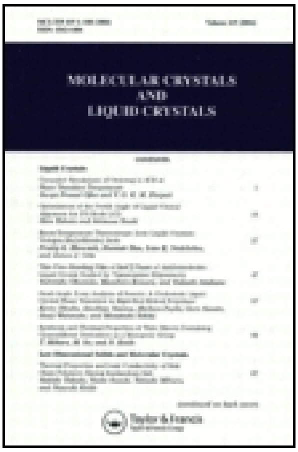

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Main Chain Order and Dynamics in a Liquid Crystalline Side-Group Polymer

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MAIN CHAIN ORDER AND DYNAMICS IN A LIQUID CRYSTALLINE SIDE-GROUP POLYMER

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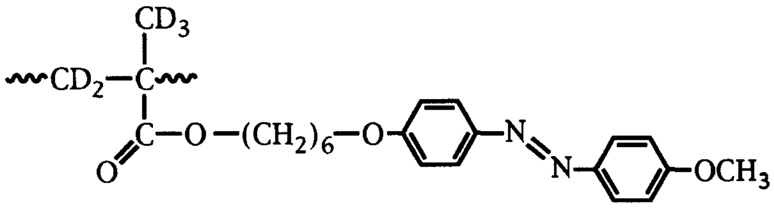
Abstract The orientational distribution function for the C-CD_3 bond on the perdeuterated polymethacrylate chain of a liquid-crystalline side group polymer was determined in the frozen S_A phase by solid-state ^2H NMR. The results are compared with the ones of two similar systems recently reported. The slow chain dynamics above the glass transition was studied via 2D ^2H NMR, which indicates a diffusive motion constrained by the partial orientational order of the mesophase.

INTRODUCTION

It has been shown by solid-state deuterium nuclear magnetic resonance (^2H NMR)[1-3] and small-angle neutron scattering (SANS)[4-6] that in liquid-crystalline side-group polymers below the isotropic-nematic transition the chain adopts an anisotropic coil conformation. A spacer of six methylene units is not sufficient to decouple completely the ordering effect exerted on the polymer backbone by the mesogenic groups through intramolecular forces. The found order parameters are low, but significantly different from zero.

So far, three systems have been investigated by ^2H NMR: a polyacrylate[1,3] and two polymethacrylates[1-3] exhibiting different mesophases. Therefore, a comparison was possible between the chain order in two systems with the same smectic A mesophase, but different chain stiffness, and between two systems with different mesophases, smectic A and nematic, but the same chain stiffness.

Now a third polymethacrylate (Figure 1) is presented, so that a comparison between two systems differing only in the mesogenic group is possible, while mesophase order and chain stiffness are kept the same. The data analysis was improved in order to detect slight differences between the two S_A systems. The fitting of the experimental line-shape to obtain the order parameters was achieved by a least-squares fit routine.



$$g \xleftrightarrow{75°C} S_{A_2} \xleftrightarrow{92°C} N \xleftrightarrow{132°C} i$$

FIGURE 1 Structure and phase behaviour of the polymer PMAM.

EXPERIMENTAL DETAILS

The synthesis and characterization of the polymer PMAM are described in Refs. 7-8. It has been the object of diffusion, viscoelasticity and X-ray studies[9-13]. The number-averaged molecular weight is reported as 74,000, the polydispersity as 3.6 (gel permeation chromatography data)[7]. The phase behaviour (Figure 1) was characterized by differential scanning calorimetry and polarization microscopy.

The 1D ^2H NMR spectra were recorded employing the solid echo pulse sequence[14] and quadrature detection simulated by TPPI on a Bruker CXP-300 spectrometer with a home-built goniometer probe-head[2]. Both a macroscopically isotropic and an aligned state were measured; the latter was obtained by slowly cooling the sample, over a period of several hours, from the isotropic phase to below the glass transition temperature inside the magnetic field of the spectrometer. The measurements were all performed on the glassy state at room temperature.

The 2D ^2H NMR spectra were recorded on a Bruker ASX-500 spectrometer employing TPPI and a five pulse sequence[15,16], which is an improvement of the older 2D ^2H four pulse exchange experiment in solids[17].

The data processing was done with our own Fortran programs on a VAX/VMS computer.

