A ^{13}C nuclear magnetic resonance study of the effect of temperature on the side-chain polysiloxane liquid crystal containing *trans*-2-[*p*-(1-undecanyl-11-oxy)phenyl]-5-[(*p*-2(*S*)-methyl-1-butoxy)phenyl]-1,3-dioxane

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Solid-state ^{13}C nuclear magnetic resonance has been used to study the effects of temperature cycling on a side-chain polymer liquid crystal. Cycling the polymer from 100°C to room temperature resulted in severe line broadening. High-resolution spectra were obtained by cycling from 70°C to room temperature. The dioxane ring undergoes a transition from a mixture of *cis* and *trans* to an all-*trans* conformation in the liquid-crystalline state. The line broadening is associated with enhanced mobility of the mesogenic unit and decreased mobility of the backbone. T_1 measurements indicate that the mesogenic unit and the spacer carbons in α positions with respect to the mesogen are rigid below T_m.

(Keywords: n.m.r. spectroscopy; liquid crystals; temperature effects)

INTRODUCTION

The polymer liquid crystals (LCs) discussed in the previous papers[1,2] were glassy below T_g and liquid crystalline above T_g and d.s.c. showed only minor changes with temperature cycling[3,4]. LC I in *Figure 1*, however, has a more rigid mesogenic unit with the addition of a second aromatic ring. The d.s.c. trace is quite different, as one observes a melt transition and an increase in the glass transition and isotropization temperatures, respectively (*Table 1*). D.s.c. measurements[4] indicate the LC to be quite sensitive to thermal history. In fact, cycling of the temperature causes the LC transition to be reduced considerably. Annealing the LCs at room temperature allowed the transitions to be recovered[5]. It was postulated that mixtures of *trans* and *gauche* conformers of the dioxane ring were obtained at elevated temperatures and the *gauche* conformers do not crystallize. It is the purpose of this paper to study the effect of thermal history on the polymeric LC by using ^{13}C solid-state n.m.r.

EXPERIMENTAL

The polymer LCs used in this study were synthesized by Hahn and Percec[3,4] and Hsu and Percec[6]. The LCs are specified on the basis of spacer length, backbone, mesogenic unit and free substituent (*Figure 1*). The d.s.c. and optical microscopy experiments are reported in the literature[4].

The ^{13}C n.m.r. spectra for LC I (s-butyl) were recorded on a Nicolet NT 150 spectrometer at 37.7 MHz. The ^{13}C n.m.r. spectra for LC II were recorded on a Bruker MSL 300 spectrometer at 75.5 MHz. Magic-angle spinning

(MAS)[7], cross-polarization (CP)[8] and dipolar decoupling (DD)[9] are used simultaneously with the cross-polarization experiments. The radiofrequency (r.f.) fields were typically 60–70 kHz. The contact time was typically 1 ms, with 2–3 s delays between transients. Some 5000 transients were taken for the CP and gated high-power decoupling (GHPD) experiments on the NT 150, and some 1600–2200 transients were taken for the relaxation experiments. Rotors machined from Al$_2$O$_3$ with Delrin and Kel-F end-caps were supplied by Doty Scientific. The chemical-shift reference was set using standard markers of adamantane (29.5 ppm), Delrin (89.1 ppm) or a silicon derivative (-1.5 ppm). Spinning frequencies were between 2 and 3.3 kHz. The free induction decay (FID) was collected in a 512 W or 1 K data size and zero-filled to 8 K before Fourier transformation. The magic angle was set by maximizing the peak intensities of glycine. The Hartman–Hahn match was set by maximizing the peak intensities of adamantane. The 90° pulse was determined by finding the 360° and 720° pulses via nulling out of the adamantane signal. The r.f. field was calculated directly from the 90° pulse.

The T_1 inversion–recovery experiments (CP) were performed using the standard pulse sequence[10,11] (*Figure 2*). Delay times of 1 ms to 4 s were plotted as a function of delay time and curve-fitted to the inversion–recovery equation on a MicroVax II.

