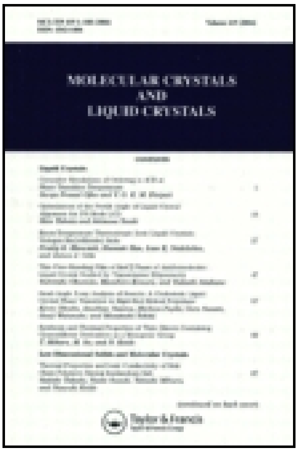

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Side Chain Liquid Crystalline Ionic Polysiloxanes

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Side Chain Liquid Crystalline Ionic Polysiloxanes

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A variety of side chain liquid crystalline ionic polysiloxanes with quaternized ammonium groups incorporated into the mesogenic moiety or into the spacer have been synthesized and studied by a combination of DSC, TGA, polarizing microscopy and X-ray diffraction. The polysiloxanes exhibit a nematic mesophase. Due to their flexible main chain, the transition temperatures are low. Thermal stability and liquid crystallinity of quaternized and unquaternized polysiloxanes are compared. It appears that in these ionic polymers the geometry of the mesogenic group plays an important part in the development of the mesophase.

Keywords: Polysiloxanes, ionic, nematic, thermotropic.

INTRODUCTION

Polymers with mesomophic order have a great potential for various applications.^{1,2}) Conventional side chain mesogens consist of rigid units and terminal polar groups, e.g. cyano, nitro, or alkoxy groups. Such groups are characterized by dipole–dipole interactions, which contribute to the anisotropy of the system. In addition to dipole–dipole interactions, ion-counterion interactions may be of importance in liquid crystal ionic polymers.^{3}) The presence of ionic groups can improve the mechanical properties of polymers such as tensile strength and impact resistance.^{4}) In addition the study of ionic liquid crystalline polymers can be useful in understanding the role of ions and counterions in more complex molecules of the bio-systems.^{4})

In a previous paper, we have described novel ion containing side chain liquid crystalline polyacrylates bearing a pyridinium ion.^{5}) It was found that quaternization increases the thermal stability of such polymers. The isotropization temperatures were shifted upwards sometimes impinging on the decomposition temperature. The mesophase range of the ionic polyacrylates was therefore difficult to determine with accuracy. New systems with lower transition temperatures are therefore required for further investigation. Polysiloxanes are promising candidates. Liquid crystalline polysiloxanes display low transition temperatures and are easily aligned by electric or magnetic fields.^{1,6}) Additionally, the polysiloxane backbone is more thermally stable than its carbon counterpart.^{7})

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This paper describes the synthesis and characterization of novel side-chain ionic polysiloxanes with low transition temperatures and stable mesophases. Three types of novel ionic side chain liquid crystalline polysiloxanes have been synthesized. One type contained a pyridyl-alkoxy-benzoate moiety in the side chain. The second type consisted of a biphenyl-methyl-piperidine mesogen, while the third contained a stilbazole mesogenic group.

EXPERIMENTAL SECTION

Characterization

Thermal properties were studied by a Perkin Elmer DSC-2C, DuPont 2000 DSC and DuPont 2995 TGA at the general rate of 20 o/min. Optical textures were observed by a Leitz Ortholux II polarizing microscope with a Mettler FP 52 heating stage. IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer. X-ray diffraction patterns of unoriented samples were obtained on a Rigaku Geigerflex X-ray diffractometer equipped with a Wahrus flat-plate camera using Ni-filtered CuKα radiation with wavelength 0.154 nm. The diffraction patterns were recorded on a flat film (Kodak DEF-5).

Synthesis:

Materials

Poly (methyl-hydrosiloxane) and platinum cyclic vinylmethylsiloxane complex were used as received from Huls America (PS 120 and PC 085, respectively). Methanesulfonyl chloride, 1-octanol, 8-bromo-1-octene, 4-hydroxybenzoic acid, 4-hydroxypyridine, 4-hydroxypiperidine, 4-(chloromethyl) biphenyl and other chemicals were purchased from Aldrich Chemical Company. Toluene was distilled over calcium hydride.

The synthetic procedures are given in Schemes 1,2 and 3. The Scheme 1 gives the reactions involved in the synthesis of monomers 1,2 and 3 as well as of the polymers 4–8.

