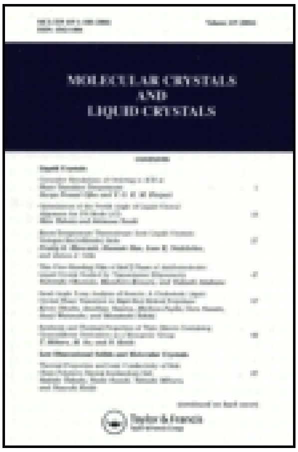

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Novel Ion Containing Liquid Crystals and Liquid Crystalline Main Chain Polymers Based on Trans-1,2-Bis(4-Pyridyl Ethylene) Mesogen

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Novel Ion Containing Liquid Crystals and Liquid Crystalline Main Chain Polymers Based on Trans-1,2-Bis(4-Pyridyl Ethylene) Mesogen

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Ion bearing liquid crystalline compounds based on trans-1,2-bis (4-pyridinium) ethylene were synthesized and studied. These compounds included low molecular mass analogues, twin model compounds and main chain ionomers. Most of these exhibited liquid crystallinity of the smectic type. As a general rule the introduction of charges into the mesogenic moiety increased the stability (transition temperature) of the mesophase. Large supercooling effects, broad mesophase intervals and tendency to polymorphism are common features of these ionic mesogenic compounds.

In the case of twin model compounds a variety of smectic phases were observed. The nature of these was dependent on the nature of the counterion and the thermal history of the compound. Tosylate or p.toluene sulfonate counterions promoted a higher degree of order in smectic mesophases as well as higher transition temperatures compared to methylsulfonate counterions. A pronounced odd-even effect of the isotropisation temperature of the twin compounds was observed. Compounds with even numbered methylene spacers display higher transition temperatures than those with an odd spacer.

Only polymers with methylsulfonate and toluenesulfonate counterions were found to exhibit both, thermotropic and lyotropic mesophases. Thermotropic mesophases were characterized as smectic mesophases of lower order (S_A). The nature of lyotropic mesophases were not determined.

High transition temperatures and concommitant oxydative crosslinking made the study of polymers with halogen counterions difficult. Polymers with halogen and perchlorate counterions were found to be poorly soluble in water precluding the formation of lyotropic mesophases. The introduction of a few siloxane bonds into the flexible spacer joining the charged mesogen moieties has a dramatic effect on lowering the transition temperatures and making possible the study of mesophases up to their isotropisation temperature. Preliminary characterization of polymers with siloxane containing spacer and methylsulfonate/tosylalte counterions suggest a smectic mesophase of lower order.

Keywords: Ion containing liquid crystals, liquid crystal ionomers

INTRODUCTION

Thermotropic and lyotropic synthetic liquid crystalline low and high molecular mass compounds have received much attention over the last two decades. This field appears to be at the peak of its development. With the exception of studies describing ionic

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amphiphiles however, there appears to be little work on synthetic charge bearing mesogenic compounds, especially of the polymeric type.

The interest of such systems is multifold: on the molecular or segmental level the existance of charges leads to strong polarity which in turn may lead to unusual orientational properties in and out of electric fields. On the macroscopic level, ionomeric liquid crystals have the ability to form both, lyotropic and thermotropic liquid crystalline mesophases as well as anisotropic gels. On the practical level, such systems can have many potential applications due to their solubility and easy (processability), high degree of anisotropy coupled with easy quenching of molecular order and the possibility of multiple thermotropic and lyotropic mesophases. Such liquid crystalline ionic polymers can be to polymer liquid crystals what polyelectrolytes and ionomers are to noncharged polymers, combining the advantages of liquid-crystals and charged polymers. In addition to the intrinsic interest in the novelty of polymeric liquid-crystalline ionomers such systems are of interest as media for molecular and charge transport, in the search for new biocompatible materials and permselective membranes. Finally, they may also play a role in the understanding of the function of ionic sites in more complex bio-systems. A great potential for innovation is therefore present.

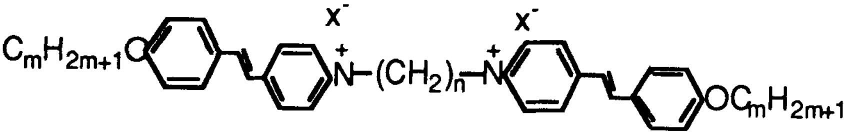
In 1984 You and Samulski[1] reported a study of ionomeric liquid crystals based on N,N-dialkyl-4,4′-bispyridinium salts and their polymeric analogs, little was said in this study about the mesomorphic properties of these compounds. The phase transition phenomena were described as "ill resolved and complex." More recently a small number of papers appeared in the literature (including our preliminary work) on synthetic liquid crystalline ionomers[2–7] and twin model compounds.[8]

In this work it is proposed to explore the synthesis and properties of a series of ion-containing main chain liquid crystals all based on a similar mesogenic moiety: starting first with low molecular mass compounds, than dimeric twin model compounds and finally, polymers of the ionene type. Special attention is paid to the trans-1,2-bis (4-pyridyl) ethylene and the alkoxystilbazole moiety both quaternized with alkyl halides, methyl and toluene sulfonates. We have attempted to explore the influence of various structural parameters characteristic of ionic compounds and of liquid-crystalline polymers on mesophase formation. Such parameters as the length and nature of the spacer, the influence of the charge and of the counterion were studied.

EXPERIMENTAL

Low Molecular Mass Compounds

The general structure of synthesized twin model compounds is:



with $m = 4, 7$ and $n = 6, 7, 8, 9, 10, 12$; $x^- = CH_3SO_3^-$, $CH_3C_6H_4SO_3^-$.

The synthesis of low *M* compounds is given in Schemes 1 and 2. Representative schemes of synthesis of alkylsulfonate quaternizing agents are given in Schemes 3 and 4. Tables I and III give the structural formulas and examples of typical elemental analysis of the synthesized low molecular mass analogs and of the corresponding ionic polymers. Selected experimental procedures are given below:

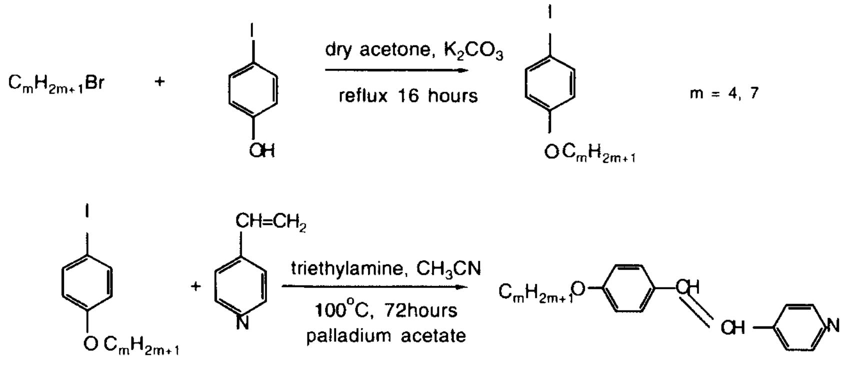
Synthesis of Alkylsulfonates and Alkyltoluenesulfonates (quaternizing agents)

The synthesis of alkylsulfonates and alkyltosylates were done according to:

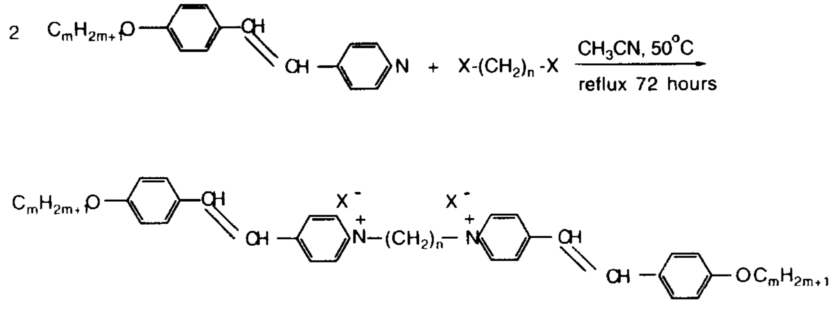
$$C_xH_{2x+1}OH + Y'Cl \xrightarrow{\text{Pyridine/0 C}} C_xH_{2x+1}Y$$

$$\text{with } x = 6\text{–}12;\ Y' = CH_3SO_2/CH_3C_6H_4SO_2;\ Y = CH_3SO_3/CH_3C_6H_4SO_3$$

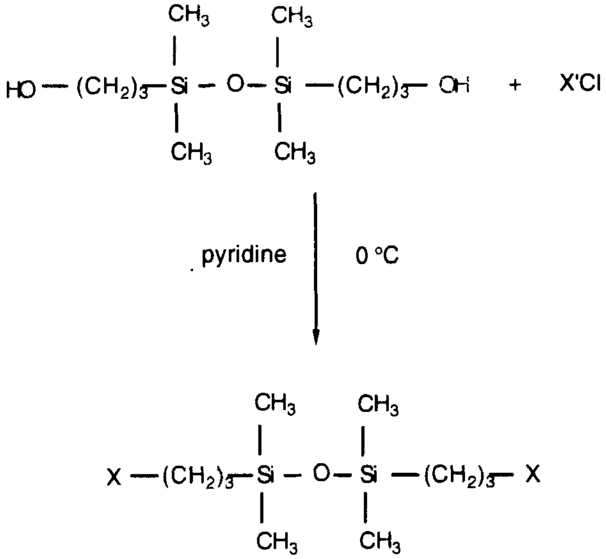
The corresponding alcohols were dissolved in pyridine (1:3 mole ratio) and kept at 0°C. To this solution a saturated solution of p.toluenesulfonylchloride/methyl sulfonylchloride in pyridine was added dropwise under stirring. The mixture was then kept refrigerated overnight, brought to room $t°$ and poured into a large excess of approximately 0.1M HCL. The oily layer was then repeatedly extracted with ether, dried over magnesium sulfate and filtered. The ether extract was then passed in a chromatographic column over aluminum oxide. After evaporation of the ether the corresponding sulfonates were recovered.



SCHEME 1



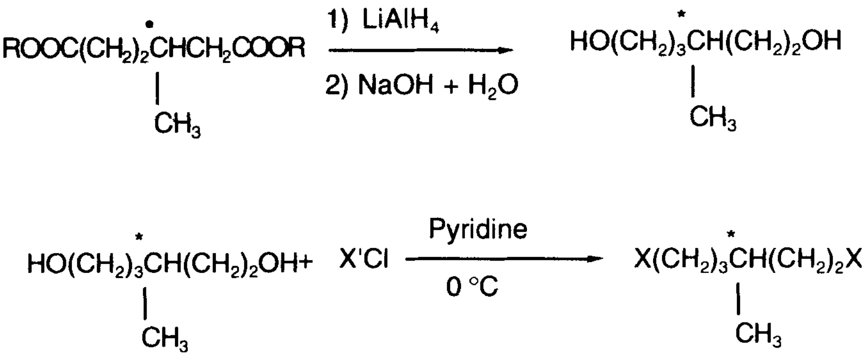
SCHEME 2



$$HO-(CH_2)_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-(CH_2)_3-OH + X'Cl \xrightarrow[\text{pyridine}]{0\ ^{\circ}C} X-(CH_2)_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-(CH_2)_3-X$$

$X' = CH_3SO_2, CH_3C_6H_4SO_2, X = CH_3SO_3, CH_3C_6H_4SO_3$

SCHEME 3



$$ROOC(CH_2)_2\underset{CH_3}{\overset{\bullet}{C}H}CH_2COOR \xrightarrow[\text{2) NaOH + }H_2O]{\text{1) }LiAlH_4} HO(CH_2)_3\underset{CH_3}{\overset{*}{C}H}(CH_2)_2OH$$

$$HO(CH_2)_3\underset{CH_3}{\overset{*}{C}H}(CH_2)_2OH + X'Cl \xrightarrow[0\ ^{\circ}C]{\text{Pyridine}} X(CH_2)_3\underset{CH_3}{\overset{*}{C}H}(CH_2)_2X$$

$X' = CH_3SO_2, CH_3C_6H_4SO_2; X = CH_3SO_3, CH_3C_6H_4SO_3;$

SCHEME 4

In the case of the corresponding disulfonates a similar procedure was followed. The reaction products separated from solution by precipitation were recrystallized from hot ethanol. Yields were in all cases 75–85%.

Trans-4-alkoxy-4′ stilbazoles:

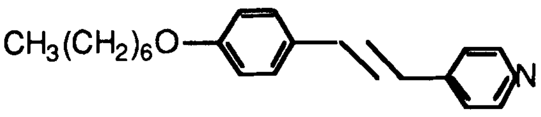


TABLE I

Elemental Analysis of low molecuclar compounds

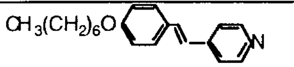
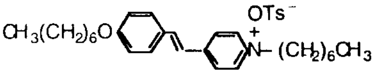
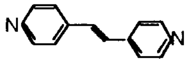
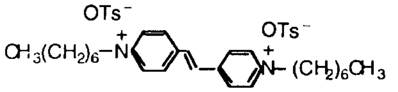
Compound	Calculated %				Found %			
	C	H	N	S	C	H	N	S
 THPPE	81.3	8.5	4.7	-	81.2	8.6	4.7	-
 THPHTE	66.8	7.4	1.9	8.7	65.2	7.3	1.9	8.7
 TBPE	79.1	5.5	15.4	-	79.1	5.6	15.3	-
 THPTE	66.5	7.5	3.9	8.9	65.2	7.5	3.8	8.8

TABLE II

Melting points and yields of alkyldisulfonates and alkylditoluenesulfonates

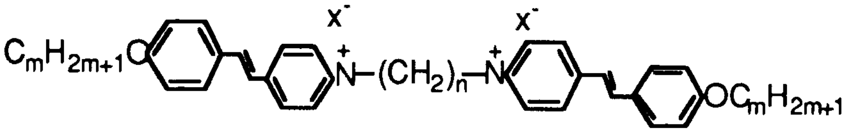
x^-	n	6	7	8	9	10	12
$CH_3SO_3^-$	T_m°C	60	53	65	57	68	70
	yield %	56	51	69	74	65	58
OTs^-	T_m°C	62	56	67	58	70	72
	yield %	61	64	70	67	67	63

trans-1-(4-heptyloxyphenyl)-2-(4-pyridyl)ethylene(THPPE) and trans-1,2-bis-4,4′ pyridylethylene(TPE) (were prepared according to the procedure of Bruce *et al.*[9] Their quaternization was done by reacting a given compound with the appropriate quaternizing agent in excess in acetonitrile at 50°C. A typical experimental procedure is as follows :

A mixture of trans-4-heptyloxy-4′-stilbazole and of alkylsulfonate/alkyltoluenesulfonate in a molar ratio of 1:2 in acetonitrile are stirred for 24 h at 50°C. After cooling to 0°C the quaternization product precipitates in the form of a yellow powder. It is filtered, dissolved in acetonitrile and precipitated into toluene. After drying in vacuo for 12 hours at room temp. the yield was 76%.

