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Reorientation of a liquid-crystalline side chain polymer

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The reorientation times of a side chain nematic polymer have been measured. The polymer samples were oriented in magnetic fields of 2.1 T and the reorientation experiments were carried out using a NMR spectrometer operating at 1.5 T. Temperature and twist angle dependencies of the proton NMR spectra were studied in detail and discussed with regard to the alignment of the mesogenic molecule groups in the polymer medium. An additional result concerns the homogeneous or inhomogeneous reorientation.

1. Introduction

In recent years the dynamics of liquid-crystalline polymers has been the subject of various experimental and theoretical investigations [1-9]. Esnault [1, 2] and Martins [10], for example, have investigated the viscoelastic properties of main chain polymers and stated the importance of systematic measurements of the twist viscosity and of instabilities in the reorientation process. Casquilho [4], Birkenheide [5], Rupp [8] and Fabre [13] have studied the viscoelastic parameters on side chain nematic polymers and combined these experimental results with results of dielectric or electro-optic relaxation methods and with theoretical approaches.

In this paper NMR measurements of mainly the reorientation time of a side chain thermotropic nematic polymer will be presented. The effect of the temperature and magnetic field on the formation of the liquid order of the rigid side groups was confirmed by studying the change of the spectra line shape as a function of the twist angle (between the preferred orientation of the axes of the mesogenic molecules, characterized by the director \bar{n} , and the external field B_0). As a result of the sample preparation under the influence of the strong magnetic field B_0 the rigid side chain molecules are, on an average, aligned parallel to the magnetic field. This alignment is reflected in the splitting of the NMR signal into a doublet. The doublet splitting allowed us to calculate an order parameter for the prepared sample. The alignment of the director (at least of the rigid molecules themselves) along the magnetic field direction has its origin in the anisotropic diamagnetic susceptibility ($\Delta\chi_a \sim 10^{-9} \text{ m}^3 \text{ kg}^{-1}$) mainly of the biphenyl groups in the side chains.

2. Theoretical considerations

The theoretical description of the reorientation experiment is quite different depending on whether the twist angle is larger or smaller than $\pi/4$. With the assumption of an ideal monodomain structure continuum theory [11-13] is used for the theoretical description of the reorientation process at twist angles smaller than $\pi/4$. Following this theory the process is characterized by the differential equation

$$\gamma_1(d\varphi/dt) + 1/2\Delta\chi_a B^2 \sin 2\varphi = 0, \quad (1)$$

where γ_1 is the rotational viscosity. This equation describes the equilibrium between the magnetic moment acting on the magnetically anisotropic groups and the viscous retardation moment of the liquid-crystalline side chain polymer. The solution of this equation is

$$\tan \varphi(t) = \tan \varphi_0 \exp(-t/\tau_0) \quad (2)$$

and

$$\tau_0 = \gamma_1 \Delta\chi_a^{-1} B_0^{-2}; \quad (3)$$

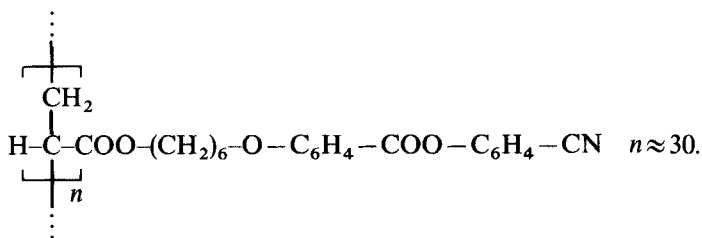
it deals with the rotation of the director of such a monodomain toward the B_0 direction.

An extensive contribution to the discussion of models describing the reorientation at angles of $\varphi_0 > \pi/4$ is given by Esnault *et al.* [2] and by Diogo [14]. Based on the assumption discussed in [14] the reorientation process can be explained by its dependence on temperature and twist angle with a combination of both the Arrhenius and the free volume model [15]. To come to an understanding of the physics of the reorientation process it is essential to take into account not only the thermal motion but also the orientational order of the molecules in the mesophase. A critical examination of existing models given in [16] confirms the dependence of the experimental data on the second rank order parameter S .

The nature of the reorientation process has been described by several authors [2, 4] as a kind of relaxation effect. Casquilho [4] studied a polysiloxane side chain polymer and found that the relaxation behaviour of a monodomain is homogeneous for all angles between the mean director and the static magnetic field. In the present work an additional experiment was carried out to decide the question as to whether the reorientation process is to be divided into quite different processes depending on the initial twist angle $\varphi_0 > \pi/4$.