ORDER

Line Shape Analysis

As in Refs. 1-3, we employed the theory for the analysis of deuterium line-shapes of partially oriented solids in high magnetic fields as developed in Refs. 18-20. For convenience of the reader we summarize it briefly.

We need to define the angular relations connecting four relevant axes, of which one is fixed in the laboratory, one in the mesophase and two on the molecule[2,18-20] (Figure 2). Around each axis cylindrical symmetry is assumed for the related physical properties.

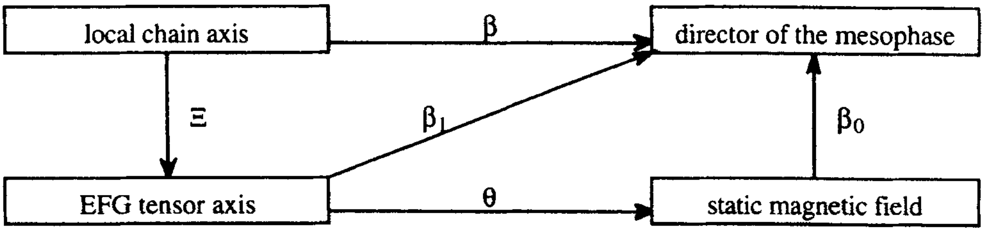


FIGURE 2 Relevant axes in the description of the molecular system. The nomenclature of the angles is consistent with Ref. 2.

We wish to determine the orientational distribution function $P(\beta_1)$, where β_1 is the angle between the director of the mesophase and the axis of the averaged electric-field gradient (EFG) tensor of the CD_3 group. This axis coincides with the $C\text{-}CD_3$ bond direction. We make use of the dependence of the deuterium resonance frequency ω on θ, defined as the angle between the EFG tensor axis and the static magnetic field:

$$\omega(\theta) = \omega_0 \pm \frac{1}{2}\delta\left(3\cos^2\theta - 1\right), \tag{1}$$

where ω_0 is the Larmor frequency and δ is the quadrupole constant, averaged by the rapid rotation of the CD_3 group. The line shape $S(\omega)$ is given by[18]

$$S(\omega) = \int \delta(\omega - \omega(\theta)) P_{\beta_1}(\theta) d\theta, \tag{2}$$

where δ is the Dirac delta function and $P_{\beta_1}(\theta)$ is the desired orientational distribution function expressed as a function of θ. An expansion in Legendre polynomials of even rank is justified by the symmetry characteristics of the system[2]:

$$P(\beta_1) = \sum_{\substack{l=0 \\ \text{even } l}}^{\infty} \frac{2l+1}{8\pi^2} \left\langle P_l(\cos\beta_1) \right\rangle P_l(\cos\beta_1) \tag{3}$$

$$P_{\beta_1}(\theta) = \sum_{\substack{l=0 \\ \text{even } l}}^{\infty} \frac{2l+1}{8\pi^2} \left\langle P_l(\cos\beta_1) \right\rangle P_l(\cos\beta_0)\, P_l(\cos\theta) \tag{4}$$

By inserting Eq. (4) into Eq. (2) and solving the integral[18], one gets a linear superposition $S(\omega)$ of subspectra $S_l(\omega)$, weighted by the sought order parameters $\langle P_l \rangle = \langle P_l(\cos\beta_1) \rangle$:

$$S(\omega) = \sum_{\substack{l=0 \\ \text{even } l}}^{\infty} (2l+1) \langle P_l \rangle S_l(\omega) \tag{5}$$

$$S_l(\omega) = \frac{1}{\sqrt{3}\delta \sqrt{2\frac{\omega}{\delta}+1}} P_l(\cos\beta_0) P_l\left(\sqrt{\frac{1}{3}\left(2\frac{\omega}{\delta}+1\right)} \right) \qquad -1 \le \frac{\omega}{\delta} \le 2 \tag{6}$$

