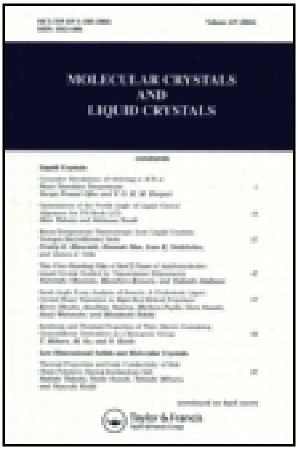


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecular Design of Thermotropic Ionic Side-Chain Liquid Crystalline Polymers

Patrick Masson [a] & Daniel Guillon

[a] Institut de Physique et Chimie des Matériaux de Strasbourg Groupe des Matériaux Organiques 23 rue du Loess, 67037, Strasbourg, Cedex, France

To cite this article: Patrick Masson & Daniel Guillon (2001): Molecular Design of Thermotropic Ionic Side-Chain Liquid Crystalline Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 362:1, 313-346

To link to this article: http://dx.doi.org/10.1080/10587250108025778

Mol. Cryst. Liq. Cryst., Vol. 362, pp. 313-346
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group.
Printed in the USA

Molecular Design of Thermotropic Ionic Side-Chain Liquid Crystalline Polymers

PATRICK MASSON and DANIEL GUILLON*

Institut de Physique et Chimie des Matériaux de Strasbourg Groupe des Matériaux Organiques 23 rue du Loess, 67037 Strasbourg Cedex, France

The design of ionic side chain polymeric systems which present a mesomorphic thermotropic behaviour, is reviewed. The different ways for the introduction of charges in the polymeric system are described, namely ionic bonds, hydrogen bonds and also the use of low molecular salts. The mesomorphic phases identified in these polymeric systems are predominantly smectic in nature, mainly due to the preponderant role of ionic charges in the arrangement of the different constituents of the polymer within the layers. The corresponding structural models are described in detail to explain the thermotropic mesomorphic behaviour. In some specific cases, nematic or columnar phases can also be obtained.

Keywords: ionic polymers; liquid crystalline side-chain polymers; smectic phases; hydrogen bond; non-covalent bond; ionic bond

1. INTRODUCTION

Conventional synthetic polymers are in our days very important materials, used in many technological areas. Now, the development of new polymeric systems with specific physical properties had become a major challenge these last years. For example, due to the large possibilities of molecular engineering, organic polymeric materials are very promising for many optoelectronic applications[1]. Among all the functional polymers, liquid crystalline polymers are of special interest. Indeed, these polymers combine the classical polymer properties (mainly the ease of processing) with the anisotropic properties of the liquid crystalline state (mainly the ease of orientation). Two types of liquid crystalline polymers have been extensively studied during the last two decades[2]. Those where the mesogenic moieties are connected head to tail and form the polymer main chain are called "main chain liquid crystalline polymers (MCLCP)"; those where

---

* Corresponding author. E-mail. daniel.guillon@ipcms.u-strasbg.fr

the mesogenic moieties are attached as side chains to the monomer units of the polymer backbone are called "side-chain liquid crystalline polymers (SCLCP)". In this paper, we will concentrate on the second type of polymers, since they offer the largest possibility of different applications (nonlinear optical, photoconductive, piezoelectric, ferroelectric...) due to the infinity of chemical natures of the side groups which can be attached onto the backbone.

The structure/properties relationship is crucial to optimise the performance of the functional materials. Therefore, it is necessary to know in detail the molecular organisation within the mesomorphic phases of SCLCP. A large number of studies have been reported and reviewed on SCLCP where the side-groups are covalently linked to the polymer backbone. A general description of their structure is based on the fact that these side-groups are alternately located on each side of the polymer backbone in a herringbone configuration[3]. However, it was also shown that this structure could be quite different, for instance in the case of some substituted polymethacrylates. By taking into account the strongly syndiotactic nature of the polymer backbone and the steric constraints, the mesogenic side groups were found to organise themselves in double rows and all oriented on the same side of the backbone in the smectic phases. Rather stretched, the macromolecules adopt the shape of very long ribbons with a width close to the side-group length and a thickness corresponding to that of a double row of mesogens[4].

In this paper we present a review concerning the specific case of ionic SCLCP for two main reasons. First, as it has been demonstrated in low molecular weight (LMW) liquid crystals that ionic interactions are strong enough to impose smectic molecular organisations in general, it is interesting to see if this behaviour is still valid in the case of polymers. Second, the use of strong non covalent interactions, such as ionic interactions, to hold together molecular components presents different advantages; for example, tailoring polymeric liquid crystalline materials becomes much easier and unique properties can be introduced by the presence of non-covalent and labile bonds.

2. IONIC POLYMERS

The introduction of charges in a polymer can be obtained by different ways depending on the nature of the polymeric backbone and also of the mesogenic side-groups. For example, low molecular salts can be present only as complexant of the polymer studied (guest-host system). In other cases, ionic bonds can be used as connectors between the various structural subunits. These ionic bonds can be obtained by ion exchange between adequate and complementary groups such as sulfonate and ammonium groups; they can also be obtained by proton transfer from acid to basic functions such as sulfonic acid to amine. Finally, strong hydrogen bonds generated between carboxylic acid and pyridine units can also be considered in the design of ionic SCLCP.

In this paper, we will present results concerning mainly side-chain or comb-like polymeric systems where a mesomorphic thermotropic behaviour is observed; LMW ionic systems are only taken into account when they can be used as models of the polymeric systems. We will consider also the role of ionic charges on the mesomorphic behaviour of SCLCP and on the molecular packing within the smectic layers. Concerning the polysoaps used in lyotropic systems, they have been well investigated and reviewed[5] before and they are not considered here. Like ionic bonds, hydrogen bonds, coordination complexes and charge-transfer interactions between complementary groups can be used in the design of liquid crystalline polymers. They are a part of "supramolecular chemistry" recently reviewed by C. T. Imrie[6] and C. G. Bazuin[7]. Here, we will describe in detail the polymeric backbones, the mesogenic side groups, the ionic species involved and their respective role on the mesomorphic behaviour. A special attention will be given to three major polymeric backbones used in this field: polymethylsiloxane, polyethyleneimine and poly(4-vinylpyridine).

2.1 Introduction of ionic low molecular weight compounds in a polymeric matrix

A. Wiesemann and co-workers[8,9] recently presented some results concerning liquid crystalline copolymers with redox-active groups. These copolymers were prepared by copolymerisation of mesogenic (methoxyphenyl benzoate groups) and ferrocene-containing acrylate monomers. The ferrocene groups can be oxidised reversibly with copper perchlorate[8] or sulfonic acid[9] (Figure 1). In addition, blends of the copolymers with amorphous polystyrene and partially sulfonated polystyrene were also studied. The mesomorphic (smectic A and nematic) phases are unchanged compared to the corresponding homopolymers and only a slight decrease of the mesophase temperature range with increasing ferrocene comonomer ratio is observed. In the oxidised state the phase transitions are slightly shifted to higher temperatures and decomposition occurs, a few degrees above, due to the presence of incorporated perchlorate counterion[8]. In all blends prepared from reduced and oxidised liquid crystalline polymers, with polystyrene or with partially sulfonated polystyrene, DSC traces show the existence of glass transitions similar in each case, independently of the starting polystyrene. Phase transitions (smectic A to nematic and nematic to isotropic) occur also nearly at the same temperatures as for pure liquid crystalline polymers. Thus the thermal behaviour of these mixtures proves that all of them are completely phase separated[9].

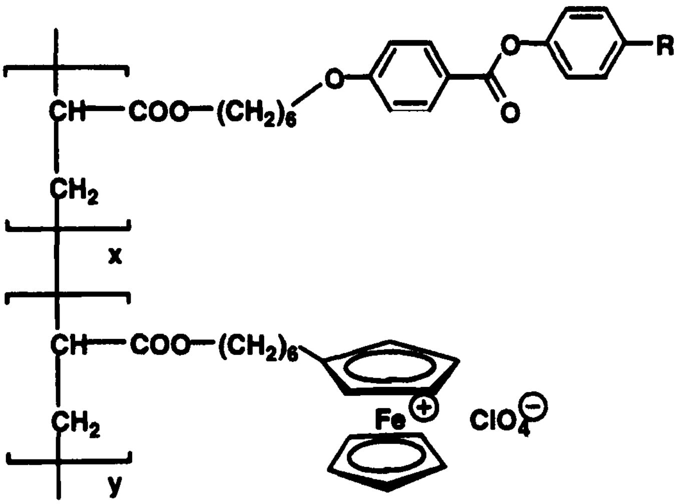
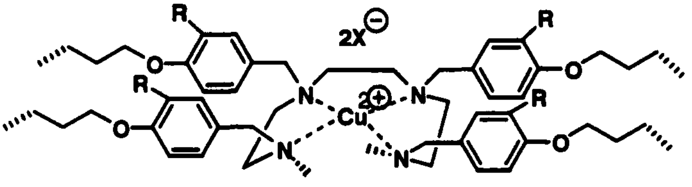


FIGURE 1 Example of polyacrylate containing ionic ferrocene side-chains moieties (see ref 8)

Other types of polymers and low molecular weight compounds have been mixed[10], where interactions between electron-accepting and electron-donating groups are involved. In the specific case of trans N-alkyl-4-nitro stilbazolium halides as ionic complexants and polyacrylates derivatives carrying (carbazolylmethylene) anilines groups[11], focal-conic fan and homeotropic textures indicating the presence of a smectic A phase, have been observed though the smectic phase did not appear in both individual components. Only a nematic phase has been reported when a 1:1 mixture of polyacrylates derivatives carrying (carbazolylmethylene) anilines groups with a non-ionic electron-accepting group (4-(hexyloxy)-N-(4-nitrobenzylidene)aniline) is involved[10].

Another example is the case of copper salts with different counter-ions (nitrate or acetate) blended with N-(3,4-dialkoxy)benzyl polyethylenimine[12]. When the acetate ion and the most substituted benzyl group are involved, a nematic columnar phase is formed where the monomer units are wound helically around the central copper ions (see Figure 2). In the other cases with the least substituted benzyl group, only smectic phases are formed[12].

The above examples show that the insertion of ionic LMW compounds can be achieved in different polymeric matrices, whatever they carry or not mesogenic



$X^{\ominus} = NO_3^{\ominus}$ or $CH_3COO^{\ominus}$

$R = H$ or $OC_{10}H_{21}$

FIGURE 2 Example of polyethylenimine derivative with copper salt presenting a nematic columnar phase (see ref 12)

groups. It is interesting to note that the thermal behaviours of these mixtures illustrate all the possible cases which can be reached in this field: complete phase separation, existence of nematic, smectic or columnar phases. The tailoring of mesomorphic properties is thus large, depending upon the nature of the polymer backbone, the molecular design of LMW compounds and the complexing metal.

2.2 Polymers negatively charged and ionically bonded with positively charged side groups

Ionic bonds can be used in the design of SCLC polymers to connect the different subunits, namely the polymeric backbone and the side groups. They can be easily obtained by simple neutralisation of a polyacid with mesogenic groups carrying a basic function (see *Figure 3*).