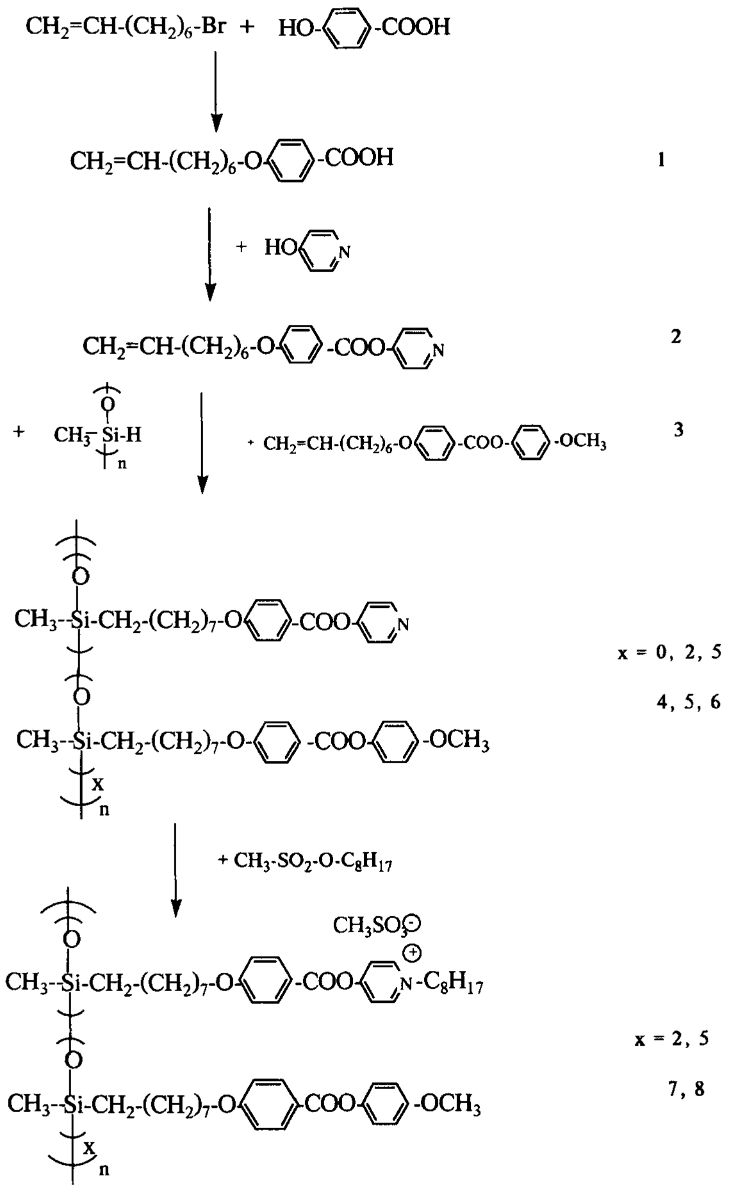
The homopolymer and copolymers **4–6** were prepared by hydrosilylation reaction of mesogenic olefins **2** and **3**. The pyridine moiety was quaternized by methanesulfonyloxy octane.

In order to change the location of the ionic site along the mesogenic side group, olefin **10** was prepared. Copolysiloxane **11** was obtained by hydrosilylation. Further quaternization gave an ionic copolysiloxane **12** (see Scheme 2).

Homopolysiloxane **16** was obtained by quaternizing heptyloxystilbazol mesogen **15** using poly[(1-methanesulfonyloxy-9-decyl)-methyl]-siloxane **14** (Scheme 3).