RESULTS

The d.s.c. and optical microscopy experiments determined by Hahn and Percec[4] are listed in *Table 1*. The chemical-shift measurements (*Table 2*) were made at room temperature, well below the LC transition. The calculated chemical shifts for the spacer, backbone,

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STANDARD FORMULA

B—S—M—F Where:
- B = Backbone
- S = Spacer
- M = Mesogen
- F = Free Substituent

B

1.
```
    CH3
    |
[ —Si—0—]n
    |
    SMF
```

2.
```
      H
[ —C—CH2—]n
      |
    0=C—0—SMF
```

S

1. B—(CH2)—MF
      11

2. B—(OCH2CH2)—MF
            3

M

1.
```
BS—0—⬡—C<H     C—0
          ⟍  C—0⟍  ⬡—F
                   C
                   H
```

2.
```
BS—0—⬡—⬡—F
```

F

1.
```
        CH3
        |
BSM—0—CH2—CH—CH2—CH3
```

2.
```
BSM—0—CH3
```

LC	B	S	M	F
I	1	1	1	1
II	1	1	1	2
III	1	1	2	2
IV	2	1	1	2
V	2	2	1	2
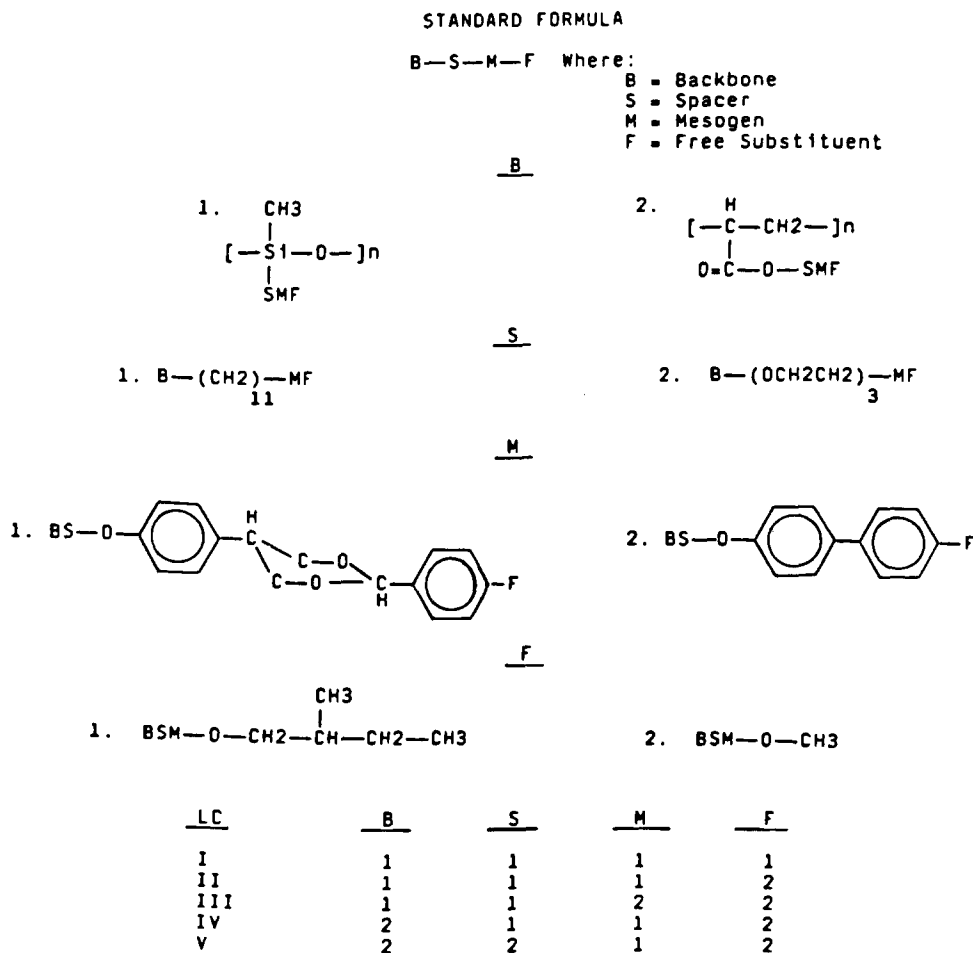
Figure 1 The chemical formulae for the LCPs used in this study. The LCPs have been separated into four distinct sections

Table 1 The transition temperatures of LCs I and II as determined by d.s.c. (°C)[a]

	I	II
T_g	30	44
T_m	71	76
T_i	146	158

[a] D.s.c. scans were run at a rate of $20°C\,min^{-1}$

Figure 2 The pulse sequence used to obtain the inversion–recovery with cross-polarization spectra

