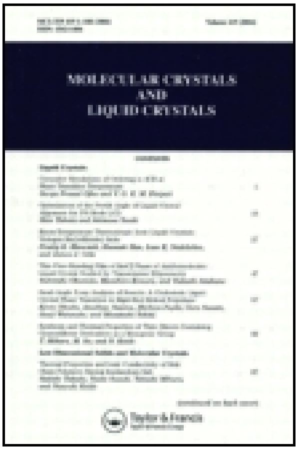

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New Thermotropic Polymers with Flexible Backbone and Mesogenic Side Chains: Blends with Small Molecule Liquid Crystals

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New Thermotropic Polymers with Flexible Backbone and Mesogenic Side Chains: Blends with Small Molecule Liquid Crystals

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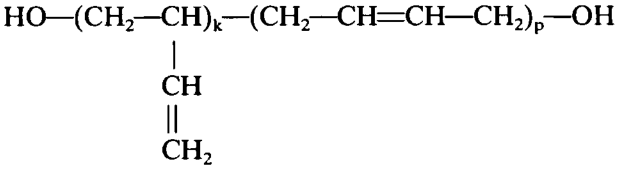
A new kind of side-chains mesomorphic polymers is described, allowing variation of spacer length and degree of substitution. Differential scanning calorimetry and polarising microscopy allow the measurement of the mesophase spread and observation of characteristic textures. A large biphasic gap is observed between isotropic and anisotropic phases. This phenomenon might be due to differences in the substitution degree and tacticity of the samples. In the case of some small molecules liquid crystal-polymer blends, a segregation of the various components also induces a new phenomenon, *i.e.*, a "pseudo reentrant" smectic phase in the biphase. Other properties of this polymer in cyanobiphenyls solutions are described such as the influence of the degree of substitution, spacer length, and low molar mass liquid crystal tail length, on phase diagrams.

INTRODUCTION

Since the synthesis of the first mesomorphic side-chain polymers, nearly ten years ago, an increasing number of studies have been performed on this type of material. Several authors have shown that, in these polymers, a relatively fast reorientation time of the optical axis by external electric fields,[1] and an optical memory effect in the glassy state associated with the presence of the flexible backbone,[2] could be obtained. To combine the properties of low molecular weight liquid crystals (SMLC), used in display devices, with the solid state properties and the memory effect achieved by quenching these polymers, it appeared of interest to study the blends of comb-like polymers with SMLC very similar to the mesogenic side chains. If miscibility studies exist in the field of nematic polymers[3,4,5,6,7] little information is available in the case of smectic polymers. Some original properties of a new side-chain material, synthesized by grafting mesogens on commercial polybutadiene, increases the interest of this study. In particular, with this new material, it is possible to modify various structural parameters of the comb-like polymer.

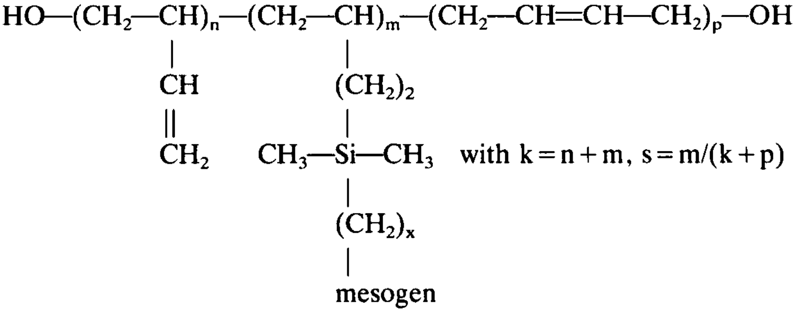
POLYMER SAMPLES STUDIED

The samples have been synthesized according to a new method[8] starting from a polybutadiene chain G 2000 from NISSO, described by the formula:



$$\mathrm{HO{-}(CH_2{-}\underset{\begin{array}{c}|\\ CH\\ \|\\ CH_2\end{array}}{CH})_k{-}(CH_2{-}CH{=}CH{-}CH_2)_p{-}OH}$$

(1–2) (k) and (1–4) (p) units are in random placement. Samples possess about 90% of (1–2) and 10% of (1–4) units. The molar mass is about 2000 g/mol corresponding to about 40 monomeric units. Various kinds of mesogens have been grafted on (1–2) units, with variable degrees of substitution: these mesogenic units are described in Table I. The side-chains polymers obtained can be represented by the following formula.



$$\mathrm{HO{-}(CH_2{-}\underset{\begin{array}{c}|\\ CH\\ \|\\ CH_2\end{array}}{CH})_n{-}(CH_2{-}\underset{\begin{array}{c}|\\ (CH_2)_2\\ |\\ CH_3{-}Si{-}CH_3\\ |\\ (CH_2)_x\\ |\\ mesogen\end{array}}{CH})_m{-}(CH_2{-}CH{=}CH{-}CH_2)_p{-}OH}$$

with $k = n + m$, $s = m/(k + p)$

TABLE I

Various mesogenic units grafted on 1,2-polybutadiene chain, leading on mesomorphic properties of the resulting polymer

