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Invited Lecture. Smectic A polymorphism from low to high molar mass systems

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Invited Lecture

Smectic A polymorphism from low to high molar mass systems

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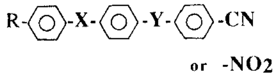
The polymorphism of smectic A phases in low molecular weight (L.M.W.) liquid crystals is associated with strong anomalies in the period defining the layers. The smectic A phases of liquid-crystalline comb-like polymers also have various modes of spacing. However, the behaviour of these polymer phases shows some peculiarities compared with L.M.W. compounds, especially due to the main chain which takes part in the smectic arrangement. To specify further the S_A polymorphism in high molar mass systems, the use of side chain polymers with partial fixation appears to be very promising: either taking advantage of better compatibility and lower viscosity in order to describe binary diagrams with L.M.W. mesogens, or through the partial insertions of long polar side groups known to generate anomalies of periodicity as for L.M.W. compounds.

1. Introduction

During the past 100 years the extensive study of the class of rod-like mesogens containing more than two aromatic rings has contributed for only the past decade:



Including a cyano or nitro end group, these compounds have revealed a very rich polymorphism [1] and consequently a considerable variety of phase diagrams have been described both experimentally and theoretically. One major result of these studies was to divide the smectic A state into several polymorphic forms. These have been classified on the basis of their layering arrangement in pure compounds: monolayer S_{A_1}, partial bilayer S_{A_d} and bilayer S_{A_2}. This classification accounts for (*a*) the value of the ratio d/l of the layer spacing to the molecular length and (*b*) the occurrence of S_A–S_A transitions [1–8]. Another remarkable point of interest was to describe iterative reentrant sequences among the nematic and smectic A phases [1, 9–13]. The modulated fluid smectics [1, 14–17], $S_{\tilde{A}}$ antiphase, $S_{\tilde{C}}$ phase and $S_{\tilde{A}_{cre}}$ crenelated phase are solutions other than the incommensurate S_A phase [18–22], found to overcome the frustration compelled by the pairing of the molecular dipoles (see figure 1).

During the same decade, interest has also been strongly focussed on the mesomorphic properties of another large class of materials: the liquid-crystalline side chain polymers [23]. Among these, comb-like polymers show an obvious inclination to form smectic phases and most often smectic A phases. Moreover, it was recognized very early that the presence of a terminal cyano or nitro group is not absolutely necessary

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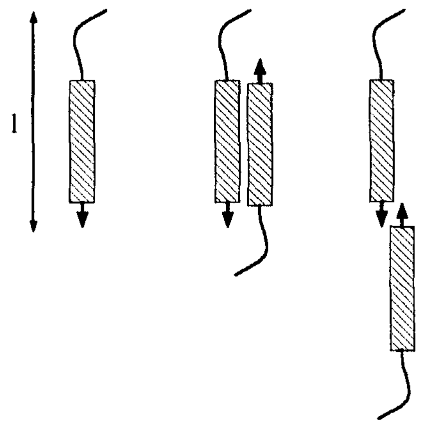


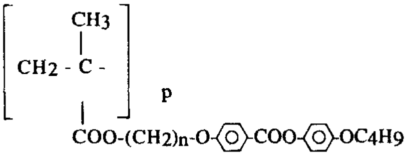
Figure 1. Schematic representation of the pairing of L.M.W. polar molecules.

to induce a partial bilayer or a bilayer S_A phase [24–38]. It is the purpose of this article to compare the different smectic A phases of L.M.W. mesogens with the layered S_A structures observed in side chain polymers.

2. Structural data on the S_A phases of liquid crystal side chain polymers

Following the criterion of the comparison between *d* and *l*, all three phases, S_{A_1}, S_{A_d} and S_{A_2}, are found to exist in liquid crystal side chain polymers. In many cases the structural modifications resulting from molecular changes cannot be compared with the behaviour of L.M.W. polar rods for which the S_{A_1} phase is always destabilized by a lengthening of the aliphatic chain with regard to S_{A_d} and S_{A_2} phases (see figure 2) [39–41].

Table 1.



	S_{A_2}	S_{C_2}	S_{C_1}	S_{A_1}
n	2	4	5	6
d/Å	46	39	23	28·8
l/Å	24	26·4	27·6	28·8
d/*l*	1·9	1·5	0·85	1

One example of the evolution of the smectic A structure in comb-like polymers is given in homologous series of polyacrylates (PAs) or polymethacrylates (PMAs). As the length of the aliphatic spacer decreases, the monolayer structure transforms into a bilayer one [24, 38]. Moreover, we show that, in contrast with what is observed in series of L.M.W. polar rods (see figure 2 and [39–41]) no modulated $S_{\tilde{C}}$ is condensed but tilted phases, monolayer S_{C_1} and bilayer S_{C_2} (see table 1), appear in the intermediate homologues.