3. Experimental considerations

The studies were performed on a side chain liquid-crystalline thermotropic polyacrylate (Röhm GmbH Darmstadt, Germany) of the general formula



Such polymers form an isotropic phase above 130°C and a nematic at temperatures lower than the clearing temperature T_{NI} . The temperature T_{NI} lies at about 115°C and the glass temperature at about 90°C . The substance was treated as follows to obtain a well-oriented sample. It was first heated in NMR tubes (5 mm o.d.) into the isotropic phase at temperatures of 20 K above T_{NI} . The NMR spectra were measured at 130°C to be sure that the isotropic state was reached. The spectra showed small linewidths due to the isotropic phase. The sample was annealed at this temperature for half an hour and then cooled down to 113°C , where the sample was kept for 6 h, followed by further cooling to room temperature. The whole temperature treatment was done in a static magnetic field of 2.1 T to obtain directed nematic domains, in the sense of a nematic monodomain [11, 12]. After this treatment the sample was ready for the reorientation

experiment. This was carried out by a turn of the sample and with it of the mean director \bar{n} from its equilibrium position about an angle φ_0 and at various temperatures. The relaxation of the director back to the initial orientation was measured for several angles ($\varphi_0 \leq 90^\circ$). For the reorientation process magnetic fields of 1.5 T were used, for example as described in [2, 6].

4. Results and discussion

Representative results are shown in figure 1; the spectra show the reorientation process. The lower spectrum in figure 1 (a) shows a 30° twist against B_0 (with a time delay of 80 s because of the measuring technique used). The relaxation from this non-equilibrium state back to the equilibrium state (i.e. $\bar{n} \parallel B_0$) is reflected by these spectra. It can be seen in which manner the broad singlet (at the bottom) changes into the doublet spectrum with time. Each spectrum corresponds to a definite instantaneous angle φ between the director \bar{n} and the magnetic field B_0 at a definite time of this relaxation

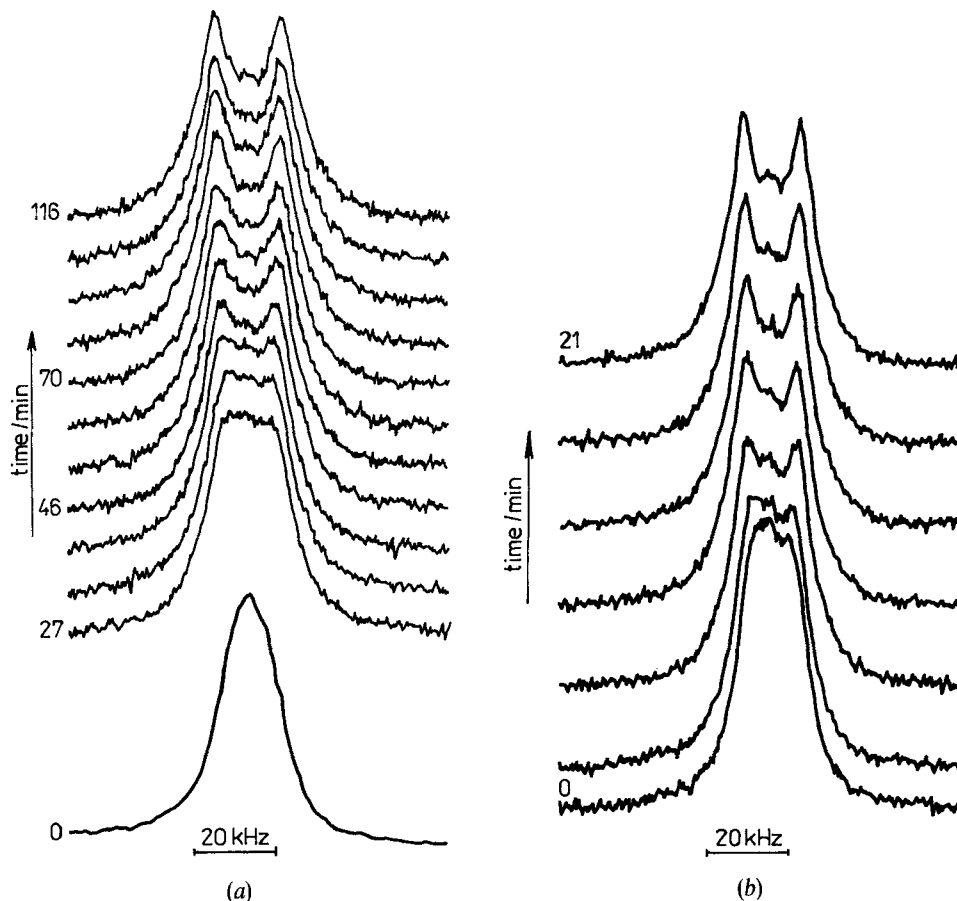


Figure 1. Time-dependence proton NMR spectrum of a sample rotated about an angle of 30° with regard to the initial position as a function of time, $B_0 = 1.5$ T. (a) $T = 75^\circ\text{C}$, (b) $T = 85^\circ\text{C}$.