Twin Model Compounds

The structure of synthesized twin model compounds is as follows:



with $n = 6$–10,12 and $m = 4,7$ and $X^- = CH_3SO_3^-$ or $CH_3C_4H_4SO_3^-$.

The synthetic route is represented in schemes 1 and 2. In order to identify the present twin compounds these compounds are abbreviated by *m,nX* where *m* denotes the number of carbon atoms in the two terminal alkoxy chains, *n* the number of carbon atoms in the spacer and *X* the counterion (toluenesulfonate = *T*, methylsulfonate = *S*). For example 4,6 *T* indicates that there are four carbon atoms in each of both terminal alkoxy radicals, six methylene units in the flexible spacer and a toluenesulfonate (tosylate) counterion. Examples of synthesis of typical intermediates and of the final twin compounds are given below.

Synthesis of Alkyldisulfonate and Alkyltoluenedisulfonate(tosylate)

The synthesis was carried out using the procedure outlined in[1]:

$HO{-}(CH_2)_n{-}OH + YCL$ (Pyridine 0°C) $Y{-}(CH_2)_n{-}Y$

The corresponding diol (0.03 mole) was dissolved in 50 ml. of pyridine(1:3 mole ratio). The reaction mixture was refrigerated for 10 min to below 0°C (about −5 to −10°C) a saturated solution of the corresponding sulfonylchloride in pyridine was then added dropwise under stirring. The mixture was kept under refrigeration overnight in a tightly sealed container. It was then poured into an excess of approx. 1–.5 N HCl at 0°C. The white precipitate of the product was filtered. It was purified by recrystallization from hot absolute ethanol and dried in vacuo. The yields and melting points Tm of obtained compounds are listed in Table II.

Synthesis of 1,3 bis(sulfonatepropyl) tetramethyldisiloxane

The synthetic procedure is similar to the one outlined above for alkyldisulfonate and alkyltoluenedisulfonate. The synthetic scheme is given (Scheme 3)

Synthesis of Alkyldisulfonate and Alkyltoluenedisulfonate with a chiral center (1,7-disulfonate-4-methyl heptane)

The synthesis is shown in Scheme 4. The experimental procedure of Marshall *et al.*[10] was as follows:

Five hundred ml of anhydrous ether were placed in a one liter 3 necked flask equipped with a gas inlet, a 250 ml dropping funnel and a condenser attached to a calcium chloride drying tube. All glassware should be rigorously dry. Dry nitrogen was made constantly to flow through the gas inlet and 13.66 g (0.36 moles) of $LiAlH_4$ powder were quickly introduced. A solution of 3 moles of diester in 200 ml of anhydrous ether was then introduced slowly dropwise into the flask under magnetic stirring so that a slow refluxing rate was maintained cooling if necessary (ice bath). After the addition was completed the solution was left under stirring to come to room temperature overnight. The reaction mixture was then gently refluxed for 24 h to insure the completion of the reaction. After cooling to 0°C (ice bath) 5 ml of 10% NaOH solution were added dropwise to the reaction mixture at a rate such as to maintain a slow reflux of the solvent. At the end an additional 10 ml of water were added dropwise to complete the hydrolysis of the $LiAlH_4$. A white residue was then separated from the liquid by filtration and washed 3 times with 100 ml of ether. The liquid portions were reunited and the ether solution was separated from the acqueous layer in a separation funnel. The acqueous layer was then repeatedly extracted with ether and the reunited ether extracts were dried over $MgSO_4$ over night. After filtration the ether was distilled off and the clear and dry ether extract was fractionally distilled under reduced pressure (1 mm). Only the fraction passing within 1°C of the literature boiling point was used. The yield was 67%.

Synthesis of trans-4-alkyloxy-4'-stilbazoles

The procedure was taken after Bruce *et al.*[9] A solution of 4-alkyloxyiodobenzene was prepared form an equimolar mixture of 4-iodophenol and 1-bromoalkane in pure and dry acetone under reflux. The solution of the product was washed with water and repeatedly extracted with ether. The combined ether extracts were washed first with a 10% water solution of NaCl followed by a 10% solution of NaOH. After extensive drying over $NaSO_4$ the ether layer was filtered and the ether and solvent were evaporated. The resultant pale yellow oil obtained in the yield of 85% was purified by chromatography.

The purified 4-alkoxy-iodobenzene, 4-vinylpyridine and triethylamine (mole ratio (1:1.2:1) were dissolved in an equal volume of acetonitrile. The mixture was placed in a thick walled Pyrex tube (Fisher-Porter type), added with approx. 0.5% (based on the weight of reactants) of palladiumacetate and the tube throughly flushed with nitrogen and sealed. The solution was placed for 70 hours in an oil bath at 100°C. After cooling the solid phase was dissolved in methylene chloride and the mixture washed with water. The separated acqueous layers were further washed with methylene chloride. The combined organic layers were then reduced in volume, dried over Na_2SO_4. The solvent was removed after filtration and the crude product (yellow-orange solid) was repeatedly extracted with *n*-hexane and recrystallized from acetone at low temperature (approx. 0°C). Pale yellow crystals. Yield 81%.

Synthesis of Twin Model Compounds: α,ω-Bis[trans-1-(4-alkoxy phenyl)-2-(4-pyridiniumethyl/toluene sulfonate)ethylene]alkane

All twin model compounds were prepared in a similar way. The synthetic path is given in scheme 2 a mixture of trans-4-alkyloxy-4'-stilbazole and alkyldisulfonate/alkylditoluene sulfonate (mole ratio 2:1) were stirred in dry acetonitrile at 50° for 24 hours. The crude product was precipitated as yellow powder on cooling to 0°. The resulting product was collected, throughly washed with ethyl ether and redissolved in acetonitrile. It was reprecipitated in toluene. The purified compound was dried in vacuo at room *t*° for 12 hours.

High Molecular Mass Compounds

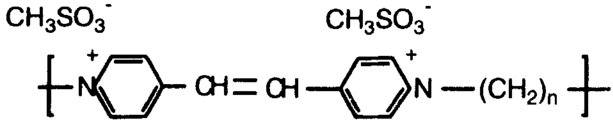
For identification purposes and in similarity to the twin compounds the mesogen moiety is designated TPE [trans-1,2-bis(4-pyridylethylene)] followed by the first initial of the counterion and the number *n* of the methylene units in the spacer. For example a polymer with a methylsulfonate counterion $n = 7$ or poly[1,2-bis(4-pyridinium-heptyl)ethylenemethanesulfonate] will be represented by TPEM7.

All polymers including the polysiloxane spacered polymers were prepared in a similar way through quaternization with the corresponding quaternizing agent. The synthetic path is given in Scheme 5 and a typical synthetic procedure is given below.

Synthesis of poly[trans-1,2-bis(4-pyridyl)-ethylene-n-alkyl-methylsulfonate]/tosylate] poly(TPEMn) or poly(TPETn)

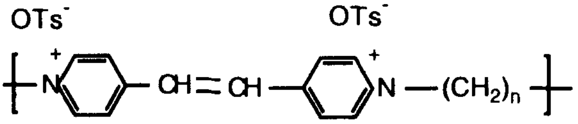
The procedure is as outlined by Moore *et al.*[11] Equimolar amounts of the trans-1,2-bis(4-pyridyl)-ethylene and of the alkyldisulfonate or alkylditoluene sulfonate were

TABLE IIIa
Elemental analysis of Poly(TPEMn)



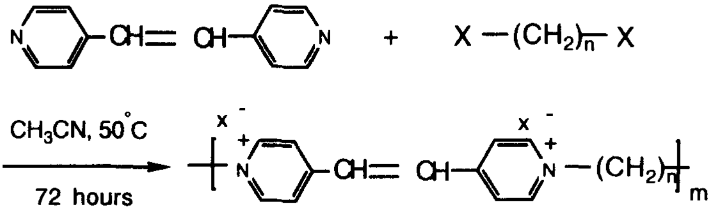
n	Compound	%	C	H	N	S
6	$(C_{20}H_{28}N_2S_2O_6)_x$	Calc.	52.60	6.18	6.14	14.04
		Found	49.26	6.36	5.75	13.00
7	$(C_{21}H_{30}N_2S_2O_6)_x$	Calc.	53.59	6.43	5.95	13.63
		Found	51.13	6.63	5.84	12.89
8	$(C_{22}H_{32}N_2S_2O_6)_x$	Calc.	54.52	6.66	5.78	13.23
		Found	50.70	6.89	5.41	12.37
9	$(C_{23}H_{34}N_2S_2O_6)_x$	Calc.	55.40	6.87	5.62	12.86
		Found	54.47	6.93	6.07	11.30
10	$(C_{24}H_{36}N_2S_2O_6)_x$	Calc.	56.22	7.08	5.47	12.51
		Found	53.45	6.92	5.45	11.79
12	$(C_{26}H_{40}N_2S_2O_6)_x$	Calc.	57.75	7.46	5.18	11.86
		Found	55.15	7.49	5.06	11.50

TABLE IIIb
Elemental analysis of Poly(TPETn)



n	Compound	%	C	H	N	S
6	$(C_{26}H_{32}N_2S_2O_6)_x$	Calc.	63.13	5.96	4.60	10.53
		Found	61.39	6.13	4.50	10.21
7	$(C_{27}H_{34}N_2S_2O_6)_x$	Calc.	63.64	6.15	4.50	10.30
		Found	61.64	6.36	4.96	10.14
8	$(C_{28}H_{36}N_2S_2O_6)_x$	Calc.	64.12	6.33	4.40	10.07
		Found	63.41	6.43	4.51	9.87
9	$(C_{29}H_{38}N_2S_2O_6)_x$	Calc.	64.59	6.51	4.31	9.85
		Found	61.24	6.72	4.96	9.17
10	$(C_{30}H_{40}N_2S_2O_6)_x$	Calc.	65.03	6.67	4.21	9.64
		Found	63.53	6.83	4.37	9.42
12	$(C_{32}H_{44}N_2S_2O_6)_x$	Calc.	65.87	6.98	4.04	9.25
		Found	63.75	7.04	4.44	8.84

reacted under stirring in dry acetonitrile at 50°C for 72 h. The polymer precipitated as a tan solid. It was filtered, dissolved in absolute ethanol and reprecipitated in ethyl acetate then dried in vacuo. The yield was 80%. Typical elemental analysis results are given in Tables IIIa and IIIb.



$n = 6, 7, 8, 9, 10, 12$; $x = CH_3SO_3, CH_3C_6H_4SO_3$; $m = 20\text{-}25$

SCHEME 5

General Methods for Counterion Exchange

Ion exchange was carried out by treating aqueous solutions of corresponding polymers with methanesulfonate counterions with an excess of saturated solution of potassium salt of the anion(Cl, Br, I and ClO_4) to be exchanged. All compounds thus prepared were significantly less soluble in water than the corresponding methane sulfonate or toluene sulfonate analogs and precipitated from water. The degree of exchange was determined by elemental analysis and in all cases exceeded 98 mole%. Only twin model compounds with methanesulfonate (mesylate) and p.toluenesulfonate (tosylate) counterions were prepared.

Measurements

Infrared spectra were recorded on a Perkin Elmer 1600 FTIR Spectrophotometer using thin films of polymer cast from solution. UV-absorption spectra of polymer solutions in ethanol were obtained on an IBM 9420 UV-visible spectrophotometer. Optical microscopy was performed using a Leitz Ortholux polarizing microscope equipped with a Mettler FP2 heating stage. Thermal analysis was carried out with a Perkin Elmer 2C differential scanning calorimeter. All scans were done at a heating/cooling rates of 20°/min and 10°/min. A Rigaku Geigerflex X-ray diffractometer using Ni-filtered Cu α radiation equipped with a thermostat controlled sample heater ($\pm 0.1°$) and a Warhus flat plate camera was used for X-ray studies. X-ray patterns of samples were recorded by two methods. In the first samples contained in sealed X-ray capillaries were heated to a predetermined temperature and rapidly cooled in dry ice. The X-ray patterns were then recorded at room temperature. The second method involved measurement of X-ray patterns of selected samples at predetermined temperatures. Both methods gave similar results.

All viscosity measurements were made at 30°C in 0.4 M acqueous solutions of sodium methanesulfonate using Cannon Ubbelohde viscometers. Variable shear rate viscosity measurements were made using a four-bulb shear dilution viscometer. Light scattering mesurements were performed on polymer samples dissolved in 0.4 M solutions of sodium methanesulfonate using a Dawn MF Laser Photometer at 30°C and $\lambda = 632.8$ nm. TGA thermograms were recorded on a DuPont 2995 thermogravimetric analyzer. Elemental analyses were performed by Atlantic Micro-Labs Atlanta, Ga.