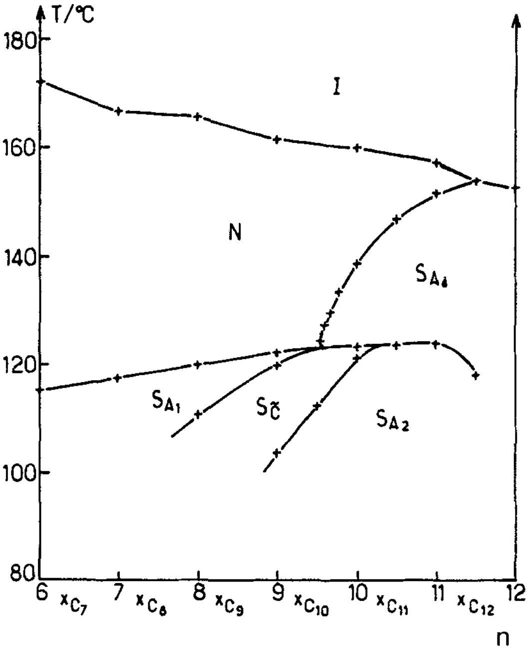
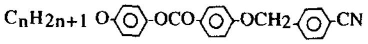
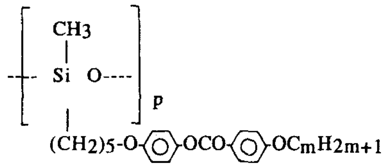


Figure 2. successive (x, T) binary diagrams in L.M.W. polar homologues in the series



(from [41]). The S_{A_l} phase is destabilized by lengthening of the aliphatic chain whereas S_{A_d} and S_{A_2} are favoured.

Table 2.



	S_{A_d}			S_{A_l}	
m	1	2	3	4	8
d/*l*	1·30	1·15	1·05	1·00	0·90

Another type of evolution is illustrated in a series of polymethylsiloxanes (PMSs) [33] in which the length of the tail is varied. The thickness of the layer is larger than the mesogenic group for short tails (thus defining an S_{A_d}) and falls to values close to this unit length for long tails (see table 2).

Once we compare *d* with *l* in polymer systems, the latter value includes the repeat unit of the main chain with no reference to the peculiar role that this part is supposed to play in the smectic structure. In terms of molecular structure, the backbone is, of course, an obvious difference with any kind of L.M.W. mesogen. Indeed, in a

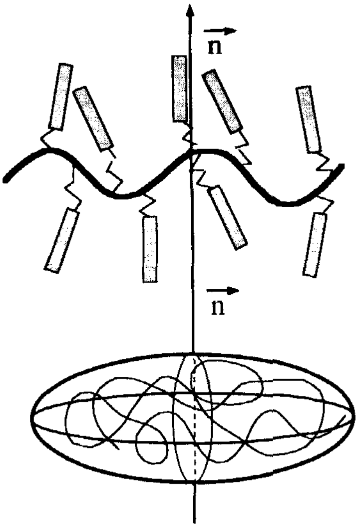


Figure 3. Oblate shape for the backbone in the nematic and the smectic A phases of PMA, PA or PMS.

smectic-like configuration the linkage to the backbone on one side and the freedom on the other side induce an asymmetry of the mesogenic moieties. The study of the overall conformation of the backbone has been performed extensively for the past 4 years via small angle neutron scattering experiments using the isotopic labelling method, mainly at the Laboratoire Léon Brillouin (Saclay, France). These investigations on a selection of different liquid crystal side chain PMAs [42–45], PAs [46] or PMSs [44, 47, 48] reveal a general tendency: the nematic and smectic A structures induce an oblate shape for the backbone (with respect to the director of the uniaxial medium) (see figure 3). Moreover, this conformational anisotropy increases as the temperature decreases.

