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Some relevant parameters on the 'jacketed' effect in side-on fixed polysiloxanes

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New 'side-on' attached liquid crystal polysiloxanes have been synthesized with different fixation ratios of side groups and various degrees of polymerization. For these syntheses, a series of random copoly(hydrogenmethyl-dimethylsiloxane)s, used a precursors, has been realized. Both thermal properties and small angle neutron scattering experiments on these polymers show a decrease in the nematic 'jacketed' effect as the number of mesogenic groups fixed to the backbone decreases and as the main chain length increases.

1. Introduction

Until recent years, the concept of side-chain liquid crystal polymers only involved materials of the 'comb' or end fixed type–often called the terminally attached type. With extensive development of these materials and for improving understanding of the effects of combining mesogenic groups with a flexible polymer backbone, these side-groups were then appended laterally [1–7]. These side-on fixed mesogenic polymers, unlike the end fixed ones, exhibit in the nematic phase, a large anisotropy of the polymer conformation as evidenced by small angle neutron scattering experiments for polysiloxanes [8, 9], as well as for polyacrylates [10] aligned by a magnetic field. Indeed, the overall quadratic size along the direction of alignment was found to be much larger than in the perpendicular direction. Thus, a so-called 'jacketed' arrangement of mesogenic groups around the polymer backbone, initially envisioned by Zhou *et al.* [11], has been confirmed. Moreover, some evidence for this arrangement has also been found from X-ray diffraction patterns of drawn fibres of 'side-on fixed' polymethacrylates [12], where the mesogenic groups are, on average, shown to be aligned parallel to the draw direction (the main chains have to be assumed to align in the draw direction).

This prolate extension of the backbone was shown to be strongly dependent upon the number of mesogenic groups and, to a certain extent, upon the molecular weight of the polymer [9, 10]. In order to obtain more insight into this unusual nematic structure, we have prepared and examined in the present study a series of polysiloxanes with various degrees of polymerization and different ratios of side-on fixed mesogenic groups to silicons in the backbone [13]. To enlarge the small number of commercial

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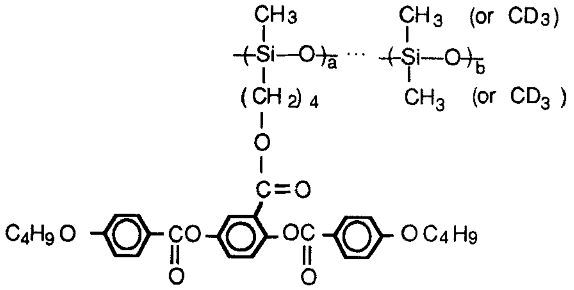
copoly(hydrogenmethyl-dimethylsiloxanes) used as the precursor backbone, we first synthesized random copolysiloxanes of this type, using perdeuteriated dimethylsiloxane units, if necessary, for neutron scattering measurements.

2. Synthesis

The polymers investigated have the following general formula:



$X = \frac{a}{a+b}$

'$P_{4,4,4}$, -X'

A short spacer of four carbons was chosen to lead to a strong coupling between the motions of the polymer backbone and the side groups. Reducing the spacer connection length tends to favour the 'mesogen-jacketed' type structure [10].

The proportion X of mesogenic groups, defined as $X = a/(a+b)$ was varied from 27 per cent to 55 per cent. In an earlier study [9], a drastic decrease in the anisotropy of the global polymer conformation has been observed on passing from the homolopolymer $X = 100$ per cent to a copolymer with $X = 30$ per cent. Thus with low contents of mesogenic groups, the polymer backbone is less restricted by the nematic ordering of the side chains, and this may result in the 'mesogen-jacketed' type structure breaking down. The aim of the present work was to investigate how this structure declines as the proportion of mesogens decreases. The degree of polymerization was also modified from $\overline{DP}_n = 55$ to $\overline{DP}_n = 90$, since this parameter has been shown to be of importance [9]. The jacketed effect is indeed reinforced when the degree of polymerization is modified from 70 to 35 [9].