Hydration and Dehydration

TGA analysis was carried out for low and high molecular mass compounds. A DuPont 2995 thermogravimetric analyzer was used. Whilst low molecular mass compounds showed often only minimal hydration, ionomers hydrated and displayed an approx. 10% weight loss on heating to 140°C. Thus dried polymers appeared to rehydrate on handling to 4–5 wt.%, especially polymers with sulfonate counterions. Samples dried at 140°C directly in the TGA apparatus followed by cooling to room temperature under dry nitrogen displayed no weight loss on subsequent heating to 300°C. (rate of heating of 20°/min.)

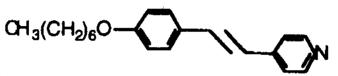
The DSC thermograms of hydrated polymers displayed a broad peak in the 80–140°C range (see Figure 12). This peak could be eliminated by drying the sample at 140°C followed by a fast transfer to a hermetically sealed DSC pan (dry box). The peak could be made to reappear on annealing in presence of water vapour. This peak is thus related to the hydration of the ionic polymer.[7]

RESULTS AND DISCUSSION

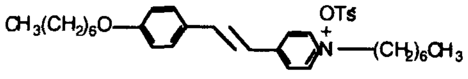
Some theoretical considerations applied to rigid mesogens point toward a weakening of mesogenic properties upon inclusion of charges by stressing the effect of repulsion between charged sites disturbing the parallel orientation of the long axes of mesogens.[12] Systematic data on such compounds are scarce. In this work we have tried to explore the evolution of mesomorphic properties on introducing charges, first into low molecular mass mesogens, than into twin model compounds and finally into polymers with all systems based on the same mesogenic moiety: trans-1,2 bis(4-pyridylethylene)(TBPE).

Low Molecular Mass Compounds

The structure of four compounds used for the study of comparative thermal behavior are given in Figure 1 and Table IV. The mesophase transition temperatures and assignments for THPPE (compound 1, Table IV) was taken from Bruce *et al.*[9]

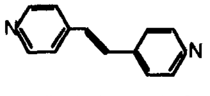


Trans-1-(4-heptyloxyphenyl)-2-(4-pyridyl)ethylene
THPPE (compound 1)

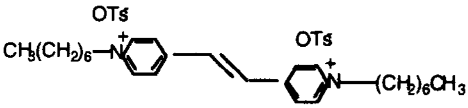


$OTs = CH_3C_6H_4SO_3^-$

Trans-1-(4-heptyloxyphenyl-2-(4-heptyloxypyridinium-p-toluenesulfonate)ethylene THPHPTE (Compound 2)



Trans1,2-bis(4-pyridyl)ethylene TBPE (Compound 3)



Trans1,2-bis(4-heptyloxypyridinium-p-toluenesulfonate)ethylene
THPTE (Compound 4)

FIGURE 1 Structure of the low molecular model compounds.

TABLE IV
Thermal properties of THPPE, THPHPTE, TBPE, THPTE

Compound	Transition°C	ΔH_1 kJ/mole	ΔH_2 kJ/mole
THPPE	C85.6S_E88.4S_B89.5I	27.38	12.53
	I88.8S_B88.2S_E#	−12.20	−
THPHPTE	C122S_A184I	0.76	7.17
	I179S_A105C	−0.99	−6.86
TBPE	C153I	21.20	−
	I152C	−19.80	−
TPHTE	C240S_A^*	0.90	23.82
	−	−	−

Data by Bruce *et al.* [16].
* no isotropization was observed, the texture was arrested after melting.

Our results indicate that both the crystal/mesophase and the mesophase/isotropic transition temperatures increase substantially on the incorporation of a charge on the mesogen. For example in the case of THPPE of Table IV (compound 1 of Figure 1) we have confirmed by polarizing microscopy and DSC the isotropization temperature of

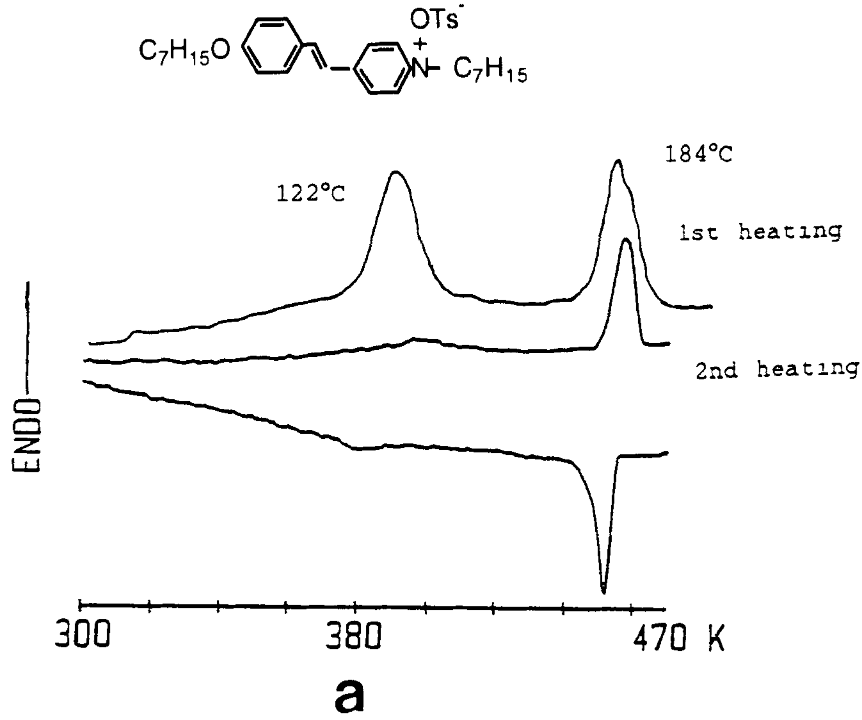


FIGURE 2 (a) Thermogram of THPHTE. (b) Polarizing Micrograph of THPHPTE. Focal conic texture developing on cooling and corresponding to an S_A mesophase (picture taken at 365°K or 92°C).

b

FIGURE 2 *(Continued)* See Color Plate I.

this noncharged compound to be 90°C (temperature of disappearence of the mosaic texture of the S_B mesophase and the development of an isotropic phase). The isotropization temperature was shifted on quaternization of the pyridine nitrogen with heptyltosylate (THPHPTE, compound 2) to 184°C. Similarly, the melting point was increased on quaternization from 85°C to 122°C. This increase in stability is accompanied by a broadening of the mesophase interval (see also Figure 2).

In passing from the uncharged TBPE (compound 3) to the double charge bearing THPTE (compound 4), the crystal melting temperature increases even more dramatically than in the preceeding case, from 153 to 240°C. At 240°C a smectic phase develops for THPTE.

The assignments for compounds 2 and 4 were made on the basis of X-ray diffraction pictures taken at temperatures 2–5°C above their DSC melting peaks of 122 and 240°C respectively. These show for the compound 2 a low angle single reflection at $d = 19.8$ Å and a halo centered around 4.2 Å. The value of 19.8 Å is very close to the length of the fully extended molecule of THPHPTE (20.5 Å).

The X-ray diffraction pattern for compound 4 is similar and shows in addition to the 4.2 Å centered halo a single low angle reflection at $d = 20.1$ Å a value very close to the length of the fully extended molecule of THPTE. Both compounds have been therefore assigned an S_A mesophase.

There is only one endotherm for the compound 4 corresponding to C/S_A transition (see Figure 3). Above this temperature the compound displays flow and birefringence. This fluidity is however progressively reduced and finally arrested and the compound becomes insoluble and opaque (dark brown). There is no isotropic transition. Cross-linking of the ethylenic double bond seems to occur before such transition, at temperatures exceeding 240°C. The central double bond of the mesogen is likely to be activated here by the adjacent nucleophilic pyridinium ring.

In summary our results indicate an increase in mesophase stability on introduction of quaternization sites on the mesogen. This is clearly apparent in considering the sequence non-charged THPPE (compound 1, Table IV and Figure 1), mono-quaternized THPHPTE (compound 2) and the diquaternized THPTE (compound 4). Such increase in the mesophase stability may be perhaps explained by the polarizing effect of the

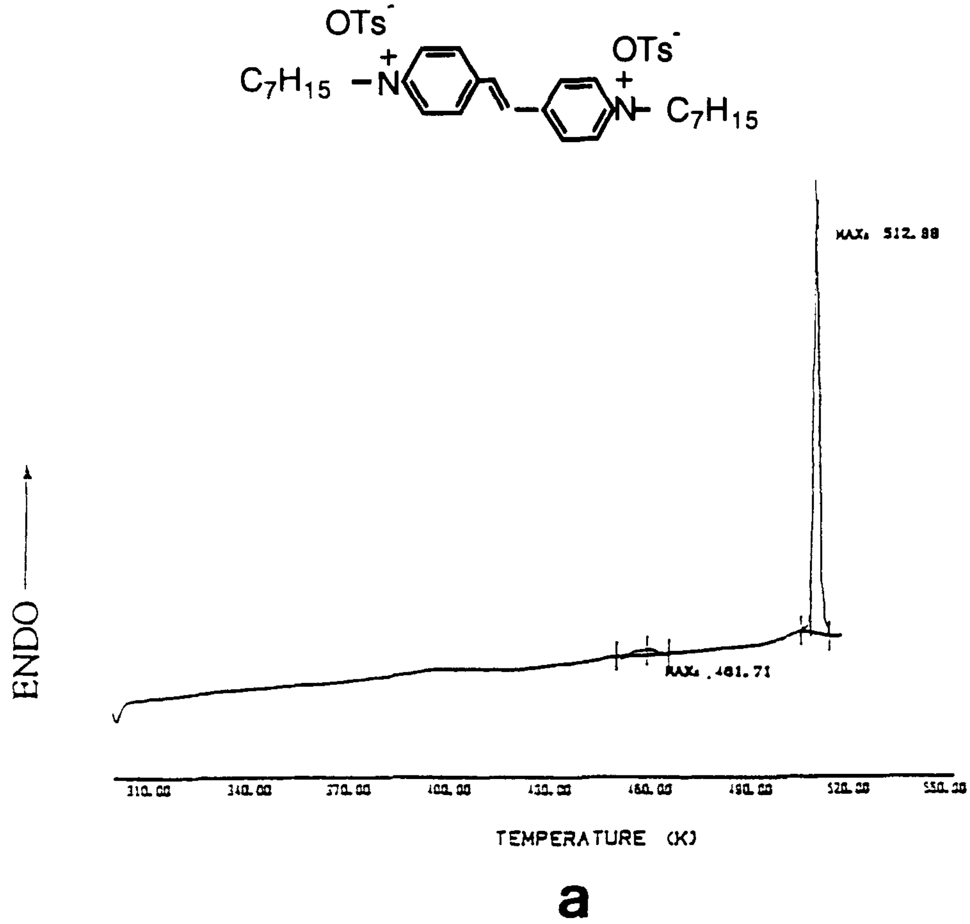


FIGURE 3 (a) Thermogram of THPTE. (b) Polarizing micrograph of THPTE (no isotropisation was observed, the granulated texture of the SA mesophase was arrested after melting of crystals at 240°C). See Color Plate.

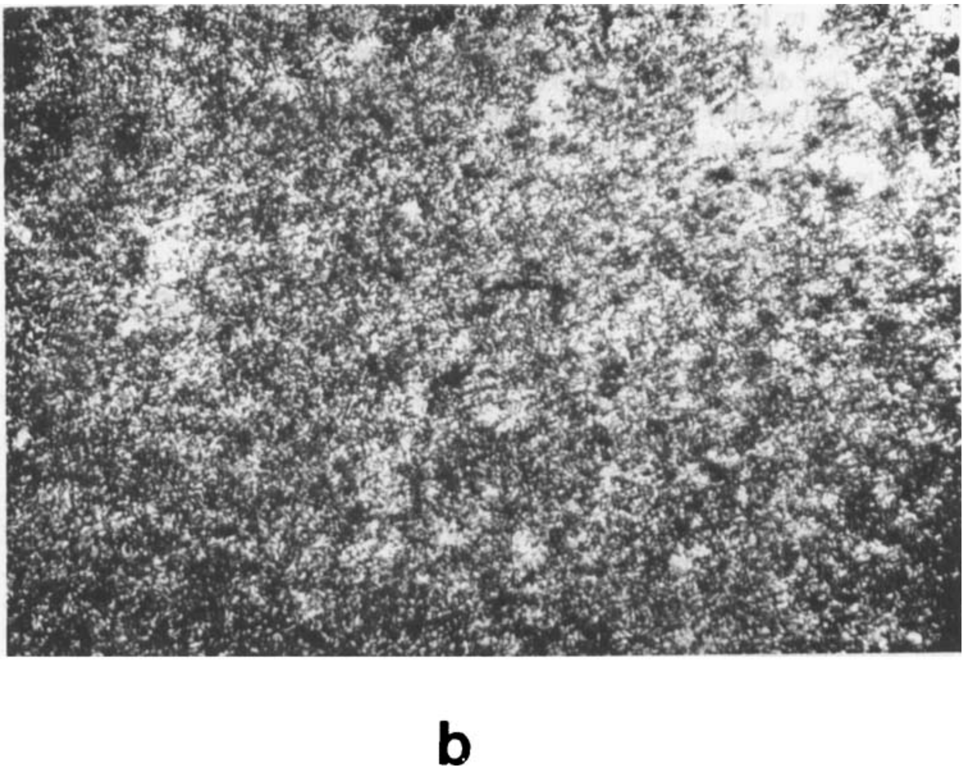
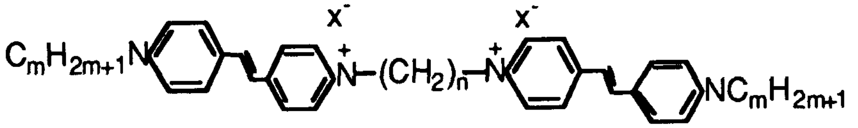


FIGURE 3 *(Continued)* See Color Plate II.

charge on the mesogenic moiety it is however at variance with some predictions from literature.[12]

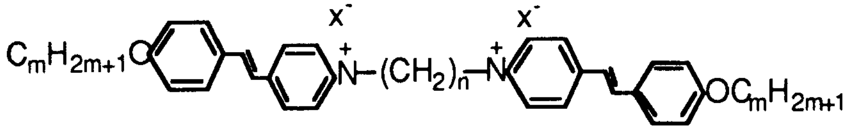
Twin Model Compounds

It is well known that two mesogenic moieties connected through a flexible sequence of atomic groups (such as a polymethylene chain) can simulate in a remarkable way the mesomorphic behaviour of a rigid-flexible main chain polymer (see for example[13-15]). The sequence of methylene units joining the two mesogenic moieties is responsible here for this similarity. Yet such "siamese twin" compounds being of low molecular mass and monodisperse are easier to characterize than polymers. We prepared therefore twin models for ionomers based on trans-1,2-bis(4-pyridyl ethylene) (TBPE) moiety quaternized with difunctional alkyl quaternizing agents such as:



$m = 7$; $n = 7$; $X^- = CH_3SO_3^-, CH_3C_6H_4SO_3^-$

In similarity to low molecular mass compounds such as THPTE(compound 4 of Figure 1) described in the previous paragraph these compounds revealed themself unstable. They darkned and crosslinked rapidly at temperatures above T_m. This lack of stability could possibly be due to the electron deficient nature of the alkyl substituent. The stability was improved considerably by replacing the alkyl with an alkoxy end group leading to 4-alkyloxy-4′-stilbazoles. The following structures were prepared:



here $m = 4,7$; $n = 6,7,8,9,10,12$; $X^- = CH_3SO_3^-$ $CH_3C_6H_4SO_3^-$.

