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X-ray diffraction study of a polybutadiene, side chain, mesomorphic polymer

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A side chain, mesomorphic polymer has been synthesized, starting from a commercial polybutadiene main chain. A preliminary X-ray diffraction study shows the influence of the degree of substitution and the spacer length on the interdigitated S_A layer thickness, particularly for strongly polar alkoxyphenyl mesogens. Some hypotheses are deduced about the particular odd-even effect observed with this backbone and on the conformation of the main and side chains.

1. Introduction

Since the first synthesis of liquid-crystalline polymers, the great majority of studies have dealt with two kinds of main chains: poly(meta)acrylate and polysiloxane. Their mesomorphic properties are induced by mobile side chains linked to a flexible backbone. Here we report results for comb-like polymers, in which the main chain is a polybutadiene [1]. The mesogen substitution process, starting from a commercial polymer, allows the variation of:

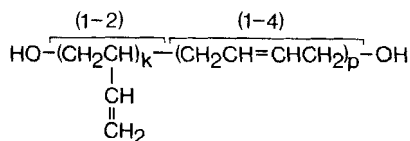
the degree of grafting,
the aliphatic spacer length,
the mesogen type.

Moreover, the industrial importance of this chain type, particularly in the rubber domain, gives it a particular interest: the aperture of the residual double bonds leads to the possibility of crosslinking the backbone.

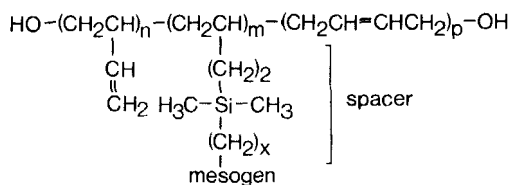
The two first mesogens grafted in Professor Fontanille's laboratory (L.P.C.O., University Bordeaux 1), gave samples which form smectic phases. They were first characterized by D.S.C. and polarizing optical microscopy [2]. Then we thought it was necessary to initiate an X-ray diffraction experiment; despite of the clear interest of this technique which is used extensively to study small molecule liquid crystals, the literature offers in fact only scarce information concerning, for example, the effect of the degree of substitution or the spacer length on the smectic layer thickness.

2. Samples studied

The samples were synthesized [1] from a polybutadiene chain G 2000 obtained from NISSO, with the formula:



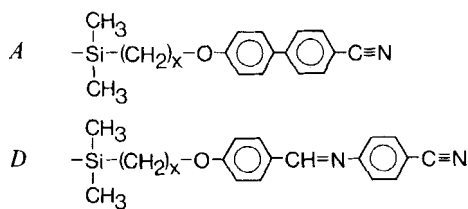
The location of the (1-2) (k) and (1-4) (p) units is random. The starting backbone is constituted from about 90 per cent of (1-2) and 10 per cent of (1-4) units. The molar mass is about 2000 g/mol corresponding to about 37 monomeric units. Two main kinds of mesogens (described in table 1) corresponding to the cyanobiphenyl (*A*) and Schiff's base (*D*) low molar families have been randomly substituted on the (1-2) units with variable degrees. The resulting mesomorphic polymers are described by the formula:



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

The mesogenic group is linked to the main chain by means of a variable length spacer ($4 < x < 7$). This spacer includes a dimethylsilane unit whose presence is associated with the synthetic route for grafting the mesogen (1); the steric hindrances induced by the two methyls are certainly very important. Preliminary trial syntheses showed the expected impossibility of obtaining mesomorphic phases when the methyls were replaced by two bulky heterocyclic rings.

Table 1. Different mesogenic units grafted onto the commercial polybutadiene chain and giving mesomorphic properties to the resulting polymer.



The designation of the samples, the glassy and anisotropic-isotropic transition temperatures are given in table 2: an important, odd-even effect, well known for low molar mass liquid crystals, [3] is observed for these transition temperatures: but this effect is reversed if compared with similar side chain mesophases.

3. Experimental diffraction patterns

The first X-rays were obtained for G24A 90 per cent in Dr. Noël's laboratory (P.C.S.M., E.S.P.C.I. Paris) with a vacuum flat-plate camera at variable temperatures up to the isotropic domain. We have made measurements at room temperature, from 16°C to 22°C on a Guinier-Hägg camera using $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5405 \text{ \AA}$) focused by a quartz monochromator. A new film holder has been built, in order to remove the small angle occultation.

