Study on the Liquid Crystalline Properties of PAoV and PAoE

1. Observation with Polarizing Optical Microscope

After heat treatment at 100–120°C for 10 mins. to remove the moisture absorbed by the samples, the samples were observed under polarizing optical microscopy during heating from room temperature to 190°C. The optical polarizing micrograph of PTUV shows that it exhibits a birefringent schlieren texture indicating its nematic phase structure at the melting temperature, however no nematic phase has been observed during cooling process (Fig. 1), hence it is a monotropic liquid crystal^[8]. Others of PAoV and PAoE were decomposed before their melting temperature.

2. DSC measurement

DSC measurements of PAoV and PAoE obtained the same results as polarizing optical microscope. After heat treatment at 100–120°C for 10 mins. to remove the moisture absorbed by the samples, there are two endothermic peaks in the DSC curves (Fig. 2). The lower peak temperature is the melting point of PTUV and the higher peak temperature corresponds to the clear point. Table 5 listed the results measured by using polarizing optical microscope and DSC.

3. X-ray Analysis

PTUV was treated at 176–178°C for 3 hours, then quenched in ice-water. From the wide angle X-ray diffraction curve of PTUV (Fig. 3), a fringing peak at $2\theta=20^\circ$ was observed which is accordance with the characteristics of nematic liquid crystal.

Acknowledgement: This work is supported by the National Natural Science Foundation of China and by the University Doctorial Research Foundation of China.

References

- [1] Akio Sasaki; *Mol. Cryst. Liq. Cryst.*, 1986, **39**, 103
- [2] Tomiki Ikeda, et al.; *ibid.*, 1990, **188**, 207
- [3] Tomiki Ikeda, et al.; *J. Phys. Chem.*, 1991, **95**, 509
- [4] S. Yitzohaik, G. Berkovic and V. Krogauz; *Macromolecules*, 1990, **23**, 3539
- [5] Zhaoxi, L. et al.; *Chinese J. of Polym. Sci.*, 1987, **5**(3), 254
- [6] Bird, C. L. and Kuhn, A. T.; *Chem. Soc. Rev.*, 1981, **10**(1), 49
- [7] Robert, J. et al.; U.S. us4,605,784
- [8] Qifeng, Z. et al.; *Macromolecules*, 1986, **19**, 247