As pointed out above twin dimers are abbreviated by indicating the number *m* of C atoms present in the terminal alkoxy group followed by the first letter of the counterion followed by the number of methylene units in the spacer. Thus the above twin is written: *mnX*.

The above compounds presented a great variety of mesophaes of high breadth and stability. The determination of thermal properties were complicated by broadening of transition peaks, easy supercooling and dependence on thermal history of the sample. Consequently the exact nature of the mesophase was often very difficult to determine. Toluenesulfonate(tosylate) counterions promoted higher transition temperatures than methylsulfonate (mesylate) counterions. Smectic mesophases of higher order were promoted over S_A and S_C mesophases by tosylate counterions. Tables V and VI recapitulate data obtained by DSC for compounds 4*nS*, 7*nS*, 4*nT* and 7*nT* respectively. Although data is presented for several members of this ionic twin family particular attention is given to the representatives with 7 methylene groups in the spacer. This is due to the relatively low transition temperatures and easier formation of characteristic schlieren textures for these compounds.

Figures 4 and 5 present in juxtaposition thermograms (taken at the rate of 10°/min.) and polarizing micrographs of 7,7,*S* and 7,7,*T*. There are at least two endotherms in the thermogram of 7,7,*S* on heating (Figure 4) the first corresponds to a (possibly polymorphic) crystal/mesophase transition, the second to a mesophase to isotropic transition. Above 150°C the sample appears isotropic however the displacement of the cover slip produces bright and dark areas indicating shear orientation (Figure 4a). On cooling a schlieren texture with points of singularity with $s = \pm 1$ (four brush singularity) characteristic of a S_C mesophase appears at 130–120°C (Figure 4b). The sample flows still easily and the schlieren texture is replaced by an undefined texture which under shear (poking of the cover glass) is represented in Figure 4c . The sample solidifies below 50°C giving a granulated texture (Figure 4d).

At 130°C the X-ray diffraction pattern presents a strong and sharp single peak at 40.7 Å in addition to the wide angle halo. This pattern is preserved on quenching the sample to room *t*°. Thus the SAX diffraction pattern confirms an S_C mesophase with a calculated tilt angle (angle between the layer normal and the molecular long axis) of approximately $\Theta = 39$–$40°$ (for a van der Waals length of the molecule of 52.5 Å) for the 7,7,*S* twin compound. It also indicates the rather unusual possibility (for a low molecular mass liquid crystalline compound) of bypassing the crystallization by rapid cooling).

Replacing the mesylate by tosylate counterions one observes two endotherms on heating and only one exotherm on cooling. The peaks are sharper than in the previous case (Figure 5) but the first endotherm at 152°C is much smaller than the second at 169°C indicating the likelihood of a smectic phase of higher order. The sample becomes isotropic above 170°C (microscopy). On cooling to 149–150°C it passes through a transition with a concommitant appearence of a focal conic fan texture illustrated in Figure 5. No crystallization was observed on further cooling. The focal conic fan texture is a natural texture for an S_A or S_B phase. It is difficult in this case to distinguish between them on the basis of microscopy alone. Based on the high value of isotropisation enthalpy we assigned this mesophase to an S_B phase.

At 130°C the X-ray diffraction pattern presents a sharp and strong peak at 37.7 Å and a much weaker (second.order) peak at 18.8 Å. The wide angle halo of the mesylate is replaced with a strong peak at 4.11 Å overlapping with a halo centered at about 4.3–4.5 Å. Such pattern is consistant with a tilted smectic phase of higher order such as a tilted S_B with an angle of tilt $\Theta = 44$–$45°$. This pattern is preserved on quenching the sample to room temperature.

It appears therefore that the replacement of mesylate counterion with tosylate in the 7,7 twin promotes mesophases of higher order and higher thermal stability and that in both cases crystallization is bypassed by rapid quenching.

TABLE V

Transition temperatures for twin model compounds 4,n*S* and 7,*nS*

Compound	Transition temperature °C
4,6S	C217I I162S
4,7S	C122S166I I110S
4,8S	C201I I167S
4,9S	C145I I130S
4,10S	C129S169I I144S117C
4,12S	C155S188I I180S
7,6S	C122S216I I182S104C
7,7S	C119S144I I145S106C
7,8S	C180I I177S
7,9S	C130S152I I133S
7,10S	C150I I130S
7,12S	C210I I151S

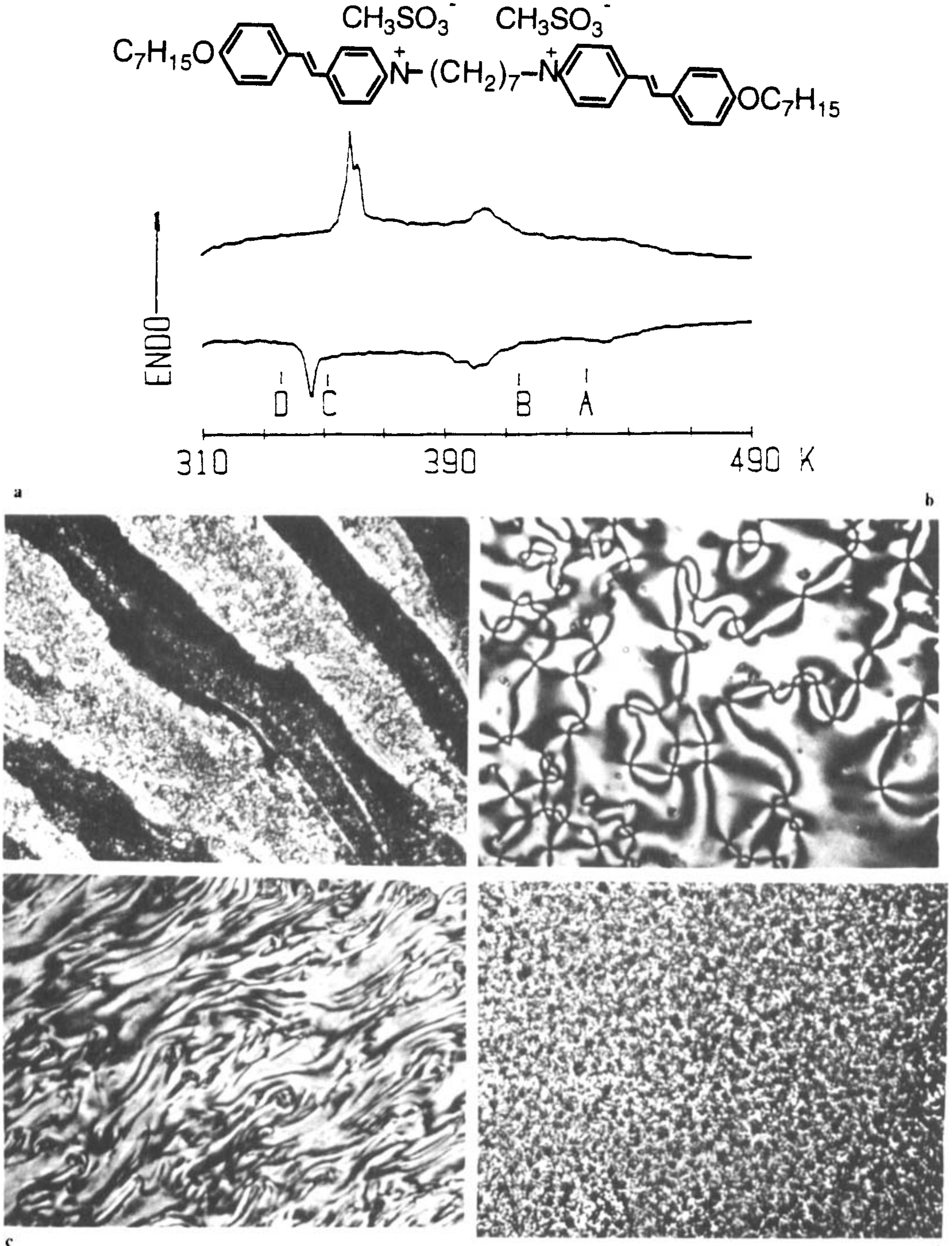


FIGURE 4 Thermogram and micrographs of textures of the 7,7*S* ionic twin model compound (in juxtaposition) at different temperatures. See Color Plate III.

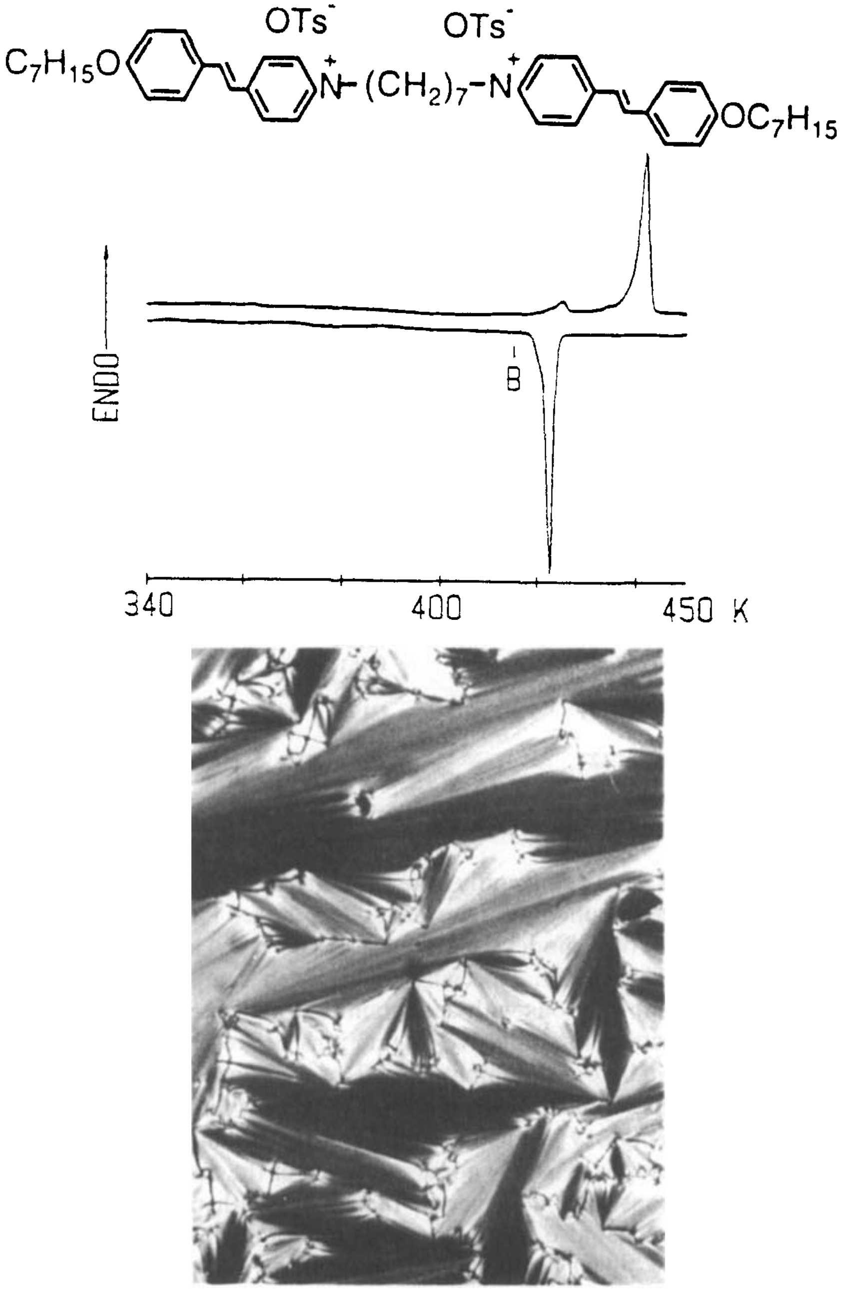


FIGURE 5 Thermogram and micrograph of textures of the 7,7*T* ionic twin model compound. See Color Plate IV.