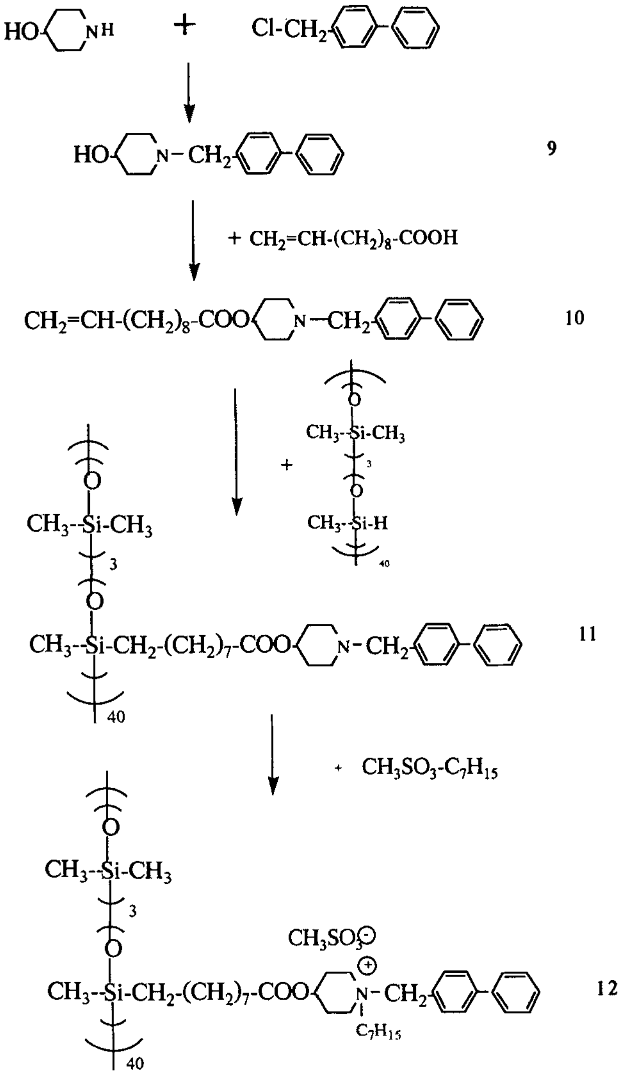
While the ionic site in copolymers 7 and 8 (Scheme 1) is on the atom of the mesogenic group external to the flexible spacer and the main chain, the ionic site in copolymer 16 is internal and adjacent to the flexible spacer (Scheme 3) and in 12 could be considered as part of the flexible spacer (Scheme 2).

Synthesis of methanesulfonyloxy octane: Modification of procedure of Martin, Ford and Bulkowski[8]) was used. 23.96 g (0.18 mol) of 1-octanol were dissolved in dry



SCHEME 1

pyridine (100 ml) in a flask. The solution was chilled to 0°C in an ice bath. 21.08 g (0.18 mol) of methanesulfonyl chloride were then added slowly over a period of 1 h. The solution was stirred at room temperature for 2 hs. 100 ml of hexane were poured into the mixture and a white solid precipitated. After adding 250 ml of ice/H_2O, the organic phase was separated and washed with 100 ml of ice/H_2O and 50 ml of concentrated



SCHEME 2

HCl, then dried over $MgSO_4$. Evaporation of solvent provided a colorless liquid product.

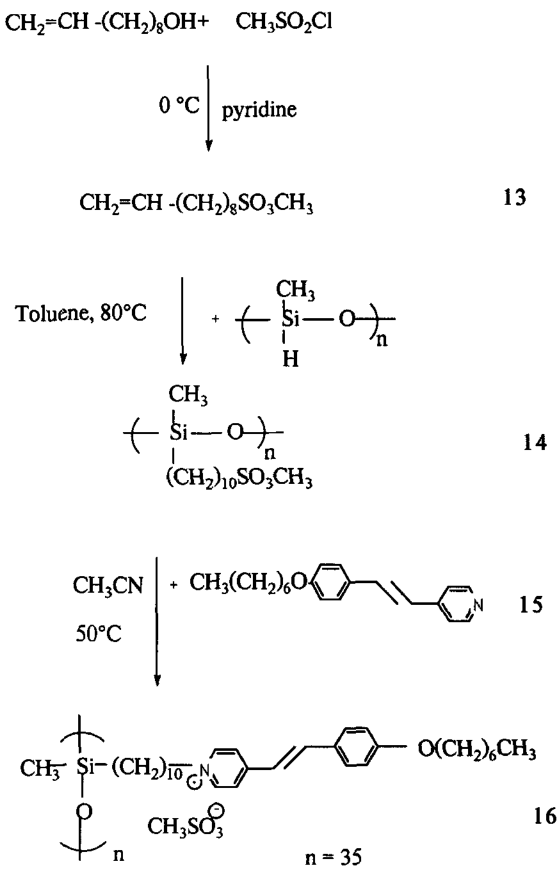
Yield: 24.09 g (63%)

IR(cm^{-1}): 1464 ($-SO_2-O-$), 1355, 1175 ($-SO_2-$)

Preparation of 4-(7-octenyloxy) benzoic acid **1**: A standard etherification method[6]) was followed by reacting the corresponding 8-bromo-1-octene with 4-hydroxybenzoic acid to give a white solid, which was recrystallized from ethanol.