Table 2. Designation of the samples and transition temperature obtained by differential scanning calorimetry and optical polarizing microscopy, for various mesogens, spacer lengths and degrees of substitution. In the code G2 XYZ per cent, G2 denotes commercial polybutadiene, X the number of methylene groups, Y the nature of the mesogen and Z the degree of substitution (s.100).

	X	S	\bar{T}_g D.S.C. increase 10°C/mn	T_c °C (increase)		T_c /°C microscope decrease		
				D.S.C. (peak) 10°C/mm	Microscope Onset End	Onset End		
A	4	0.18	-5°	-	-	-	-	
		0.44	0°	-	-	-	-	
		0.50	16°	38.5°	-	-	-	
		0.75	15°	75°	80°	84°	72°	75°
		0.90	13°	86°	88°	97°	81°	85°
	5	0.45	-3°	42°	-	-	-	-
		0.90	13.5°	109°	102°	116°	100°	112°
	6	0.45	-4°	32°	-	-	-	-
		0.90	8.5°	98°	96°	108°	93°	104°
	7	0.85	7°	115°	119°	124°	116°	122°
D	4	0.70	14°	48°	39°	50°	-	-
		0.85	-	-	57°	66°	-	-
	6	0.80	12°	102°	101°	111°	92°	98°

Samples for X-ray investigation were prepared in the following way: a small amount of polymer was placed on a nickel spatula and heated in a hot air flow until it was completely molten. The liquid was then spread out on a piece of warm glass, previous cleaned with alcohol. After cooling to ambient temperature, it was cut to a 6 mm diameter disk and then removed gently with a razor blade. The disc was fixed in the sample holder by means of sticky tape. This process was rather easy with the most substituted G2XA samples. The G2XD were more sticky and often difficult to transfer to the sample holder. G24D 85 per cent was honey-like at every temperature event in the refrigerator.

4. Results

Table 3 lists the smectic layer distances obtained with the different samples, using the first order, Bragg reflection law. The narrow, small angle lines obtained and the method used to measure the distance to the origin line allows a precision on the mean layer thickness of better than $\pm 0.3 \text{ \AA}$. In a few cases, the second order reflection is observed as a weak narrow line. A sample studied in the fibre geometry in Dr. Noël's laboratory showed diffuse lines which were not commensurate with the first order Bragg lines. They are probably associated with the coexistence of different layer structures [7, 8], X-ray experiments on oriented samples are necessary to give more accurate interpretations of these lines. Figures 1 (a) and (b) show the respective effect of the spacer length (x) and of the degree(s) of substitution on the measured thickness in the particular case of the A mesogen.

We observed other lines:

At large angles, a broad diffuse line, related to the organization of the mesogen inside the layer. It probably confirms in most cases a smectic A liquid order. The

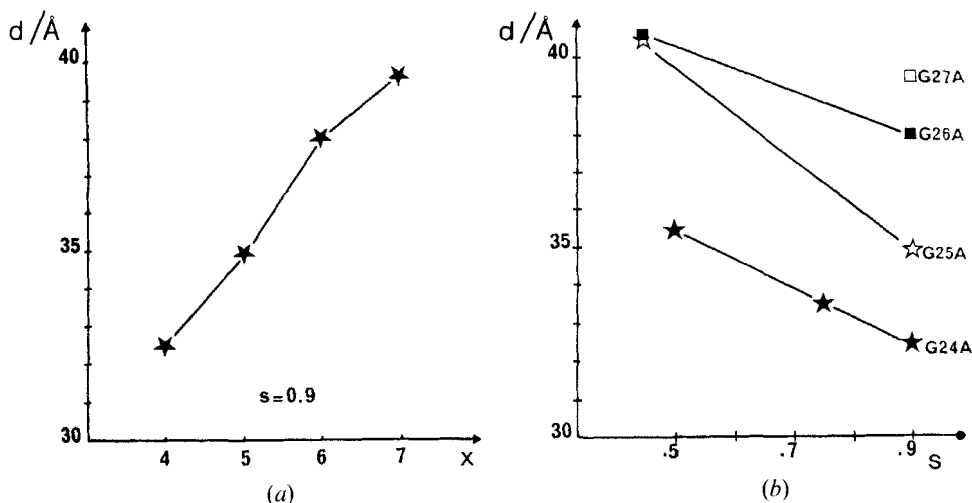


Figure 1. Effect of the number of methylene units x , (a), and degree of substitution, (b), on the smectic layer thickness.