Table 2 The calculated and observed chemical shifts for LCs I and II at 25°C

Carbon	Calculated	I	II
A	0.4	1.3	1.0
B	18	18	18
C	25	24.9	24.6
D	33	27.0	27.6
E	31.5	31.3	31.5
F	66–70	68.1	68
G	158.5	158.7	159
H	112.7	114.6	114.3
I	128.1	128.8	129
J	133.1	130.8	130
K	93	100.2	100
L	65.9	70.7, 73.8	73
M	26.6	40.2	40
N	140.9	130.8	130
O	127.5	128.8	129
P	114.1	114.6	114.3
Q	157.4	158.7	159
R	66–70	73.8	–
S	18.6	17.0	–
T	36.7	35.8	–
U	29.3	27.0	–
V	11.3	12.5	–
W	55	–	55

s-butyl and aromatic groups were discussed previously[12]
The observed assignments were made based on the LCs listed in *Figure 1* in conjunction with CP, GHPD and DD experiments. *Figures 3* and *4* are a comparison of the CP spectra of LCs I and II, which have different free substituent groups. *Figure 5* is a comparison of the

CP spectra of LCs II and III, where LC III is without the dioxane ring in the mesogenic unit. *Figure 6* is the DD spectrum of LC II at $\tau = 100\,\mu s$. *Figure 7* is the CP and GHPD spectra for LC I. The correlation of the assignments and structure is shown in *Figure 8*.
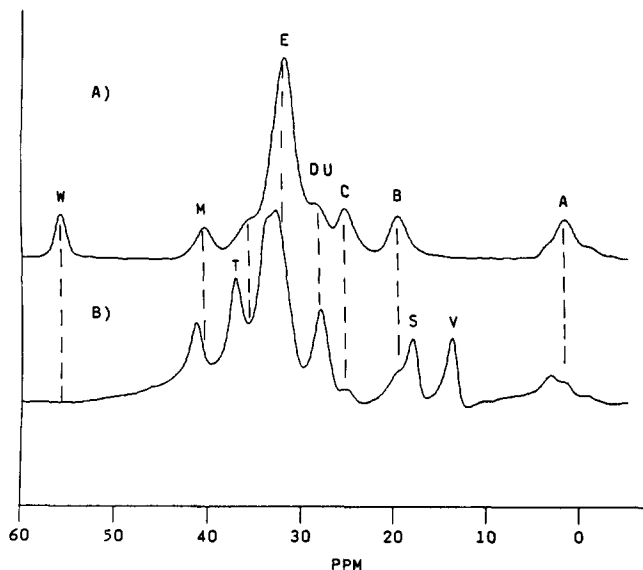
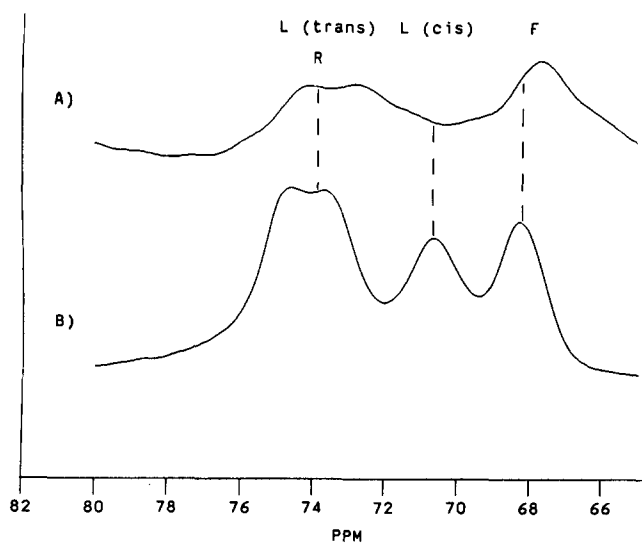**Figure 3** The CP/MAS/DD spectra of (A) LCP II and (B) LCP I

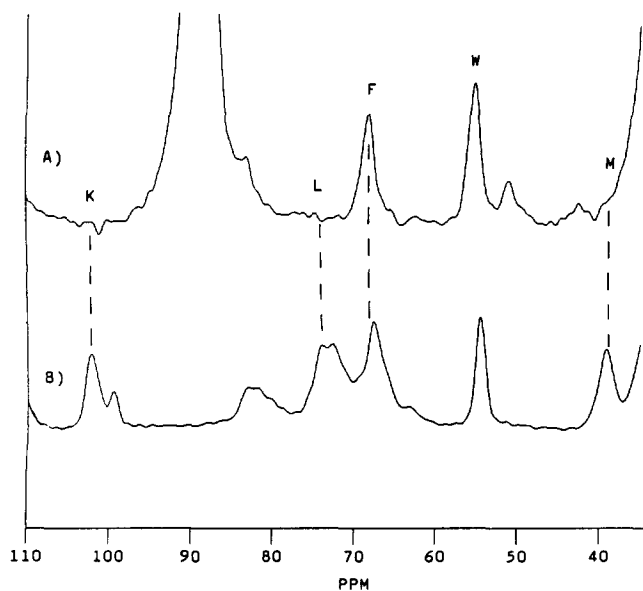**Figure 4** The CP/MAS/DD spectra of (A) LCP II and (B) LCP I