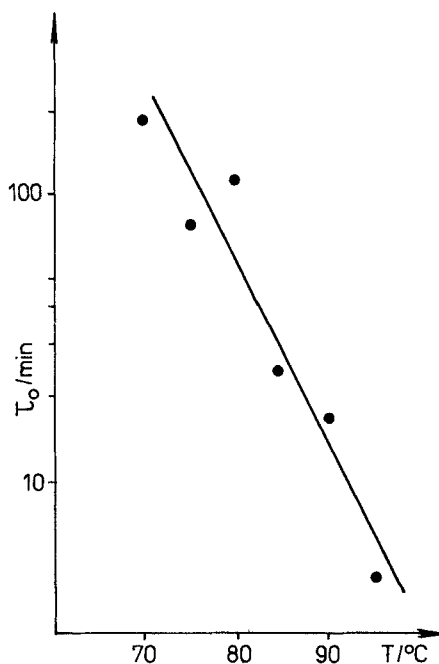


Figure 2. Relaxation time as a function of temperature at a twist angle of 30° .

process. Using the correlation between the instantaneous splitting $\Delta\nu(t)$ of the spectrum and the initial splitting $\Delta\nu_0(\bar{n}\|B_0)$ [17] via

$$\Delta\nu(t) = P_2(\cos \varphi(t))\Delta\nu_0, \quad (4)$$

this angle φ can be calculated. Using the angle φ as a function of time t of the NMR reorientation experiment the relaxation time τ_0 is calculated according to equation (2). This time τ_0 (see figure 2) measured for the reorientation process after a rotation of 30° against B_0 is nearly up to two orders of magnitude higher than the reorientation of main chain polymers [1,2] and is drastically reduced by increasing the temperature.

4.1. Reorientation time

In the following the term reorientation time is used. This time, τ_{reor} , is defined as the experimental time between the spectrum at the bottom in figure 1 (which characterizes the sample after the 30° rotation) and the spectrum at the top (with a maximum line splitting). The time necessary for the reorientation process characterized by this τ_{reor} rapidly decreases with increasing temperature, as shown in figure 3. The τ_{reor} depends on temperature (see figure 3, 30° -curve) as described by the Arrhenius type equation

$$\tau_{\text{reor}} = a \exp(b/T). \quad (5)$$

4.2. Correlation between reorientation time and twist angle

Figure 3 shows a further result: τ_{reor} also depends on the twist angle. The reorientation time increases with increasing twist angle between the director \bar{n} and the direction of the magnetic field B_0 . Figure 4 demonstrates this dependence in a twist range between 10° and 90° .

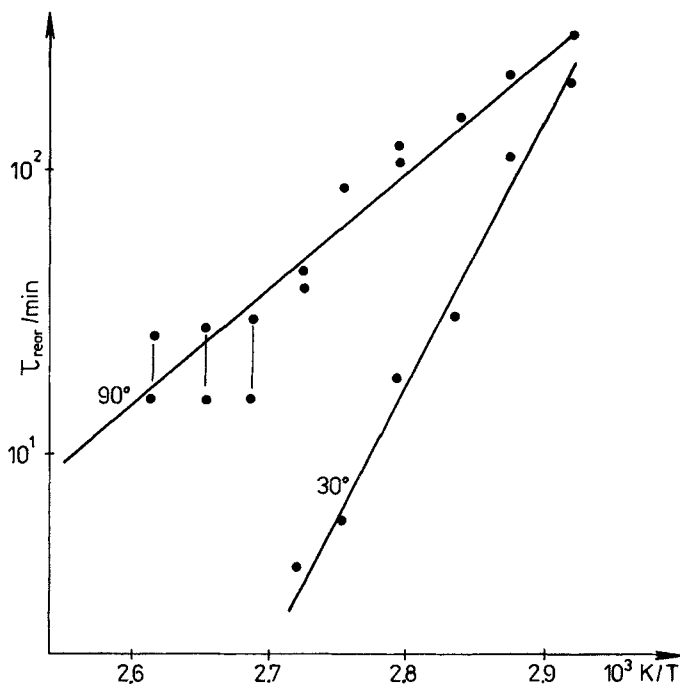


Figure 3. Reorientation time as a function of temperature for twist angles 30° and 90°.