As the experimental data are discretely sampled, we express Eq. (6) as a function of the frequency increment between the data points $\Delta\omega = (2dn)^{-1}$, where d is the dwell time and n the time domain data size. The broadening effect of the dipolar couplings is taken into account by convolution with a Gaussian $G(\omega)$. Eq. (6) becomes so

$$S_l(\omega) = \frac{1}{\Delta\omega} \sqrt{\frac{2}{3\delta}} \left(\sqrt{\omega + \frac{\delta}{2} + \Delta\omega} - \sqrt{\omega + \frac{\delta}{2}} \right) P_l(\cos\beta_0) P_l\left(\sqrt{\frac{2}{3\delta}} \sqrt{\omega + \frac{\delta}{2} + \frac{\Delta\omega}{2}} \right) * G(\omega) \tag{7}$$

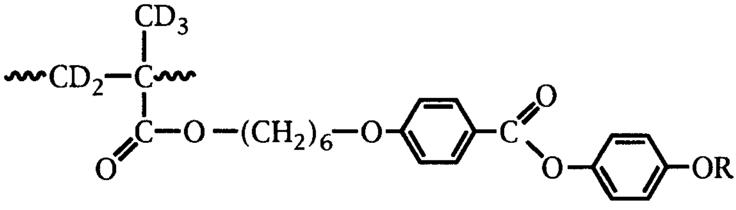
Results and Discussion

As in the previous studies[1-3], we analysed only the motionally narrowed spectrum of the CD_3 group of the perdeuterated main chain. The broader signal of the rigid CD_2 group has the drawback of a lower intensity and a significantly distorted lineshape due to the finite duration of the radiofrequency pulses. As the CD_2 group relaxes about 10 times slower than the CD_3 group, we could suppress the signal of the former by a saturation sequence preceding the solid echo.

Visual fitting of the isotropic spectrum (all $\langle P_{l>0} \rangle = 0$) yielded the value 40.04 kHz for the quadrupolar coupling constant δ and the value 2440 Hz for the full width at half height of the Gaussian $G(\omega)$ in Eq. (7). Knowledge of these quantities completely determines each individual subspectrum $S_l(\omega)$; plots are reported in the Appendix (Fig.

8). The order parameters $\langle P_l \rangle$ can easily be obtained by linear least-squares treatment of Eq. (5). Assuming that the sum of the squared residuals is the mean of a χ^2 distribution, a formal variance-covariance matrix of the fit can be obtained, providing estimates of the order parameters' standard deviations and correlation coefficients (Table I and Figures 4-6).

We re-recorded the spectra of the older polymethacrylates PMA6 and PMA64[1-3] (for the structure and phase behaviour see Fig. 3) and analysed them with exactly the same new procedure, to be sure to compare homogeneous numbers. The agreement with the previous results is excellent, except for some of the smaller order parameters, which, however, have little effect on the shape of the orientational distribution function (Fig. 6).



PMA6: $R=CH_3$ $\quad g \xleftrightarrow{47°C} N \xleftrightarrow{111°C} i$

PMA64: $R=C_4H_9$ $\quad g \xleftrightarrow{40°C} S_{A_1} \xleftrightarrow{108°C} N \xleftrightarrow{113°C} i$

FIGURE 3 Structure and phase behaviour of the polymers PMA6 and PMA64.

TABLE I Order parameters $\langle P_l \rangle$ and their estimated standard deviations s_l for the C-CD_3 bond of the three polymethacrylates, as obtained from fitting the oriented spectra of Fig. 4. Correlation coefficients among the order parameters range between 0.003 and 0.5. The number of the degrees of freedom is 5000.

	PMA6		PMAM		PMA64	
l	$\langle P_l \rangle$	s_l	$\langle P_l \rangle$	s_l	$\langle P_l \rangle$	s_l
2	0.052	.0010	0.034	.0012	-0.019	.0012
4	-0.032	.0006	-0.090	.0007	-0.114	.0007
6	-	-	0.009	.0007	0.023	.0006
8	-	-	-	-	0.007	.0009
10	-	-	-	-	-0.002	.0006