Figure 5 The CP/MAS/DD spectra of (A) LCP III and (B) LCP II

LC I is quite sensitive to thermal history as was seen in the d.s.c.[4]. The n.m.r. (CP) spectra also exhibit significant changes with temperature, as is shown in *Figure 9*. A conformational change of the dioxane ring is observed at T_m and the corresponding resonances involved are shown as a function of temperature in *Figure 10*. The plot of the relative intensity as a function of temperature cycling for the 70 and 73 ppm peaks (L) is shown in *Figure 11*. The shaded areas represent the temperature regions where the broadening of the spectra was observed. *Figure 12* shows the GHPD spectrum of LC I after cooling from 100°C.

Spin–lattice relaxation times (T_1) were calculated at 15, 40 and 70°C at two separate time periods. The results are listed in *Table 3*.
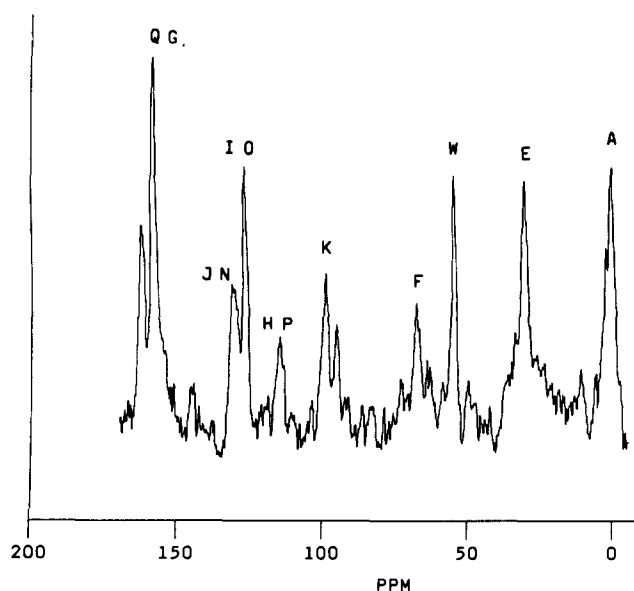

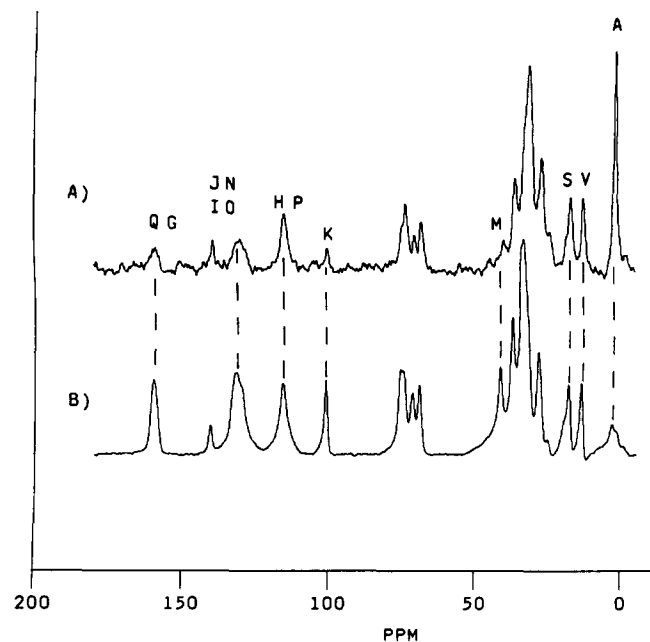**Figure 6** The dipolar dephasing spectrum with a 100 μs delay for LCP II