For example, C. M. Paleos et al[13] and D. Tsiourvas et al[14] have prepared a series of alkyl and dialkylammonium polyacrylates by neutralising poly(acrylic acid) with primary and secondary amines with linear aliphatic chains (see Figure 4). Here, the degrees of neutralisation obtained are close to the unity. When the alkyl amines have 16 or 18 methylene units, an ordered smectic B phase is observed where the alkyl chains are arranged in single layers separated from one another by the polymer backbones (see Figure 5). At higher temperatures these compounds adopt a smectic A structure where the "molten" alkyl chains are arranged now in double layers separated by the polymer backbone.

When N,N-dialkyl amines are used, the polymeric compounds exhibit, at high temperature, a smectic A phase and at low temperature an ordered smectic E

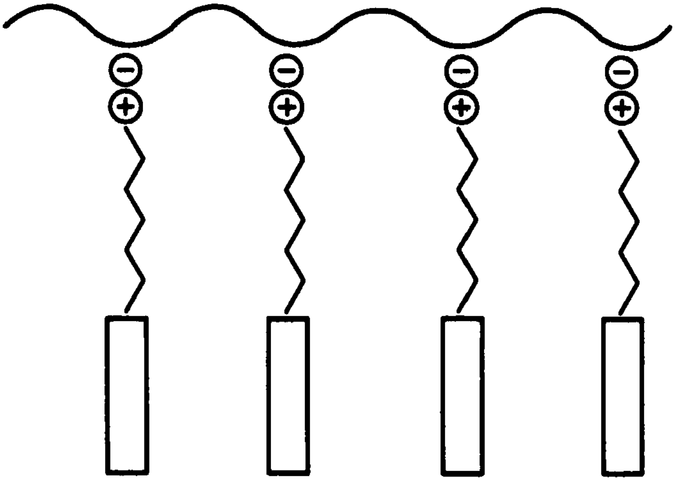


FIGURE 3 Polymer negatively charged with side groups positively charged (wavy line: polymeric backbone, ⊕ : positive charge, ⊖ : negative charge, zigzag line: spacer, rectangle: mesogenic group

phase (see Figure 6). In the latter case, the alkyl chains chemically coupled in pairs through the ammonium group, are arranged in a head to tail configuration and are standing upright in single layers separated by the polymer backbones; laterally, they are packed according to a centred rectangular lattice.

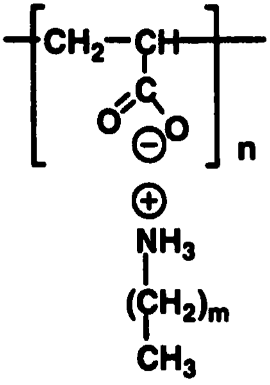


FIGURE 4 Example of alkylammonium polyacrylates presenting smectic phases (see ref 14)

In a similar way, D. Tsiourvas et al[15] have prepared SCLC polyvinylsulfonate derivatives with long chain alkylammonium, N,N-dimethyl-n-alkylammonium

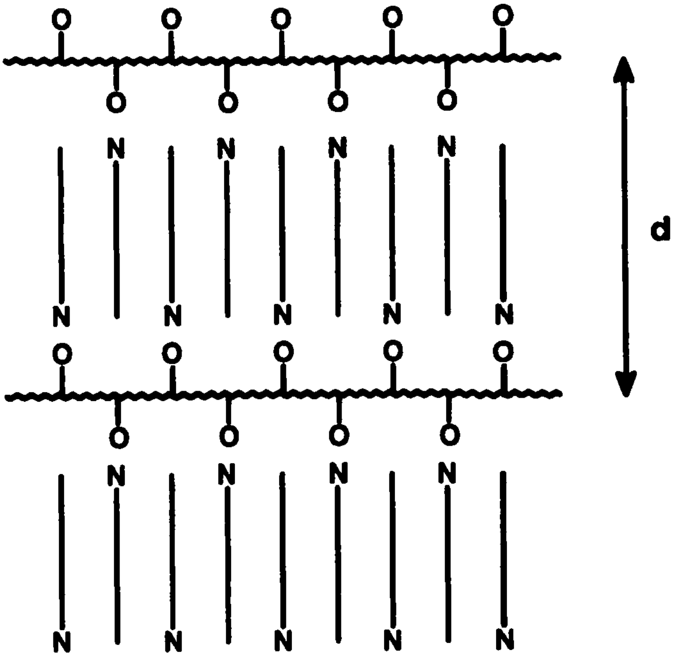


FIGURE 5 Schematic representation of alkylammonium polyacrylates in the smectic B phase (wavy line: polymeric backbone, O: carboxylate group, N: ammonium group, straight line: alkyl chain)

and quaternary N,N-dimethyl-N-cyanopropyl-n-alkylammonium as lateral polar groups (see Figure 7). These polysalts exhibit smectic B or smectic A phases depending on the length of the alkyl chains varying from 12 to 18. In a particular case, with the quaternary N,N-dimethyl-N-cyanopropyl-n-alkylammonium as side group and the shorter chains (C_{12} or C_{14}), an *Ia3d* body centered cubic phase is observed at room temperature below the smectic A phase. These results[14]show that the presence of rigid aromatic mesogenic groups is not necessary for the formation of liquid crystals from poly(acrylic acid) derivatives, liquid cristallinity being obtained by attaching simple alkyl chains onto the polymer backbones through ionic bonds.

Other mesogenic-like or non mesogenic tertiary amines derived from β-(dimethylamino)propiophenone have been used for the neutralisation of polyacids like poly(acrylic acid) and poly(methacrylic acid) by R. V. Tal'roze and co-workers[16]. The degrees of neutralisation for the polyacids are in the range 0.2 to 0.5 and smectic-like phases are observed in a large temperature range. However, DSC traces show the presence of two glass transitions which do not vary

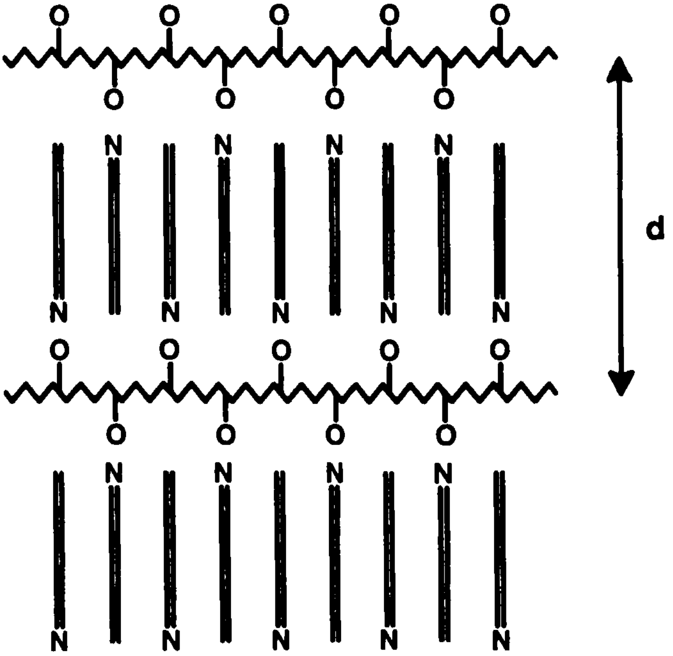


FIGURE 6 Schematic representation of dialkylammonium polyacrylates in the smectic E phase (wavy line: polymeric backbone, O: carboxylate group, N: ammonium group, double straight line: dialkyl chain)

with the polyacid complex composition. A possible explanation could be associated to the existence of a microphase separation between free acid monomeric units blocks and complexed acid units blocks, although different morphological structures are not observed by means of optical microscopy. In another case, mesogenic groups carrying at the end of the spacer an imidazole group as H acceptor have been mixed with poly(acrylic acid) as H donor by T. Kawakami et al[17] (see Figure 8). The two components are miscible over the whole range of concentration when a cyanobiphenylyle mesogenic group is used. Focal conic and homeotropic textures characteristic of a smectic A phase are observed for the mixtures containing between 33 and 75 mol% of the mesogenic group.

On the other hand, ionic complexation of polyacids with non liquid crystalline components can be achieved by proton transfer to an amine and also by ion exchange and elimination of the micro-ions. In such a case, C. G. Bazuin et al[18] used poly(acrylic acid) and poly(vinylsulfonate) sodium salt as polymeric reactant and tertiary amine or ammonium bromide derivative both carrying a 4-methoxy-4′-biphenylyloxy calamitic core (see Figure 9). Complexation ratios, close

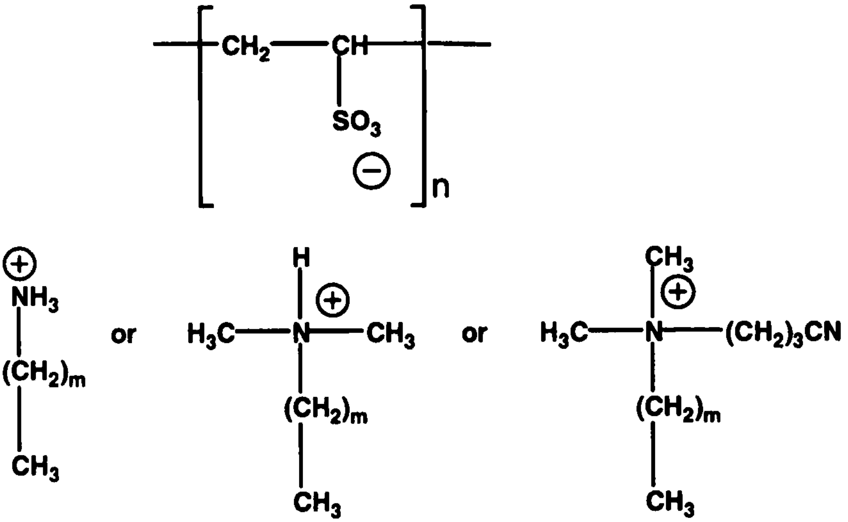


FIGURE 7 Example of alkylammonium polyvinylsulfonates presenting smectic phases (see ref 15)

to 100%, were determined by infra-red spectroscopy for polyacrylate complexes by measuring the decrease in the acid carbonyl absorption near 1700 cm^{-1} and the appearance of the asymmetric absorption of carboxylate group near 1550 cm^{-1}.

A disordered liquid crystalline phase is generated and the type of molecular arrangement corresponds to an interdigitated partial bilayered smectic A phase or to a tilted bilayered smectic C phase. The complex formed between poly(vinylsulfonate), sodium salt and the LMW ammonium bromide derivative exhibits a single-layered smectic A mesophase in a wide temperature range. Once again, these results illustrate that a mixture of simple amorphous polymers with functionalised LMW compounds which do not present mesophases can generate a liquid crystalline polymorphism. This phenomenon is more pronounced for complexes involving sulfonate rather than carboxylate moieties.