Except for defects where the backbone hops from one layer to an adjacent one [49], when the smectic A layering arrangement is locally well defined the backbone can be confined at low temperatures in the smectic layer which is, of course, composed mainly of mesogenic side groups. The backbones are probably less confined in soft S_A phases, for instance in a partial bilayer smectic A structure resulting from PMAs or PAs with a cyano group at the end of the mesogenic side group. It is well known, referring to L.M.W. polar rods, that in such an S_{A_d} phase antiferroelectric interactions of the mesogenic cores occur [50]. As a first step, this mechanism tends to move out the molecules of the smectic planes, leading to a weak segregated stacking. This kind of S_{A_d} phase with associated units can be completely destabilized at low temperatures to give a reentrant nematic phase [11, 12, 51–53]. Such reentrant behaviour is observed in a few side chain PAs with a cyano end group in the mesogenic pendents [35, 54–57]. Hence, a puzzling question is raised by the occurrence of the reentrant nematic phase: how is the anisotropy of the backbone conformation affected by this destruction of the layers below the $S_A \rightarrow N_{re}$ transition? Recent results [58] give an answer: in the reentrant nematic this anisotropy is reversed to give a prolate conformation.

Progress in this area of research is largely a matter of chemical effort, physical experience and theoretical analysis relating liquid crystal structures and polymer conformation [59–66].

3. Phase diagrams with S_A phases

As we have seen at the beginning of §2, anomalies of periodicity change with homologous series of liquid crystal side chain polymers. Then, by analogy with the investigation of L.M.W. systems, we can expect to obtain valuable information through the study of two-component systems. For example, we could imagine that striking structural modifications would occur in blends combining homopolymers with different smectic stackings. For instance, two PMAs, one monolayered and the other bilayered, or two polysiloxanes, one monolayered and the other partially bilayered. Unfortunately, even though the chemical difference is minimal between homologues, the components of such polymer blends are incompatible and all attempts to obtain homogeneous systems have failed [67].

As an alternative to this physical mixing, the synthesis of statistical copolymers in which two side groups inducing different structural behaviour are associated [67–72] might appear an interesting means of investigation. In this connection we note the striking similarity in the non-monotonic variations of the layer spacing for copolymers embodying non-polar and polar mesogenic parts [70, 73] and for binary mixtures of non-polar L.M.W.-polar L.M.W. liquid crystals [74] (see figure 4). Although this kind of result is really helpful in the analysis of smectic structures, this method of chemical mixing is not convenient for extensive systematic studies.

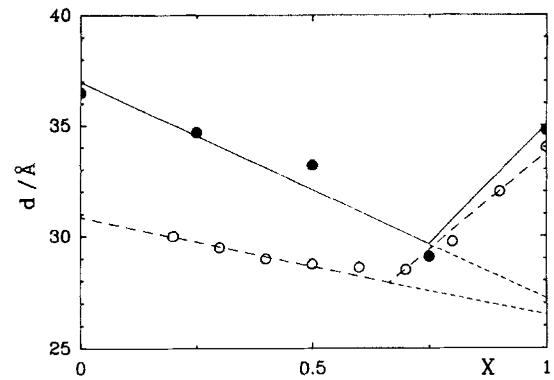
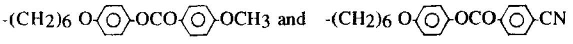


Figure 4. Layer spacing, *d*, versus composition for (○) mixtures of non-polar L.M.W.-polar L.M.W. liquid crystals (from [74]) and (●) copolymers (PMS) with two different mesogenic pendants (from [73]):



Finally, the systems which are likely to provide accessible and major information on the smectic modifications in liquid crystal side chain polymers are temperature–concentration phase diagrams involving an L.M.W. liquid crystal as the second constituent. In particular, two non-ideal behaviours have been observed very frequently in these diagrams; they can be interpreted as consequences of periodicity anomalies:

enhanced or induced S_A phases [75–77] (see figure 5) and
reentrant nematics [78] (see figure 5).