Our data in Tables V and VI show that an odd-even effect of the isotropisation temperature T_i takes place for the 4,*nS* and 7,*nS* as well as for 4,*nT* and 7,*nT* series on heating and on cooling. This effect (on heating) is illustrated in Figure 6 and Figure 7. Here T_i decreases with increasing number *n* of methylene units in the spacer. The

TABLE VI
Transition temperatures for twin model compounds 4,*nT* and 7,*nT*

Compound	Transition temperature °C
4,6T	C251S269I I239S
4,7T	C142S162I I106S
4,8T	C206S217I I192S
4,9T	C155I I99S
4,10T	C234I I176S
4,12T	C191S219I I195S
7,6T	C263I I251S
7,7T	C152S169I I149S
7,8T	C2261 I212S
7,9T	C161S180I I146S
7,10T	C191I I162S
7,12T	C114S192I I182S94C

compounds with *n* odd have significantly lower T_i than the even. This is not surprising as such effects have been abundantly reported and discussed for low molecular mass compounds (see f.ex.[16]), twin model compounds(see f.ex.[13–15]) and main-chain polymers (see f.ex.[17–20]) The spacer, especially in the even samples tends to assume preferentially trans conformations with concommitant higher mesophasse stabilities than in odd ones. Electrostatic repulsive interactions between mesogens make this effect particularly sallient here as the amplitude of T_i oscillations can reach nearly 100°C.

The stability of the mesophase does not appear to be very sensitive to the nature of the terminal group (heptyloxy versus butoxy) while the stabilizing effect of tosylate counterions on the mesophase is very apparent. Most of the above twin compounds with tosylate counterions have a higher T_i than those with mesylate counterions. Tosylate counterions appear also to influence the formation of higher molecular order in the mesophases. The higher assymmetry, polarizability and packing ability of the aromatic tosylate counterion are factors here.

Figures 8–11 give DSC thermograms and textures for some of the synthesized twin compounds. Thermograms show endotherms related to the crystal to smectic transition, and smectic to isotropic transition. In the case of 4,12*T* for example DSC thermograms display two endotherms during heating: the first is small and corresponds to the melting of crystals; the second is relatively large and corresponds to a mesophase/isotropic transition. The mosaic texture is characteristic of a smectic mesophase

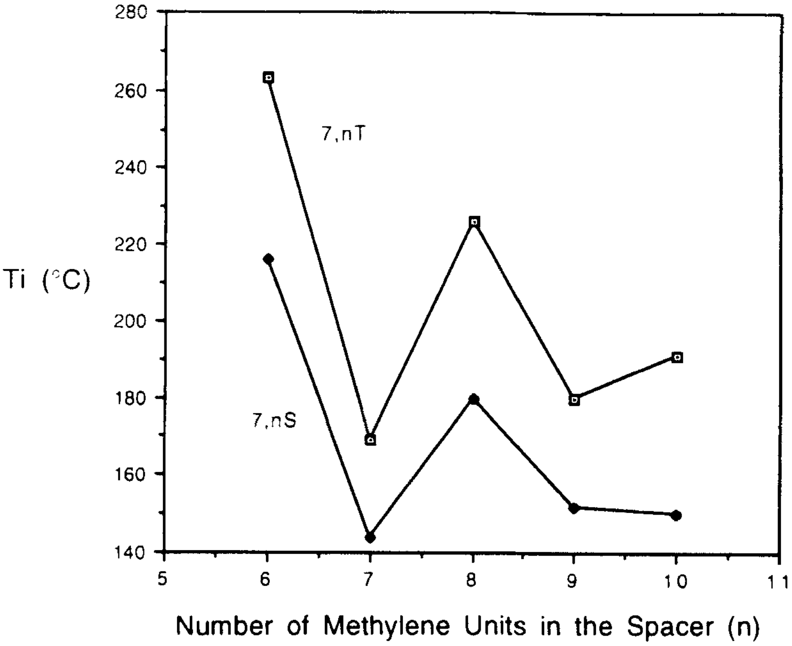


FIGURE 6 The odd-even effect of isotropisation temperature T_i of the 7,*nS* and the 7,*nT* series of the ionic twin model compounds.

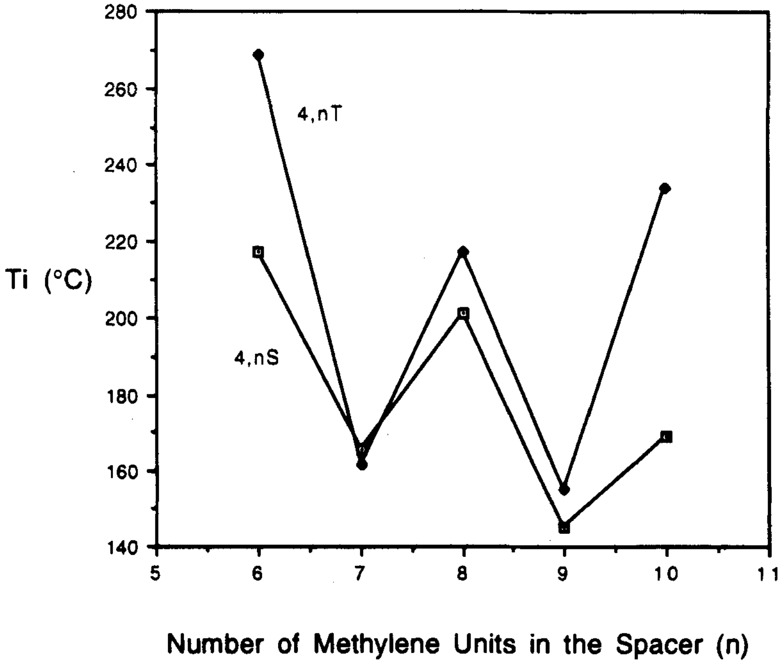
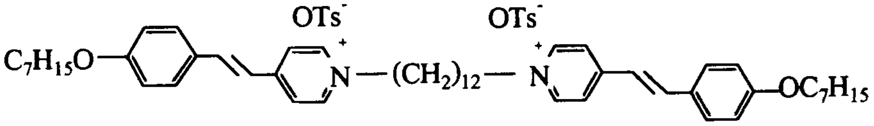
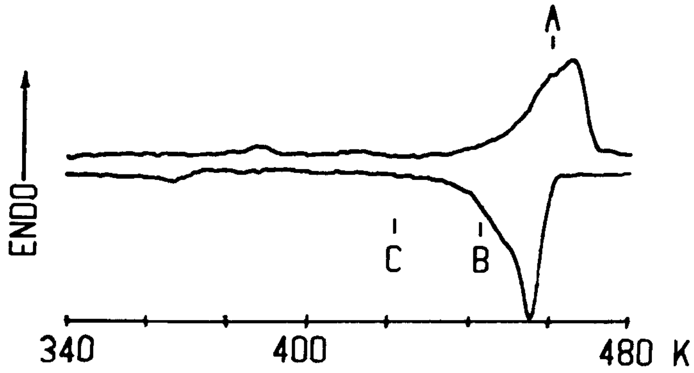
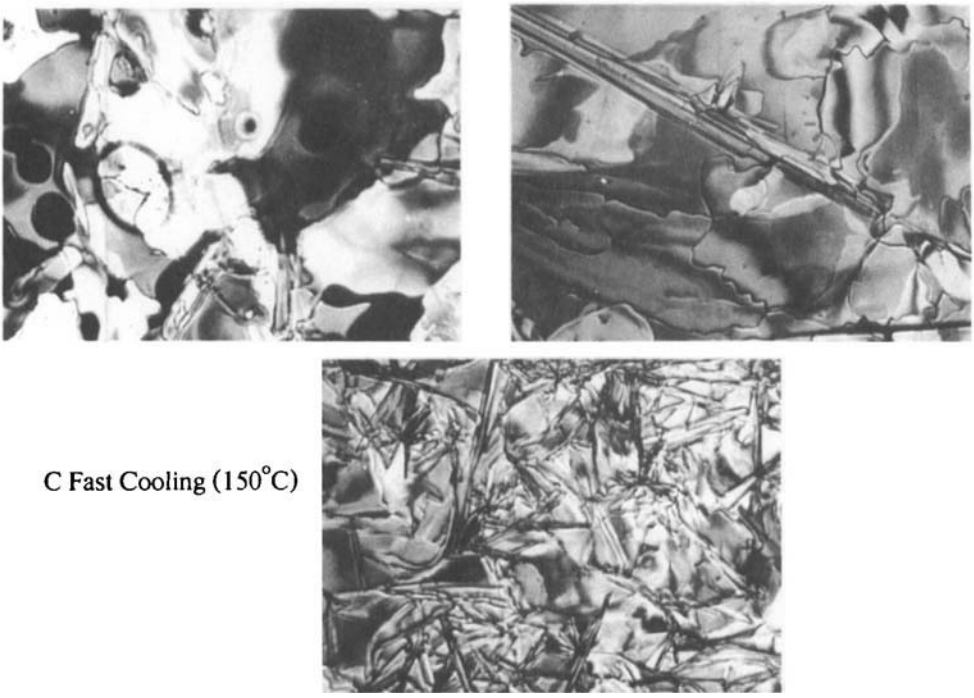


FIGURE 7 The odd-even effect of T_i for the 4,*nS* and the 4,*nT* series of the ionic twin model compounds.



(7,12T)



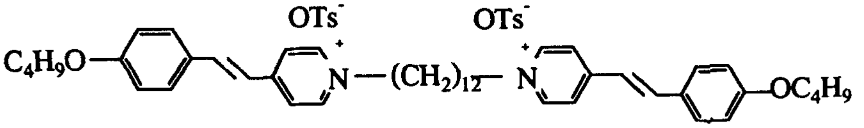


A (186°C)

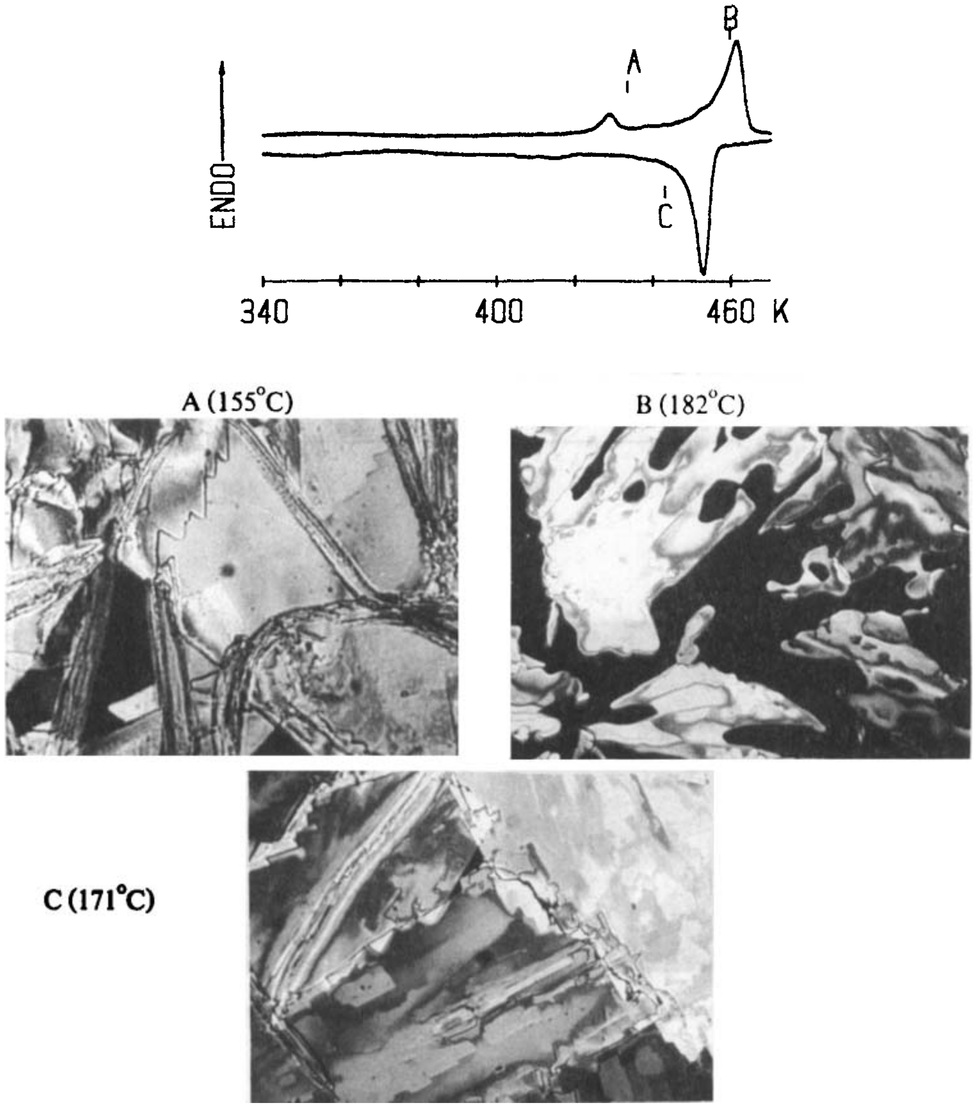
B (180°C)

C Fast Cooling (150°C)

FIGURE 8 Thermogram and micrographs of the 7,12*T* ionic twin model compound. See Color Plate V.