intermesogen mean distance D calculated from the expression $2D \sin \theta = 1.117\lambda$ [4, 5, 12] where θ is the angle for the line, is about 5.4 Å [6]. It corresponds to distances varying from 4 to 7 Å .

In some cases a particularly broad (probably double) wide angle line, and several narrow lines (see figure 2 (b)) may correspond to the possible existence of a more ordered smectic or crystalline phase [7, 8] at room temperature. This was indicated by the observation of the striation on the fan-like textures appearing at room temperature (see figure 3 (a, b)).

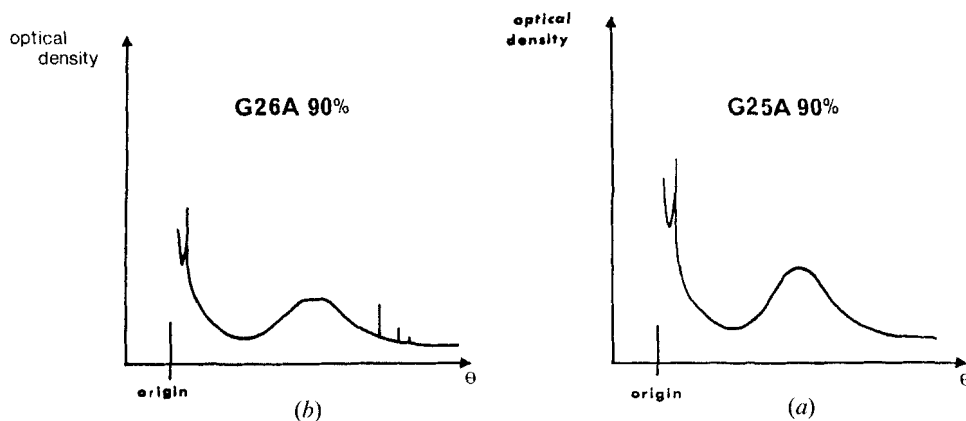
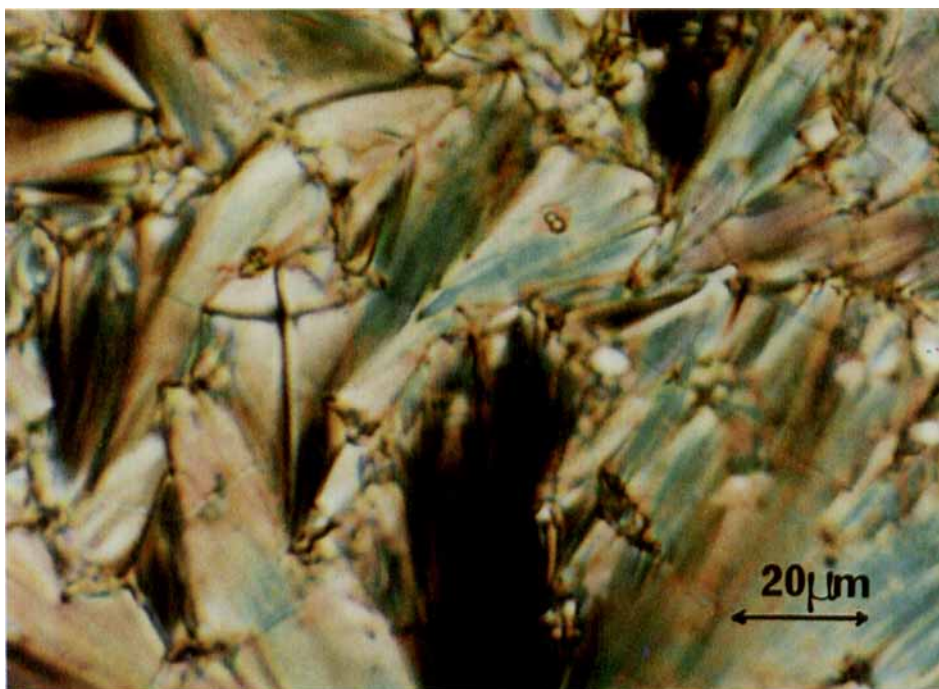