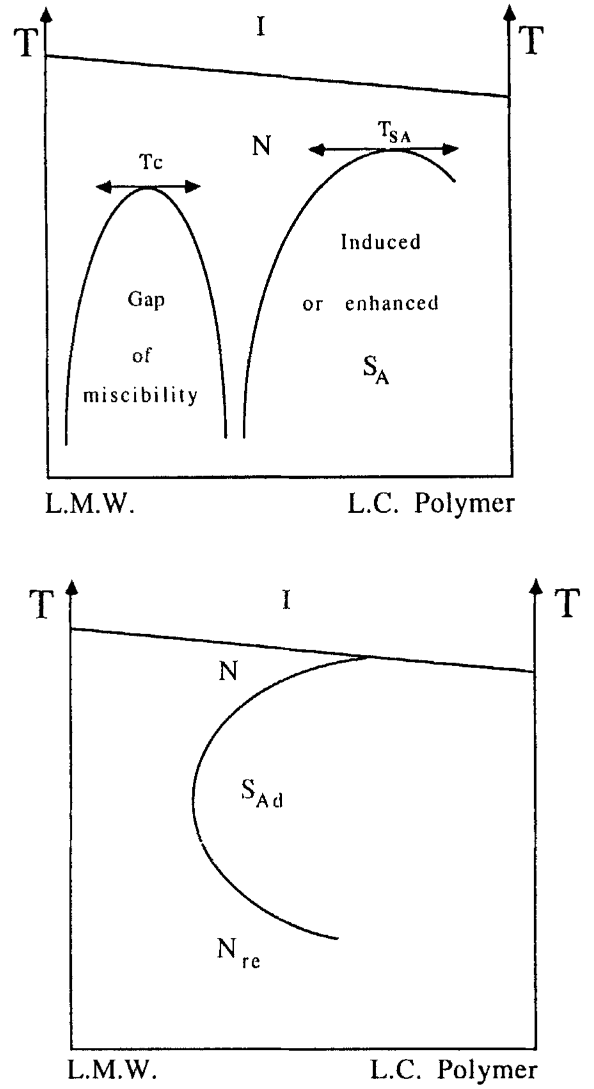


Figure 5. Schematic drawings of L.M.W.-polymer binary diagrams. Three types of non-ideal behaviour are frequently found. A nematic–nematic immiscibility and an enhanced or induced S_A phase (which can coexist in the same phase diagram) and nematic reentance.

However, a third non-ideal phenomenon, the immiscibility of the two components either in the nematic state (see figure 5) or in the isotropic phase, introduces an obvious difficulty in the study of binary mixtures [68, 75, 79–81]. Thus it is necessary to remove such miscibility gaps in order to describe uninterrupted monophasic domains. To this end we know that some conditions applied to the chemical nature of the L.M.W. solvent are favourable [75, 80, 81]. We have found it more efficient to use copolymers known as partially fixed side chain polymers [70, 82–90]. Table 3 illustrates that partial substitution on a PMS backbone strongly promotes the miscibility in a given L.M.W. compound compared with cases of totally substituted or unsubstituted chains. A decreasing number of substituted positions is obtained by the

Table 3. A nematic–nematic phase separation is observed between an L.M.W. and a fully substituted polysiloxane (X = 100 per cent). Partial fixation ($0 < X < 100$ per cent) leads to a complete miscibility in the mesomorphic state. Of course, the ungrafted chain (X = 0) is fully immiscible with any L.M.W. mesogen.

X/per cent				
100	50	30	9	0
N–N phase separation		No phase separation Complete miscibility		Not miscible

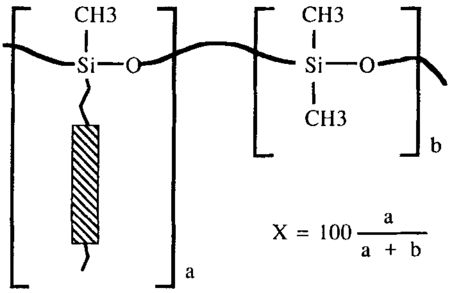


Figure 6. Partially fixed polysiloxanes; X is the fixation ratio.