Yield: 59%

DSC: k 82 s 98 n 140 i



SCHEME 3

Preparation of 1-methylbiphenyl-4-hydroxypiperidine **9**: This compound was obtained by a modification of the standard procedure[9]) and recrystallized from ethanol/ether 1:1.
Yield: 54%.
IR (cm^{-1}): 3367 (-OH), 2789 (-N-)
DSC: k 150 i 135 s 80 k (monotropic)

General procedure for preparation of 4-pyridyl-4-(7-octenyloxy) benzoate **2**, *4-(methoxyl) phenyl-4 (7-octenyloxy) benzoate* **3** *and N-(4-biphenylmethyl)-piperidyl-4-(10-undecenoate)* **10**: These compounds were prepared by reacting the corresponding acids and alcohols, respectively, using literature reported DCC/4-PPY esterification procedure.[10]) Yields ranged from 51 to 60%. A general procedure for the esterification is given below:

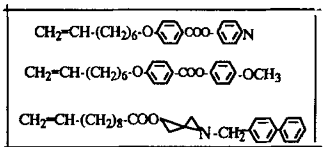
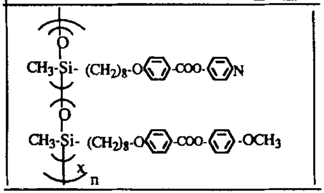
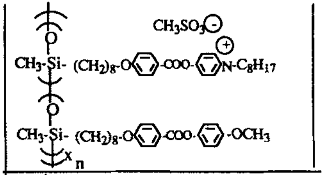
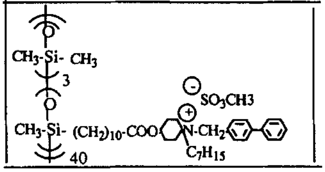
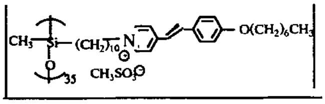
4-Pyridyl-4′-(7-octenyloxy)-benzoate **2**: 2.2 g (8.86 mmol) of the acid **1**, 0.93 g (9.75 mmol) of 4-hydroxypyridine and 0.15 g (0.98 mmol) of 4-pyrrolidinopyridine (4-PPY) in 30 ml of $CHCl_3$ were stirred at 0°C. Then 2.02 g (9.75 mmol) of dicyclohexylcarbodiimide (DCC) in 10 ml of $CHCl_3$ were added. The mixture was stirred at room temperature for 12 hs. After filtration and then evaporation of the solvent, the product was purified by flash chromatography and petroleum ether/ethyl acetate as elution medium.

Phase transitions of the compounds are given in Table 1 and elemental analysis in Table 2.

General procedure for synthesis of mesogenic polysiloxanes: Addition of corresponding mesogenic olefin to the poly (methyl hydrosiloxane) was carried out in toluene at 80°C with platinum cyclic vinylmethylsiloxane complex as catalyst. In order to complete the addition, a 10 mol% excess of olefin related to the Si—H bonds was used. After complete addition followed by disappearance of the Si—H absorption[6]) at 2140 cm^{-1}, the polymers were precipitated several times from THF in hexane/ethyl acetate 3:1 and dried in vacuo.