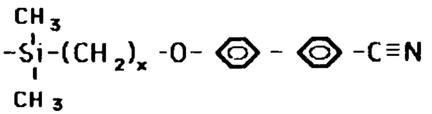
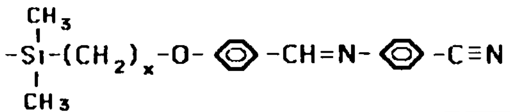
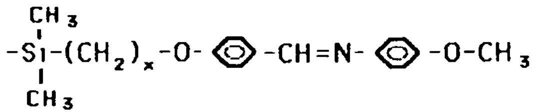
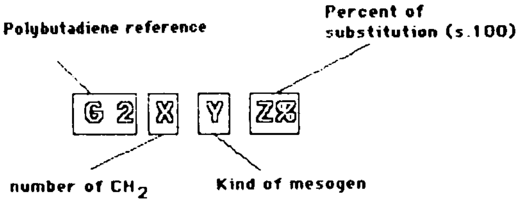
A	
D	
E	

TABLE II

Identification of the samples and transition temperatures obtained by differential scanning, calorimetry and optical polarizing microscopy, for various mesogens, spacers length and degree of substitution.



	X	S	$\overline{Tg}$ DSC increase 10°/mn	Tc (increase)			Tc microscope decrease	
				DSC(peak) 10°/mn	microscope onset	microscope end	onset	end
A	4	18	-5°	▨	▨	▨	▨	▨
		44	0°	▨	▨	▨	▨	▨
		50	16°	38.5°	▨	▨	▨	▨
		75	15°	75°	80°	84°	72°	75°
		90	13°	86°	88°	97°	81°	85°
	5	45	-3°	42°	▨	▨	▨	▨
		90	13.5°	109°	102°	116°	100°	112°
	6	45	-4°	32°	▨	▨	▨	▨
		90	8.5°	98°	96°	108°	93°	104°
	7	85	7°	115°	119°	124°	116°	122°
D	4	70	14°	48°	39°	50°	▨	▨
		85	▨	▨	57°	66°	▨	▨
	6	80	12°	102°	101°	111°	92°	98°
E	4	85	20°	▨	85°	110°	▨	▨

It must be pointed out that the grafting of the mesogen is performed by means of spacers somewhat different from the commonly used aliphatic chains since a dimethylsilane unit is introduced. The length of the spacer is variable ($4 \leq x \leq 7$). The resulting polymers are described in Table II.

SMLC USED IN THE BLENDS

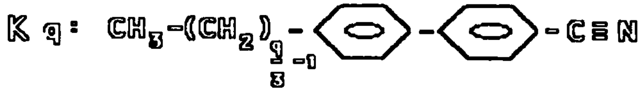
A family of SMLC, cyanobiphenyls, corresponding to the main mesogenic group grafted on the chain as well as a well-known Schiff base, MBBA, have been used in the studied blends. Table III describes these compounds and their transition temperatures.

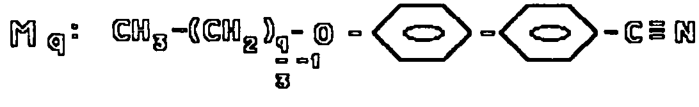
EXPERIMENTAL

Differential scanning calorimetry and polarising optical microscopy are used to obtain the transition temperatures of the crude polymers and of the blends. Polarising optical microscopy was used to observe polymer–SMLC contacts in the blends as well as in samples of well-defined composition prepared by direct weighing of the glass slides and homogenization in the isotropic phase. Near the transition

TABLE III

Chemical constitution and transition temperature of cyanobiphenyl small molecule liquid crystals family used as solvent of the polymer





S.M. Liquid crystal	K-N or K-SA transition	SA-N	N-I or SA-I
k15	24(N)	-	35.3
k18	14.5(N)	-	29
k21	30(N)	-	42.8
k24	21.5(SA)	33.5	40.5
k30	44(SA)	-	50.5
M15	48(N)	-	68
M24	54.5(SA)	67	80

temperatures, measurements were performed by optical polarising microscopy, according to the experimental method described in Figure 1.

The onset and the end temperatures of the anisotropic–isotropic transition from the curve I(T) = transmitted light intensity are defined as follows:

$T_c = T_1$ corresponds to 90% of I max.

T_2 corresponds to 10% of I max.

A slow heating and cooling rate of 0.34°/nm was generally used. Near T_c, an important increase in the birefringence is often observed when heating, as a result

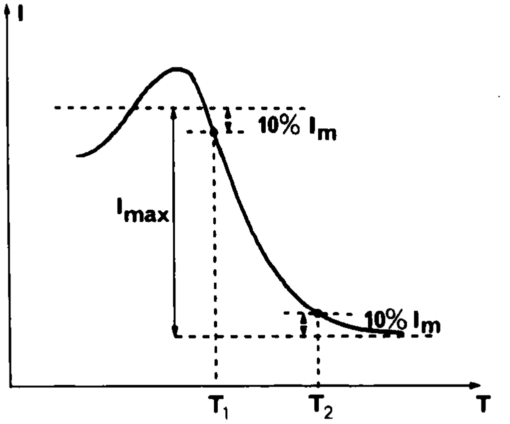


FIGURE 1 Variation of the light intensity transmitted between polars when the mesomorphic polymer sample is heated above the isotropisation temperature: the onset and end temperatures of this transition are defined in this way.

of the fluidification of the smectic mesophase (9). To suppress this behaviour the anisotropic phase was generally annealed in the vicinity of T_c. Then, after a variable time, observation of the characteristic textures of the smectic A phase was possible. Just after the preparation of the samples, it was often only possible to observe a thinly-textured, unidentifiable, strongly diffusing morphology (9). For a longer period of annealing an increase of domains size was obtained.