Figure 7 A comparison of the (A) gated high-power decoupling and (B) cross-polarization spectra for LCP I
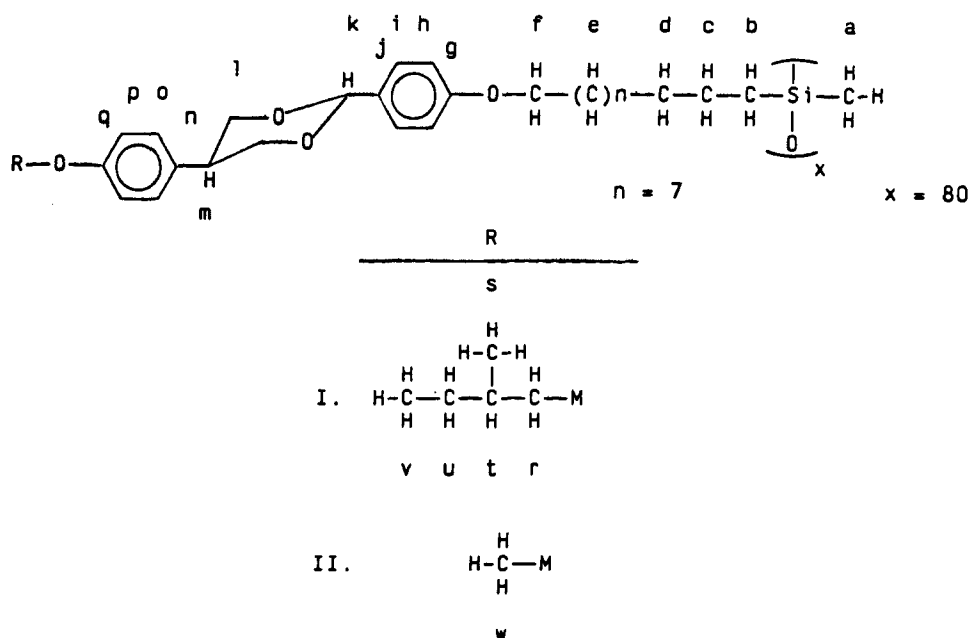
Figure 8 The structure and related chemical-shift assignments for LCPs I and II

DISCUSSION

Chemical-shift assignments

The assignment of the spacer carbons and s-butyl carbons are made by comparing the spectra of LCs I and II in *Figure 3*. LC II experiences a loss of peaks V, S and T, indicating that they belong to the s-butyl group. Additionally, a decrease in the relative intensities of the resonances D, U and L indicates that these are composite peaks (*Figures 3* and *4*). Comparison of LCs I and III in *Figure 5* clearly shows the disappearance of the peaks M, L and K. The resonance at 68 ppm remains and is assigned to carbons F in the spacer.

Three distinct methoxy peaks appear at 68, 70 and 73 ppm for LC I (R, L, F). The peak at 73 ppm is partly due to the methoxy carbons in the s-butyl group (R) and the peak at 68 ppm is due to spacer methoxy carbons (F). The spectra are complicated by the fact that the dioxane ring can exist in the *cis* or *trans* conformation. Previous experiments in solution[13,14] on derivatives of cyclohexane observed an upfield shift for the higher-energy conformer due to steric interaction. The bulky substituent attached to the dioxane ring on LC I will tend towards the *trans* conformation[15], and thus the *trans* conformer should appear at lower fields. So we assign the composite peak at 73 ppm to the s-butyl methoxy (R) and the *trans* methylenes in the dioxane ring (L). The 70 ppm resonance is due to the *cis* dioxane methylene carbons (L), which include one axial and one equatorial substituent. The peaks M and K are assigned to the methine carbons in the dioxane ring.