TABLE 1

Characterization of monomers and side chain polysiloxanes

No.	Structure	x	DSC Phase Transition (°C)	Remarks
2			k 48 i[a] (23.1)[b]	
3			k 57 n 65 i (16.5)(4.7)	Nematic mesophase, schlieren texture
10			c 69 i (25.1)	
4		0	g 9 s 74 i (7.6)	Smectic mesophase, schlieren texture
5		2	g 7 s 107 i (4.13)	Undefined texture
6		5	g 3 s 103 i (1.36)	Schlieren texture
7		2	g 18 n 70 i (0.88)	Undefined texture
8		5	g 34 n 82 i (1.46)	Undefined texture
12			g 33 n 78 i (0.23)	Undefined texture
16			k 147 n 173 i (7.3)	Enantiotropic nematic mesophase

[a] k: cristalline; s: smectic; n: nematic; i: isotropic; g: glass transition temperature

[b] ΔH value in kJ/mol

TABLE 2

Elemental analysis of mesogens and quaternized polymers

No		C	H	N	S	Degr of Quatem[a]
2	Calculated	73.82	7.12	4.31		
	Found	73.56	7.18	4.28		
3	Calculated	74.55	7.39			
	Found	74.98	7.47			
10	Calculated	80.32	9.07	3.23		
	Found	79.53	9.06	2.99		
12	Calculated	58.04	8.75	1.54	3.52	
	Found	50.44	8.28	1.39	3.37	95.7
16	Calculated	66.26	9.15	2.49	5.71	
	Found	65.71	9.35	3.02	5.65	98.9

[a] Expressed in mole% based on the sulfur content.

General procedure of quaternization: The polysiloxane and 10 mol-% excess of methanesulfonyloxy alkane were dissolved in acetonitrile/hexane (1:1) and stirred at 50°C for 72 hs. The quaternized polymers were precipitated several times from THF into ethyl acetate, then dried in vacuo. Degree of quaternization was estimated based on the weight percentage of sulfur.

Synthesis of 1-methanesulfonyloxy 9-decene **13**: 0.03 mole of corresponding alcohol were dissolved in 50 ml pyridine (1:3 mole ratio) in a reaction flask. The flask was kept in ice water containing saturated NaCl for 10 minutes, then the methylsulfonyl chloride was added drop wise into the reaction flask. The reaction mixture was kept under stirring for 1 hour in salt ice water bath and 1 hour at room temperature, then stored at 0°C overnight. The reaction mixture was poured into acidified ice water (50 ml conc. HCl in 950 ml ice water). Oil-like liquid was formed. After repeat extraction by ether, the combined ether layers were dried over magnesium sulfate for four hours. After filtration the ether solution was passed through a chromatography column using an aluminium oxide packing. The pure product was obtained by evaporating the excess ether using a rotary evaporator. Yield was 78%.

Synthesis of polysiloxane **14**: The addition of **13** to siloxane polymer backbone was done using a standard method described in the literature.[6]) Typical elemental analysis of the ionic poly(siloxanes) is given in Table 2.

RESULTS AND DISCUSSION

The thermal characteristics of monomers and polymers are given in Table 1.

Thermal and Liquid Crystalline Properties Before Quaternization

Monomer **3** displayed schlieren textures by annealing on cooling at 59°C under microscope (Figure 1a). Two endothermic peaks were observed on second heating at 57 and 65°C by DSC. The enthalpy values were 16.5 and 4.7 kJ/mol respectively. On cooling, enthalpy values were 4.7 and 15.3 kJ/mol at 61°C and 16°C. On cooling a