(4,12T)



A (155°C)

B (182°C)

C (171°C)

FIGURE 9 Thermogram and micrographs of the 4,12*T* ionic twin model compound. See Color Plate VI.

of higher order. In the case of the 7,6*S* (Figure 10) the first sharp endotherm is related to the transition from crystal to a higher order mesophase, the second sharp endotherm appears to be related to a transition to a lower order smectic whilst the small and broad peak about 195°C corresponds to the isotropisation of the compound. On cooling it is

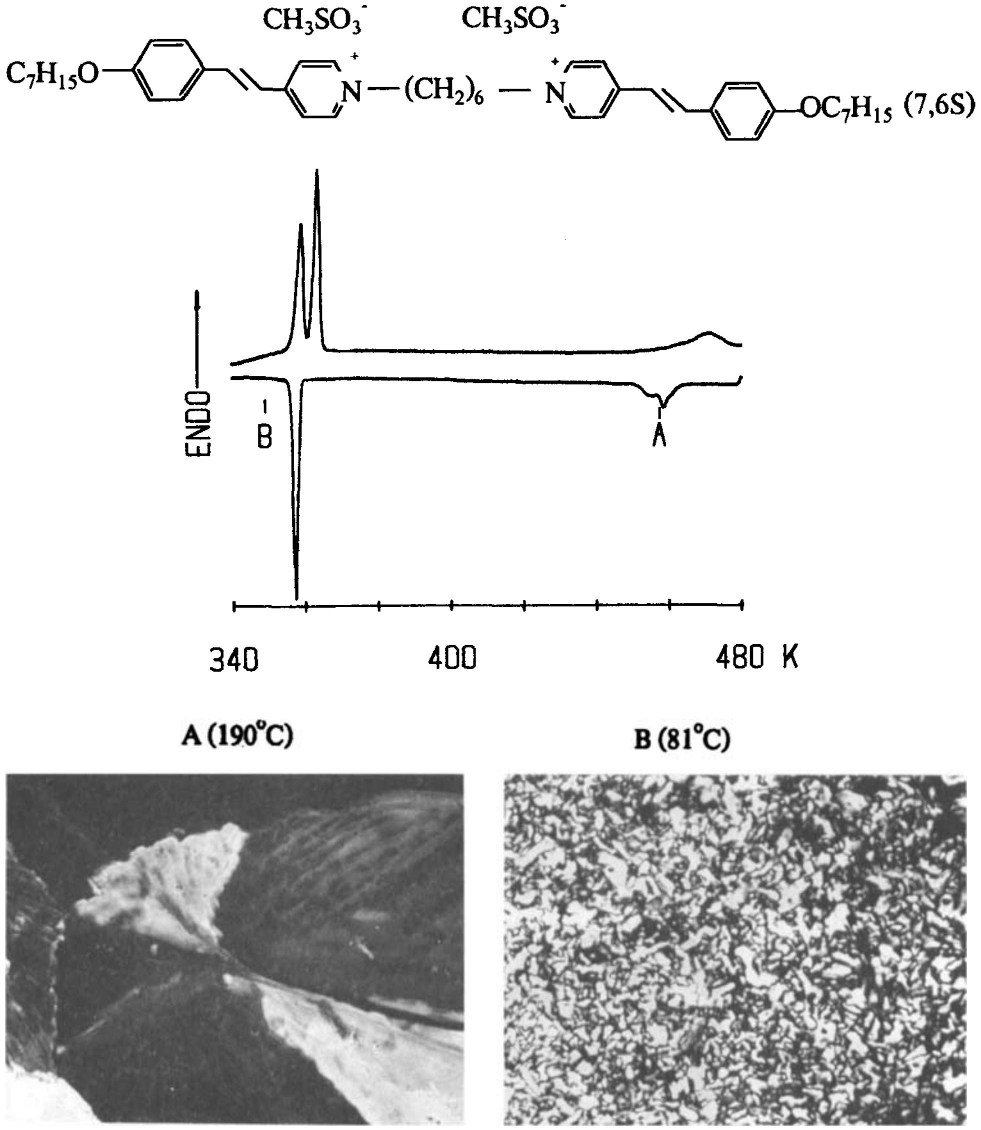


FIGURE 10 Thermogram and micrographs of the 7,6*S* ionic twin model compound. See Color Plate VII.

possible to bypass the crystallization peak. Some twin compounds such as 8,7*T* are clearly crystalline. (Figure 11)

Typically, ionic twins supercool easily. Supercooling is easier for twins with odd rather than even spacered mesogens and for mesylate rather than even spacered mesogens and for mesylate rather than tosylate counterions. Thus 7,7*T* supercools easier than 7,8*T* and 7,12*T* which crystallize under the same conditions while 7,7*S* is even easier to supercool than 7,7*T*.

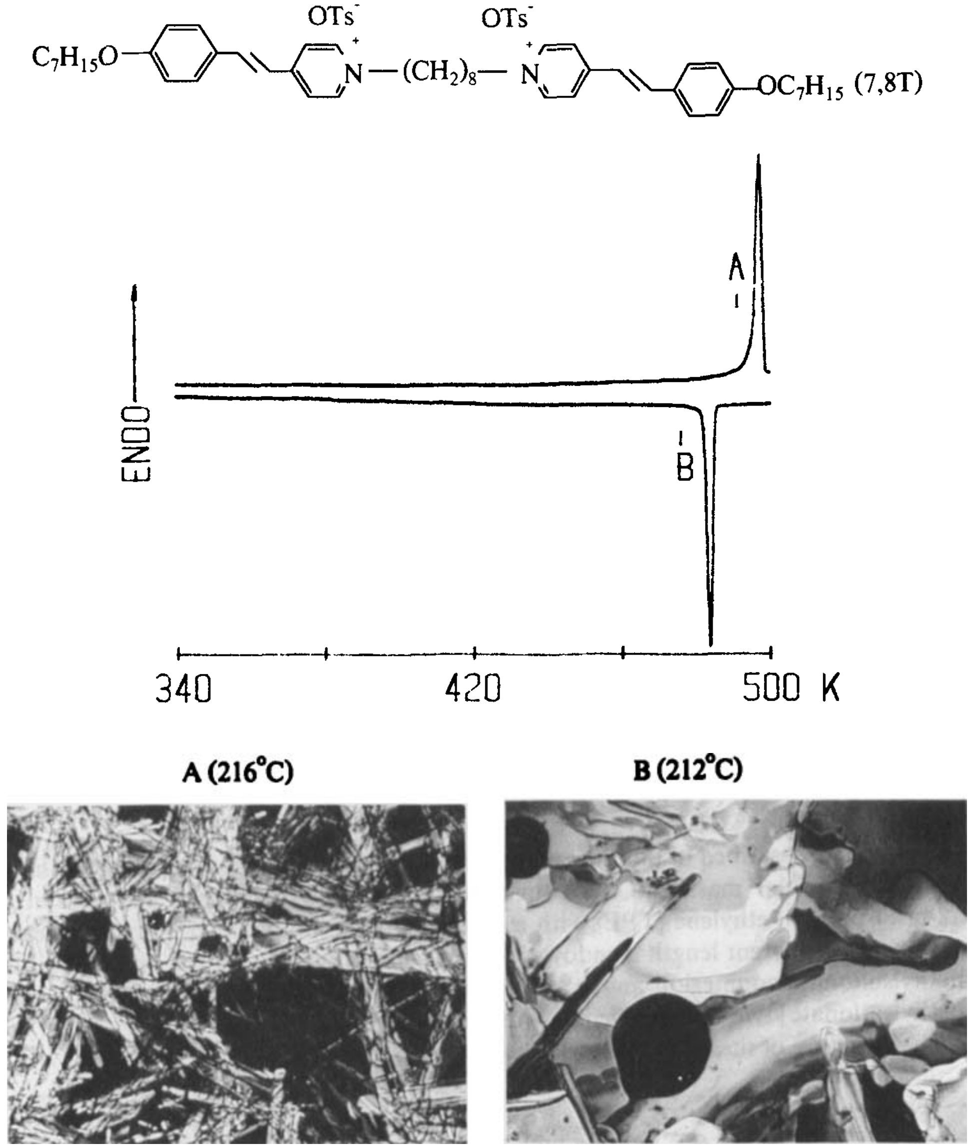
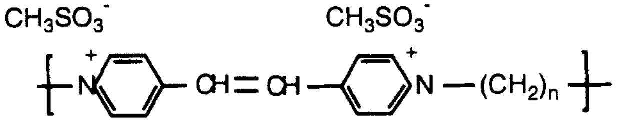


FIGURE 11 Thermogram and micrographs of the 7,8T ionic twin model compound. See Color Plate VIII.

Sensitivity to the thermal history make assignment of mesophases difficult, and although many members of the homologous series of twins exhibit focal conic or mosaic textures, an assignment of the nature of the smectic phase could be made in a few cases only. Such difficulties are not typical of low molecular mass liquid crystals which in contrast to the above compounds usually crystallize and transit reversibly and

TABLE VII

Intrinsic viscosity [η] and molecular weight (Mw) of poly(TPEMn)



n	$[\eta]_{\gamma}-0$[a] (dl/g)	Mw[b] (g/mole)
6	0.38	14000
7	0.29	11000
8	0.35	14500
9	0.32	12000
10	0.20	10200
12	0.22	10700

[a] Intrinsic viscosity measured in 0.4 M aqueous $CH_3SO_3^-Na^+$ solution at 30%C.

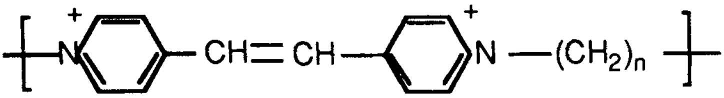
[b] Measured in 0.4 M aqueous $CH_3SO_3^-Na^+$ solution at 30°C. $\lambda = 632.8$ nm $dn/dc = 0.2\ cm^3/g$.

without significant supercooling. Strong intermolecular electrostatic forces promoting long molecular relaxation times and opposing flow could here again be responsible for such behaviour in the charged twin compounds.

Polymers

The polymers described in this paragraph bear the same rigid mesogenic moiety than the low molecular mass and the twin model compounds described above: trans-1,2-bis(4-pyridyl) ethylene (TPE) with a flexible spacer composed of polymethylene sequences of different length n endowed with a counterion X^-. Thus a polymer with methylsulfonate counterion and $n = 7$ or poly[1,2-bis(4-pyridinium heptyl)ethylene methylsulfonate] will be identified as poly(TPEM7).

The structure of these polymers is as follows:



$$n = 6, 7, 8, 9, 10, 12;$$

$$x = CH_3SO_3^-, CH_3C_6H_4SO_3^-, Cl^-, Br^-, I^-, ClO_4^-$$

Some properties of the above polymers were described in a preliminary publication.[7] Table VII shows the weight average molecular mass of various polymer samples used in this study which is between 10,000 and 15,000 g/mole as well as the intrinsic viscosity extrapolated to zero shear. All measurements were done in 0.4 M aqueous sodium methyl sulfonate.

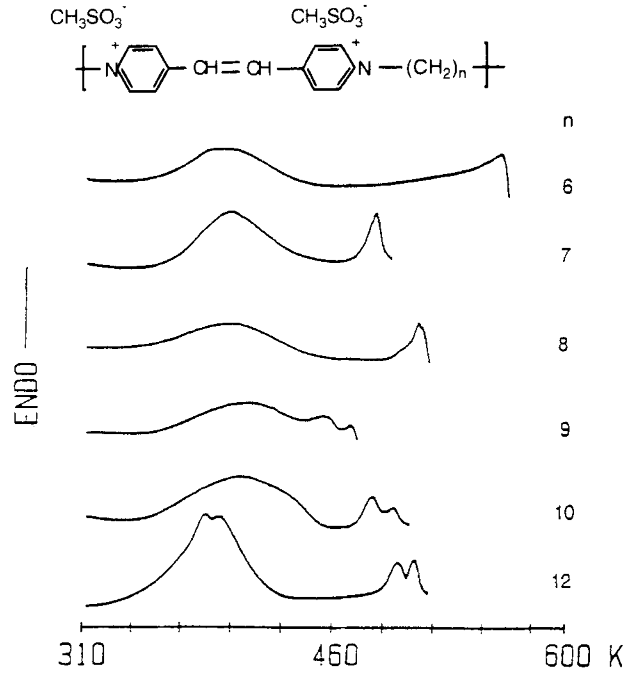


FIGURE 12 Thermograms of the poly(TPEMS) ionic polymers on heating.

Figure 12 gives some typical DSC thermograms obtained on heating for the series of poly(TPMn). It was found that these ionomers display typically two DSC endotherms at T_1 and T_2, the first rather broad, centered around 130°C, the second sharper than the first located at a temperature dependent on the particular polymer and in some cases (polyTPEM9,10 and 12) giving a doublet or a shoulder (see Figure 12). Given the narrowness of the interval between these doublets it was not possible to decide whether they are due to the formation of an additional mesophase or to recrystallization.

The nature of the first peak was assigned to hydration it was discussed in an earlier publication.[7] While the position of the first peak was independent of *n*, the position of the second peak varied with *n* according to an oscillating odd-even mode which is illustrated by Figure 13 and Figure 14 and in the Table VIII.

The X-ray diffraction indicates crystallinity in these polymers. This crystal pattern weakens somewhat on heating but is present up to T_2. This can be seen in Figure 15, indicating that crystallinity for poly(TPEM7) is present up to T_2. No new phase formation associated with "ionic clustering"[22] was detected here.

On rapid heating above T_2 (second peak) poly(TPEM7), poly(TPET7), poly(TPEM9) and poly (TPET9) displayed simultaneous flow and birefringence. At this point the X-ray pattern becomes that of a smectic of lower order with a peak at low angles and a halo at about 4.0 Å. This pattern can be preserved by quenching to below T_2. Polarizing microscopy and the X-ray pattern indicates therefore that the second peak corresponds

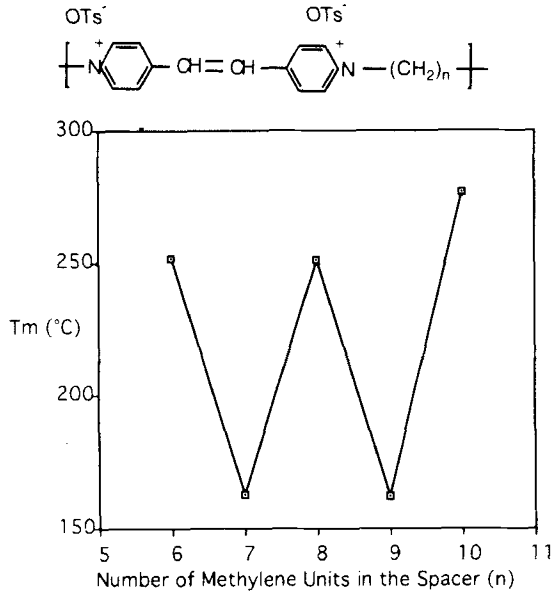


FIGURE 13 The odd-even effect of *Tm* for the poly(TPETn) (on heating).