The circumstance that the reorientational velocity at smaller twist angles differs remarkably from those at larger angles results from the need to take into account the theoretical description of the reorientation process to distinguish between $\varphi_0 > \pi/4$ or $\varphi_0 < \pi/4$. This $\tau_{\text{reor}} - \varphi_0$ relation refers to different influence magnitudes on the reorientation process. It may be possible that the order decreases during the reorientation process especially at larger twist angles and that his decrease is comparable with the effect of the temperature on the order. This assumption was confirmed by the temperature dependence of the order parameter S , as figure 5 shows. This parameter is taken from the doublet splitting $\Delta\nu$ of the ^1H NMR spectrum according to

$$S = 2\Delta\nu(3\cos^2\varphi - 1)^{-1}\alpha^{-1}, \quad \alpha = 3/4\gamma^2hr_{jk}^{-6}, \quad (6)$$

where γ is the magnetogyric ratio, and r_{jk} is the proton-proton separation. As a consequence of the experimental result discussed it seems to be reasonable to modify equation (5) and, using the concept of Fabre [13], to describe the temperature/twist angle dependence of the reorientation time by

$$\tau_{\text{reor}} = S^2/(\Delta\chi_a B^2) \exp(\varepsilon_a(S^2)/T), \quad (7)$$

where ε_a is an effective energy which depends on S^2 and where the correlation time $\tau_{\text{reor}} = \gamma_1 \Delta\chi_a^{-1} B_0^{-2}$ is used.

At first the structure of the side chain polymer was taken into consideration in a former experiment [18] where it was observed that the order parameter of the siloxane polymers investigated increases with the length of the end alkyl chain. The larger chains (more conformations possible) effect a better alignment of the mesogenic side chains

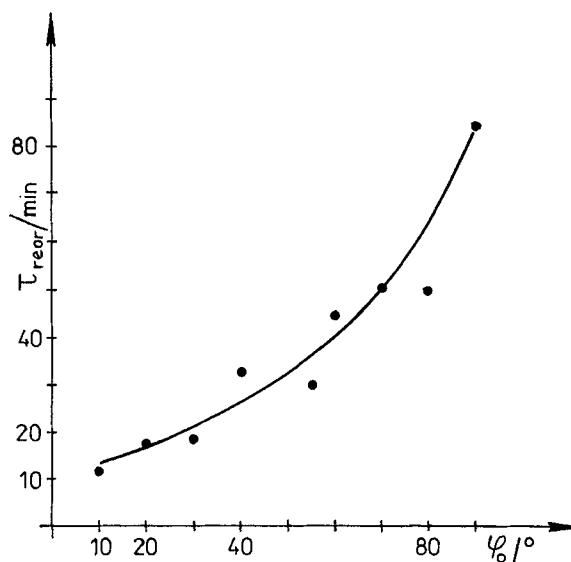


Figure 4. Reorientation time as a function of twist angle at $T=90^\circ\text{C}$.

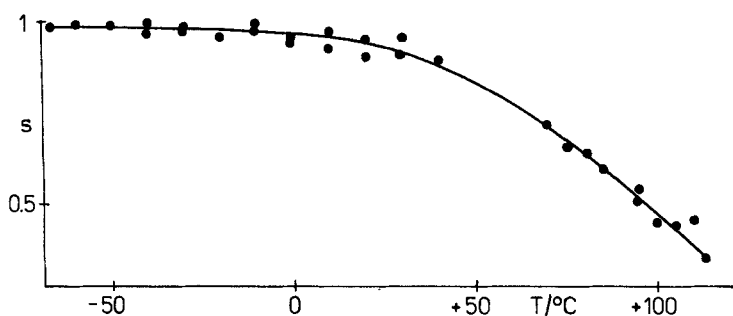


Figure 5. Order parameter S as a function of temperature.

than the shorter ones. This was found to be valid up to a certain length of the alkyl chain. Investigations of the dependence of the clearing temperature on the length of the alkyl chain gave the same relation and thus also suggested the importance of the structural order of the substance for reorientation.

