Polymer Bulletin 35, 351–356 (1995)

Polymer Bulletin

Liquid crystalline polysurfactant

S. E. Wang, T. R. Fang, Y. Li, H. F. Zhang, Z. S. Mo*

Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022,
People's Republic of China

Received: 17 September 1994/Revised version: 6 March 1995/Accepted: 13 March 1995

Summary

A new kind of amphiphilic polymer ($PAMC_{16}S$) has been synthesized where the amphiphilic moiety is attached as a side chain via the hydrophilic end to the polymer backbone. DSC, POM, and WAXD study revealed that the polysurfactant formed thermotropic liquid crystalline phase. The liquid crystalline domains appeared after annealed at the melt for a period of time, and evolved with annealing. It was indicated that the thermodynamic effect played a significant role on the self—aggregation of hydrophobic ends, so as to form liquid crystalline structure. X—ray investigation suggested that the mesophase structure could be described as smectic with lamellar type of packing, in which alkyl tails aggregated to form layer. A model of supermolecular structure was given.

Introduction

Low molecular amphiphiles have the tendency of forming mesomorphic structures which are often in forms of micelles and vesicles. Polymerizable amphiphiles have been synthesized where the amphiphilic moiety is ether within the polymer main chain or attached as a side chain via the hydrophilic or hydrophobic end to the polymer backbone(1). Detailed investigation of binary phase diagram of monomeric and polymeric surfactants in aqueous solution have proven that the polysurfactants and amphiphilic copolymers form liquid crystalline phases in water. These polymers exhibited phase structure similar to that of low molecular lyotropic liquid crystals(2). To the best of our knowledge, thermotropic liquid crystalline property has never been reported on these polysurfactants.

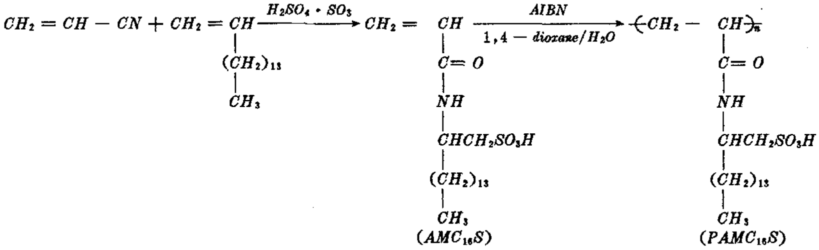
In this paper, the supermolecular structure and thermotropic behaviour of a kind of novel comb—like amphiphilic polymer ($PAMC_{16}S$) was investigated and a chain packing model was given.

---

* Corresponding author

Materials

The synthesis of polymer was described in previous papers(3,4):



$$CH_2=CH-CN+\underset{\substack{|\\(CH_2)_{13}\\|\\CH_3}}{CH_2=CH}\xrightarrow{H_2SO_4\cdot SO_3}\underset{\substack{(AMC_{16}S)}}{CH_2=\underset{\substack{|\\C=O\\|\\NH\\|\\CHCH_2SO_3H\\|\\(CH_2)_{13}\\|\\CH_3}}{CH}}\xrightarrow[1,4-dioxane/H_2O]{AIBN}\underset{\substack{(PAMC_{16}S)}}{\left(CH_2-\underset{\substack{|\\C=O\\|\\NH\\|\\CHCH_2SO_3H\\|\\(CH_2)_{13}\\|\\CH_3}}{CH}\right)_n}$$

The polymerization recipes were given in Table 1.

Table. 1 Raw materials and viscosities of polymers

Sample Code	1,4—dioxane (ml)	H_2O (ml)	$AMC_{16}S$ (g)	AIBN (g)	$[\eta]^{30℃}_{THF}$ (ml/g)
SP1	46	4	4.5	0.02	39.2
SP5	10	40	4.5	0.02	32.6
SP8	46	4	4.5	0.005	16.3

Characterization

The resulting polymer was found to be soluble in THF, DMF, and ethanol. Contrary to the monomer, $PAMC_{16}S$ is insoluble in water and dioxane—water mixed solvents. The IR spectrum of polymer indicated the absent of the characteristic peak of the C=C double bond at $1620CM^{-1}$(Fig. 1). After heat treatment at 80℃ under vacuum, the polymer showed melting and crystallization peaks at ca. 240℃ and 225℃, respectively. The lower peaks might be resulted from residual solution (Fig. 2). The most interesting character in the WAXD patterns for the polymers was the appearance of a strong diffraction peak at low angles, indicating the existence of long range order in solid state(Fig. 3).