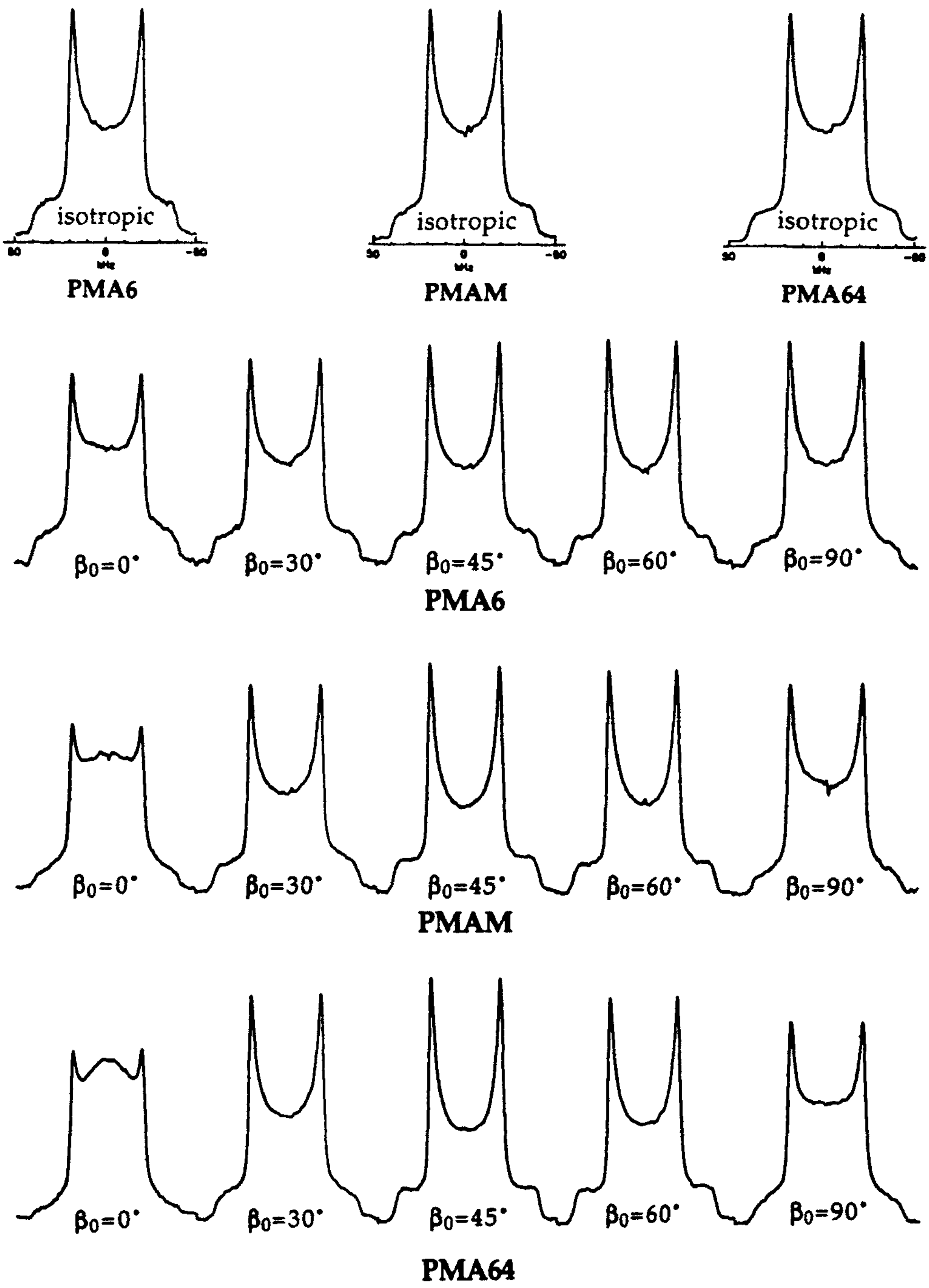


FIGURE 4 Experimental isotropic and oriented spectra of the three liquid-crystalline polymethacrylates. β_0 is the angle between the static magnetic field of the spectrometer and the director of the mesophase.