Materials were prepared by a hydrosilylation reaction between the silane functions of the precursor polymer and the appropriate terminal alkene side chain [14] using dicyclopentadienyl-platinum (II) chloride as catalyst and a 20 per cent excess of alkene. The synthesis of the mesogenic groups has already been described [5]. The proportion X of mesogenic groups and the $\overline{DP}_n$ values of the final products were predetermined by the composition and the length of the initial copoly(hydrogenmethyl-dimethylsiloxane), since the hydrosilylation reaction is assumed to be complete and free from any polymer fractionation during the process. The precursor copolysiloxanes were synthesized by acid catalysed equilibration [15–17] of cyclic 1,3,5,7-octamethyltetrasiloxane, or its deuteriated analogue, and linear polyhydrogenmethylsiloxane prepolymer ($\overline{DP}_n = 30$ or 67 from Petrarch Systems). Reaction was performed in bulk at 60°C by using a sulphonated silica Spherosil$^{(R)}$ resin (0·59 meq H^+g^{-1} from Rhône Poulenc Society) as initiator (see example). Previous preliminary tests had been carried out with other catalytic resins, but the copolysiloxanes synthesized were not statistical. The use of a solid catalyst makes the process of elimination easier. Before use, the resin must be carefully washed and filtered in order to eliminate the smallest particles. The reaction time required was at least 24 h so that equilibrium conditions were reached.

Synthesis of the copolymer 4. Into a flask, fitted with magnetic stirrer and a nitrogen inlet–outlet purge system, are placed 0·1 g of Spherosil[(R)] resin; 2·15 g (29 mmol) of 1,3,5,7-octamethylcyclotetrasiloxane and 2·85 g of the linear polyhydrogenmethylsiloxane prepolymer (43 silane mmol, $\overline{DP}_n = 30$ from Petrarch Systems) are introduced by syringe. The mixture is stirred under nitrogen for 3 days at 60°C. After this time, the cyclic or linear oligomers generated by the reaction [18] are evaporated under vacuum. The remaining mixture is then taken up in toluene and carefully filtered. The low to intermediate molecular weight homologues are removed from the polymer by semi-preparative gel permeation chomatography using two 19 × 300 mm Ultrastyragel columns (500 Å, 10^3 Å) from Waters Associates and toluene as eluent. The polydispersity is in this way substantially reduced and is estimated to be narrower than $\overline{M}_w/\overline{M}_n = 1{\cdot}5$ in all cases. The average number molecular weights of the poly(hydrogenmethylsiloxane-co-dimethylsiloxane)s were measured by tonometry experiments. The composition of the copolymers was determined by 270 MHz ^{1}H NMR spectroscopy. Table 1 summarizes the reaction conditions and the characterization of the synthesized polymers.

The sequence of distribution of dimethylsiloxane and hydrogenmethylsiloxane units was investigated by 39·76 MHz ^{29}Si NMR spectroscopy as previously described [19, 20]. As shown in figure 1 each type of silicon is clearly split into triads connected with the nature of the nearest neighbours. In each region, the intensities of the different triads have been measured and the contribution of the various sequences agrees well with a Bernouilli type random distribution (see examples in table 2). Besides, the silicon spectroscopy confirms the ratio X.

All these copolymers have been substituted by the same mesogenic group reported earlier. The extent of completion of hydrosilylation was assessed by the ^{1}H NMR band associated with Si–H. We noted that this band has vanished in all the synthesized copolymers.

Table 1. Synthesis and characterization of poly(hydrogenmethylsiloxane-co-dimethylsiloxanes)s.

Polymer number†	X_0‡	X§ ± 0·02 (^{1}H NMR)	Theoretical ¶ $\overline{DP}_n$	Measured $\overline{DP}_n$ ± 5 (tonometry)
1	0·30	0·27	100	70
2D	0·30	0·30	100	70
3	0·35	0·35	100	85
4	0·60	0·55	50	55
4D	0·60	0·55	50	55
5	0·60	0·56	110	90
5D	0·60	0·55	110	90

†**D** denotes polymers with perdeuteriated dimethylsiloxane units.