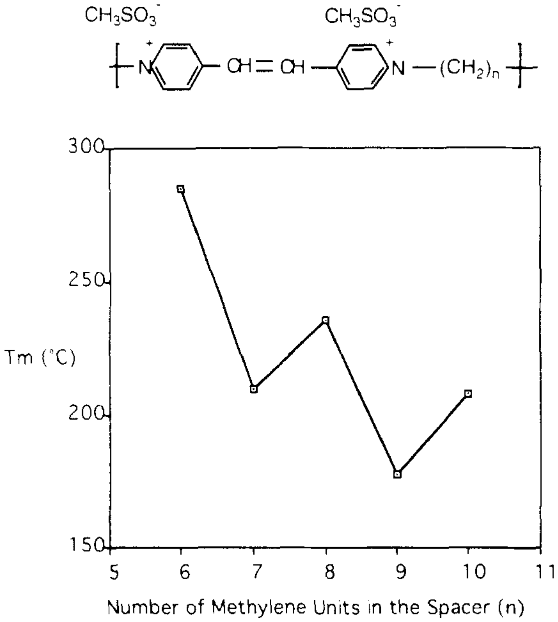
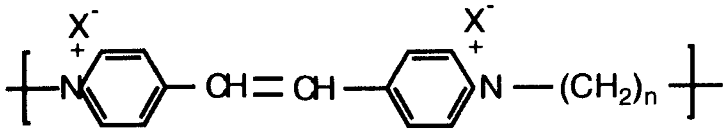


FIGURE 14 The odd-even effect of *Tm* for the poly(TPEMn) (on heating).

to a crystal/smectic transition. For TPEM7 for example the X-ray diffraction peak is at $d = 18.2 \pm 0.5$ Å (length of the r. u. = 18.7 Å). This suggests that the repeating unit has a tendency to orient normally to the plane of the layers and that the smectic phase is of the S_A type. The X-ray pattern remains similar on replacing the mesylate counterion by

TABLE VIII

Transition temperatures and enthalpies for poly(TPEMn) and (TPETn)



$n = 6, 7, 8, 9, 10, 12$; $X^- = CH_3SO_3^-, CH_3C_6H_4SO_3^-$

counterion	n	6	7	8	9	10	12
$CH_3SO_3^-$	T_1 (K)	390	397	398	405	400	382
	ΔH_1 (kJ/r.u.)	6.48	7.90	9.36	6.98	7.11	10.03
	T_2 (K)	558	483	508	451	481	506
	ΔH_2 (kJ/r.u.)	15.26	8.15	9.28	10.12	9.11	12.83
$CH_3C_6H_4SO_3^-$	T_1 (K)	395	400	402	407	402	392
	ΔH_1 (kJ/r.u.)	7.73	7.94	10.45	7.52	7.52	10.45
	T_1 (K)	525	436	524	435	550	536
	ΔH_2 (kJ/r.u.)	6.27	7.94	9.20	7.11	7.11	9.07

the tosylate with the exception of the low angle X-ray diffraction peak which is very slightly shifted to $d = 19.0 \pm 0.5$ Å again indicating an S_A mesophase. Similarly to poly(TPEM7) and poly(TPET7) the crystalline X-ray pattern of the poly(TPEM9) disappeared at T_2 and was replaced by a pattern of a smectic phase of lower order with a sharp small angle diffraction ring at 22 Å (length of the r. u. = 21.1 Å) and of a broad halo at about 4 Å. This data suggest that in this case also an S_A mesophase prevails.

If the sample is maintained above T_2 the mobility of the birefringent phase is rapidly reduced and finally arrested. Samples with halogen counterions darkened more rapidly than polymers with sulfonate counterions at this temperature. At this stage the polymer becomes rapidly insoluble suggesting crosslinking. Typical TGA analysis (performed on carefully dehydrated poly(TPEM7)) showed no significant weight loss up to 350°C, thereby confirming that crosslinking is the process limiting the flow of the mesophase at temperatures above T_2.

Effect of the Counterions

The effect of counterions on the magnitude of both DSC endotherms was investigated for the poly(TPEX7). Table IX gives T_1, T_2 and the corresponding enthalpies ΔH_1 and ΔH_2 for various counterions X^-. As already pointed out above ΔH_1 is related to the dehydration process. Its magnitude depends strongly on the nature of the counterion and on the thermal history of the sample. In the halogen series ΔH_1 linearly decreases with 1/(radius of the counterion) as can be seen in Figure 16. This suggests that the electric field at the counterion surface plays an important part in this process (possibly through ion-dipole interactions). Ions of more complicated geometry than spherical were not considered in the graph.

The meaning of ΔH_1 is however not completely clear as polymers with the highest ΔH_1 values (polymers with Cl^- and Br^- counterions) are less soluble in water than

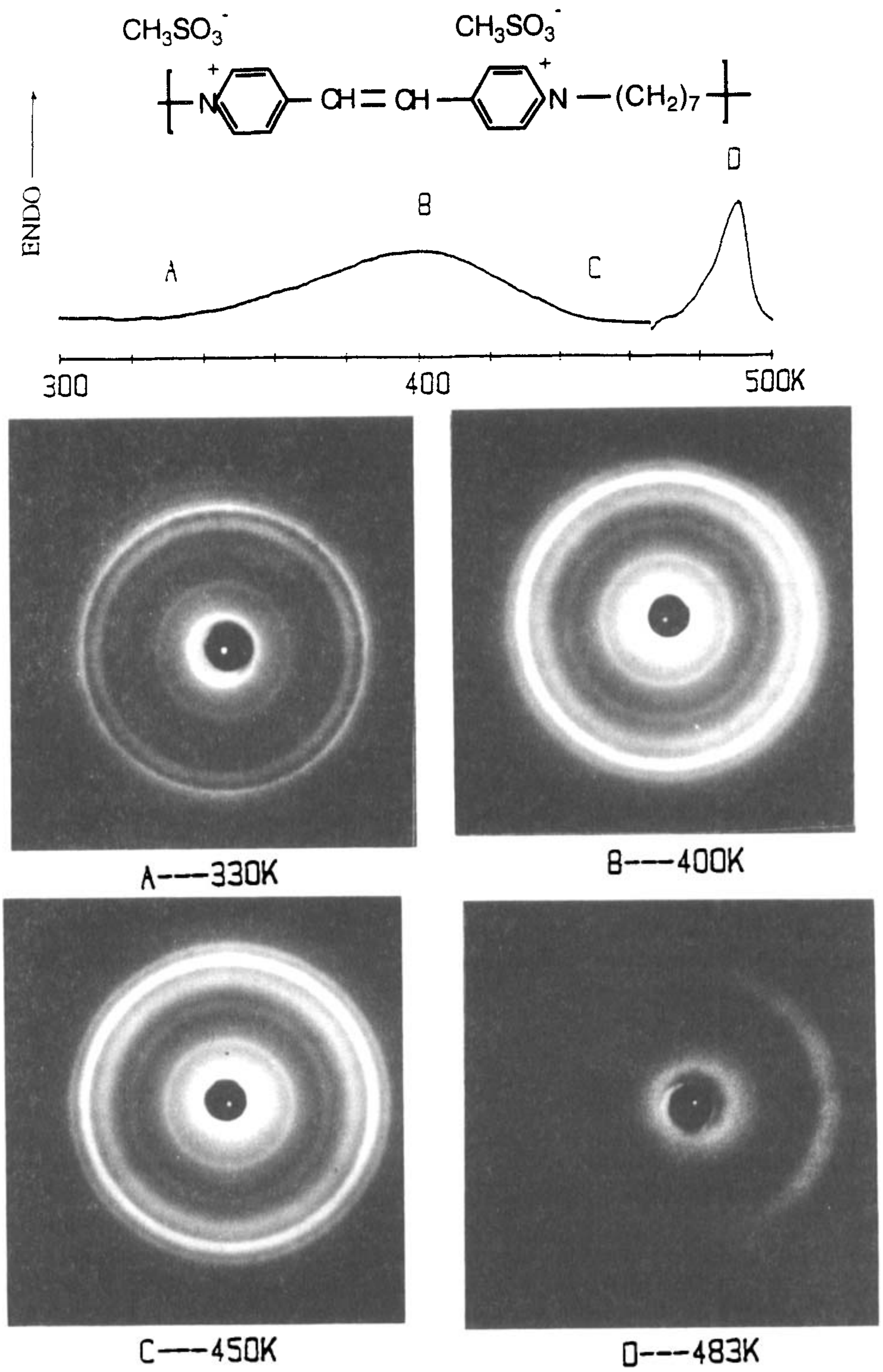
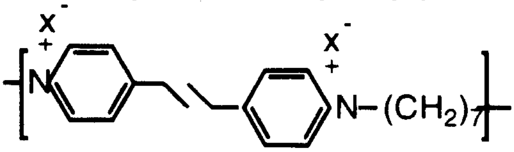


FIGURE 15 X-ray (Laue) diffraction patterns at different temperatures given along the DSC thermogram for poly(TPEM7).

TABLE IX

Transition temperatures and enthalpies for poly(TPEX7)



$X^- = Cl^-, Br^-, I^-, ClO_4^-$

counter ion X	T_1 K	ΔH_1 kJ/r.u.	T_2 K	ΔH_2 kJ/r.u.
Cl^-	416	61.57	543	10.99
Br^-	415	41.01	525	9.53
I^-	392	20.02	479	1.71
ClO_4^-	362	12.37	–	–

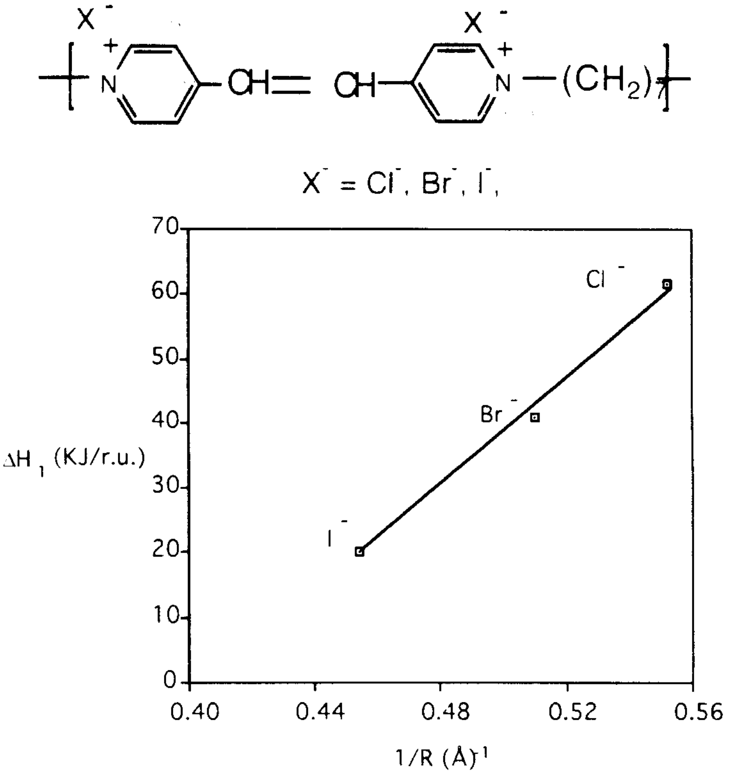


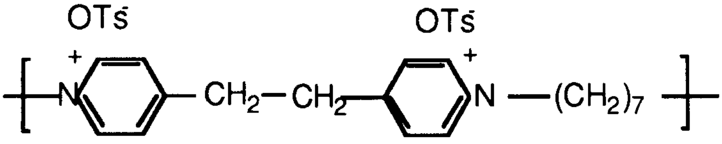
FIGURE 16 Hydration enthalpy ΔH_1 plotted against 1/ionic radius of counterion (R) for the halogen series of poly(TPEX7).

polymers with mesylate or tosylate counterions for which ΔH_1 is smaller (see Table IX). Apriori one would expect the opposite if a simple correlation between ΔH_1 and the degree of hydration were prevalent. It is possible that the departure of hydration water is here connected to a polymorphic crystal/crystal transition. More studies performed on a full range of counterions are necessary to understand the mechanism of hydration and dehydration of these ionic polymers.

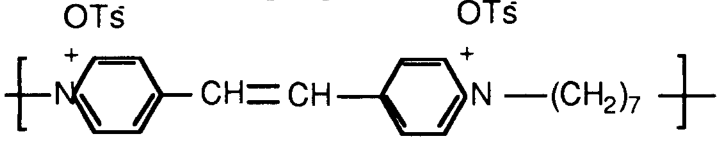
It is apparent from Table IX that the counterion influences both, the degree of crystallinity (ΔH_2) and the crystal/liquid crystal transition temperature T_2. The increase of the size of the counterion decreases both parameters. Thus in the halogen series the degree of crystallinity decreases substantially from Cl^- to Br^- to I^-. While the X-ray pattern of polymers with $Cl^-$and Br^- displayed decreasing crystallinity at room temperature, little crystallinity could be detected for the I^- containing polymer. The values of T_2 are high for polymers with halogen counterions. No mesophases were detected above T_2 as samples crosslinked and darkened rapidly making the microscopic observation impossible. Similarly the polymer with the large ClO_4^- counterion did not show any mesophases or crystallinity. In contrast to the halogen and perchlorate ion containing polymers polymers containing organic counterions such as methanesulfonate and toluenesulfonate do not fit this trend as significant crystallinity is present in both, poly(TPEM7) and poly(TPET7) inspite of the size of the counterion. Also, lower T_2 than in the case of halogens allow for an identification of the mesophase which can also be easily quenched by rapid cooling to room temperature before the crosslinking and oxydation sets in. Finally, polymers with halogen counterions in addition to having high T_2 appear to be less thermally stable than those with organic mesylate or tosylate counterions.