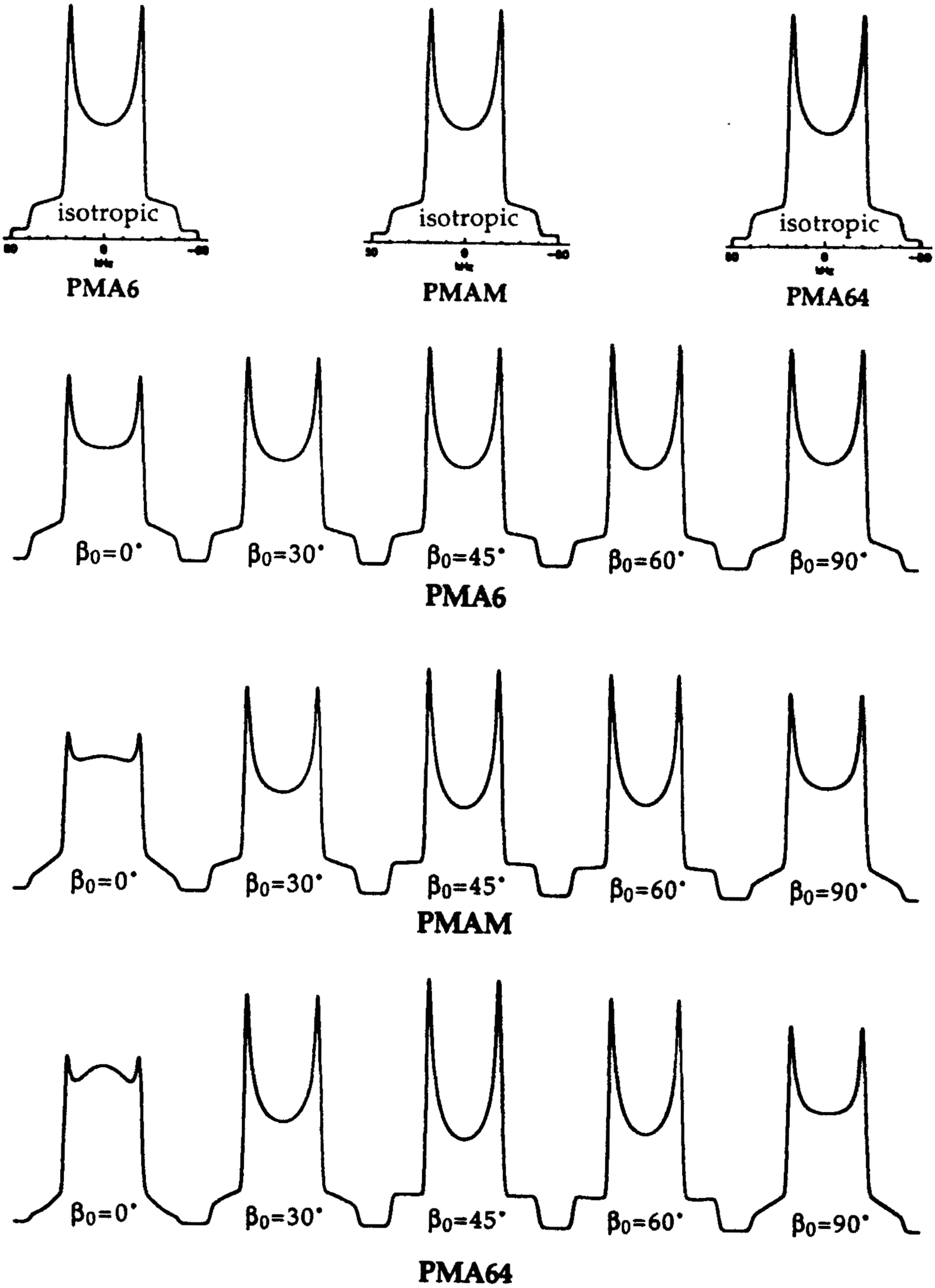


FIGURE 5 Calculated isotropic and oriented spectra of the three liquid-crystalline polymethacrylates. β_0 is the angle between the static magnetic field of the spectrometer and the director of the mesophase.