1. Results concerning bulk polymers

Transition temperatures. Table II and Figure 2 show the transition temperatures of the various samples. An odd–even effect is observed with the increase of the

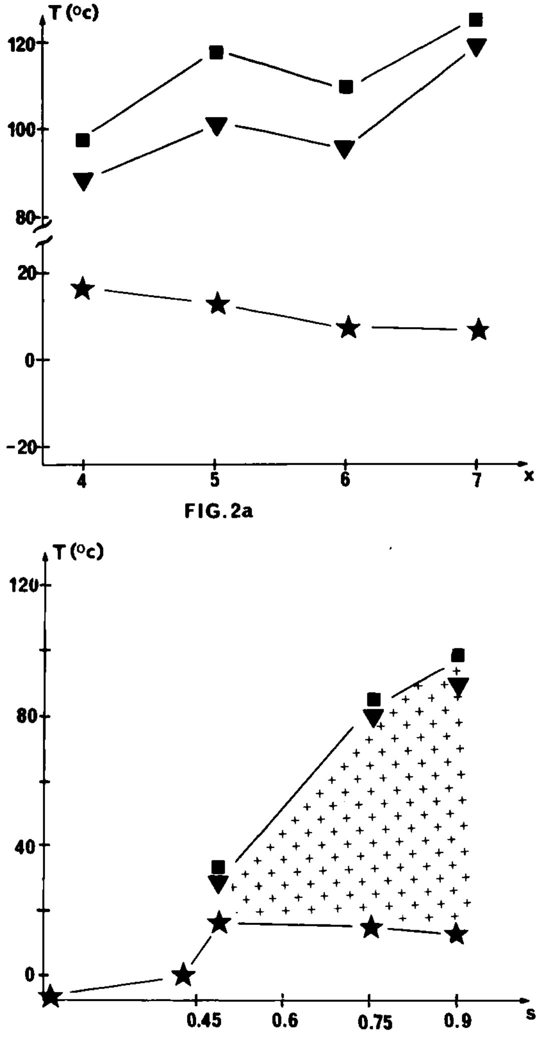


FIG.2a

FIG.2b

FIGURE 2 Glass (*), and iso-aniso (onset and end) transition temperatures as function of: a) length x of the variable part of the spacer, b) the degree of substitution s.

spacer length.[9,10] A decrease of T_c with the degree of substitution $s = m/(p + k)$ is observed while the glass transition temperature Tg is only slightly modified in these cases. For $s = 0.45$ no mesomorphic phase can be observed. In the case of high substitution rates and long spacers, the annealing allowed the observation of fan-shaped textures corresponding to S_A phase (Picture 1). In other cases, extremely long annealing (1 week) did not always allow these characteristic textures to occur. The observations in the biphase suggest that a S_A phase is also present in such cases. An X-ray study is in progress to clarify this point.

Biphases. For a temperature range of about ten degrees, a biphase is observed near transition A–I corresponding (Figure 1) to the decrease in the transmitted light intensity with temperature T. In all cases a typical texture is observed corresponding to isotropic black areas of ever increasing size, finally filling the field except for birefringent long needles (Pictures 2a and b). An important anisotropy of surface tension between directions perpendicular and parallel to the smectic layers, results in the numerous "angles" observed in this kind of biphase,[11] as opposed to a globular nematic morphology. This type of biphase has been observed with other side-chains polymers, but the temperature range is wider in the material studied.

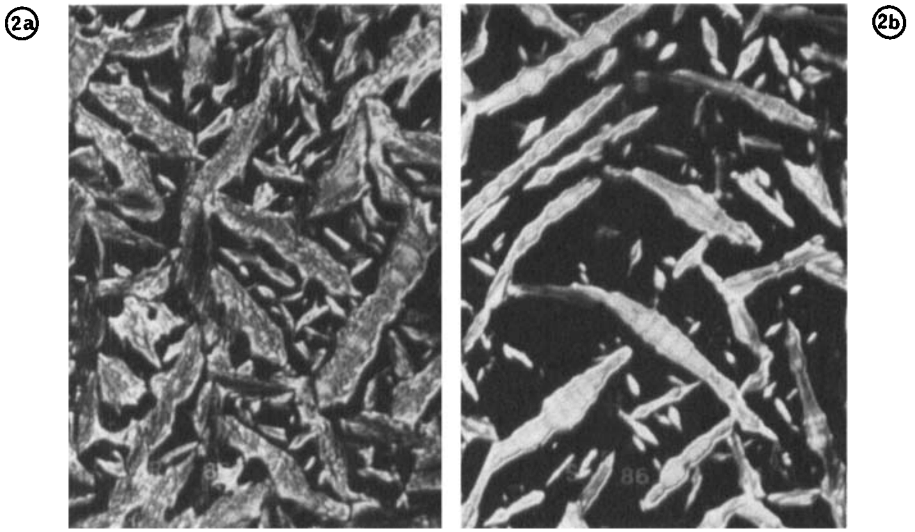
In the case of main-chain mesomorphic polymers a marked biphasic structure has been observed, and ascribed to the partial segregation of the low T_c short chains (Figure 3a) in the isotropic phase and that of high T_c longer ones in the anisotropic phase. A fractionation of chains with different molecular weights is obtained in this way.[12,13]