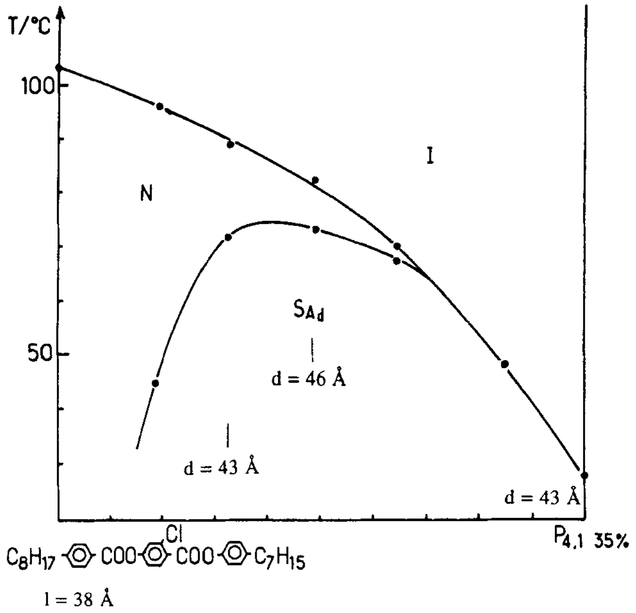
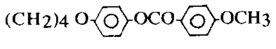
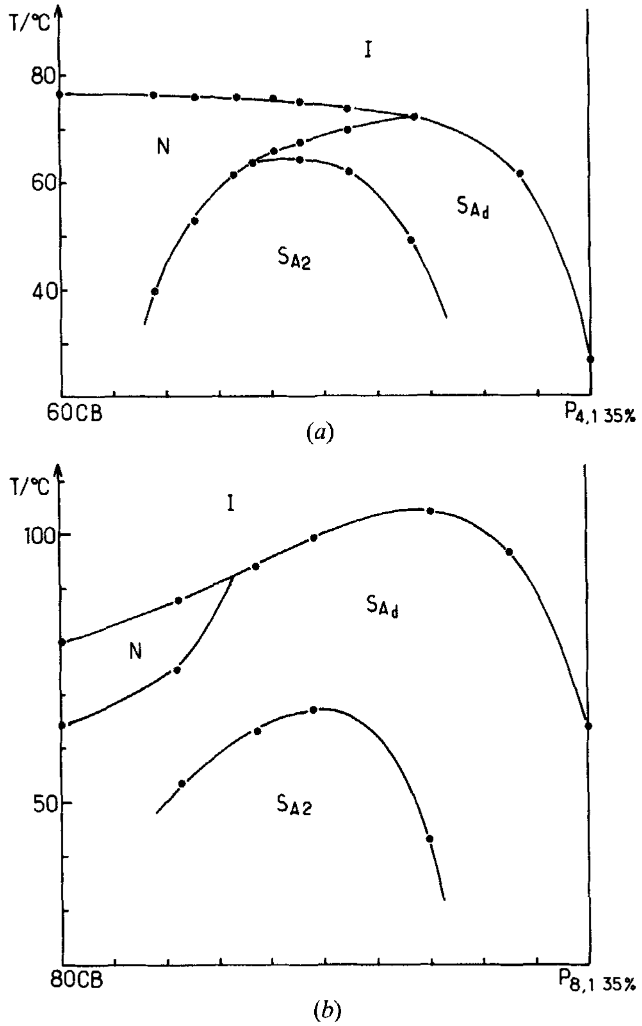


Figure 7. Non-polar L.M.W.–non-polar polymer binary diagram; the polymer is a partially fixed polysiloxane (X = 30 per cent) with



as side group.

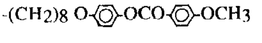


(*a*)

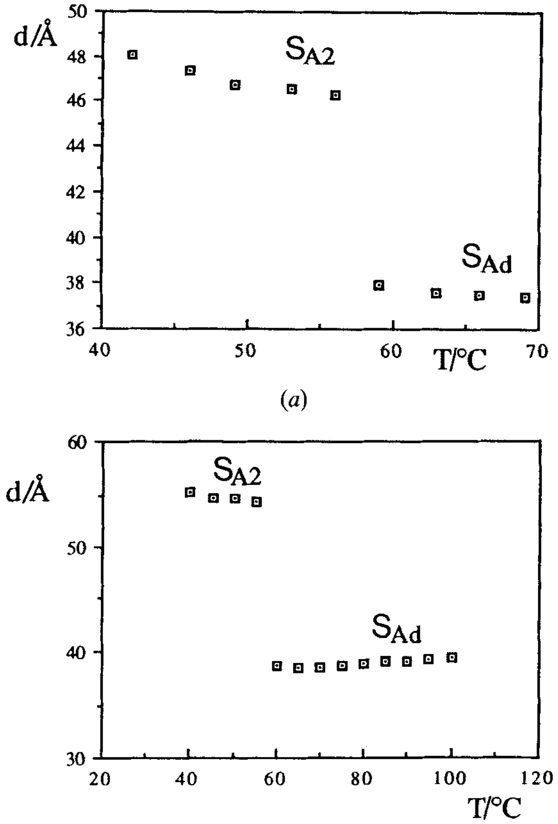
(*b*)

Figure 8. Temperature–concentration binary phase diagram involving a polar L.M.W. and a non-polar polymer. (*a*) L.M.W.: 4-*n*-hexyloxy-4′-cyanobiphenyl (6OCB) P.M.S. partially fixed (X = 30 per cent) with the mesogenic group

(*b*) L.M.W.: 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB) PMS partially fixed (X = 30 per cent) with the mesogenic group



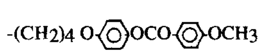
use of chains with an increasing content of dimethylsiloxane segments (see figure 6). In addition, this partial fixation provides two advantages which make the study of mixtures easier, namely the clearing temperature of the polymer is lowered and the bulk viscosity drops dramatically. From the investigation of a large number of these diagrams coupling a partially fixed liquid crystal polymer and an L.M.W. mesogen, a general trend emerges: the smectic A phase of the polymer is boosted resulting most often in a large domain of so-called enhanced smectic (see figures 7, 8 and 10).