Complexes between polymeric backbones such as polyvinylsulfonate[19] polymethacrylatesulfonate[20] and polystyrenesulfonate[21] with respectively bis(2-hydroxyethyl) hexylethylammonium[19,20] (see Figure 10) and alkyltrimethylammonium[21] liquid-crystalline derivatives have also been considered. S. Ujiie et al[19] have compared the mesomorphic behaviour of the iodide (LMW salt) and polyvinylsulfonate of bis(2-hydroxyethyl)ethyl(6-((4-((4-nitrophenyl)azo)phenyl)oxy)hexyl)ammonium to the behaviour of the amine derivative with the same mesogenic group but without ionic character. Both ionic

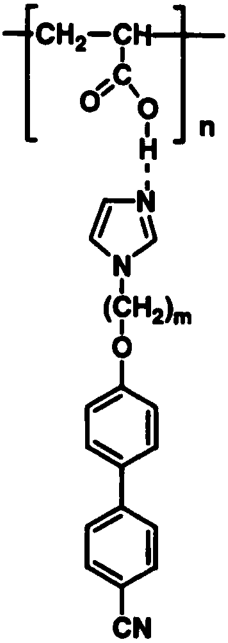


FIGURE 8 H-bond interaction between polyacrylate acid and an imidazole group at the end of the spacer of the mesogenic group (see ref 17)

complexes presented homeotropic textures which remained unchanged on cooling into the solid state or below Tg, whereas the non ionic molecule does not present this homeotropic texture. The smectic layers consist of the sublayers formed with mesogenic groups and ionic moieties. The thermal stability is therefore enhanced in comparison with non-ionic liquid crystalline compounds.

A similar thermal behaviour and layer packing is found in the liquid-crystalline polymer with poly(sulfopropylmethacrylate) acting as the polyanion[20], and the same mesogenic group acting as the lateral cationic group. Another case is reported by M. Antonietti et al[21] who prepared ionic complexes of poly(styrenesulfonate) and different alkyltrimethylammonium derivatives (12, 14, 16, and 18 methylene units) by common precipitation in water and who then processed them in flexible and highly transparent films. The corresponding X-ray scattering patterns of the different complexes can be explained by a lamellar structure of alternating alkane and ionic layers where the alkane side chains are intercalated.

The molecular recognition process by hydrogen bond especially between carboxylic acids and pyridines or tertiary amines has been widely used by T. Kato et

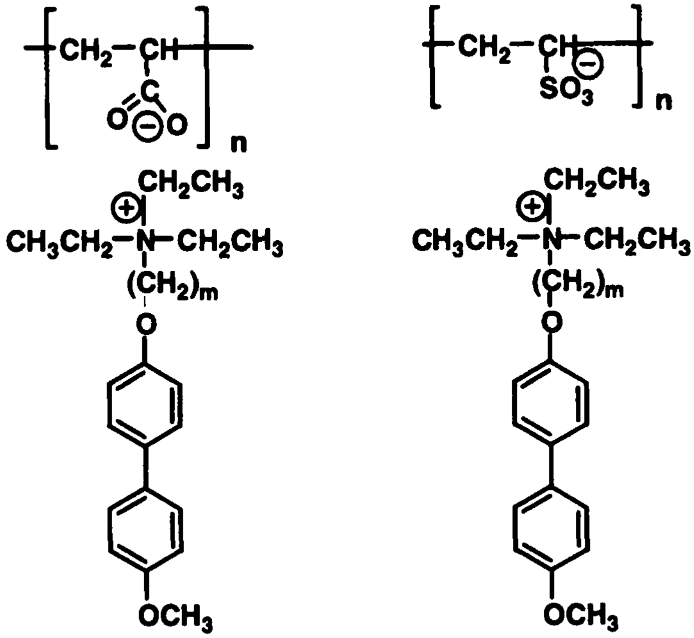


FIGURE 9 Mesomorphic polyacrylate and poly(vinylsulfonate) derivatives obtained by proton transfer and ion exchange respectively (see ref 18)

al[22] for the formation of mesogenic side-chain polymeric complexes. The hydrogen bonding can be used as the connecting bond between the main chain and the side-chain mesogen, or else can be used to form the lateral mesogenic core (see Figure 11). Polyacrylates derivatives containing in its side chain a hexamethylene or a undecanemethylene spacer terminated with a 4-oxybenzoic acid unit have been used as H-bond donors, stilbazole derivatives with alkoxy tails or with more polar groups being used as H-bond acceptors. These complexes exhibit stable smectic mesophases (essentially S_A and S_B) in a wide range of temperature especially when a polar tail is present (isotropisation above 200°C). Copolymer structures were also prepared when the polyacrylate with the pendant carboxylic acid is complexed with a mixture of two different H-bond acceptors. These copolymers exhibit a stabilisation of their smectic phases (wider temperature range and higher enthalpies of isotropisation) than the homopolymer ones, especially when the H-bond acceptors are in the same quantity. Low molecular weight complexes with structures related to the polymers have also been prepared to compare the effects of dipolar interactions but the clearing temperatures and the nature of the phases were similar.

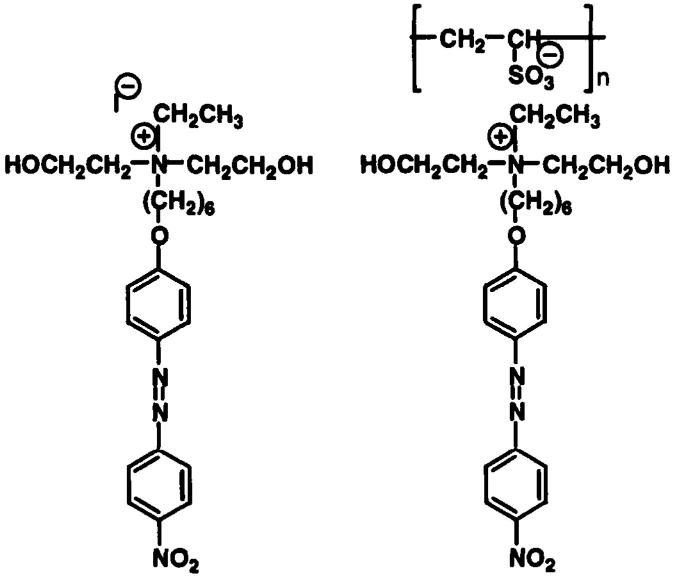


FIGURE 10 Iodide LMW salt and poly(vinylsulfonate) derivative carrying an azobenzene mesogenic group (see ref 19)

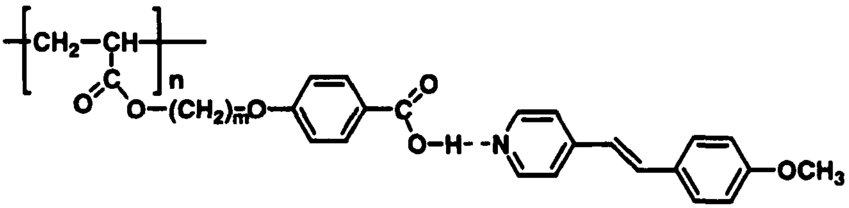


FIGURE 11 Example of polyacrylate derivative where H-bond is present in the mesogenic core (see ref 22)

Other stilbazole derivatives with longer alkoxy tails[23] or with paramethoxybenzoic group[24] as H-bond acceptor were complexed with the same polyacrylate derivatives as described before. In the last case, the stilbazole alone exhibits a nematic phase and polymeric complexes present a strong enhancement of this mesophase. Doubly hydrogen-bonded molecular complexes were also formed between 2-(acylamino)pyridines[25] and polyacrylates carrying carboxylic acids (see Figure 12) and, in this case, a monotropic mesophase in a small range of temperature was observed.

By a simple neutralisation of a polyacid with mesogenic groups carrying a basic function or by ion exchange between polysalts and appropriate LMW salts

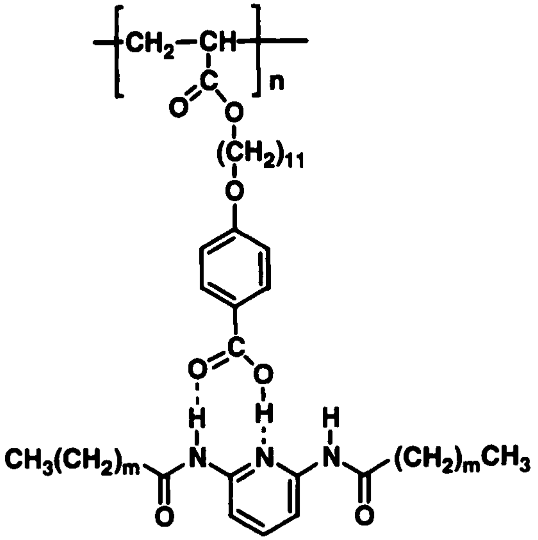


FIGURE 12 Double H-bond complexes between 2-(acylamino)pyridine and a polyacrylate derivative (see ref 25)

and elimination of the micro-ions, numerous SCLCP negatively charged and ionically bonded with positively charged side groups can be obtained. The identification of the ionic bonding is performed by IR spectroscopy, by observing the modification of the carbonyl band near 1700 cm^{-1} when the carbonyl group is present in the polymer backbone. It is important to stress out that simple alkyl chains containing an amine function are enough to produce smectic mesophases when complexed along a polyacid chain. In many cases, the lateral moieties do not need to be mesomorphic by themselves to generate liquid crystallinity when they are ionically bonded to a polymer backbone. More generally in these systems, the formation of smectic phases is predominant, though microphase separation could occur in some specific cases[16].

2.3 Polymers positively charged and ionically bonded with negatively charged side groups

Another way for the preparation of thermotropic liquid-crystalline polymers containing ionic groups is the use of polymers carrying amine groups (see Figure 13) and then potentially positive charges.

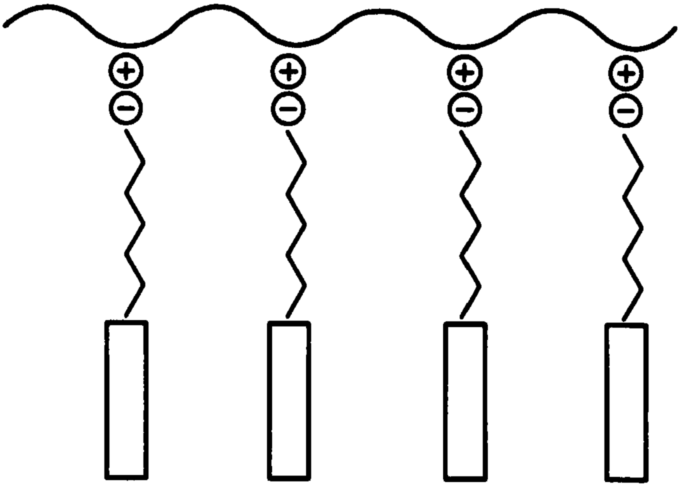


FIGURE 13 Polymer positively charged with side groups negatively charged (wavy line: polymeric backbone, ⊕ : positive charge, ⊖ : negative charge, zigzag line: spacer, rectangle: mesogenic group

In this context, S. Ujiie et al[26] synthesised first a methacrylate monomer derivative by ion-exchange reaction between sodium 4-(4-diethylaminophenylazo)benzene sulfonate and methacryloyloxy-2-ethyltrimethylammonium chloride. Then, copolymers are formed by radical polymerisation of this monomer with other methacrylate derivatives carrying biphenyl or 4-nitroazobenzene group (see Figure 14). Both types of copolymers exhibit enantiotropic mesomorphic phases, namely nematic and smectic when biphenyl groups are present, and only smectic phases when 4-nitroazobenzene groups are present. However, homopolymers synthesised only from charged monomers do not exhibit any mesophase. In this particular case, it seems necessary to introduce classical mesogenic side groups to obtain a mesomorphic behaviour.

Monomers with an acrylate type unsaturation and carrying a pyridyl-alkoxy-benzoate mesogenic group have been prepared by C. Lin et al[27]. The polyacrylate derivatives obtained by free radical polymerisation and the starting monomers exhibit smectic phases. On the other hand, the ionic polymeric derivatives, prepared by quaternisation of the pyridyl terminal side-chain group with an alkyl tosylate reactant, present birefringent schlieren textures. However, the exact nature of the mesomorphic phase was not definitively identified by the authors[27].