The influence of the backbone length in comb-like polymers has stressed various authors[14,15] (Figure 3b) but, in the present case, a new kind of polydispersity must be taken into account:

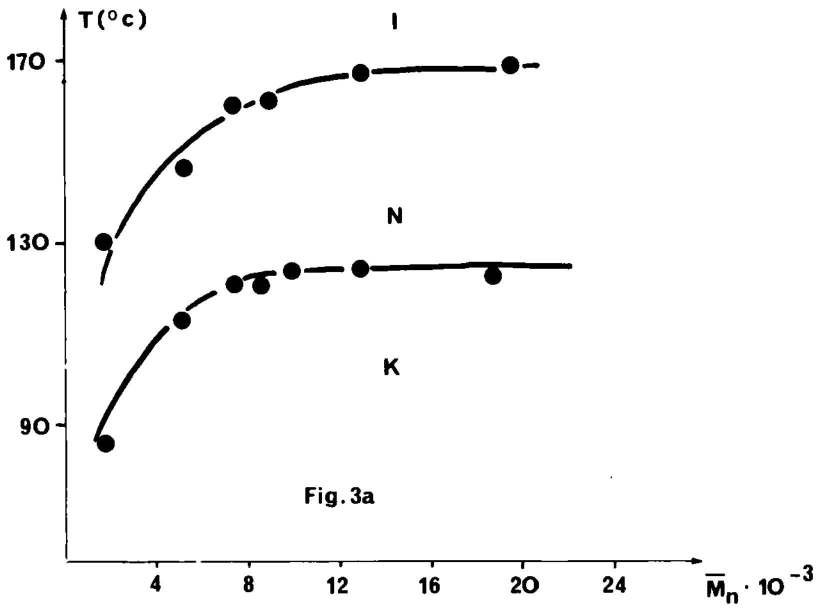
— it has been shown that an asymptotic chain length effect is reached when about 10 substituted units are linked[14]

①

Typical fan-shaped smectic texture obtained with G24A90%, after a 24 hour annealing. Enlargement = 80.

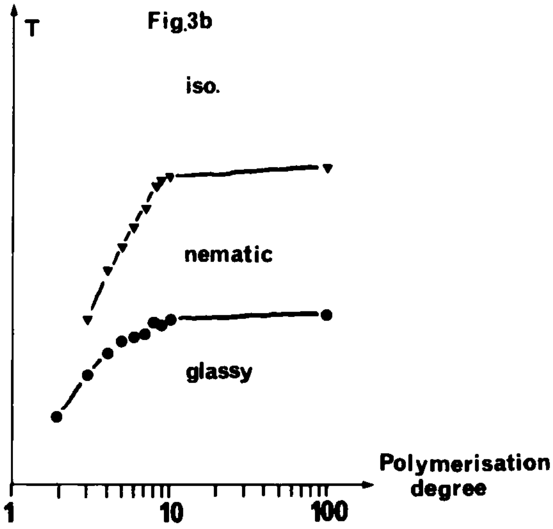


Needle textures obtained with G24A90%, in the biphasic gap a) near the onset of the biphase 90°C, b) near the end of the biphase 95°C. Enlargement = 400.



(a)

FIGURE 3 Examples of variation of aniso-iso transition temperature, function of the molecular weight: a) for a main chain aromatic polyester from Reference 12, b) for a side-chains polysiloxane from Reference 14.



(b)

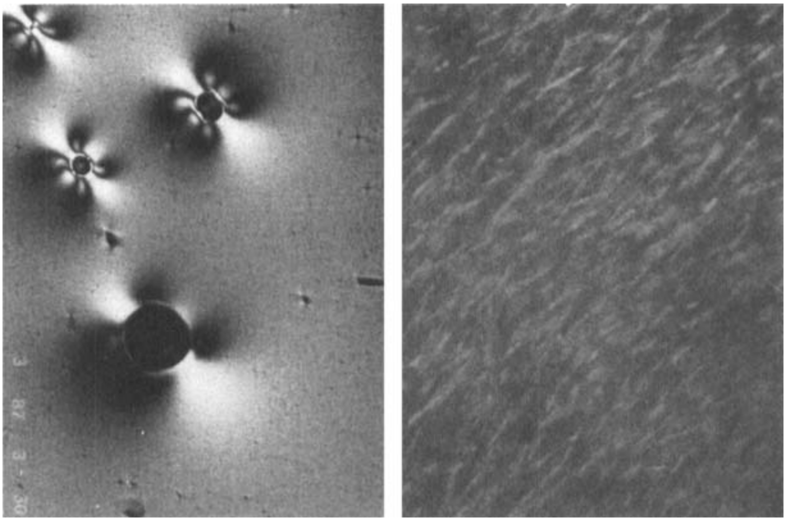
FIGURE 3 (*continued*)

— in addition the biphasic gap observed in the present case is too wide considering that the starting polybutadiene used possesses low polydispersity

— the different widths of the biphasic gaps between different samples (G25A, G27A for example) cannot be explained from chain lengths.