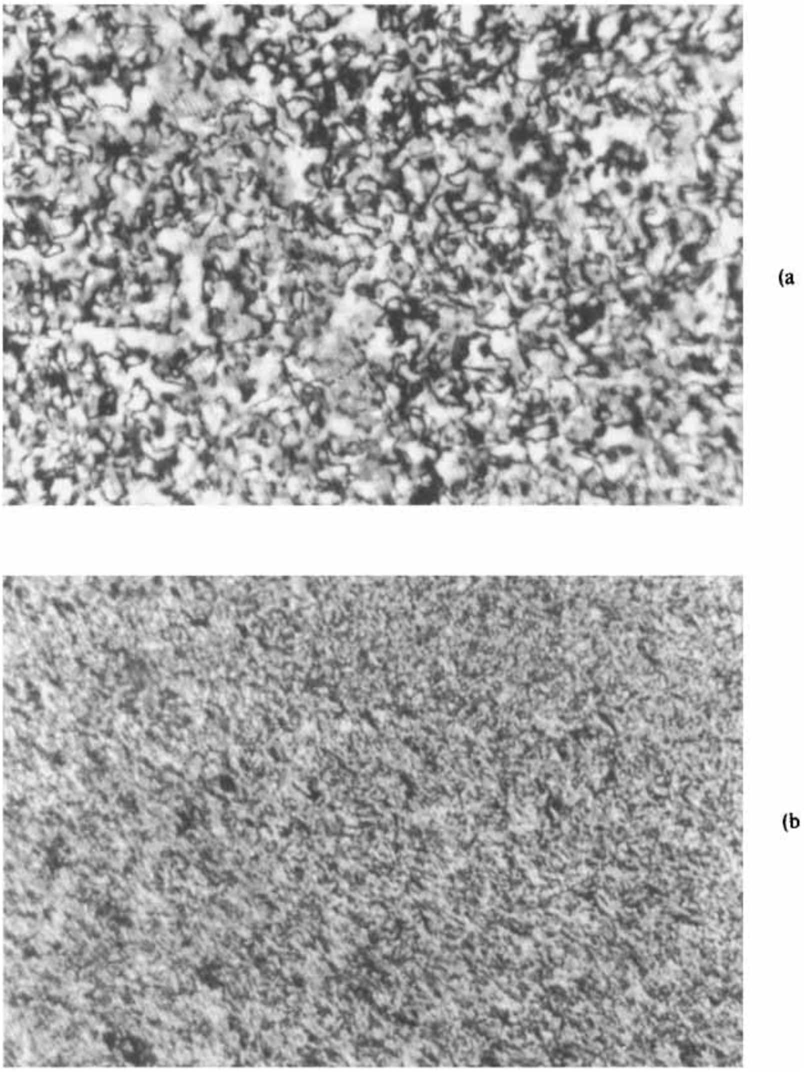


FIGURE 1 Crossed polarizers, magn. 200X: a) Schlieren texture of mesogenic compound 3 at 590°C, b) Texture of polysiloxane 6 at 78°C. See Color Plate X.

weak schlieren pattern was developed under microscope suggesting a nematic phase. Monomers **2** and **10** showed only a crystal to isotropic transition.

In the case of homopolysiloxane **4**, weak and difficult to determine schlieren textures were observed under microscope. At 74°C the sample became isotropic. A glass transition at 9°C and a transition from liquid crystal to an isotropic phase at 74°C were also found by DSC. The corresponding value of enthalpy change of 7.6 kJ/mol was in agreement with a transition from a smectic phase of lower order to an isotropic phase.

The thermogravimetric analysis (TGA) of polymer **4** showed a weight loss of about 21.7% at 215°C. A sudden weight loss (42.8%) appeared at 441°C. As expected, the decomposition temperature of the polysiloxane is higher than that of the corresponding polyacrylate (180°C).

Copolysiloxane **5** displayed undefined textures under microscope. At 107°C it became isotropic. Polymer **5** showed a glass transition at 7°C by DSC and a mesophase to isotropic transition at 107°C with enthalpy value of 4.13 kJ/mol. These transitions were reproducible (see Figure 2). TGA of copolymer **5** showed a sudden weight loss of 65.9% at 433°C.

Slowly cooled from the isotropic phase and annealed for two days at room temperature thin films of copolymer **6** displayed schlieren textures (Figure 1b). Texture development is difficult with these ion containing polymers and long annealing times have to be applied. The film became isotropic when heated to 103°C. A glass transition at 3°C and a mesophase to isotropic transition at 103°C were observed on heating. Copolymers **5** and **6** showed broader mesophase intervals and increased thermal stability in comparison with the homopolymer **4**.

All homo- and copolysiloxanes **4**–**6** show mesophases. In comparison to polyacrylates polysiloxanes present better thermal stabilities. They display lower glass transition temperatures and lower mesophase to isotropic transition temperatures.

Thermal and Liquid Crystalline Properties After Quaternization

The quaternized polymer **7** annealed at 68°C displayed undefined birefrigent textures. The DSC thermograms showed a glass transition at 18°C and a possible LC to isotropic transition at 70°C. TGA showed a weight loss of about 50% at 442°C.