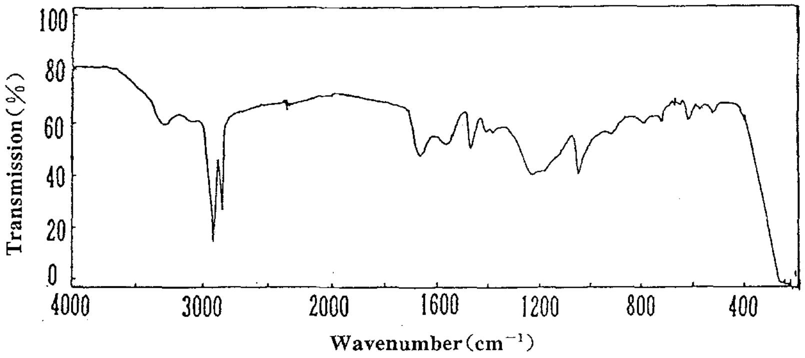


Fig. 1 IR spectrum of $PAMC_{16}S$

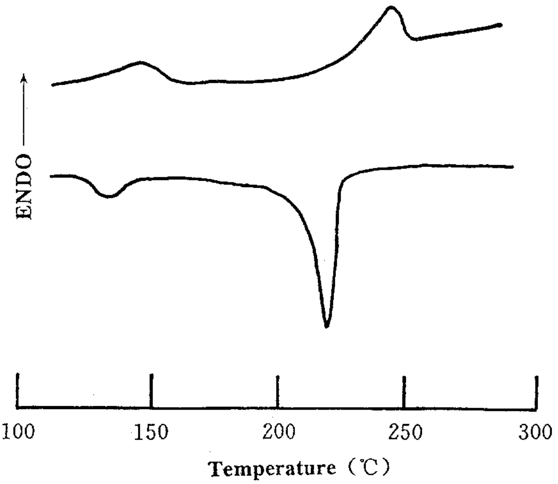


Fig. 2 DSC heating and cooling curves for PAMC$_{16}$S(SP5)

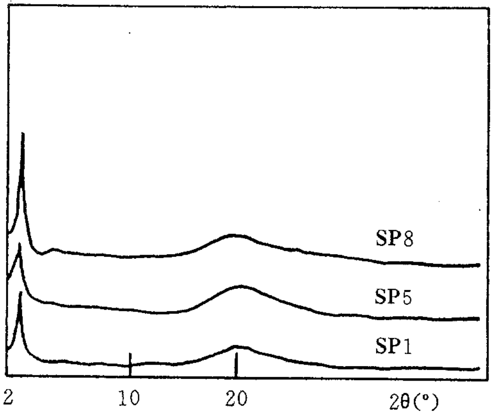


Fig. 3 WAXD patterns for the original samples

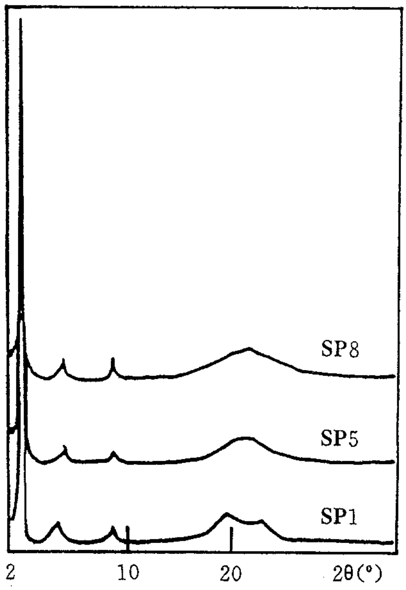


Fig. 4 WAXD patterns for the heat treated samples

The result inspired our further investigation on its supermolecular structure and mesophase behaviour.