It can therefore be assumed that a particular behaviour is thus obtained, due to the variable degree of substitution. The random spatial distribution of these substituents could be responsible for an important effect on T_c. A fractionation induced either by the various degrees of substitution or by the variable structure of the monomeric units may result in the separation of the biphase components.

Textures observed. As pointed out previously in the case of high degrees of substitution and long spacers, the focal conic fan-shaped textures of S_A are readily observed. This ready macroscopic reorganization is related to fluidity and enhanced by annealing in anisotropic phase, far from Tg.[9] For low values of s and x and for D and E mesogens, when (T_c − Tg) is lower than about 50°C, annealing must be extremely long and the observed textures show a very different aspect. The smectic phase can be identified only by the observation of long needles at the end of the biphase. The general aspect of the textures for temperatures near Tg looks like that of a birefringent, nearly homogeneous medium similar to a strongly viscous nematic one (Picture 3a). However, extinctions occurring in the vicinity of bubbles and other defects, clearly show an important difference with nematics. These defects are separate and do not appear as aggregates as in nematics. This could be due to the long range relaxation of deformations (the whole of associated disclination strengths equals 0). Very long annealing of these textures allows, in the most favourable cases, (T_c − Tg > 30°C) the observation of a needle texture (Picture 3b): these needles prove to be the basic units of a kind of "macro nematic" phase

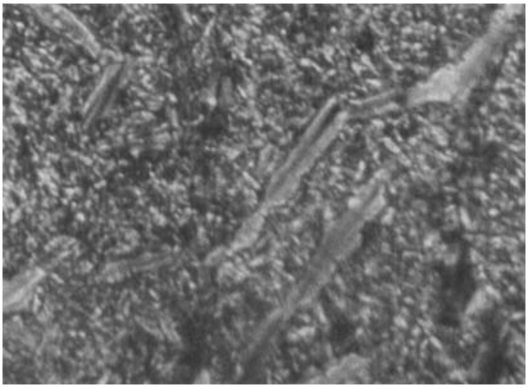


(3a) (3b)

a) Uniform texture and some particular defects observed just after preparation of a G24D70% sample. Enlargement = 150. b) After a long annealing (1 week at 60°C) oriented needles become visible for an alignment at 45° of the polars. Enlargement = 400.

(S_A at the molecular level) with very low elastic constant. A preferential orientation of these "needles" under flow and near surfaces accounts for the observed defects.

The medium around these needles can be either an isotropic one, far from Tg, or a smectic, very thinly-textured and strongly-diffusing one, corresponding, on a smaller scale, to the observed texture resulting from the quenching of a high T_c sample after annealing in the biphasic domain (Picture 4).



④

Texture obtained after quenching a G26A90% sample. Starting from a 110°C temperature in the biphasic gap, long needles are still visible in a diffusing medium.

2. Polymers in solutions[3,4,5,6,7]

Observation of contact domains/G2XA + SMLC cyanobiphenyls. With all these systems, no phase separation was observed far from the solid-S_A or S_A-isotropic transitions. In the contact area with the SMLC nematic phase, the concentration gradient shows a continuous transition from the concentrated polymer smectic phase to SMLC-rich nematic phase.

Most of the contact domains observed correspond to the textures described in Figure 4. Particularly for low x values the S_A–N transition occurs in a homeotropic anchoring zone, where the two phases can be distinguished only after application of a slight shear on the slides, leading in the S_A phase to the appearance of a grid of filament instability (Picture 5). It is however possible, in several cases, to observe a direct change from smectic A "fans" to the nematic "schlierens" (Picture 6).

G2XD, E + K15 or MBBA. In this case, the behaviour observed by the contact method seems to indicate a lesser compatibility with the used SMLC than in the former one. Along the concentration gradient, an isotropic or biphasic zone appears at temperatures for which the polymer or the SMLC when pure, are fully anisotropic. Areas equally appear when anisotropic–anisotropic separation occurs. Some