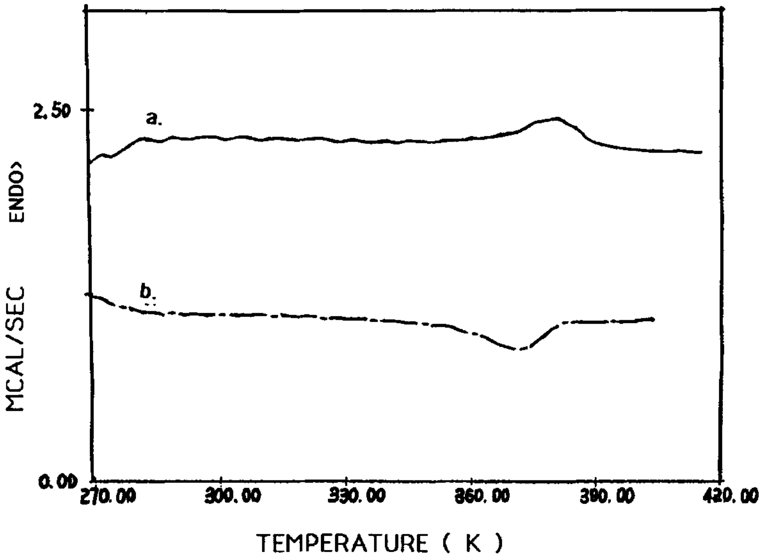


FIGURE 2 DSC Thermograms of copolysiloxane 5: a. heating b. cooling.

An X-ray powder diffraction pattern from an unoriented sample of 7 displayed a diffuse inner and a diffuse outer ring indicating absence of a well defined smectic order. The observation of birefrigence under the polarizing microscope, the low value of enthalpy (0.88 kJ/mol) and the absence of a defined X-ray pattern suggested therefore the existence of a nematic phase for this polymer.[12])

Quaternized copolymer **8** displayed X-ray diffraction patterns similar to 7 (absence of sharp inner and outer rings). The DSC thermogram exhibited on heating a glass transition at 34°C and a mesophase to isotropic transition at 82°C. A weight loss of about 18% at 261°C and a sudden weight loss of 65.5% at 445°C were observed by TGA.

The copolysiloxane containing a quaternized alkyl amine in the mesogenic side-group (polymer **12**) showed undefined mobile textures under microscope when annealed at 76°C. The DSC thermogram on heating showed a glass transition temperature and a peak corresponding to the isotropization of the polymer in agreement with microscopic observations. The small value of enthalpy (0.23kJ/mol) is consistent with the absence of a smectic phase. A weight loss of about 52% at 283°C as well as a weight loss of 43% at 392°C were observed by TGA. In contrast to polyacrylates described previously,[5]) the copolysiloxane **12** is thermally more stable and its mesophase can be studied.

After quaternization the glass transition temperature of homo- and copolysiloxanes increases somewhat. However isotropization temperatures of the quaternized polysiloxanes are lower than those of the corresponding unquaternized polymers. It is possible that the long alkyl terminal group (C8) of the quaternizing agent is responsible for this effect.

Polysiloxane **16** became mobile at 147°C and isotropic at 173°C. During cooling the birefringence occurred at 123°C, but the sample was still very mobile. The crystallization took place at 104°C. Two endothermic transition peaks were observed on second heating, while only one endothermic peak was observed on second cooling.

At room temperature the polymer 16 displayed Laue X-ray diffraction patterns characteristic of a crystalline phase. At 160°C, the X-ray diffraction pattern showed only a diffuse halo at about 5.1 Å suggesting the absence of a smectic mesophase. A nematic phase is therefore also proposed for this polymer.

It is interesting to note that while the unquaterized side chain polysiloxanes 4–6 appear to tbe smectic, the corresponding ionic analogues appear nematic irrespectively of the charge density and of the fact that a long alkyl chain (usually favoring smectic behaviour) has been added to the quaternized nitrogen atom. Also the change in the position of the ionic site within the side groups did not alter the nematogenic character of the above polymers This may be due to the change in the geometry of the mesogen introduced by quaternization (from a flat non ionic nitrogen site to a three-dimensional quaternary ionic nitrogen site) unfavorable to the packing of mesogenic groups, and would suggest that in this case, unlike in the system studied by Gramain *et al.*,[11] the geometry of the mesogen and not the charge is an important factor in the development of mesomorphic properties.

These results are of course fragmentary and much more systematic work on structure variation is necessary to elucidate structure-property correlation of such ionic polymers.

Acknowledgement

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