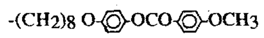
(*a*)

(*b*)

Figure 9. Thermal variations of the layer spacing, *d*, in polar L.M.W.–non-polar polymer systems, giving evidence for an S_{A_d}–S_{A_2} transition. In the S_{A_2} phase two orders of reflection are detected. (*a*) L.M.W.: 4-*n*-hexyloxy-4′-cyanobiphenyl (6OCB) P.M.S. partially fixed (X = 30 per cent) with the mesogenic group



mixture with polymer weight fraction 0·54. (*b*) L.M.W.: 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB) PMS partially fixed (X = 30 per cent) with the mesogenic group



mixture with a polymer weight fraction of 0·48.

In the case of binary system of figure 7 (non-polar liquid crystal polymer–non-polar L.M.W.) we note that, from a structural point of view, the evolution of the layer spacing *d* as a function of the molar fraction of L.M.W. is a maximum for mixtures close to the composition corresponding to the maximum of the enhanced S_A phase. The opposite (i.e. a minimum layer thickness) is observed in mixtures of two L.M.W. liquid crystals.

However, the induced or enhanced S_A phenomenon in L.M.W.–L.M.W. binary systems are due mostly to the combination of a non-polar and a polar mesogen [15, 50, 74, 91–98]. In liquid crystal polymers partially fixed with non-polar side groups–polar L.M.W. binary systems, not only is the S_A phase of the polymer

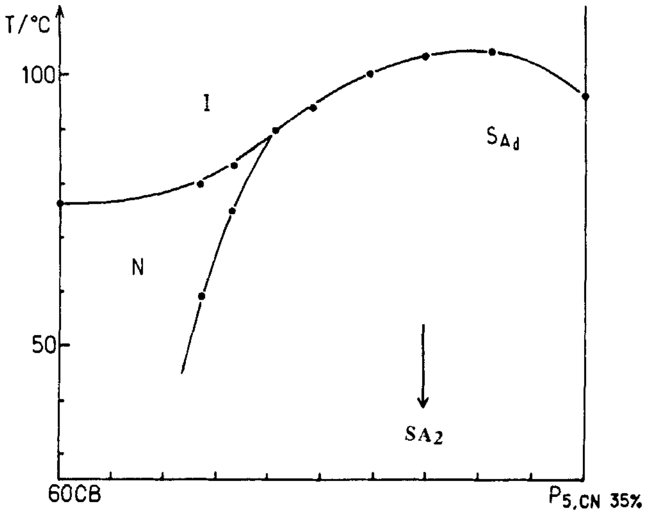
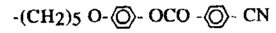


Figure 10. Temperature–concentration binary phase diagram involving polar L.M.W. and a polar polymer. L.M.W.: 4-*n*-hexyloxy-4′-cyanobiphenyl (6OCB) PMS partially grafted (X = 35 per cent) with the mesogenic group



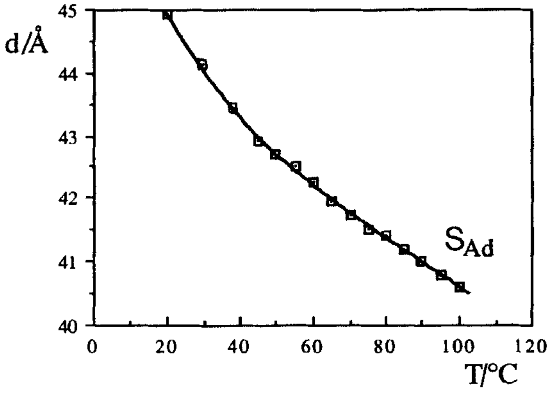
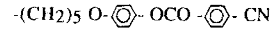


Figure 11. Continuous evolution of the layer spacing in a polar L.M.W.–polar polymer system. L.M.W.: 4-*n*-hexyloxy-4′-cyanobiphenyl (6OCB) PMS partially grafted (X = 35 per cent) with the mesogenic group