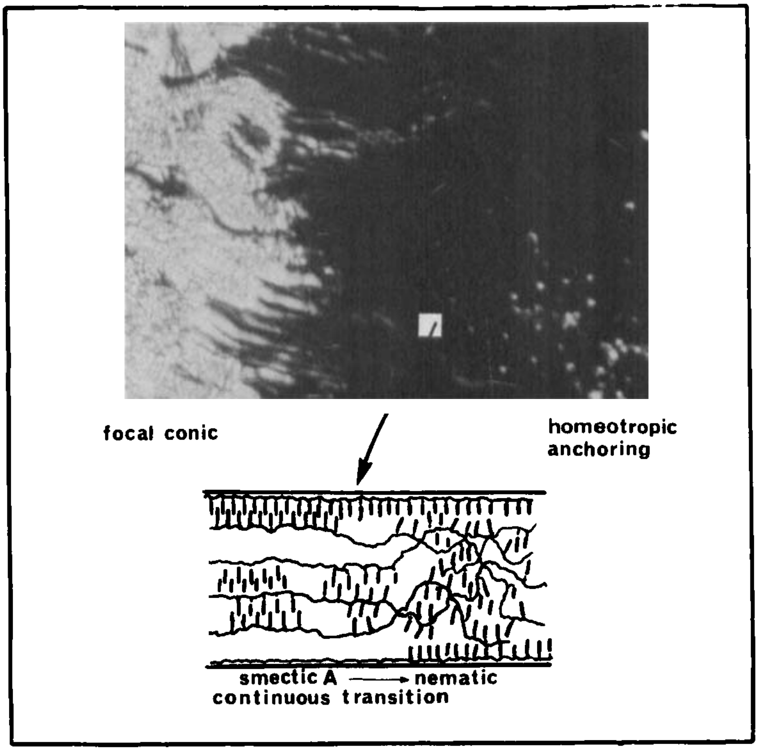
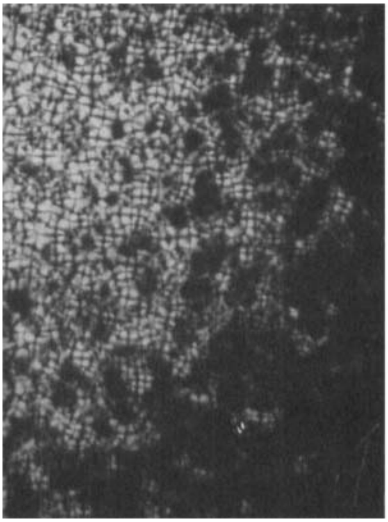


FIGURE 4 Micrography of the concentration gradient domain in a contact area of G24A90%—K18, and figure showing the transition from smectic A focal conic to smectic A homeotropic and to nematic homeotropic texture.



⑤

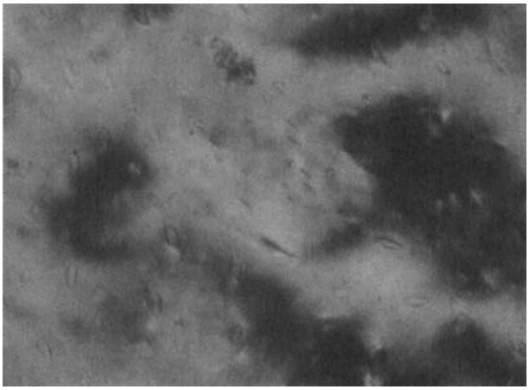
Polygonal smectic instability observed after shearing the upper slide of a homeotropic texture. Enlargement = 400.

⑥

Transition from a fan-shaped smectic texture to a schlieren nematic one (contact G26A90%—K10). Enlargement = 400.

smectic needles are visible (Picture 7) in the nematic medium particularly, for the $N-S_A$ transition obtained by cooling.

Phase diagrams. The phase diagrams obtained with the polymer family G2XA and SMLC cyanobiphenyls (Figure 5) show that the spacer length x, the SMLC aliphatic tail length q, and the polymer degree of substitution, equally affect the transition temperature T_c of the blends and the extent N of the nematic phase. Because of the odd–even effect of x and q, it is however necessary to compare



⑦

Observation of smectic needles with nematic texture. Gradient concentration in a G26D85%—K15 contact zone. Enlargement = 400.