Nature of the Mesogen

In order to check the influence of the mesogenic trans-1,2-bis(4-pyridyl ethylene moiety on the formation of mesophase we have synthesized the poly[1,2-bis(heptylpyridyltoluenesulfonate)ethane] (PTET7) and compared it to the corresponding poly(trans-1,-bis(4-pyridyl)ethylene or poly(TPET7).



poly (PTET7)



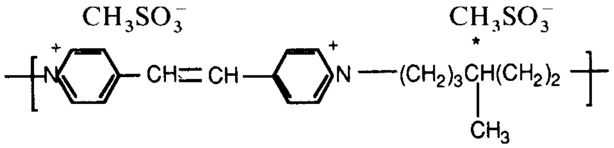
poly (TPET7)

The molecular mass of this unconjugated flexible and stable ionomer was in the range of 10,000 g/mole, similar to poly(TPET7). This polymer was exclusively crystalline with an observed melting point of C186°I and a single ΔH of 176 J/g (6.37 kJ/mole) on heating displaying a single crystallization point of I 155°C and a single ΔH of 17.1J/g (6.19 kJ/mole) on cooling. These transitions were reversible. No transition to a liquid crystalline state was observed. This can be compared with the transition at 170°C from crystal to an S_A mesophase with a ΔH_2 of 9.7 J/g (3.50 kJ/mole) for poly(TPET7). The absence of mesophase in the ethane analogue of the poly(TPET7) suggests that the conjugation between the two pyridine rings is indispensible for mesophase formation quite independently from the presence of charges and counterions on the chain and that in analogy to flexible main-chain polymers a rigid mesogenic moiety is a factor favoring the formation of liquid crystalline phases in main chain ionomers as well. It is interesting to recall that an ionomer based on halogen salts of a shorter but also conjugated bipyridinium moiety incorporated into a flexible main chain was described by Samulski as "yielding ill resolved and complex transition phenomena"[1] our observations using optical microscopy indicated that such melts do display liquid-crystallinity.

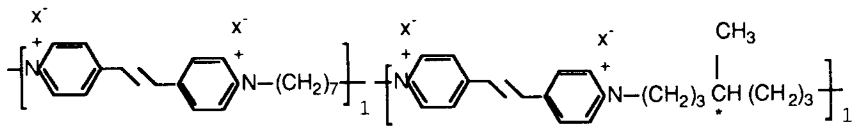
Nature of the Spacer

From the preceding section it is clear that the parity and the length of the spacer affects the transition temperature T_2. We have shown that odd numbered spacers and mesylate counterions provide for lower T_2 than even numbered spacers and tosylate counterions. Nevertheless T_2 is still to high to insure stability of the smectic phase. We have therefore tried two well known approaches to decrease T_2 by modifying the nature of the spacer.

The first approach consisted to replace a linear with a branched spacer such as the (+)3-methylhexane:



An even more pronounced lowering of T_2 could be expected from a copolymer of statistically mixed branched and linear spacers such as:

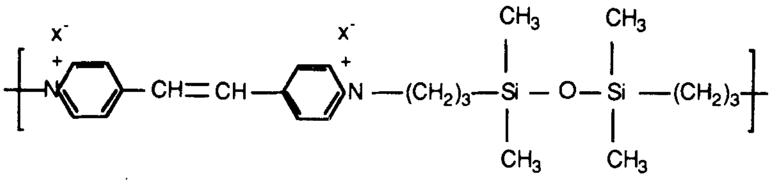


$$X = CH_3SO_3^-, CH_3C_6H_4SO_3^-$$

The DSC thermograms of these copolymers were very similar to the linear homopolymers discussed in the previous paragraph.

For the homopolymer with the branched, chiral group in the spacer the thermogram displays 2 endotherms, one very broad centered about 140°C, the second corresponding to the transition from crystal/smectic centered about 225°C. Thus T_2 is not lowered by the methyl substitution alone. The ionic copolymer with statistically mixed spacers and mesylate counterions displays in addition to the broad dehydration endotherm centered at 140°C a second and sharper endotherm at T_2 of 160°C. This transition temperature is significantly lower than that of the homopolymer. Under microscope the sample displays birefringent viscous flow soon arrested above 160°C. The mobile texture of the mesophase is similar to the texture of the poly(TPEM7). Judging by the mobility of this mesophase in analogy to the poly(TPEM7) we are inclined to assign it to a smectic of lower order.

The second approach consisted in replacing the alkyl spacer with 1,3 bis propyl tetramethyldisiloxane spacer:



$x = CH_3SO_3^-, CH_3C_6H_4SO_3^-$

Such replacement is known to lead to significant lowering of transition temperatures in rigid-flexible thermotropic linear polyesters.[22] This siloxane spacered polymer (with the mesylate counterions) is characterized by a rather strong endotherm at 114°C followed immediately by a broader (peak at 137°C) (see Figure 17). These transitions were reproducible on heating and cooling (97°C and 85°C). Under microscope birefringent flow occurs at 114°C indicating the presence of a mobile mesophase with an undefined texture that could be either nematic or smectic of lower order. Based on the value of ΔH we tentatively assign it to the latter. At 137°C the fluid becomes isotropic. Thus in contrast to alkyl spacered ionic polymers stable linear liquid crystalline ionic polymers with much lower transition temperatures are obtained by introducing a few siloxane bonds into the spacer. Such liquid crystalline polymers can be comfortably studied throughout the complete interval of mesophases extending into the isotropic phase without danger of decomposition or crosslinking.

Lyotropic Mesophases

If a solvent is totally miscible with a liquid crystalline compound there ought to be a critical concentration above which lyotropic liquid crystallinity is displayed. In the majority of cases this concentration is extremely high because of the fast destruction of molecular order by a non mesomorphic solvent. The investigation of such systems becomes consequently very difficult. This becomes obvious if one tries to study solutions of the above polymers and their model compounds: the diffusion of solvent (water) into the crystals of the twin model compounds with mesylate or tosylate counterions is so fast and complete that we have not been able to experimentally determine this critical concentration which certainly is very high.

In the poly(TPEXn) series only the mesylates and tosylates are soluble enough to give on swelling with water lyotropic mesophases of sufficient stability to be studied. Figure 18 gives the critical concentration of the poly(TPEM7) in water for the birefringence to be observed as a function of temperature (determined by diffusion of known amounts of water into carefully preweighed samples of the polymer placed in tubes of small diameter). Several colored textures could be obtained in placing a drop of

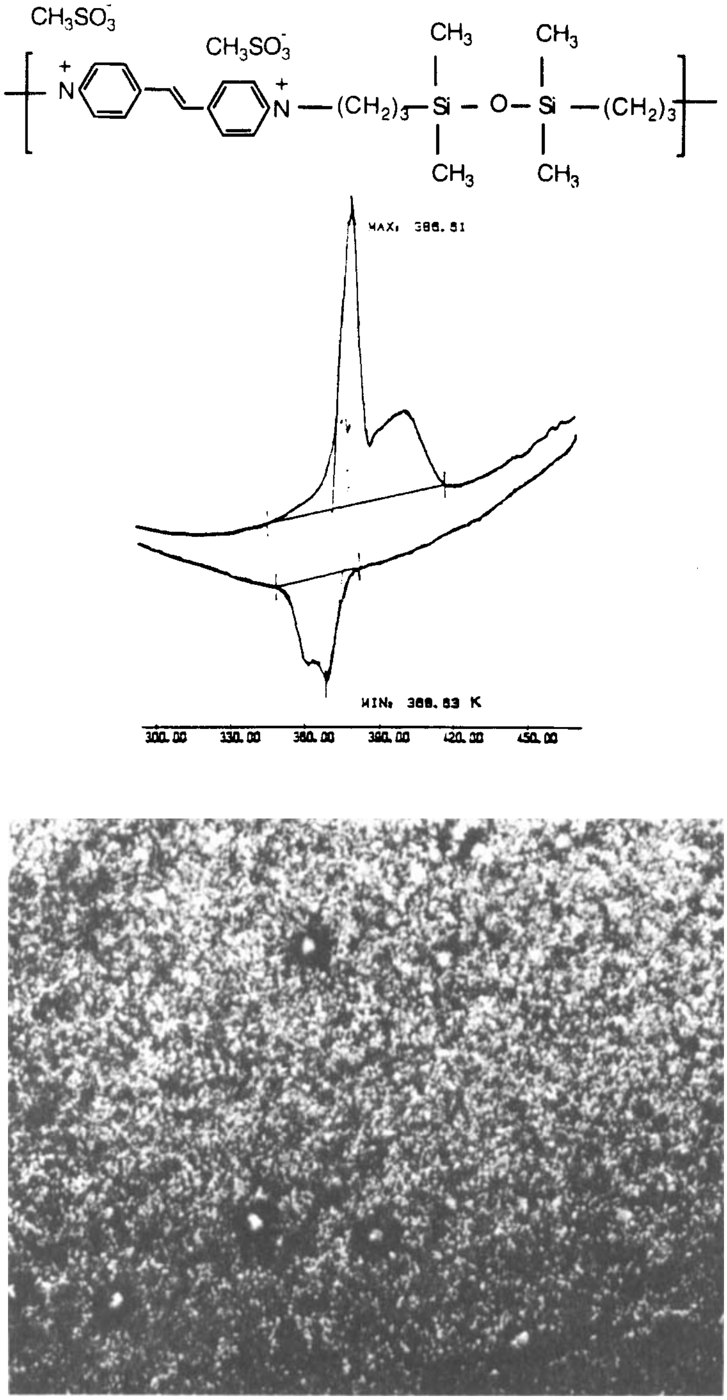


FIGURE 17 Thermogram and micrograph of the mesophase of the ionic polymer with spacer containing siloxane units (micrograph taken at 85°C on cooling from the isotropic phase). See Color Plate IX.

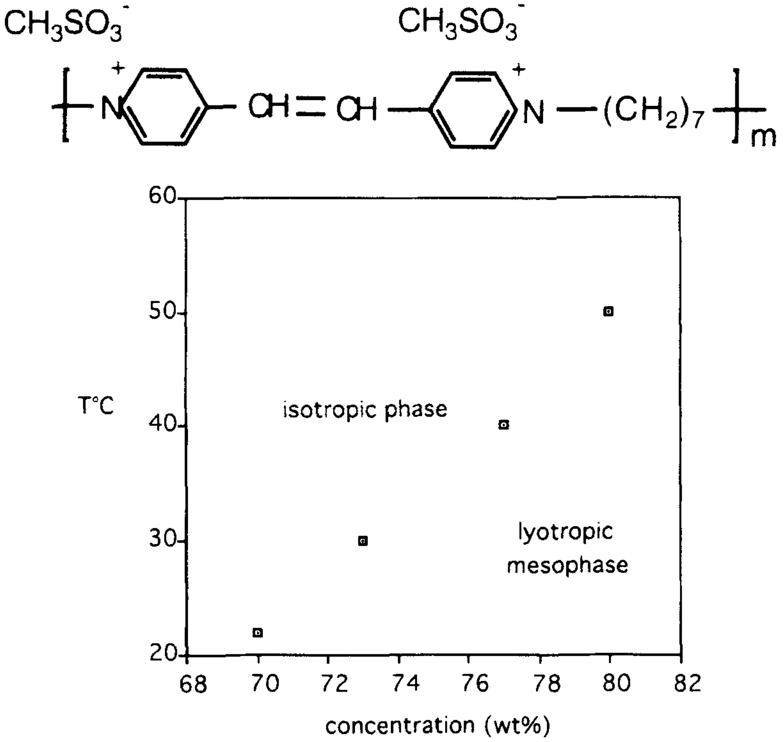


FIGURE 18 Critical concentration for lyotropic mesophase formation for poly(TPEM7) in water at various temperatures.

water in contact with a film of polymer between slide and cover glass and observing the sequence of mesophases as solvent diffused into the polymer. Thus in the case of $n = 8$ and $n = 10$ such as poly(TPEM8) poly(TPET8) as well as poly(TPEM10) and poly(TPET10) at least 2 different colored textures were observed. For $n = 7$ only one colored texture was observed. The nature of these lyotropic mesophases has not been studied.

CONCLUSION

Ion bearing liquid crystalline compounds based on trans-1,2-bis(4-pyridinium)ethylene were synthesized and studied. These compounds included low molecular mass analogues, twin model compounds and main chain polymers of the ionene type. Most of these exhibited liquid crystallinity of the smectic type. No nematic mesophases were observed. As a general rule the introduction of charges into the mesogenic moiety increased the stability (transition temperature) of the mesophase. Large supercooling effects, broad mesophase intervals and tendency to polymorphism are features of these ionic mesogenic compounds. The role of the counterion is important in lowering the transition temperature and influencing the solubility and the nature of mesophase.

Thus methylene sulfonate and toluenesulfonate were found to promote solubility and mesophase formation (thermotropic and lyotropic alike) over halogen counterions.

In the case of twin model compounds a variety of smectic phases were observed. The nature of these was dependent on the nature of the counterion and the thermal history of the compound. Toluene sulfonate counterions promoted higher order in the smectic mesophases as well as higher transition temperatures compared to methylsulfonate counterions. A pronounced odd-even effect of the isotropisation temperature of the twin compounds was observed. Compounds with even numbered methylene spacers displaying higher transition temperatures than those with odd spacers.

Only polymers with methylsulfonate and toluensulfonate counterions were found to exhibit both, thermotropic and lyotropic mesomorphism. High transition temperatures and concommitant oxydative crosslinking made the study of polymers with halogen counterions difficult. Polymers with halogen and perchlorate counterions were found to be poorly soluble in water precluding the formation of lyotropic mesophases. An oscillation (odd-even effect) of the *Tm* was observed. The introduction of a few siloxane bonds into the flexible spacer joining the charged mesogen moieties has a dramatic effect on lowering the transition temperatures and making possible the study of such enantiotropic smectic mesophases beyond their isotropisation temperatures. Introduction of flexible bonds into the rigid mesogen moiety destroyed the mesophase all other structural factors remaining equal.

It is possible to conclude that while the rigidity of the mesogenic moiety plays an important role in the formation of the liquid-crystalline order, the existance of charges and counterions on the mesogen is not unfavorable. Quite to the contrary the stability (transition temperatures) of the mesophases are increased. The temperature range of such mesophases is also augmented as well as their variety. Complete characterization of such liquid crystalline main chain ionic polymers remains to be established.

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