The use of complementary hydrogen bonding between two non-liquid crystalline species, a flexible aliphatic polymer namely poly(2-(dimethylamino) ethyl

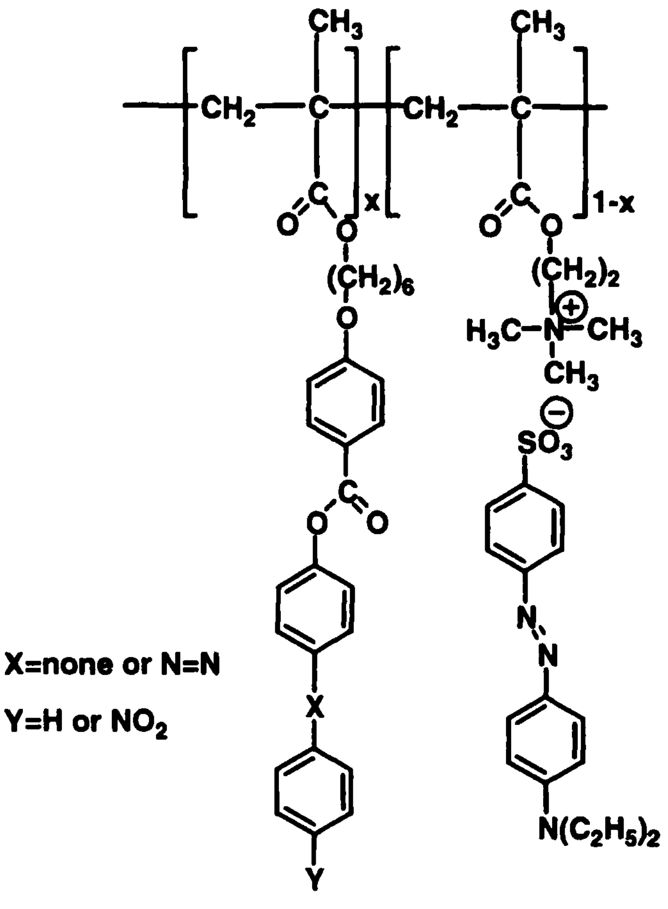


FIGURE 14 Copolymer of polymethacrylate derivatives with biphenyl or azobenzene group and 4-(4-diethylaminophenylazo)benzene sulfonate ion (see ref 26)

methacrylate) and rigid aromatic phenolic derivatives (see Figure 15) generates mesomorphic phases[28]. From the same backbone, copolymers are obtained by varying the concentration of the rigid core molecules in the binary mixture; the mesophase temperature ranges are quite large for the highest side group concentrations. In this case, even if polarising microscopy and X-ray diffraction techniques have been used, the exact nature of the mesophases could not be determined.

T. Kato et al prepared polyamides by polycondensation of 2,3-bis(amino)pyridine with α,ω-alkylenedicarboxylic acids. They prepared the corresponding 1:1

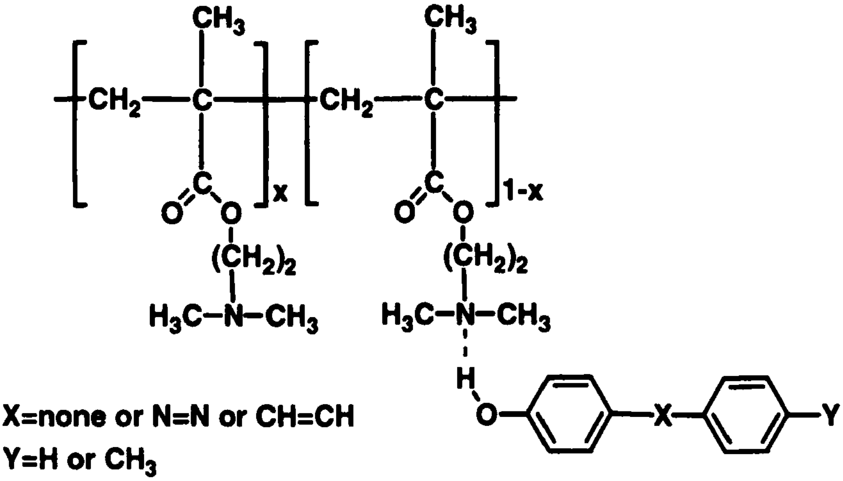


FIGURE 15 H-bond interaction between rigid aromatic phenolic derivatives and poly(2-(dimethylamino) ethyl methacrylate) (see ref 28)

complexes with 4-alkoxybenzoic acids derivatives[29] or 4-(4′-octyloxy)phenyl)benzoic acid[30]. When a chloro supplementary substituent is present in the 3 position on the benzoic acid (see Figure 16), all the complexes exhibit an enantiotropic mesophase[29]. When simple 4-alkoxybenzoic acids are used, a phase separation between these LMW acids and polyamide occurs. In contrast, for low molecular weight model complexes, monotropic smectic B phases are observed, while the complex with a chloro substituent exhibits no mesomorphism.

Polymers positively charged and ionically bonded with negatively charged side groups are less studied than the polymers negatively charged reviewed previously. However, the same thermal behaviours have been found. Let us remark that these positively charged SCLCP can be prepared by a symmetric neutralisation process as the negatively charged polymers or by polymerisation of ionic methacrylate or acrylate derivatives.

2.4 Poly(methyl)siloxane derivatives

In the design of SCLC polymers with ionic charges, polysiloxane backbone has been considered for its flexibility and then for the low transition temperatures shown generally by the liquid crystalline polysiloxane derivatives. Indeed, this flexible backbone favours in general a good orientation of the samples. Poly(methylsiloxane) derivatives carrying a cyclohexyl benzoate group at differ-

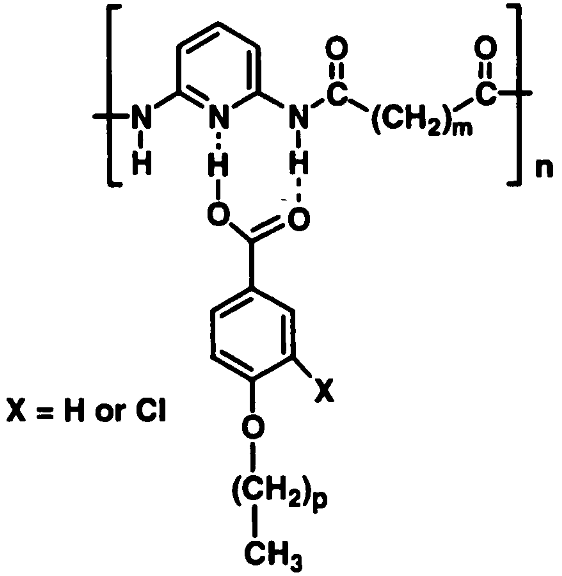


FIGURE 16 Example of polyamides derivatives where double H-bonds are present between amines functions of the backbone and the 4-alkoxybenzoic acid derivatives (see ref 29)

ent ratios (5 to 100%) have been prepared by M. Schellhorn et al and G. Staufer et al[31]. Two hydroxy functions are also present on the cyclohexyl ring and aggregation via intermolecular hydrogen bonding between different diol units leads to the formation of mesomorphic supramolecular structures (see Figure 17). This phenomenon is increased by the flexibility of the chain and by the amphipathic character of these polymeric derivatives where all the moieties, except the hydroxy functions are lipophilic. In all cases, a hexagonal columnar mesophase is formed. For the homopolymer, a supplementary cubic mesophase structure is present at lower temperatures.

Poly(methylsiloxane) containing a pendant propyloxy benzoic acid functionality acting as a H-bond donor and stilbazole[32] or stilbazole-N-oxyde[33] derivatives acting as H-bond acceptors have been used by U. Kumar et al to give H-bonded polymeric assemblies. The starting polymer presents a smectic C phase due to intermolecular dimerisation of the pendant benzoic acid units. The complexation of this polymer with stilbazole derivatives (see Figure 18) leads to the formation of H-bond between these antagonistic groups and to the stabilisation of the smectic phase on a wider temperature range.

For the ionic SCLCP mentioned previously, ionic groups are located in most cases within or near the polymer backbone, or within or near the mesogen. A

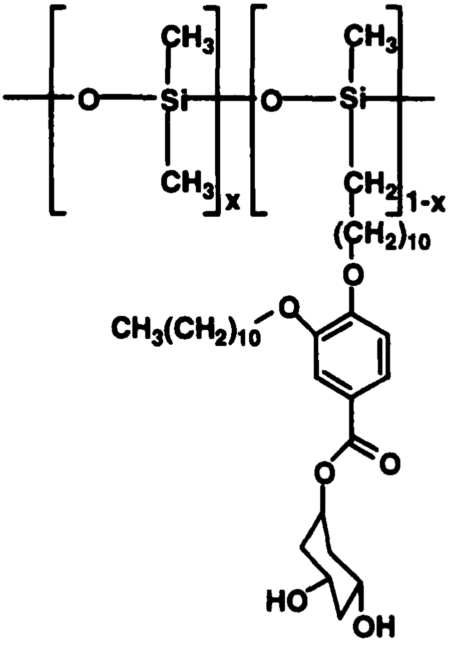


FIGURE 17 Poly(methylsiloxane) derivative carrying a cyclohexyl benzoate group which generates a hexagonal columnar mesophase (see ref 31)

new polysalt structure has been prepared by A. Ikker et al[34]; in this case, ionic pyridinium groups are located on the alkyl spacer between a poly(methyl)siloxane backbone and a 4-alkoxy(biphenylyl)oxy mesogenic group (see Figure 19). The polymers were obtained in a four steps process from poly(methylhydrosiloxane) with a final degree of functionalisation larger than 80%. Thermotropic smectic A and smectic B phases were identified[35] for the poly(methyl)siloxane derivatives with a methoxy tail attached to the mesogenic group; smectic E phases were also observed when a 2-methylbutoxy tail is attached to the mesogenic group.