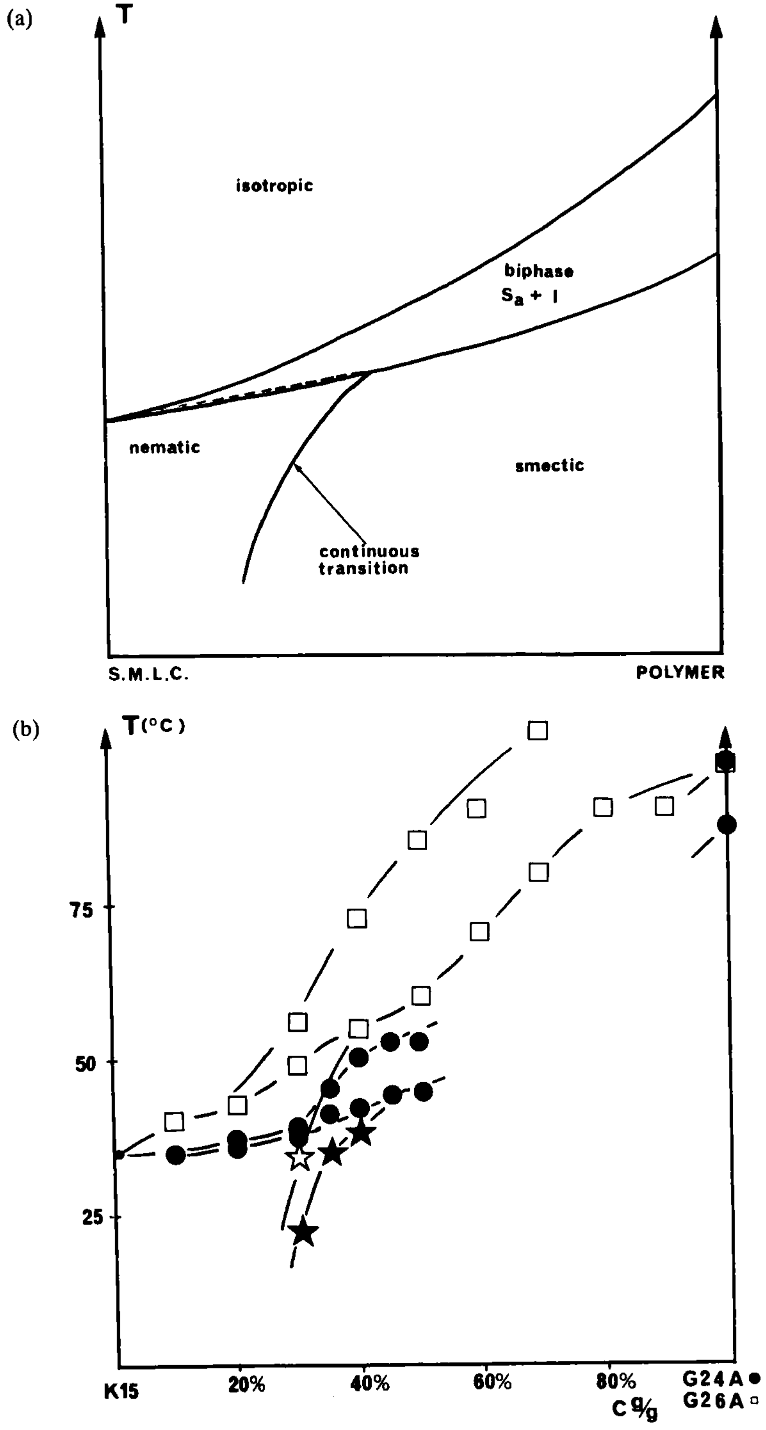


FIGURE 5 Effect of various structural parameters b) length of the spacer, c) degree of substitution, d) length of the aliphatic tail of the SMLC, on the phase diagrams G2XA-Alkylcyanobiphenyls.