Supermolecular structure and mesophase behavior

1. *Supermolecular structure*

The WAXD patterns for the heat treated samples were quite different from those of original ones (Fig. 4). Two new diffraction peaks at low angles could be clearly seen for the former. The degree of crystallinity were greatly enhanced, especially for polymer SP1 and SP8 (Table 2).

Table. 2 The degree of crystallinity (Wc,x%) in samples

sample code	$W_{c,x}$%	
	before annealing	after annealing
SP1	37. 1	54. 8
SP5	42. 2	45. 1
SP8	24. 7	44. 3

These results indicated that there exists a kind of order structure in long range which was enhanced by thermal treatment. Considering that there are long hydrophobic alkyl tails attached to the backbone by hydrophilic heads, these different parts of polymer chain tend to self—aggregate, as a result, the supermolecular structure with lamellar type of packing was formed (Fig. 5).

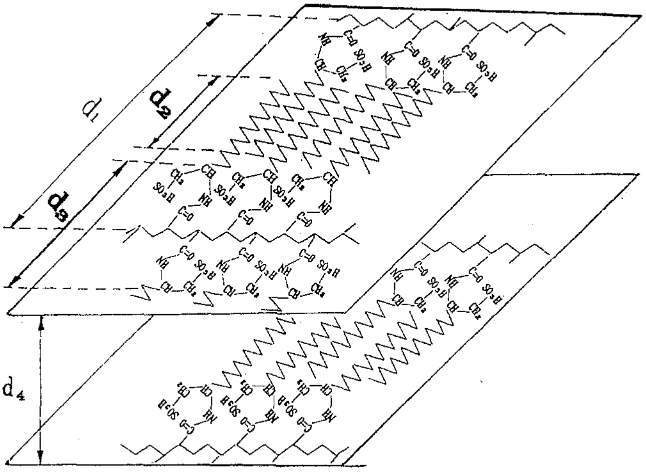


Fig. 5 Supermolecular chain packing model of $PAMC_{16}S$

The calculated spacings (d) data according to the model (by all trans—conformation) were fairly close to the experimental results (Table 3).

Table. 3 Interplanar spacings (d) after annealing and calculated data

sample code	d(Å)(experimental)				d(Å)(calculated)		
	d_1	d_2	d_3	d_4	d_1	d_2	d_3
SP1	29. 9	14. 8	10. 3	4. 98			
SP5	30. 4	14. 4	10. 0	4. 90	30. 2	15. 1	10. 1
SP8	30. 4	14. 7	10. 0	4. 86			

2. *Mesophase behavior*

Another interesting aspect of PAMC$_{16}$S was the unique character of the melt. It is supposed that the rigid core would be needed for the mesophase formation. There is no rigid or even semirigid segment in PAMC$_{16}$S. It seems that the polymer melt would not behave as a mesophase. However, after holding the melt at 250℃ for a period of time, the bright birefringence gradually appeared and evolved with time (Fig. 6). After the melt was supplied with a shear action, the band texture was gradually formed (Fig. 7). Fig. 8 gave the WAXD diffraction patterns for the melt quenched samples (quenched with liquid Nitrogen), it was observed that there still existed three diffraction peaks at low angles, suggesting that the long range orders of the solid state were retained in the melt. The inner diffraction spots perpendicular to the fibre direction on the X—ray fibre pattern indicated that the melt structure could be ascribed to the Smectic mesophase structure with lamellar type of packing, in which alkyl tails aggregated to form layer (5) (Fig. 9).