Pyridyl-alkoxy-benzoate or biphenyl methyl piperidine as mesogenic groups[36] have been introduced through their α-olefinic derivatives in a poly(methylhydrosiloxane) using a platinum catalyst. In the presence of methanesulfonyloxy alkane, a reaction of quaternisation occurs on the amine functions on the side chain. The ionic sites were on the mesogenic group in an external position with respect to the main chain when the pyridyl-alkoxy-benzoate group was involved, and were part of the flexible spacer for the biphenyl methyl piperidine group (see

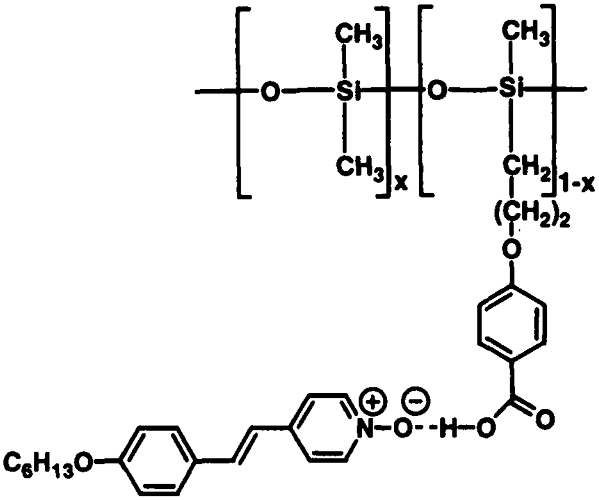
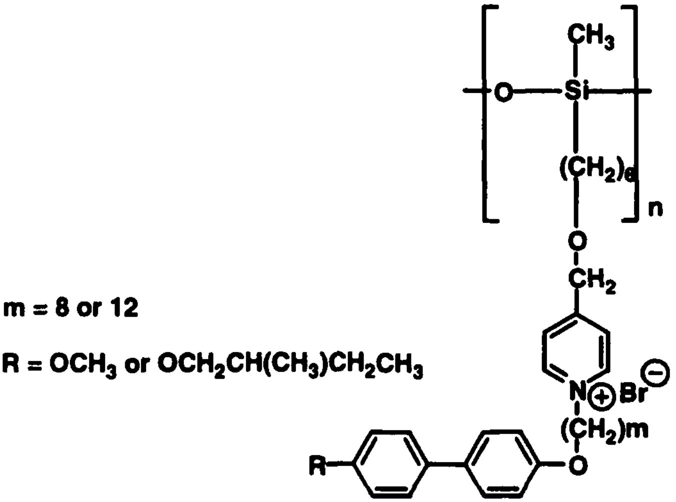


FIGURE 18 Complexation of stilbazole group with a poly(methylsiloxane) derivative (see ref 33)



m = 8 or 12

R = OCH_3 or $OCH_2CH(CH_3)CH_2CH_3$

FIGURE 19 Poly(methylsiloxane) derivative where the ionic group is present on the spacer (see ref 34)

Figure 20). When a stilbazole mesogenic group is fixed on a poly(methylsiloxane) carrying an appropriate alkyl side chain, the ionic site obtained by a quaternisation reaction, could be on the mesogenic group in an internal position to the main chain and adjacent to the flexible spacer. Homo and copolysiloxanes derivatives with a pyridyl-alkoxy-benzoate mesogen show smectic mesophases before quaternisation and nematic phases after quaternisation. The ionic poly(methylsiloxane) derivatives with the two other mesogenic groups present also nematic phases and the change in the position of the ionic site within the side groups does not change the nematogenic character of these polymers.

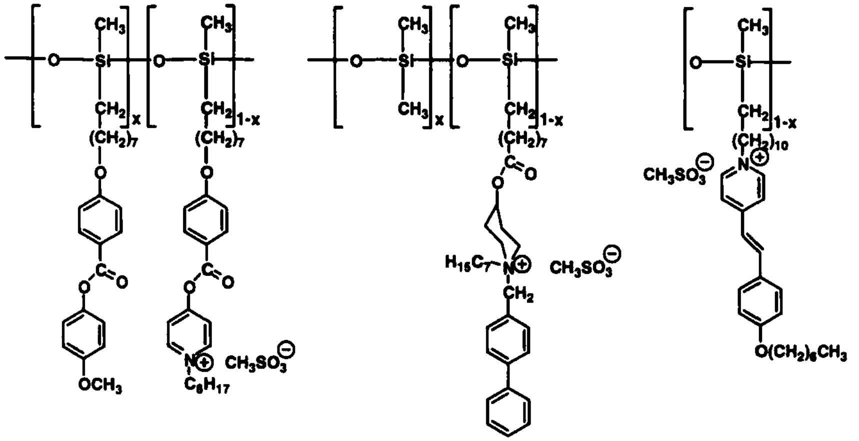


FIGURE 20 Poly(methylsiloxane) derivatives where the ionic groups are present at different positions along the mesogenic core (see ref 36)

Hexagonal columnar and cubic mesophases are formed with poly(methylsiloxane) derivatives carrying a two hydroxycyclohexyl group through intermolecular H-bond formation. Poly(methylsiloxane) backbones have also been used in the design of ionic SCLCP where the ionic groups can be introduced by appropriate chemical reactions in different positions along the mesogenic side chain. Nematic and smectic phases were obtained depending on the nature of the mesogenic group and on the presence and the position of the charge.

2.5 Poly (ethyleneiminium) salts alkylated with mesogenic side groups

In the case of vinyl polymers, the pendant mesogenic groups can be present every two atoms along the polymeric backbone; in the case of alternating vinyl polymers, they can be present every four atoms along the chain. With linear poly(ethyleneimine) (PEI) obtained from poly (2-ethyloxazoline) the intermediate case can be reached; moreover this stiff chain with two carbon atoms between each amine function offers the possibility to prepare N-alkylated and then

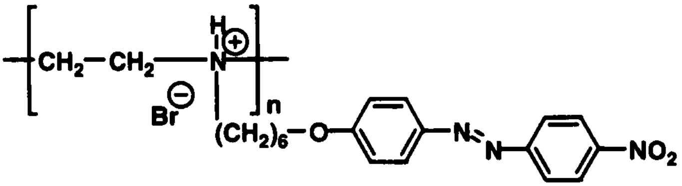


FIGURE 21 PEI derivatives with 4-(4-nitrophenylazo)benzene mesogenic group (see ref 37)

N-quaternised polymers. In this domain, S. Ujiie and K. Iimura[37] have prepared poly(ethlyleneiminium) halides derivatives by a quaternisation reaction between PEI and 4-(4-nitro phenylazo)-6-bromohexyloxybenzene (see Figure 21). Ammonium and trisubstituted amine of low molecular weight were also synthesised with the same mesogenic group. Ionic polymeric and LMW derivatives[37] present enantiotropic smectic phases. The trisubstituted amine of low molecular weight exhibits also an enantiotropic smectic phase with a lower clearing temperature. With 4-(6-bromohexyloxy)phenylazo-4′-methylbenzene[38] S. Ujiie and K. Iimura have also obtained ionic and non ionic PEI derivatives which present respectively smectic and nematic phases.

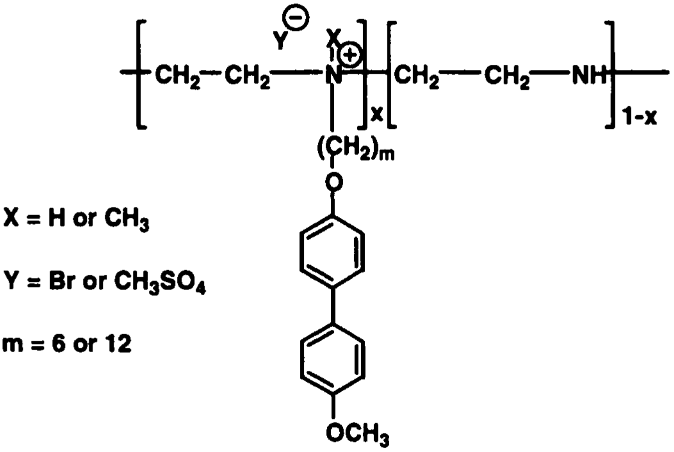


FIGURE 22 PEI derivatives carrying methoxybiphenyloxyalkyl group and different types of charges along the backbone (see ref 39)

A two steps process for the functionalisation of linear PEI has been developed by P. Masson et al.[39] where N-alkylated and N-quaternised polymeric derivatives are successively obtained. First, a controlled N-alkylation with bromide mesogenic agents permits to obtain PEI carrying methoxybiphenyloxyalkyl groups with ratios of functionalisation varying from 50% to 100%. All these derivatives exhibit only a crystal to isotropic transition. Second, by using bromohydric acid or dimethylsulfate on such polymers, N-quaternised poly(ethyleneimine) derivatives are obtained; here the ratios of functionalisation vary from 30% to 100% (see Figure 22).

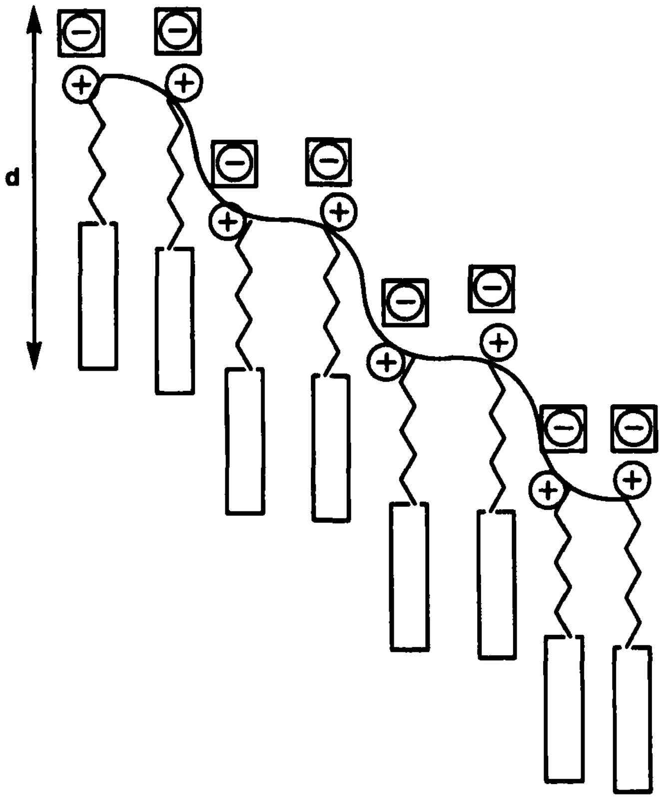


FIGURE 23 Conformational model of a ionic PEI derivative in a single layered (d) smectic A phase where the mesogenic groups are on the same side of the backbones (se ref 40) (wavy line: PEI backbone, zigzag line: spacer, rectangle: mesogenic group, ⊕ : ammonium group on the backbone ⊖ : negative counter-ions)

All the ionic PEI derivatives present a mesomorphic behaviour corresponding to a disordered single layered smectic A phase[40]. A conformational model of the polymer chain is proposed with all the pendant groups on the same side of the polymer backbone, the ionic substructures giving rise to two superposed sublayers. These ribbons within a layer are oriented in a randomly up and down fashion and the superposed smectic layers are positionally uncorrelated with one another (see Figure 23). Despite the presence of mesogenic side groups along the PEI backbone, the ammonium moieties are predominant for the formation and the stabilisation of the smectic layer structure.

Various carboxylic acid-functionalised mesogens were blended with PEI[41]. Almost complete complexation occurs in these systems, as indicated by IRTF analysis, conducting to ion-pair interactions which are thermally stable up to the isotropisation temperature. For mesogen with alkoxy tails and a short spacer (C_6), an ordered smectic E phase is obtained and the molecular organisation within smectic layers is similar to that of pure mesogen alone except for the lamellar spacing (see Figure 24). When cyano tails are involved, X-ray data registered for these PEI complexes indicate the existence of a smectic C phase.