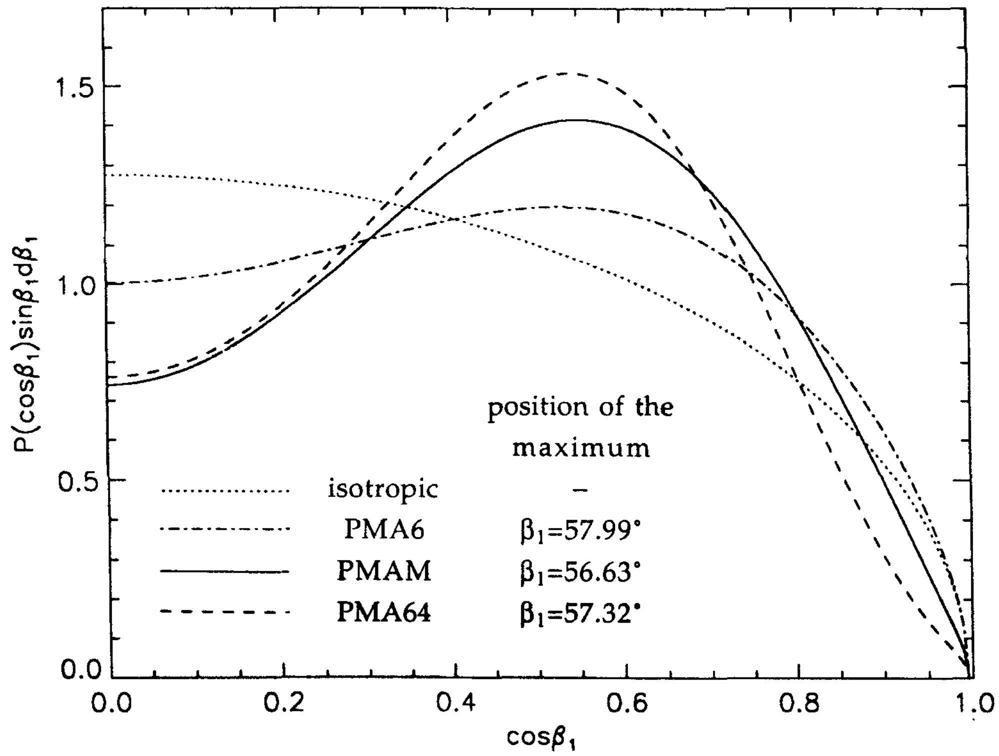


FIGURE 6 Orientational distribution functions of the C-CD$_3$ bond of the three l.c. polymethacrylates. The representation as a differential probability has been chosen in accordance with the previous literature[1-3].

The increase of the orientational order among the three polymer chains is evident from the superposed plot of the orientational distribution functions (Fig. 6), but can be inferred as well from direct inspection of the spectra (Fig.4). It is remarkable that all three orientational distribution functions exhibit a maximum close to the same angle, and differ only in the broadness and intensity of the peak. Qualitative consideration of the local geometry of the quaternary carbon at the link between the backbone and the spacer confirms that the local chain axis is prevalently aligned perpendicular to the director of the mesophase[2]. This conclusion may be drawn even if the angle Ξ (Fig. 2) is unknown and an exact expression of the orientational distribution function of the local chain axis P(β) cannot be obtained.

An investigation of further systems of this kind will be needed to completely elucidate how main chain order depends on different parameters as structure (i.e. spacer lenght and mesogenic group), mesophase order, chain stiffness and molecular weight.

DYNAMICS

Theory

Deuteron 2D exchange NMR is a powerful tool to investigate ultra-slow molecular motions in the solid state. A spectrum obtained by this method is interpreted as the two-time joint probability density function of finding a nucleus with resonance frequency ω_1 at time t_1 and the *same* nucleus with resonance frequency ω_2 at time t_2. The time interval t_2-t_1, also called mixing time t_m, is limited upwards only by the longitudinal relaxation time T_1 of the observed nucleus. We refer readers to Refs. 15-17 and 21-23 for a detailed description of the experiment and interpretation of the 2D exchange spectra. We point out that the exchange pattern yields information on the distribution of correlation times as well as on the molecular geometry of the motion, allowing to differentiate between diffusive processes and discrete jumps. In this latter case, it is easy to read out the jump angle directly from the specrum. On the contrary, the distribution of correlation times is accessible only by comparison with simulated 2D line shapes. In some favourable cases, it is possible to determine also the orientational distribution function from simulations of the 2D exchange pattern of macroscopically oriented samples[24].

Results and discussion

We recorded several 2D exchange spectra of the three liquid-crystalline polymers with different mixing times. The samples were macroscopically isotropic. The temperature ranged between 10 and 30 degrees above the glass transition T_g, in order to observe the slow chain dynamics, which actually manifested itself in off-diagonal spectral intensity. We report a typical spectrum as a representative example in Figure 7.