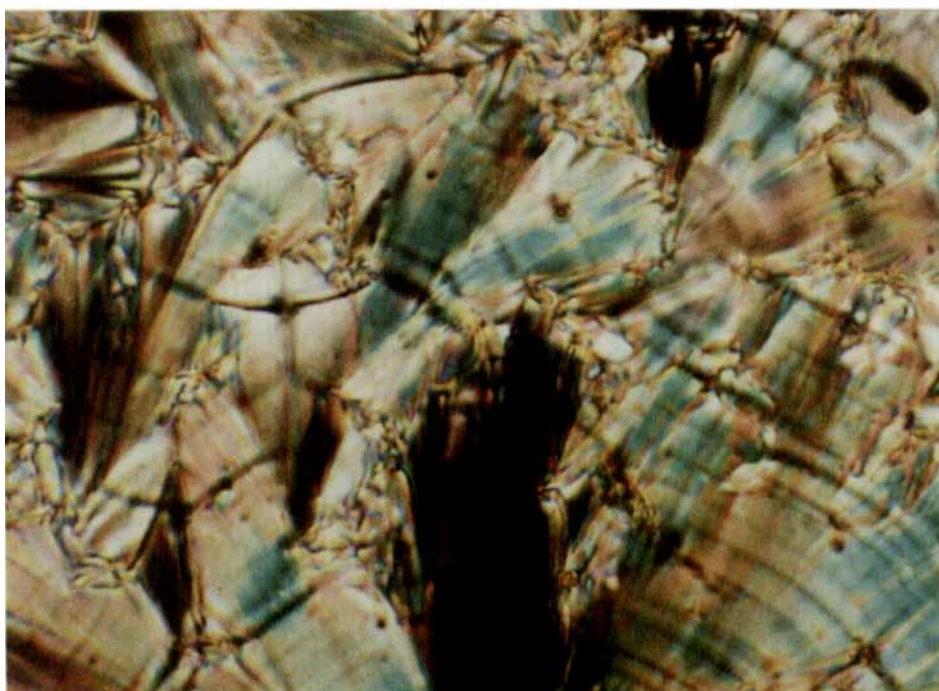
Figure 2. X-ray diffraction spectra obtained at room temperature with an even (b), and an odd (a) number of aliphatic bonds in the spacer.

We note that G24D 85 per cent did not give any small angle line, even after several treatments such as annealing, freezing, and leaving for several weeks. Its aspect and texture did not evolve at all, and X-ray patterns remained unchanged: they show merely a broad diffuse line at wide angles.

The temperature experiments on G24A showed a very small increase of the diffraction angle across the mesomorphic range: the corresponding layer thickness



(a)



(b)

Figure 3. Photomicrographies of G24A 90 per cent showing the focal conic textures observed between crossed polars: (a) the normal smectic A fan-like texture at 70°C; (b) the striated pattern obtained at room temperature.

Table 3. Thickness of the smectic layer as a function of the mesogen type, spacer length and degree of substitution

	<i>X</i>	<i>S</i>	Interlayer distance 1/Å	Number of orders observed
<i>A</i>	4	0.18	—	—
		0.44	—	—
		0.50	35.4	1†
		0.75	33.5	2†
		0.90	32.5	1
	5	0.45	40.1	1
		0.90	34.7	2
	6	0.45	40.6	1
		0.90	38.1	2†
	7	0.85	39.6	2
<i>D</i>	4	0.70	35.3	1
		0.85	—	—
	6	0.80	38.6	1

† Narrow lines at large angles.

decreased by about 1 Å. It can be related to the disorganization of the aliphatic spacers [7, 9], or to a decrease in the orientational order parameter decrease [10]. On raising the temperature into the isotropic phase there is a significant increase of the small angle from 1.48° to 1.76°: this increase is associated with a broadening of this line. Calculation of *l* using the formula [11, 12] given for completely disordered media

$$2/\sin \theta = 1.229\lambda$$

leads to a 30.8 Å molecular length in the isotropic phase. It is the same range as the smectic layer thickness. In fact, there is probably some short range order even in the isotropic phase [12]. Then the presence of a 25 Å molecular length, derived from a simple Bragg relation would be a better interpretation.