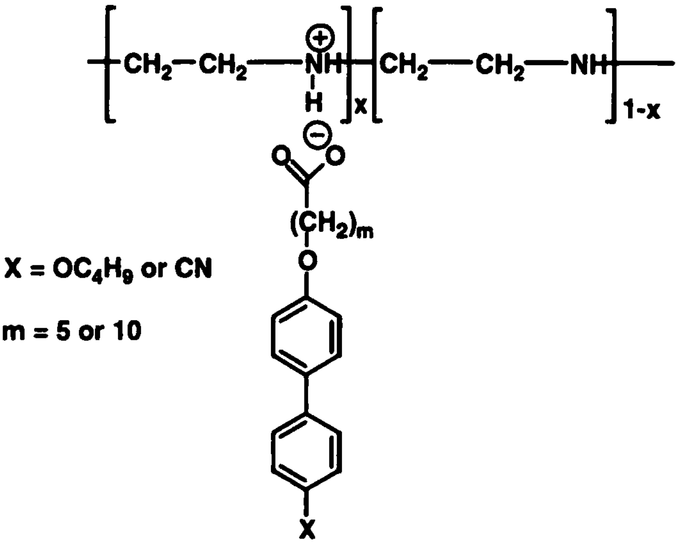
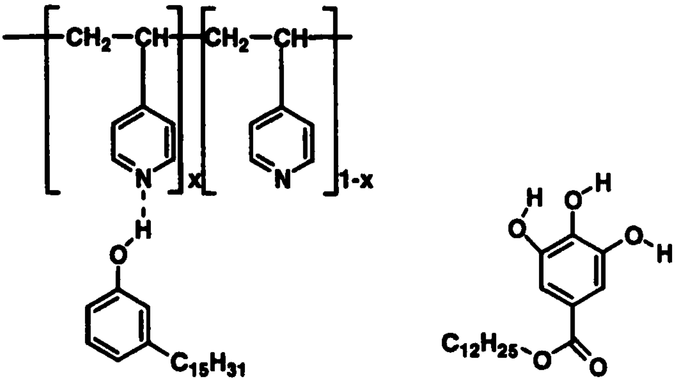


FIGURE 24 PEI derivatives obtained by proton transfer with carboxylic acid-functionalised mesogens (see ref 41)

Linear PEI offers the possibility to prepare N-alkylated and then N-quaternised polymers which present an absence of mesomorphic phase or a nematic phase for the non-ionic compounds and smectic phases for the ionic derivatives. Again, this behaviour illustrates the strong smectogenic power of the ionic groups along the polymeric backbone.

2.6 Poly (4-vinylpyridinium) salts fully or partially quaternised with mesogenic side groups

In the design of ionic SCLCP, a large number of poly (4-vinylpyridine) (P4VP) derivatives have been prepared since the amine functions in 4 position of the aromatic rings are easily accessible along the backbone. In a first approach, P4VP derivatives obtained by hydrogen bonding between side groups as phenol, pyrogallol or carboxylic acid and backbone were studied by J. Ruokolainen et al[42].



3-pentadecylphenol **lauryl gallate**

FIGURE 25 P4VP derivatives obtained by hydrogen bonding between the amine function and phenolic groups (see ref 42,43)

With 3-pentadecylphenol[43] and 4-nonadecylphenol[44], the hydrogen bonding is enough to yield mesomorphic lamellar structures and a full complexation is achieved when equimolar amounts of reactants are used. By dynamic mechanical spectroscopy, it is shown that these comb-like copolymers[45] have a similar behaviour to that of di- and triblock copolymers. With pyrogallol group (see Figure 25), the prepared P4VP derivatives[42] are smectic in nature at room temperature and the layer spacing grows with the increase of molar surfactant ratio probably due to the multifunctionality of the head group. Complete complexation is not achieved with alkylcarboxylic acid surfactant as seen by IRTF. J. Ruokolainen et al[42] claim that the repulsive polar-nonpolar interactions seem to be too small to form mesomorphic structures. But, using the p-dodecylbenzenesulfonic acid[46] (see Figure 26) it was not possible to observe the formation of mesomorphic layered structures in bulk and in xylene solution.

The introduction of zinc dodecyl 4-benzyl sulfonate salt in a P4VP matrix (see Figure 26) has been studied by J. Ruokolainen et al[47]. The complexation

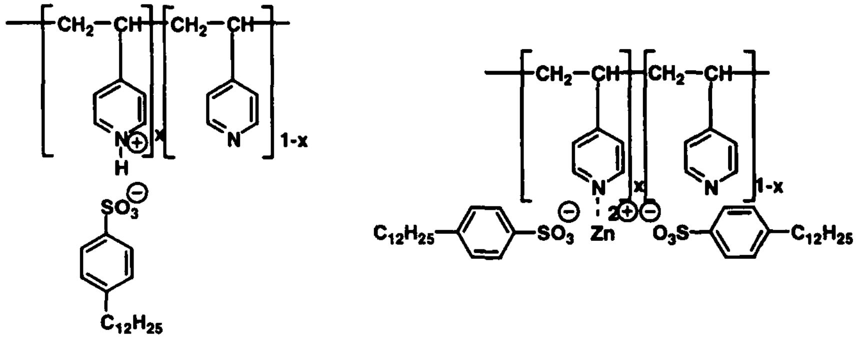


FIGURE 26 P4VP derivatives obtained by transfer proton with benzyl sulfonate function (see ref 46) or by complexation with a zincsulfonate salt (see ref 47)

between the cation and pyridine ring is sufficient to yield mesomorphic behaviour. The layer spacing increases only from 26Å to 28Å when the molar ratio varies from 25% to 100% and can be compared to the 23.7Å value of the ionic salt alone. The authors develop the same model for the zinc salt and the complexes and suggest that the ionic layers which separate the alkyl tails, are thicker when the P4VP chains are present in these ionic layers.

The interactions between mesogens carrying at the opposite alkyl spacer end a carboxylic acid function and homopolymers or copolymers of 4-vinylpyridine were studied widely. For example, butoxybiphenylyle mesogens with a carboxylic acid function were mixed to vary proportions of P4VP (see Figure 27) by F. A. Brandys and C. G. Bazuin[48]. Strong hydrogen-bonding occurs between these opposite functions as checked by IRTF. At low mesogen concentrations, miscible amorphous blends are formed; at higher concentrations, mesogens tend to form highly ordered or crystalline domains at low temperatures. Above the melting point of the mesogen, the miscibility of the two components is enhanced and the molecular organisation within layers, after quenching, corresponds to a smectic E phase as for the pure mesogen.

D. Stewart and co-workers[49] and K.I. Alder et al[50] have even studied the thermal behaviour of blends of mesogenic groups (azobenzene type) carrying a carboxylic function with polystyrene, poly(2-vinylpyridine) and P4VP at different molar ratios. The two components are essentially immiscible when polystyrene is used, and no significant interaction exists between acid and polymer. The blends for the two isomers of poly(vinylpyridine) have approximately the same thermal behaviour, which is driven by hydrogen bond formation between the acid and pyridine rings revealed by the broadening of the carbonyl region of the IR spec-

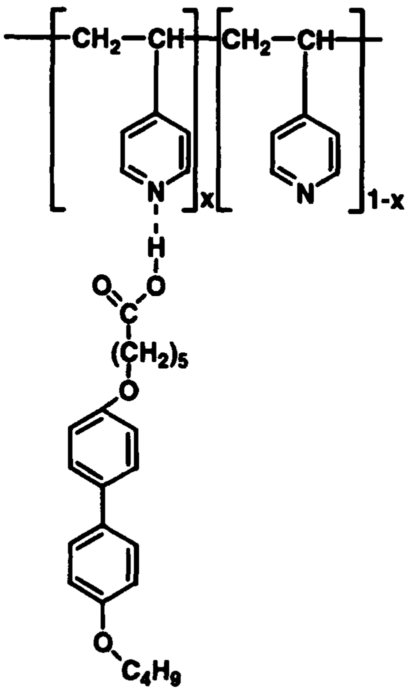


FIGURE 27 Strong hydrogen bonding between a mesogen carrying a carboxylic acid function and the amine function of the P4VP chain (see ref 48)

tra. However, two phenomena occur concurrently in these systems and are probably in dynamic equilibrium: the presence of self associated acid dimers and at the same time the presence of acid-pyridine hydrogen-bonded groups which act as an isotropic solute in the nematic phase of the starting acid mesogenic group.

Copolymers of 4-vinylpyridine and styrene[51] as H-bond acceptor have been complexed with two mesogens such as azobenzene and cyanobiphenylyle acting as H-bond donor and linked to a carboxylic acid function through a flexible spacer. Enantiotropic smectic phases are observed for the 1:1 blend. T. Kato et al[51] have also studied the complexation of these mesogens with a copolymer of 4-vinylpyridine and an acrylate monomer carrying a p-cyanophenylbenzoate group. No phase separation was observed for the H-bonded complexes which show nematic phases. D. Stewart and C. T. Imrie[52] have used the same process with copolymers synthesised from methacrylate carrying a methoxyazobenzene group and styrene or 2-vinylpyridine or also 4-vinylpyridine as comonomer; the LMW compound is the ω-hexanoic acid derivative with the same mesogenic group (see Figure 28). In the first case, the components are essentially immiscible; when 2-vinylpyridine is the comonomer, the behaviour of the blends (prepared with an equimolar ratio of mesogenic acid and 2-vinylpyridine units in the copolymer) is the same than that previously observed for the low rate of methacrylate derivative in the copolymer composition. For the higher rates, blends are miscible and exhibit a nematic phase above the glass transition. When 4-vinylpyridine is the comonomer, blends have the same behaviour and exhibit a nematic phase as in the case of 2-vinylpyridine; in this case, the hydrogen bond formation between acid function and pyridine group cannot be revealed by the modification of the carbonyl range in IR spectra due to the presence of the methacrylic carbonyl band of the polymer.

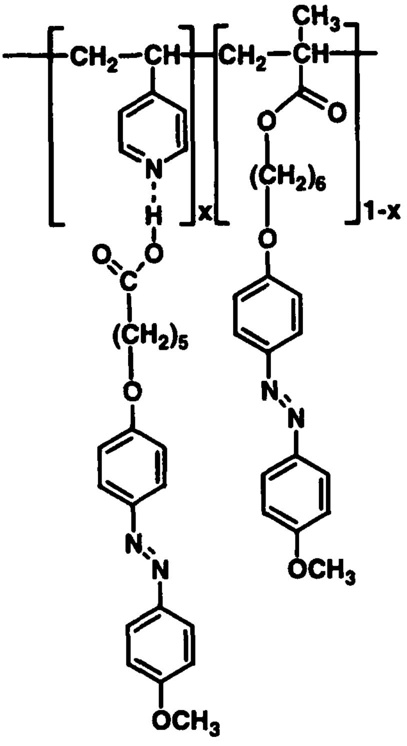


FIGURE 28 Copolymers of methacrylate derivative carrying a methoxyazobenzene group and 4-vinylpyridine where H-bond occurs between amine function of the backbone and a mesogen carrying a carboxylic acid function (see ref 52)

The presence of antagonistic functions such as a pyridine ring and a methylene bromide group carried by the extremity of the spacer of mesogenic groups permits the synthesis of numerous poly 4-vinylpyridinium bromide derivatives to obtain ionic SCLCP. Similarly, poly 2-vinylpyridinium bromide derivatives were synthetised and the corresponding LMW ionic compounds were also prepared as models of the polymeric systems. This field has been widely investigated by D. Navarro-Rodriguez[53–56], E. Bravo-Grimaldo[57,58], C. Chovino[59] and P. Masson[60] et al. The incorporation of the mesogenic groups and thus the formation of the pyridinium ring could be achieved through two different ways: the first one is a chemical modification of a P4VP chain and the second one is the synthesis of the ionic monomer followed by its polymerisation. In the first approach, the quaternisation of P4VP with ω-bromoalkyl mesogenic agents produces easily partial ratios of functionalisation of the polymeric backbone; but due to kinetics and steric limitation, a total conversion in P4VP is difficult to reach[53]. In the second one, the 4-vinylpyridinum bromide ionic monomer carrying a mesogenic group is prepared; it polymerises spontaneously by an anionic mechanism and leads to a fully quaternised polymer. These compounds like the LMW ionic models are thermally stable up to 200–250°C depending upon the mesogenic groups present; above these temperatures a dequaternisation process occurs first. The hygroscopic character of these ionic polymers, typically a half or one water molecule per pyridinium unit, requires a careful deshydratation process before thermal characterisation. Poly4-vinylpyridinium bromide carrying a methoxybiphenylyleoxy mesogenic group were the first to be prepared[54] following the two routes described above (see Figure 29); LMW ionic model with different halide counter-ions were also synthesised[55].