As can immediately be seen, the dynamics is of a diffusive kind, and the exchange patterns are similar to the ones of chain-deuterated amorphous polymers above T_g, like polystyrene[22,25] or atactic polypropylene[26]. There is, however, a difference: in the liquid-crystalline systems the correlation loss among the frequencies before and after the mixing time is lower than in the amorphous systems, and spectral intensity tends not to diffuse to regions far away from the diagonal even for long mixing times. We attribute this difference to the partial orientational order of the mesophase, rather than to steric hindrance of the bulky side groups. In order to appreciate the information contained in 2D exchange spectra, we relate them to the fast exchange 1D spectra commonly used to determine the order parameters in l.c. phases[21]. A complete exchange spectrum as in amorphous polymers[22,25,26] corresponds to an isotropic motion, $\langle P_l \rangle = 0$. Conversely, a finite order parameter $\langle P_l \rangle > 0$ leads to only partial exchange intensity in the 2D exchange spectrum[24]. Indeed, the difference from amorphous systems increases with growing order of the mesophase, i.e. from PMA6 through PMAM to PMA64.

The recorded 2D exchange spectra are compatible with the order parameters of Table I, and with a log-normal distribution of correlation times with a mean of the order of 10 ms and a full width at half height of about 2.5 decades.

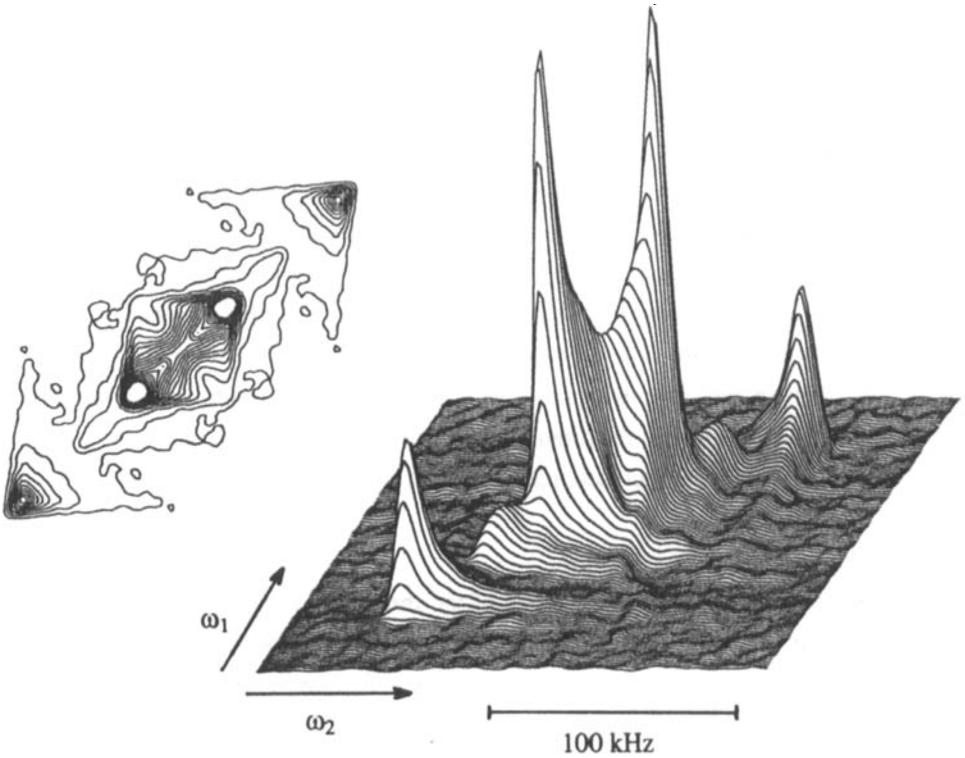


FIGURE 7 Deuteron 2D exchange spectrum of the l.c. polymer PMAM (contour plot and stacked plot). Temperature = 85°C (10° above T_g), mixing time = 15 ms, sweep width in both dimensions = 208 kHz. The outer peaks are attributed to the methylene group, the inner peaks to the methyl group.