5. Discussion

The use of angles and bond lengths given in the literature [7, 13] gives a value of 22 Å to the shorter mesogen (see figure 4) (G24A) for an extended conformation of the aliphatic spacers. A probable disorder of the rigid parts [12] is described by the orientational order parameter *S*. The large discrepancies found in the literature for this kind of smectic side chain polymer ($0.5 < S < 0.9$) may be associated with a mean angle ranging from 15° to 35° between the cores and the normal to the smectic layers. Several authors [6, 12, 14, 15, 18]) claim a partial interdigitation of the layers for low molar mass mesogens and polymer smectic mesophases including comparable polar mesogens. Such a phenomenon may be responsible for the factor of 1.5 leading from the 22 Å molecular length to the 32 Å layer thickness. We must take into account too a small amount of main chain interlayer thickness [6]. It probably does not exceed 3 Å in the most substituted samples, according to a few layer thickness measurements made on cyanobiphenyl liquid crystals [12, 14].

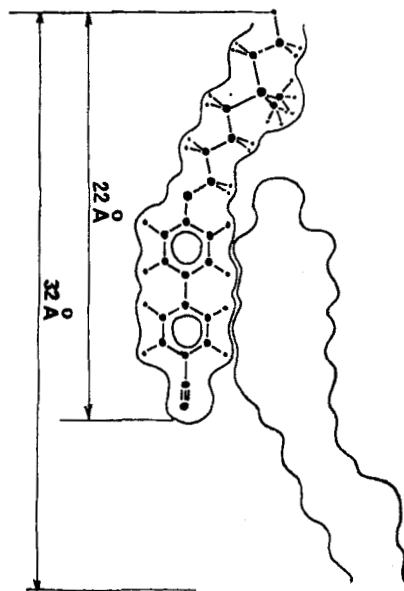


Figure 4. Interdigitated model of the smectic layer organisation for the strongly polar alkoxyphenyl mesogen.

If we pay attention to the thickness variation observed (see figure 1(a)) as a function of x , we can build some hypothesis about the conformation of the spacer. When we compare the same parity values of x , we find a mean variation of 2.6 \AA per carbon. This variation is very important [16, 17, 18] when compared to the 2.3 \AA per carbon given by the fully extended model shown in figure 5. It seems to confirm the hypothesis of an all-trans spacer conformation. Furthermore, the liquid crystal-isotropic transition temperatures show an important odd-even effect. Until now the

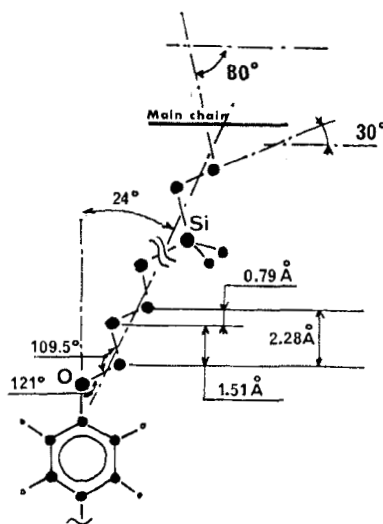


Figure 5. Fully extended spacer model giving the probable angles and bonds lengths between the main chain and the rigid core.