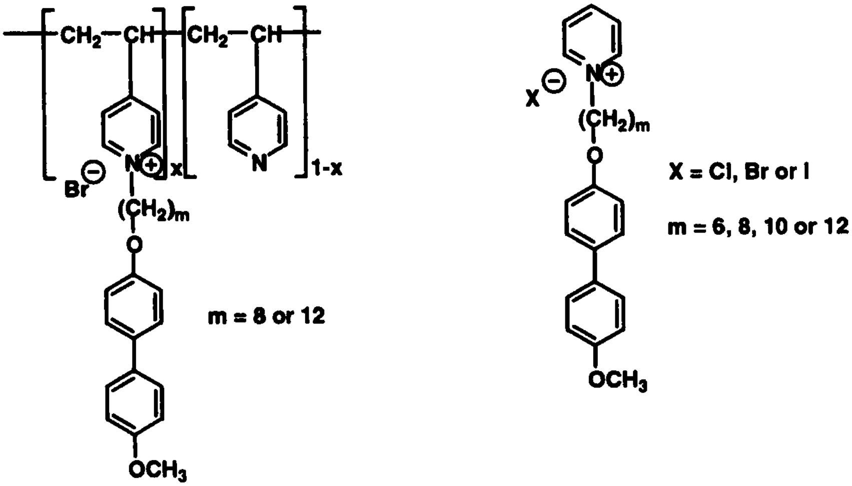


FIGURE 29 Poly4-vinylpyridinium bromide carrying a methoxybiphenylyleoxy mesogenic group (see ref 54) and LMW model salts (see ref 55)

These LMW model compounds exhibit smectic A, B and E phases depending upon the length of the alkyl spacer and the nature of the counter-ion. The smectic structures are all single layered, with the molecules oriented on average perpendicular to the smectic planes and laterally arranged head to tail (see Figure 30). Fully quaternised polymers[56] have the same thermotropic polymorphism and present the same smectic structure with a smectic period slightly larger due to the presence of the polymer backbone. For partially quaternised polymers, the lamellar spacing of the disordered smectic phases decreases monotonically as a function of the degree of functionalisation; the excess of smectic period suggests that the non-quaternised pyridine rings are located in between the layers together with the polymer backbones.

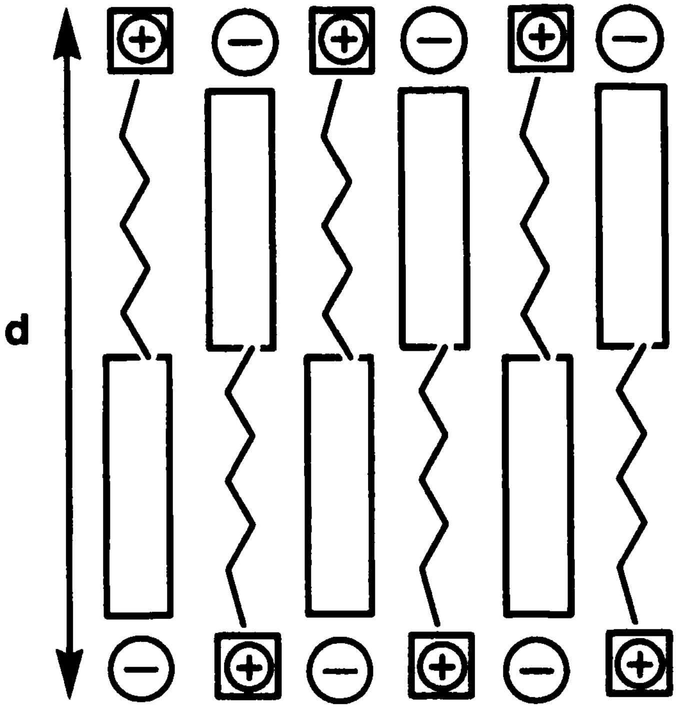


FIGURE 30 Schematic representation of the head-to-tail arrangement of the LMW ions within the smectic layers (see ref 55) (⊞ : pyridinium group, ⊖ : negative counter-ions, zigzag line: spacer, rectangle: mesogenic group)

This study has been extended to the preparation of poly(2-vinylpyridinium) bromide salts[57] with the same methoxybiphenylyleoxy mesogenic group (see Figure 31). In this case, mesogenic groups are in the ortho position with respect to the polymer backbone and the development of ordered smectic phase must be hindered; it is not the case with the low molecular weight 2-ethylpyridinium bromide model[58] and with the previous poly(4-vinylpyridinium) bromide salts where the mesogenic groups are in a para position.

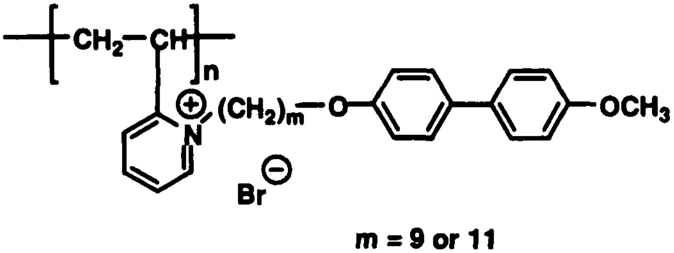


FIGURE 31 Poly(2-vinylpyridinium) bromide salt with a methoxybiphenylyleoxy mesogenic group (see ref 57)

Other biphenylyleoxy mesogenic groups carrying a cyano tail or a chiral optically active tail have been used[59]; LMW ionic model and fully quaternised P4VP derivatives have been prepared. Cyano tail was chosen since it promotes the formation of double or partially double layered structures. Likewise, the introduction of chiral optically active mesogenic groups into SCLCP promotes a polar ordering with tilted smectic phase formation (see Figure 32). LMW compounds present a smectic A phase except the salt with the chiral tail and the C_{12} spacer which presents smectic B and E phases; fully quaternised P4VP derivatives show also a smectic A phase. At lower temperatures, a supplementary smectic E phase is observed when a chiral tail is present on mesogenic groups. In spite of the presence of cyano or chiral groups on the side chain, only smectic mesophases consisting of single layers of upright molecules were identified for the compounds studied.

A mesogenic group known for its nematogenic character, namely 4-methoxyphenyl 4'-oxybenzoate, has been used[60] to prepare fully quaternised P4VP and LMW salts (see Figure 32). Here also, only smectic A phases were observed; by comparison between the measured stacking periods and the calculated lengths, the authors concluded that the monomer units are not in their most extended conformation. In the proposed model (see Figure 33), the in-layer structure is similar to that previously described for poly(4-vinylpyridinium) with a methoxybiphenylyleoxy mesogenic group[56], except that the aromatic parts are laterally arranged head to tail and the alkyl spacers are in a disorganised conformation in order to satisfy the interactions between aromatic cores.

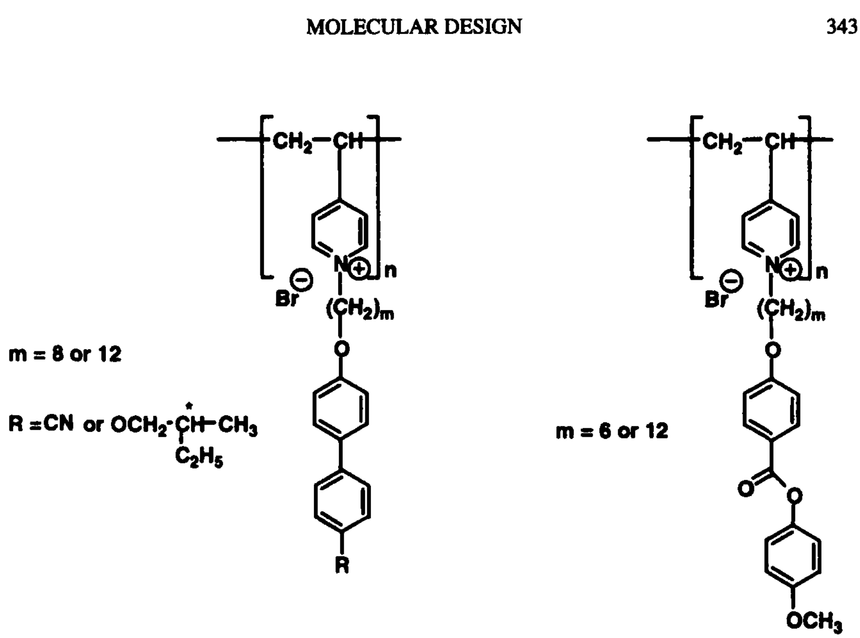


FIGURE 32 Poly4-vinylpyridinium bromide with biphenylyleoxy mesogenic group with cyano or optically active tail (see ref 59) or with 4-methoxyphenyl 4′-oxybenzoate mesogenic group (see ref 60)

3. CONCLUSION

In the design of ionic SCLCP, many polymeric backbones and a large diversity of mesogenic or non-mesogenic side-groups have been considered. In addition, it has been shown that several ways can also be followed to introduce ionic charges in the polymer depending on the nature of the backbone and of the side-groups. It is interesting to note that, when H-bonds are involved, these being less energetically stable (1 or 2 orders of magnitude less than that of ionic bond[42]), they lead to less stable interactions between the antagonistic groups, with the possibility of phase separation[16,50]. Let us also stress out that the presence of mesogenic side-groups is not necessary to obtain mesomorphic phases; simple alkyl chains[14,15] are enough in some cases.

Most of the mesophases obtained with the ionic SCLCP are smectic phases. Ionic interactions are necessary to induce smectic A phase in some PEI derivatives[39]. The systematic study[53-56,59,60] on P4VP derivatives with different side chain groups shows that only smectic phases are obtained in spite of the specific mesomorphic character of the mesogenic groups used in some cases. The models proposed to describe these smectic phases take into account the ionic interactions which bring the major contribution in the stabilisation of the layers.