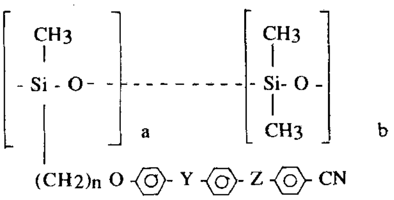
mixture with a polymer weight fraction of 0·70.

enhanced but an additional induced S_A occurs. Thus, two S_A domains coexist in the phase diagram which, in some cases are connex (see figure 8). Under these conditions microscopic observations and differential scanning calorimetry (D.S.C.) experiments give clear evidence for an S_A–S_A phase boundary line. An X-ray analysis indicates a phase transition of the S_{A_d}–S_{A_2} type (see figures 9 (*a*) and (*b*)), the S_{A_2} phase being induced since it is not observed in either the pure polymer or the pure polar L.M.W. (see figures 8 (*a*) and (*b*)). As shown in figure 8 (*b*), complete miscibility of the L.M.W. and the liquid crystal polymer can be obtained over the whole concentration range in the S_{A_d} phase.

Incorporating a cyano mesogenic side group containing two phenyl rings, the polymer also exhibits an S_{A_d} phase. We recall that in the case of substitution on the polysiloxane backbone by polar side groups, the fully substituted compounds have high transition temperatures and the reduction obtained with partial fixation is of great interest for the physical studies. When mixed with polar L.W.S.s of the cyano-biphenyl series (see figure 10), a clear tendency to a bilayered phase exists but the evolution toward an S_{A_2} phase appears continuous and no phase transition is revealed (see figure 11) in contrast to the case of the non-polar polymer. Of course, this is in good agreement with the theoretical description where the S_{A_d} and S_{A_2} phases appear to be of the same symmetry [99].

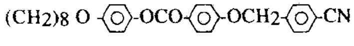
Thus, the various binary systems between an L.M.W. mesogen and a partially fixed polymer with mesogenic groups containing two phenyl rings exhibit strong variations of the layer spacing involving or not involving S_{A_d}–S_{A_2} transitions. Such evolution is reported for L.M.W. compounds [1, 2].

From the experience gained in the study of polar L.M.W. mesogens [1] a convenient choice for more-exhaustive investigations of periodicity anomalies need polymers with cyano mesogenic side groups containing three phenyl rings:

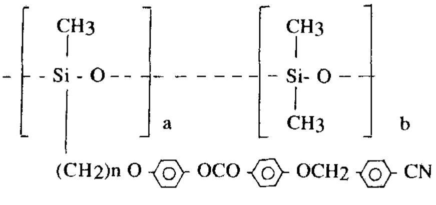


As expected, these partially fixed polymers are compatible with L.M.W. long cyano rods, and the binary phase diagrams display a variety of topologies including a reentrant nematic phase, an S_{A_d}–S_{A_2} transition and S_{A_d}–S_{A_1} transitions (see figures 12(*a*)–(*c*)). These recent studies are in progress and an appropriate choice of the polar pendants in these systems should permit us to extend the phase behaviour of liquid crystal polymers to all kinds of fluid mesophases even in pure polymers [55, 100].