‡X_0 initial proportion of hydrogenmethylsiloxane units versus the total number of siloxane units in the reaction mixture.

§X, proportion of hydrogenmethylsiloxane units in the polymer determined by ^{1}H NMR.

¶Theoretical $\overline{DP}_n$ based on the ratio between the whole number of siloxane units and the number of end groups without taking into account the formation of cycles and oligomers.

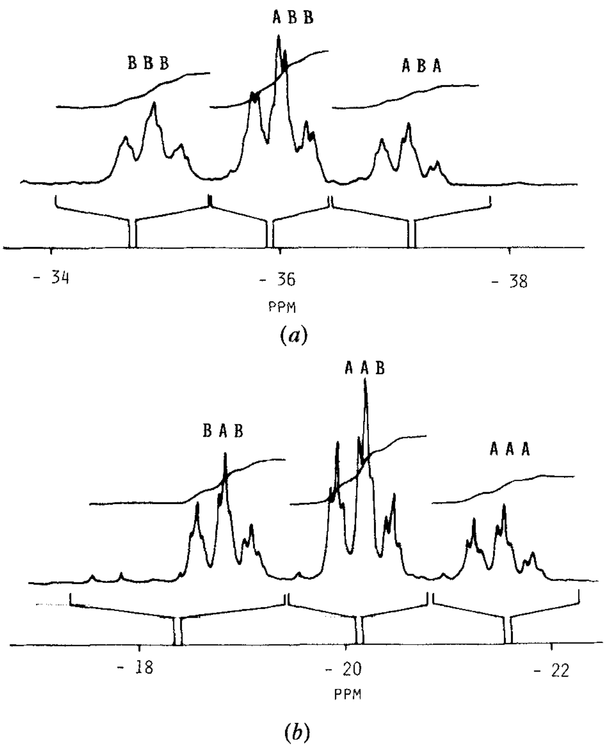


Figure 1. A typical 39·76 MHz ^{29}Si NMR spectrum of a copoly(hydrogenmethyl-dimethylsiloxane). $M_2 A_{23} B_{30}$ average composition, (*a*) B region, (*b*) A region, M, end group; A: dimethylsiloxane unit; B, hydrogenmethylsiloxane unit.

Table 2. Ratios of the different triad sequences measured by ^{29}Si NMR or calculated using a random distribution in two poly(hydrogenmethylsiloxane-co-dimethylsiloxane)s.

Polymer number	Triad†	Measured intensity	Calculated intensity
3	AAA	0·415	0·422
	AAB	0·457	0·455
	BAB	0·128	0·123
	BBB	0·125	0·123
	ABB	0·450	0·455
	ABA	0·425	0·422
5	AAA	0·194	0·194
	AAB	0·490	0·492
	BAB	0·316	0·314
	BBB	0·305	0·314
	ABB	0·495	0·492
	ABA	0·200	0·194

†A, dimethylsiloxane unit; B, hydrogenmethylsiloxane unit.

3. Thermal properties

The characterizations of the '$P_{4,4,4-X}$' polymers are listed in table 3. The clearing temperatures were determined by optical microscopy with decreasing temperature. The enthalpies of transition, ΔH_{IN}, and the glass transition temperatures were analysed by differential scanning calorimetry. All the polymers, even with low contents of mesogenic groups (27 per cent), present nematic phases, as already observed for Polymer **2** [9]. As usually observed for 'diluted' side chain polymers, after extrapolation to $\overline{\mathrm{DP}}_n$, both the glass transition temperature and the clearing temperature decrease with the proportion of mesogenic groups.