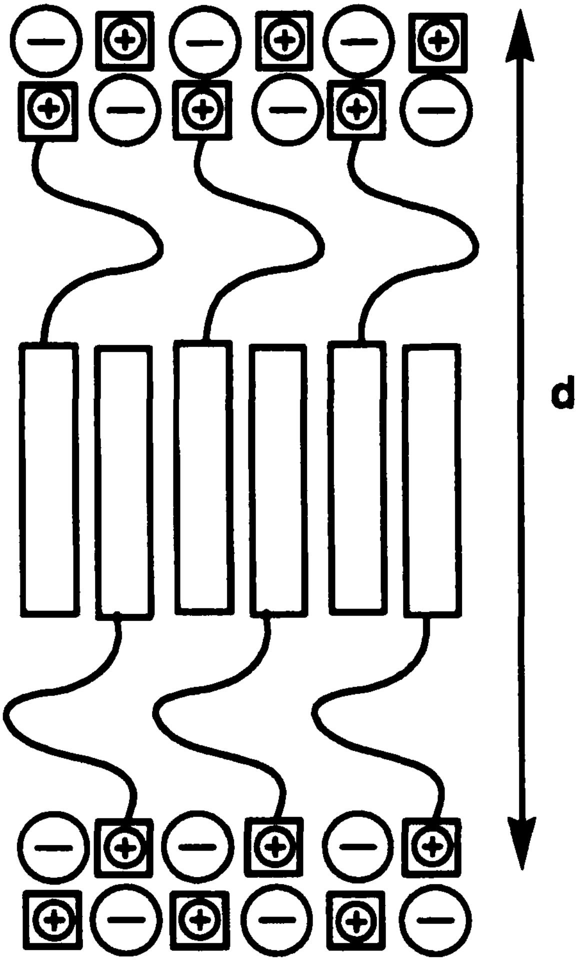


FIGURE 33 Schematic representation of LMW salts (see ref 60) in the smectic A phase inside the layers with a head to tail arrangement of the mesogenic groups, an interdigitation of the ionic species and a disoraganised conformation of the spacers (⊕ : pyridinium group, ⊖ : negative counter-ions, wavy line: spacer, rectangle: mesogenic group)

A regular alternation of opposite charges satisfies the coulombic interactions and promotes the smectic arrangement. Then, within the layers, an arrangement of the other parts of ionic SCLCP is proposed; it takes also into account the steric parameters and the amphipathic character of the non-ionic parts[61]. As a whole, all these results confirm the primordial role of the ionic interactions in the establishment of the smectic structure, and therefore the strong mesogenic power of ionic SCLCP. Finally, let us note also that several ionic SCLCP[36] show nematic phases depending on the backbone and on the mesogenic group. Even columnar mesophases can be generated when the flexibility of the chain allows for a helical structure around central ions[12] or H-bond systems[31].

References

1. *Functional Organic and Polymeric Materials*, Ed. T.H. Richardson, (John Wiley & Sons, New York, 2000).
2. *Handbook of Liquid Crystals*, Ed. D. Demus, J. Goodby, G.W. Gray, H-W. Spiess and V. Vill, (Wiley-VCH, Weinheim, 1998), Vol. 3.
3. V.P. Shibaev, *Liquid-Crystal Polymers*, Ed. N.A. Platé, (Plenum Press, New York, 1993), p. 193.
4. R. Duran, D. Guillon, P. Gramain, A. Skoulios *J. de Physique*, **49**, 1455 (1988).
5. A. Laschewsky, *Adv. Polymer Sci.*, **124**, 1 (1995).
6. C.T. Imrie, *Trends Polymer Sci.*, **3**, 22 (1995).
7. C.G. Bazuin, *Mechanical and Thermophysical Properties of Polymer Liquid Crystals*, (Chapman and Hall London, 1998) Vol. 3, Chap. 3 pp. 60–100.
8. A Wiesemann, R Zentel, T. Pakula, *Polymer*, **33**, 5315 (1992).
9. A Wiesemann, R Zentel, *Liquid Crystals*, **14**, 1925 (1993).
10. Y. Kosaka, T. Uryu, *Macromolecules*, **27**, 6286 (1994).
11. Y. Kosaka, T. Kato, T. Uryu, *Macromolecules*, **28**, 7005 (1995).
12. H. Fischer, T. Plesnivy, H. Ringsdorf, M. Seitz, *J. Mate. Chem.*, **8**, 343 (1998).
13. C. M. Paleos, D. Tsiourvas, P Dais, *Liquid Crystals*, **5**, 1747 (1989).
14. D. Tsiourvas, C. M. Paleos, A. Skoulios, *Macromolecules*, **30**, 7191 (1997) D. Tsiourvas, M. Arkas, C. M. Paleos, A. Skoulios, *Polym. Prepr. ACS*, **38**, 233 (1997).
15. D. Tsiourvas, C. M. Paleos, A. Skoulios, *Macromolecules*, **32**, 8059 (1999).
16. R. V. Tal'roze, S.A. Kuptsov, T. I. Sycheva, V.S. Bezborodov, N.A. Plate, *Macromolecules*, **28**, 8689 (1995).
17. T. Kawakami, T. Kato, *Macromolecules*, **31**, 4475 (1998).
18. C.G. Bazuin, A. Tork, *Macromolecules*, **28**, 8877 (1995) C.G. Bazuin, F.A. Brandys, T.M. Eve, M. Plante, *Macromol. Symp.*, **84**, 183 (1994).
19. S. Ujiie K. Iimura, *Macromolecules*, **25**, 3174 (1992).
20. S. Ujiie K. Iimura, *Chem. Lett.*, **1991**, 411.
21. M. Antonietti, J. Conrad A. Thünemann, *Macromolecules*, **27**, 6007 (1994) M. Antonietti, J. Conrad, *Angew. Chem. Ed. Engl.*, **33**, 1869 (1994) M. Antonietti, C. Burger, J. Effing, *Adv. Mater.*, **7**, 751 (1995).
22. T. Kato, H. Kihara, S.Ujiie, T. Uryu, J.M.J. Fréchet, *Macromolecules*, **29**, 8734 (1996).
23. T. Kato, H. Kihara, T. Uryu, A. Fujishima, J.M.J. Fréchet, *Macromolecules*, **25**, 6836 (1992).
24. T. Kato, J.M.J. Fréchet, *Macromolecules*, **22**, 3819 (1992).
25. T. Kato, M. Nakano, T. Moteki, T. Uryu, S.Ujiie, *Macromolecules*, **28**, 8875 (1995).
26. S. Ujiie, Y. Tanaka, K. Iimura, *Chemistry Letters*, 1037 (1991).
27. C. Lin, A. Blumstein, *Polymer Preprints ACS*, **33,2**, 118 (1992).
28. S. Malik, P. K. Dhal, R. A. Mashelkar, *Macromolecules*, **28**, 2159 (1995).
29. T. Kato, O. Ihata, S. Ujiie, M. Tokita, J. Watanabe, *Macromolecules*, **31**, 3551 (1998).
30. T. Kato, Y. Kubota, T. Uryu, S. Ujiie, *Angew. Chem. Ed. Engl.*, **36**, 1617 (1997).
31. M. Schellhorn, G. Lattermann, *Macromol.Chem. Phys.*, **196**, 211 (1995) G. Staufer, G. Lattermann, *Macromol. Chem. Phys.*, **196**, 211 (1995).
32. U. Kumar, T. Kato, J.M.J. Fréchet, *J. Am. Chem. Soc.*, **114**, 6630 (1992) K. Araki, T. Kato, U. Kumar, J.M.J. Fréchet, *Macromol. Chem. Phys. R. C.*, **16**, 733 (1995) U. Kumar, J.M.J. Fréchet, T. Kato, S. Ujiie, K. Timura, *Angew. Chem. Ed. Engl.*, **31**, 1531 (1992).
33. U. Kumar, J.M.J. Fréchet, *Adv. Mater.*, **4**, 665 (1992).
34. A. Ikker, Y. Frère, P. Masson, Ph. Gramain, *Macromol. Chem. Phys.*, ***192***, 2421 (1991).
35. A. Ikker, P. Masson, Ph. Gramain, D. Guillon, in preparation.

36. C. Lin, P. Cheng, A. Blumstein, *Mol. Cryst. Liq. Cryst.*, **258**, 173 (1995).
37. S. Ujiie, K. Iimura, *Chemistry Letters*, 995 (1990).
38. S. Ujiie, K. Iimura, *Polym. J.*, **25**, 347 (1993) S. Ujiie, K. Iimura, *Chemistry Letters*, 1969 (1991) S. Ujiie, K. Iimura, *Mol. Cryst. Liq. Cryst. Letters*, **8**, 111 (1992).
39. P. Masson, B. Heinrich, Y. Frère, Ph. Gramain, *Macromol. Chem. Phys.*, **195**, 1199 (1994).
40. P. Masson, Ph. Gramain, D. Guillon, *Macromol. Chem. Phys.*, **196**, 3677 (1995).
41. F. A. Brandys, P. Masson, D. Guillon, C.G. Bazuin, in preparation.
42. J. Ruokolainen, M. Torkkeli, R. Serimaa, S. Vahvaselka, M. Saariaho, G. Ten Brinke, O. Ikkala, *Macromolecules*, **29**, 6621 (1996) G. Ten Brinke, J. Ruokolainen, O. Ikkala, *Europhys. Lett.*, **35**, 91 (1996).
43. J. Ruokolainen, G. ten Brinke, O. Ikkala, M. Torkkeli, R. Serimaa, *Macromolecules*, **29**, 3409 (1996).
44. J. Ruokolainen, J. Tanner, O. Ikkala, G. ten Brinke, E.L. Thomas, *Macromolecules*, **31**, 3532 (1998).
45. J. Ruokolainen, M. Torkkeli, R. Serimaa, E. Komanschek, G. ten Brinke, O. Ikkala, *Macromolecules*, **30**, 2002 (1997).
46. O. Ikkala, J. Ruokolainen, G. ten Brinke,, M. Torkkeli, R. Serimaa, *Macromolecules*, **28**, 7088 (1995).
47. J. Ruokolainen, J. Tanner, G. ten Brinke, O. Ikkala, M. Torkkeli, R. Serimaa, *Macromolecules*, **28**, 7779 (1995).
48. F. A. Brandys, C.G. Bazuin, *Chem. Mater.*, **8**, 83 (1996).
49. D. Stewart, C.T. Imrie, *J. Mater. Chem.*, **5**, 223 (1995).
50. K.I. Alder, D. Stewart, C.T. Imrie, *J. Mater. Chem.*, **5**, 2225 (1995).
51. T.Kato, N. Hirota, A. Fujishima, J. M. J. Fréchet, *J. Pol. Sci. Pol. Chem. Ed.*, **34**, 57 (1996).
52. D. Stewart, C.T. Imrie, *Macromolecules*, **30**, 877 (1997).
53. D. Navarro-Rodriguez, Y. Frère, Ph. Gramain, *J. of Polym. Sci A Pol. Chem.*, **30**, 2587 (1992) Y. Frère, Ph. Gramain, *Macromolecules*, **25**, 3184 (1992).
54. D. Navarro-Rodriguez, Y. Frère, Ph. Gramain, *Macromol. Chem. Phys.*, **192**, 2975 (1991).
55. D. Navarro-Rodriguez, Y. Frère, Ph. Gramain, D. Guillon, A. Skoulios, *Liq. Crystals*, **9**, 321 (1991).
56. D. Navarro-Rodriguez, D. Guillon, A. Skoulios, Y. Frère, Ph. Gramain, *Macromol. Chem. Phys.*, **193**, 3117 (1992).
57. E. Bravo-Grimaldo, D. Navarro-Rodriguez, D. Guillon *Makromol. Chem. Phys.*, **198**, 3863 (1997).
58. E. Bravo-Grimaldo, D. Navarro-Rodriguez, D. Guillon, A. Skoulios, *Liq. Crystals*, **20**, 393 (1996).
59. C. Chovino, Y. Frère, D. Guillon, Ph. Gramain, *J. of Polym. Sci. A Pol. Chem.*, **35**, 2569 (1997).
60. P. Masson, Ph. Gramain, D. Guillon, *Makromol. Chem. Phys.*, **200**, 616 (1999).
61. A. Skoulios, D. Guillon, *Mol. Cryst. Liq. Cryst.* **165**, 317 (1988).