One can use dipolar dephasing and GHPD to distinguish quaternary and protonated carbons. The DD experiment with a 100 μs delay for LC II is shown in *Figure 6*. There are five major peaks present, (Q, G), (J, N), E, W and A. The first two are quaternary carbons while the last two are methyl carbons. The resonance, E, is due to the central methyl carbons of the spacer. The fact that it has not totally dephased is an indication that those carbons are quite mobile, thus reducing the C–H dipolar interaction.
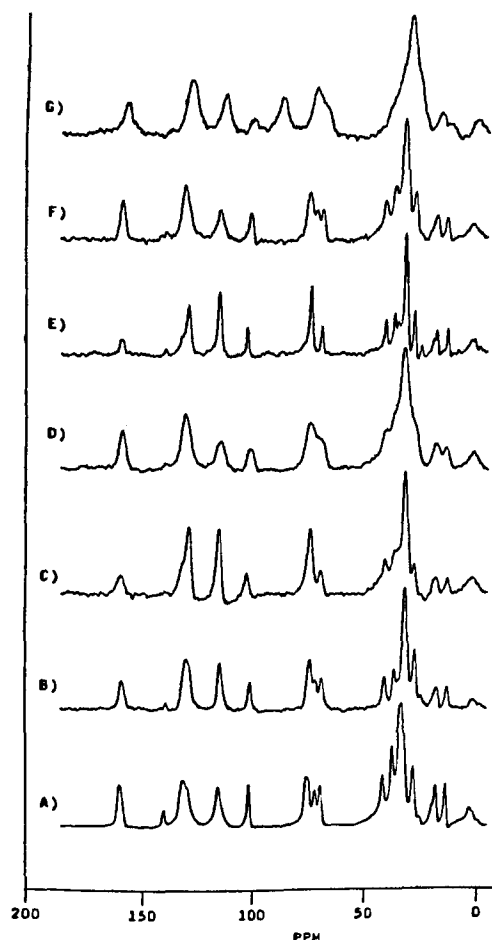

Figure 9 The CP/MAS/DD spectra of LCP I as a function of thermal history: (A) 20°C, (B) 40°C, (C) 70°C, (D) 20°C after cooling from 100°C, (E) 70°C, (F) 20°C after cooling from 70°C, and (G) 20°C after cooling from 100°C

The CP and GHPD spectra for LC I are shown in *Figure 7*. There is a decrease in intensity for the non-protonated aromatic carbons (Q, G). The resonances (I, O) and (H, P) (composites) are assigned to protonated
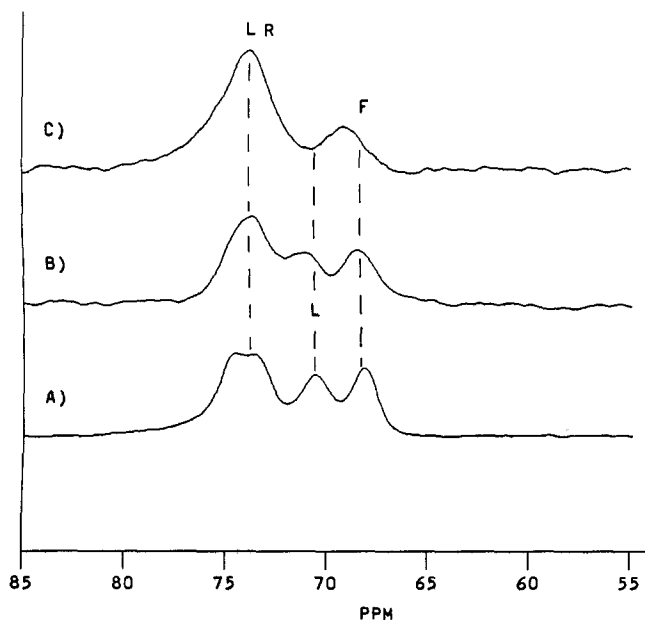
Figure 10 The effect of temperature on the dioxane ring resonances (CP/MAS/DD): (A) 20°C, (B) 40°C, and (C) 70°C

aromatic carbons. One should note the increase in relative intensity of the backbone methyl carbons (A) for the GHPD experiment relative to the CP experiment. This is in comparison to the minor increase in intensity for the s-butyl methyl carbons (S, V). This is an indication that the backbone is very mobile at this temperature.

Thermal history

The thermal history of the LC I has a dramatic effect on the n.m.r. spectrum. The LC as received is a crystalline polymer, as the peaks are quite narrow and CP is quite efficient (*Figure 9A*). As T_m is approached (40°C), one observes a decrease in intensity and an upfield shift of the L (*cis*) resonance and a subsequent increase in the L (*trans*) and R intensity (*Figure 9B*). At the LC transition (70°C), the L (*cis*) resonance is completely shifted downfield to L (*trans*) and R (*Figure 9C*). One would expect rapid exchange of the *cis* and *trans* conformations in the melt so the methoxy peak would have an average chemical shift. In this case, the *cis* peak (70 ppm) shifted, indicating that the dioxane ring is in a completely *trans* conformation in the LC state. In addition, there is no observed shift of the central spacer carbons (E). The chemical-shift values indicate that a significant number of *gauche* bonds exist at the temperature studied[16,17]. If the temperature is raised to 100°C, then lowered to room temperature, one observes a homogeneous broadening of the entire spectrum (*Figure 9D*). This is indicative of an amorphous polymer that experiences a broadening phenomenon relative to the crystalline polymer because of the larger number of available conformations. This is also seen in the spectra of epoxies[18]. Although the lines are broad, one can see that the dioxane ring exists in both conformations and the relative intensities are quite similar to the spectrum in *Figure 9A* (*Figure 11*). Thus the *cis* and *trans* conformations exist in both the crystalline and amorphous polymers below T_m. The presence of the *gauche* conformers is not the major contributing factor to the loss of the LC properties.