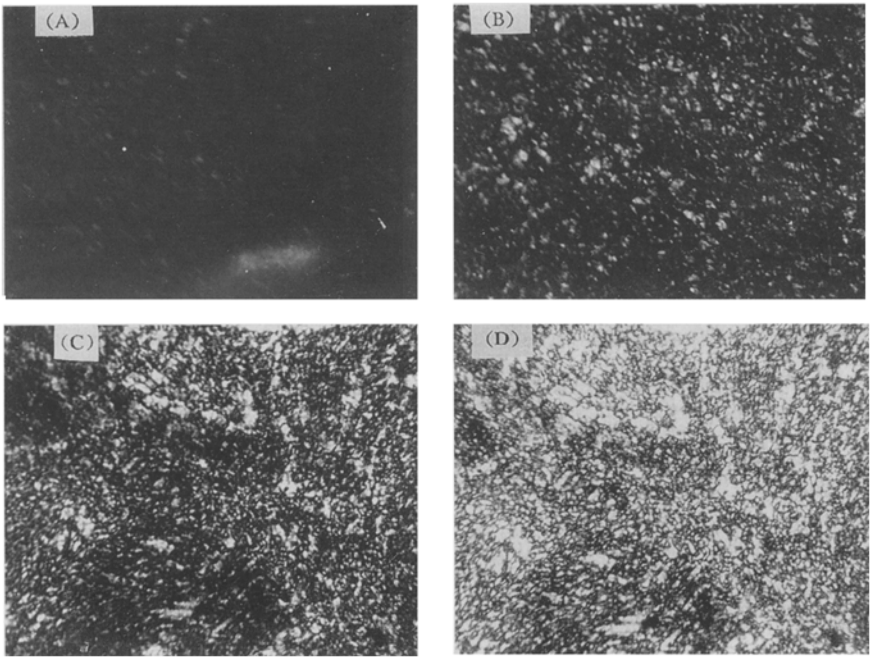


Fig. 6 The optical texture evolution of PAMC$_{16}$S With annealing time at 250℃, (A): 10 sec, (B): 30 sec, (C): 60 sec, (D): 120 sec, cross polarized (× 320)

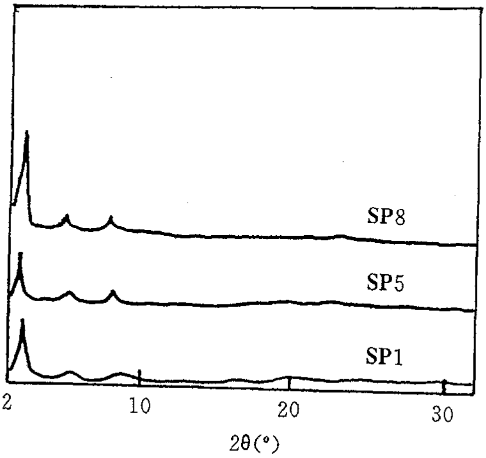


Fig. 8 WAXD patterns for the quenched samples

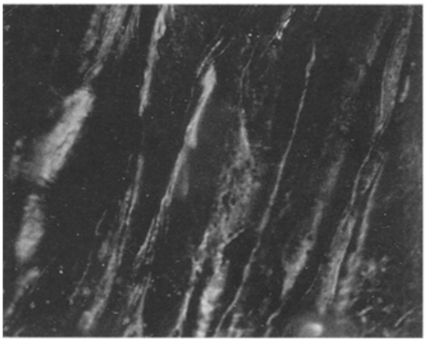


Fig. 7 Band texture after shear

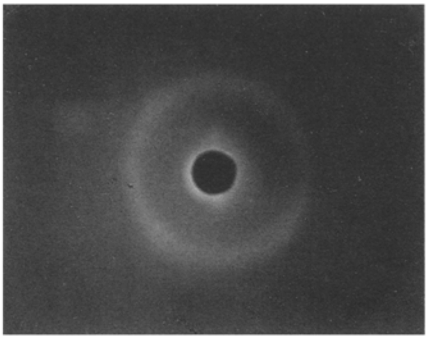


Fig. 9 X—ray fibre pattern for SP5

Acknowledgement

The financial support of National Natural Science Foundation of China is gratefully acknowledged.

References

1. Ringsdorf H, Schlarb B, Tyminski PN, Brien DFO' (1988) Macromolecules 21:1620
2. Ringsdorf H, Schmidt G, Schneider J (1987) Thin Solid Films 152:207
3. Fang TR, Zhu XB (1991) Polymer Bulletin 25:467
4. Wang SE, Li Y, Huang XY, Fang TR, Mo ZS (1993) Functional Polymer(Chinese) 6:248
5. Nöel C (1985) Recent Advance in Liquid Crystalline Polymer, Elsevier, London