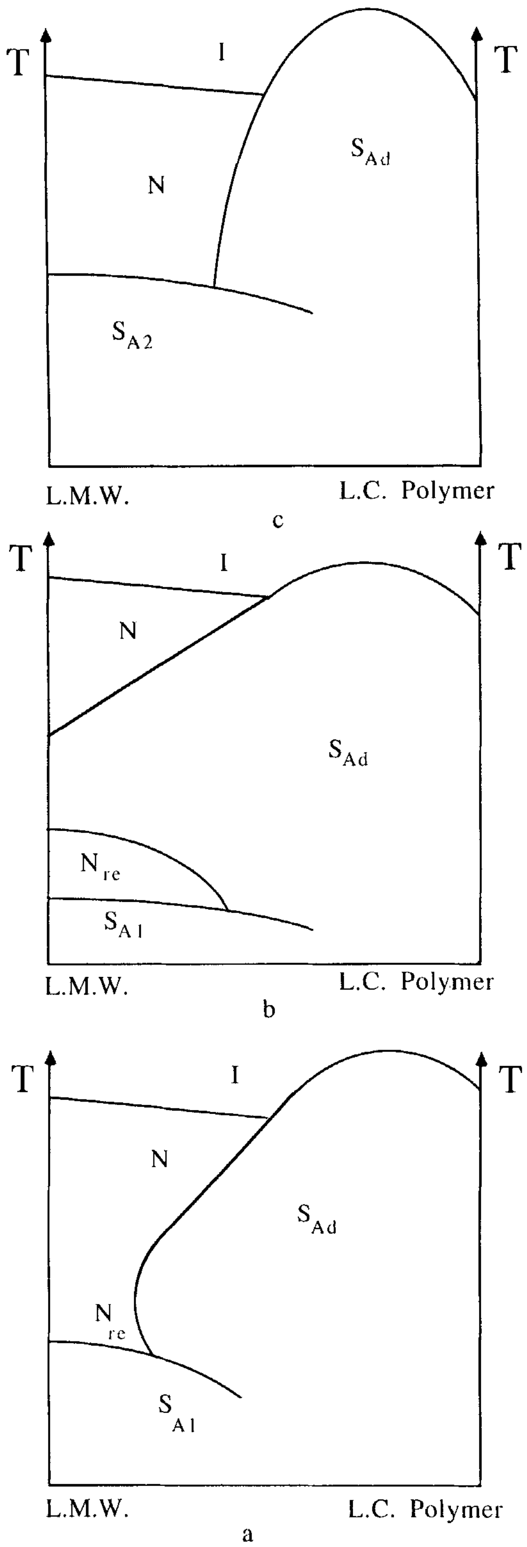
In a series of non-polar liquid crystal side chain polymers bidimensional fluctuations are sometimes observed in the S_{A_1} phase [25, 31, 34, 43]. Locally they reflect a lateral modulation or periodic defect walls superimposed on the smectic structure. However, no modulated smectic phase has so far been revealed. Thus, it was not known whether two dimensional fluid mesophases are really difficult to condense in polymers. This uncertainty has now been solved by partial fixation on the PMS backbone of the vinyl parent of the polar rod



This L.M.W. compound has an S_{A_1}–$S_{\tilde{C}}$ transition (see figure 2 and [41]). The corresponding partially fixed polysiloxane



$$I \xrightarrow[200°\mathrm{C}]{} S_{Ad} \xrightarrow[115°\mathrm{C}]{} S_{\tilde{C}}$$


T
I
T
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S_{A2}
L.M.W.
L.C. Polymer
c
T
I
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N_{re}
S_{A1}
L.M.W.
L.C. Polymer
b
T
I
T
N
S_{Ad}
N_{re}
S_{A1}
L.M.W.
L.C. Polymer
a

has an S_{A_d}–$S_{\tilde{C}}$ sequence, detected by optical observations and D.S.C. analysis. By analogy with the L.M.W. derivative [39, 101], the signature of this latter phase is given by $\bar{1}1$ and 01 Bragg reflections in the X-ray patterns. By changing some molecular parameters of the side group, we can now expect rapid advances in this subject [102].

4. Conclusion

We have shown that analogies can be found between the smectic A modifications of liquid crystal side chain polymers and of M.W. mesogens. Although the nomenclature used is the same, the small angle neutron scattering results demonstrate that the backbone has an oblate shape in the S_A arrangements of the polymers. More experiments should specify how it participates to produce complex periodicity anomalies.

On the other hand, the occurrence of a modulated phase in a polymer confirms that part of the rich polymorphism of long polar L.M.W. compounds extends to systems of high molar mass. However, to what extent we can refer to this description for the polymorphism of polymers is still an open question. In this regard the study of binary systems between L.M.W.s and polymers is of prime importance.

In phase diagrams involving a polymer component, strong non-ideal behaviours is frequently observed, especially originating from the enhancement and the induction of smectic A phases of different kinds. In this context the use of partially fixed polymers gives a lower viscosity and better compatibility with L.M.W.s [103], and so is of great help in overcoming the drawbacks encountered with fully substituted chains (for example, immiscibility and poor textures).

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Figure 12. Schematic binary phase diagrams involving a partially fixed polysiloxane (X = 30 per cent) with a cyano mesogenic group containing three phenyl rings (n = 8, Y = –COO–, Z = –) and a long polar L.M.W. mesogen:

a) C_7H_{15} O -⌬-COO -⌬- CH=CH -⌬- CN (I, N, S_{A1})

b) C_8H_{17} O -⌬-COO -⌬- CH=CH -⌬- CN (I, N, S_{Ad}, N_{re}, S_{A1})

c) C_5H_{11} O -⌬-OCO -⌬- OCO -⌬- CN (I, N, S_{A2})

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