Variation in X has a significant effect on the clearing transition enthalpies, ΔH_{IN}, and entropies, ΔS_{IN}, values. The overall trend is a decrease in ΔH_{IN} and ΔS_{IN} as X is decreased. We can note first that a similar behaviour was found for the nematic to isotropic transitions of 'end fixed' side chain homo- and co-polysiloxanes [21], and secondly that the values obtained for the homopolymers are larger than those associated with 'end fixed' side chain polysiloxanes [22]. According to the prolate conformation model N_{III} proposed by Wang and Warner [23], in the nematic phase of a laterally-attached polymer, the backbone is stretched out towards being a rod by the aligning field of the mesogens, thus losing more entropy than it would in the oblate conformation [7]. Decreasing the number of mesogenic groups leads to lower restriction of the polymer chain by the nematic ordering of the side chains: for the lowest contents of mesogenic groups ($X \cong 30$ per cent), the chain conformation is almost isotropic as already noted [9], and the entropic contribution becomes less important.

The effect of polymer length was investigated for two systems: $X = 0{\cdot}55$ and for the homopolymer ($X = 1$). In each case, there is a slight decrease in T_g as the molecular weight is increased. This unusual improvement in flexibility corroborates the tendency, observed by neutron scattering experiments on homopolymers [9], towards a weakening of the 'jacketed effect' with greater $\overline{\mathrm{DP}}_n$. In the case of homopolymers, in which the coupling between the main chain and the mesogenic groups is maximal, this

Table 3. Phase transition temperatures (°C) for the '$P_{4,4,4-X}$' polymers.

Precursor polymer	X	$\overline{\mathrm{DP}}_n$ (tonometry)	T_G§	N		I	$\Delta H_{IN}/\mathrm{J\,g^{-1}}$	ΔS_{IN}¶$/\mathrm{J\,K^{-1}\,u^{-1}}$
1	0·27	70	7	●	71	●	0·8	0·5
2†‡	0·30	30	10	●	74	●	0·7	0·5
3	0·35	85	16	●	82	●	0·7	0·5
4	0·55	55	26	●	100	●	1·7	1·7
4D	0·55	55	22	●	97	●	1·7	1·7
5	0·56	90	21	●	100	●	1·8	1·8
6†	1	36	39	●	129	●	3·4	5·3
7†	1	67	36	●	130	●	2·1	3·2

† Commercial product from Petrarch Systems.

‡ From [9].

§ T_G, glass transition temperature.

¶ ΔS_{IN}, entropy of transition at the clearing point calculated for one average unit (W, molecular weight, $W = X$ substituted methylsiloxane unit molecular weight $+(1-X)$ dimethylsiloxane unit molecular weight).

effect finds expression in a greater rise in the entropic contribution for $\overline{DP}_n = 36$ than for $\overline{DP}_n = 67$. Besides, we notice that for an appreciable dilution of about two thirds ($X = 0{\cdot}35$; $0{\cdot}30$; $0{\cdot}27$), the glassy transition temperatures decrease as X decreases, so the main factor is no longer the backbone length, but the dilution.

4. Neutron scattering experiments

Small angle neutron scattering (SANS) experiments have been carried out on $P_{4,4,4} - 55$ per cent with $\overline{DP}_n = 55$ (precursor polymers numbers: **4** and **4D**). Labelling the polymer in the main-chain allows the direct determination of the backbone conformation. The SANS measurements were performed by following the usual procedure [8, 9, 24] using a 50/50 weight ratio mixture of protonated polysiloxane with the homologous selectively deuteriated polysiloxane. Aligned nematic phases were obtained by cooling the sample through the isotropic–nematic phase transition in a magnetic field (1·4 T). The scattering intensity was collected on the SANS-XY position multidetector 'PAXY' of the Laboratoire Léon Brillouin (CEA/CNRS, CEN Saclay,