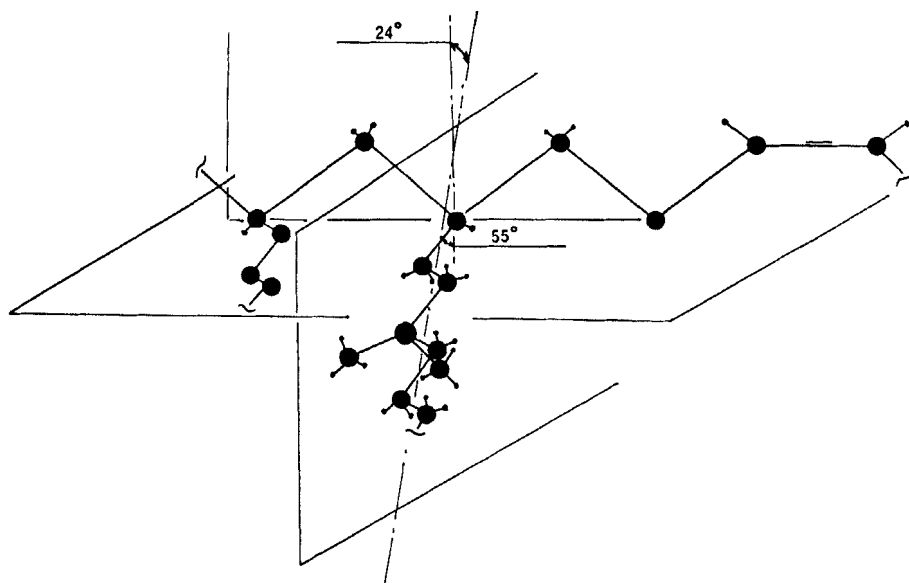


Figure 6. A simplified model showing a probable conformation of the main and side chain, for the A mesogen and for high degrees of substitution

literature of side chain mesomorphic polymers described odd-even effects in only two cases: an alkyl terminated smectic polyacrylate [19] and a $C\equiv N$ terminated polysiloxane [20]. In these two cases the observed effect was comparable with the odd-even effect in low molar mass liquid crystals such as the cyanobiphenyl families [21]. An even number of aliphatic CH_2-CH_2 bonds in the spacer leads to higher transition temperatures than an odd one; this is related to the last bond direction, increasing the axial ratio of the molecule only in the first case. For G2XA 90 per cent we observe the opposite effect. The mesophase seems to be more stabilized when the last aliphatic bond near the main chain has a tangential position relatively to the smectic layer. This can be explained by an arrangement of the main chain shown in figure 6 for which the 35° angle between this last segment and the layer plane greatly favours a trans conformation of the main and lateral chains. The presence of the strongly packed dimethylsilane unit in the smectic plane has certainly an important part to play in this particular effect. The difference with the other examples mentioned can probably be found in a very different conformation of the polyacrylate and polysiloxane main chain in the interlayer.

Another effect should be pointed out; when x is increased by one, from an even to an odd number of bonds in aliphatic chain, the layer thickness increases by 1.6 \AA though odd to even leads to an increase of 3.3 \AA . Here, we are in qualitative agreement with the description in the figure 4. This effect is not observed for polymers with low degrees of substitution. This fact may be related to a much more disordered conformation of the main chain and to the presence of small pendants due to unsubstituted units.

The interlayer thickness l increases as the degree of substitution decreases. For example, we can see that a variation of s from 0.9 to 0.45 leads to an increase of l by 2.5 \AA for the samples having an even number of spacer bonds and by 5 \AA when this number is odd (G25A). Owing to the comparable densities of the lateral parts and the

polybutadiene chains, ($0.97 < \rho < 1.02$ for the alkycyanobiphenyl low molar mass family in the mesomorphic phase [22] and $\rho \approx 0.95$ for a polyethylene polymer) we may assume a main chain interlayer thickness l' proportional to the ratio of the respective molecular weights. For the lateral parts of G24A, $M_w = 338$, for the main chain part, $M_w = 29.7$ with $s = 0.9$ and $M_w = 77.4$ with $s = 0.45$. This gives $l' = 2.86 \text{ \AA}$ for $s = 0.9$ and $l' = 7.44 \text{ \AA}$ for $s = 0.45$. The increase of layer thickness observed is in agreement with these values. For an even number of spacer bonds, the less dense and more disordered packing of the main chains for large s is probably responsible for the smaller increase observed. On the other hand, this small increase for the even spacers could explain the rapid disappearance of mesomorphic properties for $s < 0.45$. Though for a siloxane backbone [23] these properties are maintained up to $s = 0.1$. With the decrease of s , a large part of the main chain possibly crosses the smectic layers and disorganizes them.