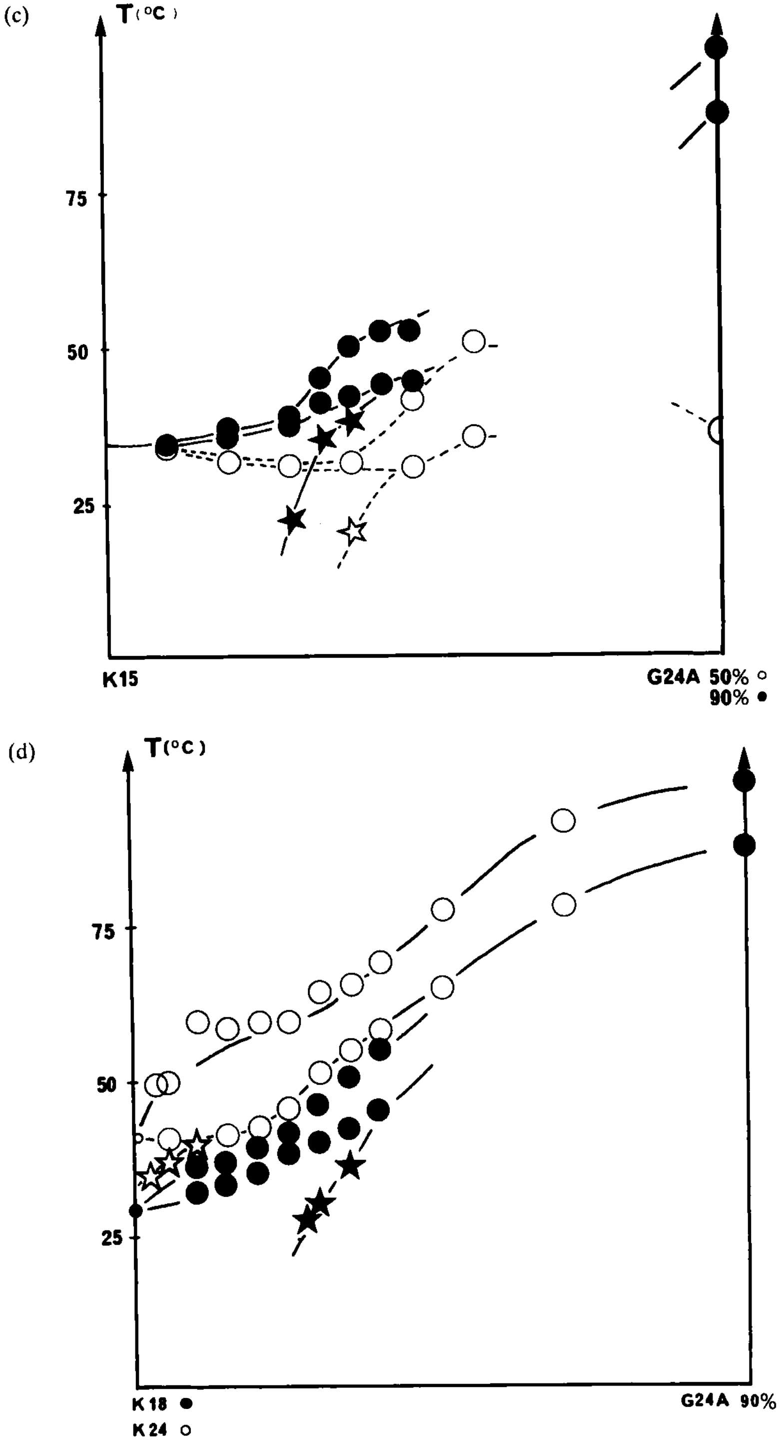
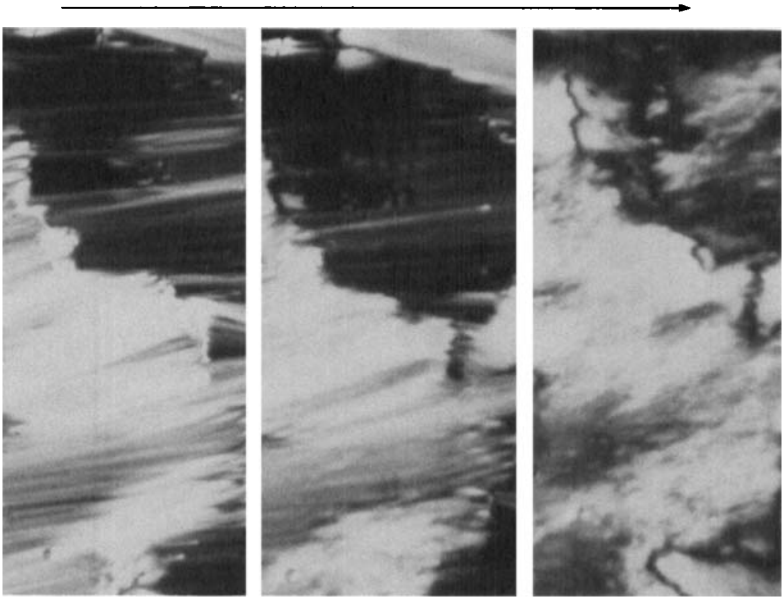
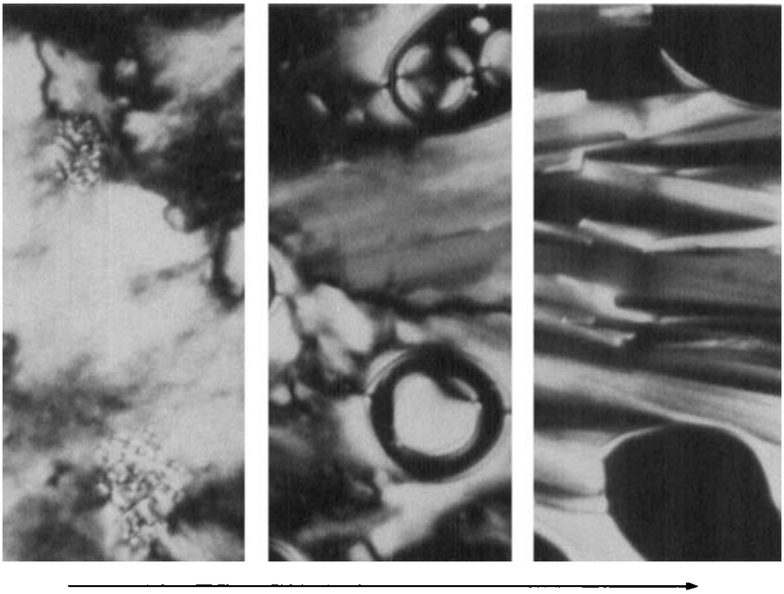


FIGURE 5 (continued)



Successive textures observed during a temperature increase with a G26A 90% in K15 blend. Following the arrow: 40°C smectic, 44°, 45° nematic.



⑧

48° Beginning of the biphase, 48.5° appearance of smectic domain in the nematic–isotropic biphase, 49°biphase smectic–isotropic. Enlargement = 400.

only components of the same parity. Then, an increase of *x*, *q* or *s* leads to an increase of T_c and a decrease of N, and to the ultimate disappearance of N in K30. The series of micrographies marked 8 show the previously described behaviour in the biphase above the nematic phase, leading to a smectic A–isotropic biphase. On heating, and on appearance of the first nematic droplets, the characteristic defects of the nematic phase lead to "fans" and to characteristic angles of smectic phases. These biphases probably correspond to the rapid diffusion of the SMLC with low T_c towards the isotropic phase.

CONCLUSION

Remarkable effects are associated with the substitution degree of this new kind of side-chains mesomorphic polymers. By blending these polymers with low molecular weight liquid crystals, some new properties such as the smectic–isotropic biphase above the nematic phase, are observed.

X-rays diffraction, differential scanning calorimetry and dielectric investigations, would provide better understanding of the molecular mechanisms inducing these effects.

The possible modification of many structural parameters as degree of substitution, blending with small molecules liquid crystals, flexibility of the main chain, etc., should allow the adjustment of this material to specific uses, particularly in the domain of electro-optical devices.

Acknowledgment

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