The higher-resolution lines can be obtained by raising the temperature to 70°C as is seen in *Figure 9E*. The

polymer can crystallize when lowered from 70°C to 20°C as is seen in *Figure 9F*. Cycling the temperature to 100°C was repeated and the same results were obtained (*Figure 9G*).

Crystallization involves reordering of both the backbone and main chain so three-dimensional order can be obtained. Ringsdorf *et al.*[19] have shown that the side-chains are ordered in the LC state but the siloxane copolymer backbones with paired side-chains are disordered due to their flexibility. Spiess[20] has also shown that methacrylate backbones have very little order in the LC state. The lack of order among the backbone and the *cis–trans* isomerizations of the dioxane ring imply the existence of a large kinetic effect on crystallization. Cooling from 100°C, which is well above T_m, does not allow the polymer chains time to reorganize and as a result an amorphous polymer is obtained. This results in broad lines in the n.m.r. spectrum and a greatly reduced LC transition. Crystallization does occur when the LC is cooled from 70°C, which indicates that the polymer chains are not as disordered at this temperature. D.s.c. was not run in this particular cycling scheme. It was, however, noted that allowing LC I to anneal at room temperature resulted in the growth of the T_m peak[5]. The mesogenic units are quite rigid at room temperature,
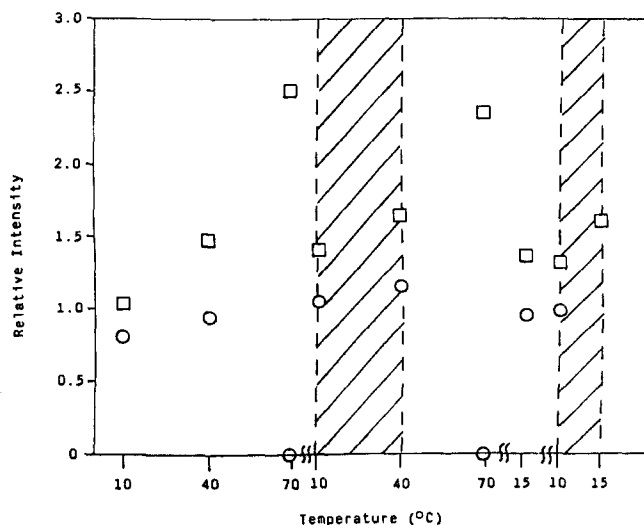

Figure 11 The effect of temperature cycling on the relative intensities of the *cis* and *trans* carbons of the dioxane ring: (□) carbons L (*trans*) and R; (○) carbons L (*cis*). The shaded regions are synonymous with the broadening that was observed in the CP/MAS/DD spectra

Table 3 The ^{13}C T_1 spin–lattice relaxation times as a function of temperature for LC I at 37.7 MHz[a]

	Peak	15°C	40°C	70°C	10°C	40°C	70°C
Methylene carbons[b]	C	0.17	0.29	0.34	0.13	0.24	0.31
	E	0.19	0.30	0.45	0.19	0.29	0.19
	F	0.68	1.0	0.23	0.84	1.0	0.23
	L	1.1	0.86	–	1.2	0.96	–
	L, R	0.69	0.66	0.31	0.67	1.1	0.15
Methyl carbons[c]	A	1.7	1.8	2.9	1.8	1.4	3.8
	V	0.76	1.2	1.7	0.77	0.71	2.0
	S	0.27	0.48	0.91	0.36	0.40	0.74

[a] Experimental error is ±15%
[b] First data set run on LC annealed at room temperature
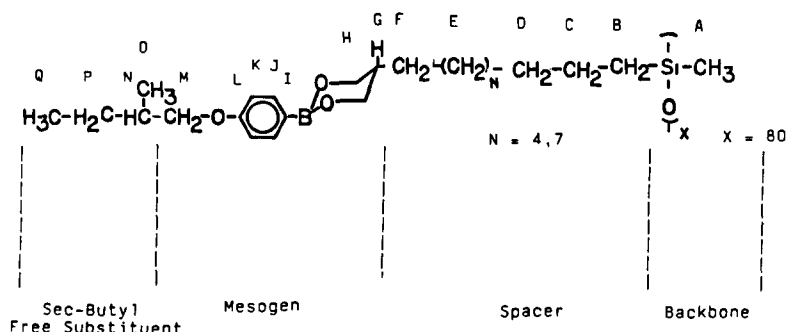[c] Second data set run on LC cooled from 70°C