The small number of samples prepared and investigated with the D mesogen does now allow us to draw any valuable conclusions.

6. Conclusion

The first results reported here for a family of side chain mesomorphic polymers by X-ray diffraction leads to original results concerning influence of the spacer length and the degree of substitution on the smectic layer thickness: these results show the great importance of the main chain conformation on the mesophase properties. This influence cannot be summarised only in term of rigidity as many authors do. In particular, the description of the odd-even effect of the spacer length needs, in this side chain case, a more complex model than for low molar mass liquid crystals.

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References

- [1] ROBERT, P., VILLENAVE, J. J., FONTANILLE, M., GILLI, J. M., and SIXOU, P., 1988, *Molec. Crystals liq. Crystals*, **155**, 161.
- [2] GILLI, J. M., FULCHERI, C., SIXOU, P., ROBERT, P., VILLENAVE, J. J., and FONTANILLE, M., *Molec. Crystals liq. Crystals* (to be published).
- [3] GRAY, G. W., HARRISON, K. J., NASH, J. A., CONSTANT, J., HULME, D. S. KIRTON, J., and RAYNES, E. P., 1974, *Liquid Crystals and Ordered Fluids*, Vol. 2, edited by J. F. Johnson and R. S. Porter (Plenum), pp. 617-643.
- [4] DE VRIES, A., 1970, *Molec. Crystals liq. Crystals*, **10**, 219.
- [5] DE VRIES, A., EKACHAI, A. and SPIELBERG, M., 1979, *J. Phys., Paris, coll. C3*, Suppl. au No. 4, T **40**, 147.
- [6] RICHARDSON, R. M., and HERRING, M. J. 1985, *Molec. Crystals liq. Crystals*, **123**, 143.
- [7] DOUCET, J., 1978, Thèse, Université Paris Sud.
- [8] DAVIDSON, P. 1984, Thèse, Université Paris Sud.
- [9] DIELE, S., BRAND, P., and SACKMAN, H., 1972, *Molec. Crystals liq. Crystals*, **16**, 105.
- [10] DE VRIES, A., EKACHAI, A., and SPIELBERG, M., 1979, *Molec. Crystals liq. Crystals Lett.*, **49**, 143.
- [11] DE VRIES, A., 1970, *Molec. Crystals liq. Crystals*, **11**, 361.
- [12] LEADBETTER, A. J., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press) pp. 285-316.
- [13] *Interatomic distances*, Chemical Society, special publication Nos. 18 and 11.

- [14] LEADBETTER, A. J., DURRANT, J. L. A. and RUGMAN, M., 1977, *Molec. Crystals liq. Crystals Lett.*, **34**, 231.
- [15] GUILLON, D., SEURIN, P. and SKOULIOS, A. 1979, *Molec. Crystals liq. Crystals*, **51**, 149.
- [16] PAPE, E. H., 1984, *Molec. Crystals liq. Crystals Lett.*, **102**, 271.
- [17] ACHARD, M. F., HARDOUIN, F., SIGAUD, G., and MAUZAC, M., 1986, *Liq. Crystals.*, **1**, 203.
- [18] MAUZAC, M., HARDOUIN, F., RICHARD, H., ACHARD, M. F., SIGAUD, G., and GASPAROUX, H., 1986, *Eur. Polym. J.*, **22**, 137.
- [19] GEMMELL, P. A., GRAY, G. W., LACEY, D., ALIMOGLU, A. K., and LEDWITH, A., 1985, *Polymer*, **26**.
- [20] SIMON, R., and COLES, H. J., 1986, *Polymer*, **27**, 811.
- [21] GRAY, G. W., 1982, *Polymer Liquid Crystals*, edited by A. Ciferri, W. R. Krigbaum, R. B. Meyer (Academic Press).
- [22] DUNMUR, D. A. and MILLER, W. H., 1979, *J. Phys., Paris*, **40**, Suppl. No. 4, coll. C3, 141.
- [23] RINGSDORF, H., and SCHNELLER, A., 1982, *Makromolek. Chem. rap. Commun.*, **3**, 557.