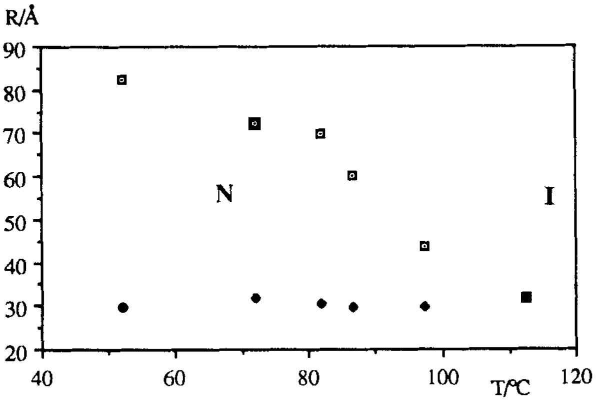


Figure 2. Quadratic size (Å) in the parallel ($R_{\parallel}$) (□) and perpendicular ($R_{\perp}$) (◆) directions to the magnetic field as a function of temperature for $P_{4,4,4} - 55$ per cent with $\overline{DP}_n = 55$.

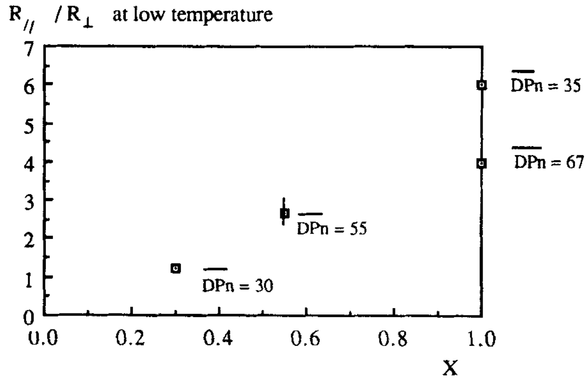


Figure 3. Anisotropy ($(R_{\parallel}/R_{\perp})$) of the '$P_{444}$, X' polymer as a function of X. (□, polymer labelled on the aliphatic tails of the mesogenic groups from [8, 9]; ⌶, polymer labelled in the main chain).

Orphée reactor) and the apparent quadratic sizes $R_\perp^2$ and $R_\parallel^2$ (perpendicular and parallel to the magnetic field) were deduced. The temperature dependences of $R_\perp$ and $R_\parallel$ are reported in figure 2. On cooling from the isotropic state, an anisotropy of the polymer conformation appears in the nematic phase and increases upon further cooling until a maximum value ($R_\parallel/R_\perp \cong 2{\cdot}7$) is reached. The polymer backbone is strongly stretched in the average direction of the mesogens, unlike $P_{4,4,4}-30$ per cent whose conformation was quasi-isotropic [9]. It is somewhat difficult to compare this value of backbone anisotropy quantitatively with the overall anisotropy of the homopolymer ($X=1$) which is perdeuteriated on the aliphatic tails [8, 9]; however it appears that the observed 'jacketed' structure already exists, but is less marked in a 55 per cent copolysiloxane than in a fully substituted homopolymer (figure 3). In addition, we notice that at low temperature, $R_\perp$ in $P_{4,4,4}-55$ per cent ($R_\perp = 30$ Å) is greater than would be expected for a completely extended chain; this difference suggests formation of elbows in the polymer backbone in the nematic phase.

The influence of the molecular weight on the backbone conformation of this polymer is currently under study by SANS experiments.

5. Conclusion

Those new systems allow a better approach to the nematic phase organization for 'side-on fixed' liquid crystalline polysiloxanes; the SANS studies confirm the large participation of the main chain in the nematic order.

In proportion, as the dilution increases, the nematic 'jacketed' effect becomes weaker and the nematic phase is destabilized [9]. This effect is still operative in a 55 per cent copolysiloxane, but weaker than in the homopolymer. For a dilution of about two thirds ($X=0{\cdot}30$), there is no longer any backbone anisotropy: the prolate conformation in the nematic phase is very weak and the 'jacketed' structure vanishes, as well as the influence of $\overline{DP}_n$ on the mesophase stability.

Finally, considering the previous SANS results on 'side-on fixed' polymers [8–10], we can claim the 'side-on' fixation causes strong coupling between the polymer backbone and the mesogenic groups, so that the persistence length depends, for the same spacer length, on both the 'dilution' along the polymer backbone and the main-chain length.

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