Figure 12 GHPD spectrum of LC I after cooling from 100°C

when the spectrum has narrow peaks. However, the backbone mobility is quite evident based on the GHPD experiment of *Figure 7*. Annealing at room temperature must involve reorganization, which leads to enhanced backbone mobility in conjunction with more efficient packing and reduced mobility of the mesogens (*Figure 7*).

RELAXATION MEASUREMENTS

It is desirable to probe the motions involved in the LC transition in more depth, so ^{13}C spin–lattice relaxation times were chosen to probe the dynamics of the LC transition. The temperature trends are reproducible as two sets of temperature experiments were run with the LC in the semicrystalline state (*Table 3*). The first set of data were run on the LC as received, so considerable annealing had occurred. The second set of data was run on the LC after having been cooled from 70°C. There are some absolute value deviations, most notably the protonated aromatic carbons. Since the aromatic rings are involved with the packing in crystalline and LC states, it is not surprising to see enhanced mobility for LCs that have been cycled in temperature relative to annealed LCs.

Methylene carbons

Four resolvable spacer methylene carbons are present, B, C, E and F. Over the limited temperature range studied, we observe an increase in T_1 with temperature for the B, C and E carbons and there is no motional heterogeneity along this part of the spacer chain. The spacer is quite mobile at all temperatures. The spacer carbon in the α position with respect to the mesogenic unit (F) is quite rigid at 15°C and experiences a sharp decrease in T_1 with temperature, indicating that decoupling along the spacer is quite efficient below T_m. The rigidity of the α carbon in side-chain LCs has been observed by Lauprêtre[21]. The proximity of T_g and T_m on the n.m.r. timescale precludes differentiation between the two transitions[22]. The composite peak (L, R) is also rigid at 15°C and shows a sharp decrease with temperature, indicating that the dioxane ring and/or the s-butyl group have large-scale motional increases at T_m. The large-scale increase in molecular motion accompanies the conformational change in which the dioxane rings adopt a *trans* conformation, i.e. both substituents adopt an equatorial conformation. The motions could involve transitions between diequatorial and twisted chain conformations.

Methyl carbons

Three methyl carbons are distinguishable, A, V and S. An expected, the T_1 values of these carbons lie on the fast side of the T_1 minimum. The T_1 values of the backbone methyl carbons are substantially longer than those of the s-butyl carbons, which is expected if the polymers are above T_{g1} (ref. 12). The difference in T_1 values persists at elevated temperatures, and thus the backbone methyls are not hindered in the LC state. The enhanced mobility at 15°C agrees with the GHPD spectrum, indicating that ample mobility is present to allow reordering. One also observes the trend observed earlier for glassy LCs[1,2,12]. The terminal methyl carbons (V) always have larger T_1 values than do the branched methyl carbons (S). This may be due to a packing constraint in the LC phase, which would be expected in a smectic LC phase where the side-chains are ordered in layers.

CONCLUSIONS

The semicrystalline LCs used in this study are quite sensitive to thermal history, as broadening is observed when the temperature is lowered from 100°C. D.s.c. also showed a sharp drop in the melt transition area. The inability of the LC to crystallize reduces the melt transition on the second heating scan, which resulted in amorphous broadening of the n.m.r. spectra. There is also an apparent enhancement in the mobility of the mesogens and a reduction in mobility of the backbone carbons in the 'broad-line' state. The LC transition can be obtained by annealing at room temperature. The n.m.r. results indicate that the backbone is indeed very mobile at room temperature. N.m.r. also indicates that temperature cycling from 70°C to room temperature allows crystallization to occur.

The T_1 measurements indicate that the mesogenic unit is fairly rigid below T_m but has a substantial motional increase at the transition that coincides with the dioxane ring adopting an all-*trans* conformation. The spacer carbons α to the mesogenic unit behave in a similar manner to the mesogen. The majority of the spacer carbons are relatively mobile below T_m, indicating efficient decoupling of motions of the backbone and mesogen.

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