APPENDIX

We report in Figure 8 the subspectra $S_l(\omega)$ (Eq. 7) used as basis functions for fitting the angular-dependent oriented monodimensional spectra of Figure 4.

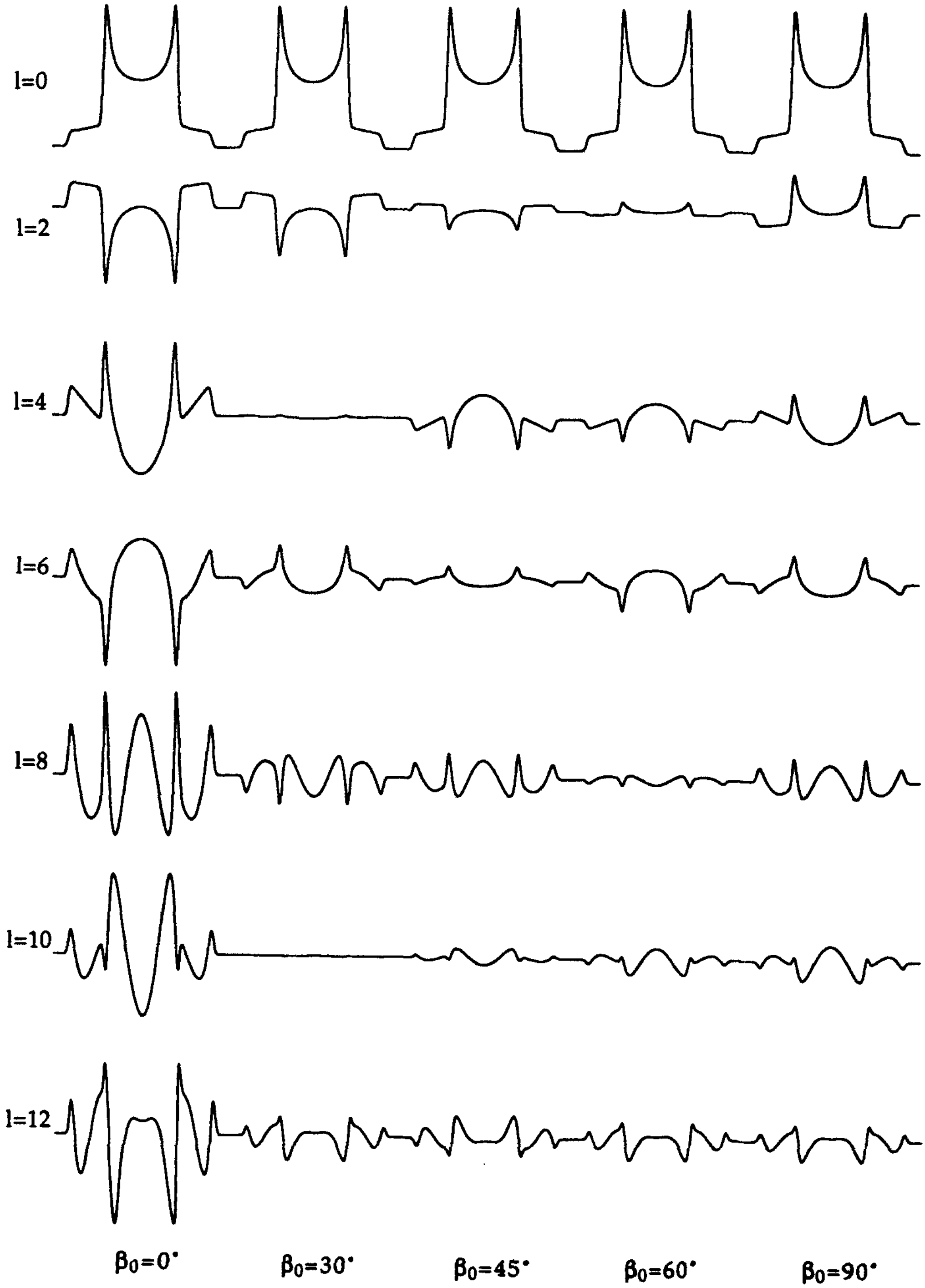


FIGURE 8 Subspectra $S_l(\omega)$ (Eq. 7) used as basis functions for fitting the angular-dependent oriented monodimensional spectra of Figure 4.

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