4.3. Homogeneous or inhomogeneous reorientation ?

It was observed that the experimental data τ_{reor} measured at the twist angle of 90° (see figure 3) had greater deviations from the fitted curve than those at the twist angle of 30° . For the 90° measurements the experimental data would be better interpreted by two curves with different slopes. This means that different energetically activated processes were represented by the experiment. It would be necessary to include this perception into the further discussion.

Thus it can be concluded from the NME measurements first, at angles φ_0 smaller than $\pi/4$, the director field relaxes homogeneously, undisturbed, the aligned domains relax as a whole and second, the director relaxes inhomogeneously at angles larger than

$\pi/4$. After a $\varphi_0 > \pi/4$ turn a backward flow takes place. This viscosity-dependent flow passes an experimental state, where either the monodomain itself is disturbed or the domains have lost their joint alignment (to a macroscopic order). After this disturbance the orientation is built up again.

This assumption had to be checked. For that reason the following NMR experiment was carried out:

- (1) At 90°C the sample was twisted about 90° . At zero time a proton spectrum was measured (see figure 6, left row, the second lowest spectrum). The lowest spectrum corresponds to the initial one with the order parameter $S \approx 0.6$.
- (2) Further spectra were measured at intervals of some minutes. The change of the line shapes with the current reorientation process was remarkable.
- (3) When the signal with the narrowest line was reached the sample was taken out of the spectrometer and cooled down from 90°C to 30°C in a stream of nitrogen gas.
- (4) The spectral measured at 30°C (see figure 6, right) do not show a difference between 0° and 90° position to the B_0 -direction. The sample is not ordered

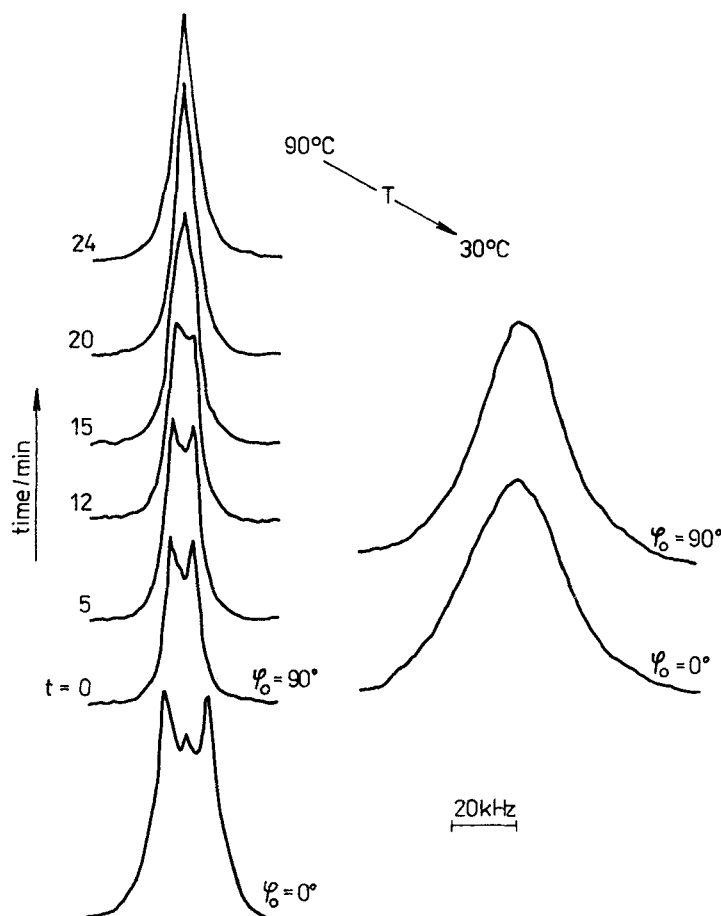


Figure 6. Proton NMR spectra (left) as a function of residence time in the magnetic field at 90°C (T_g) and (right) as a function of twist angle 0° and 90° at $T=30^\circ\text{C}$ ($< T_g$).

($S \sim 0$). The unordered state is even visible macroscopically! Spectra measured at temperatures between 40°C and 90°C (near the glass temperature) confirm this statement (see figure 7). (The spectra of 0° and 90° differ slightly from one another with increasing temperature. We might have failed the situation where the backward-flow step changed into the built-up step of the reorientation process).

- (5) At a temperature of 90°C the built-up process was continued, see left-hand side of figure 8, (as the second step of the reorientation process) until the spectra corresponded to the initial state of order with $S \sim 0.6$.
- (6) After taking the sample out of the spectrometer and cooling it down again to 30°C the spectra measured at different temperatures (see right-hand side of figure 8) showed the characteristic difference between 0° and 90° which is valid for oriented samples.

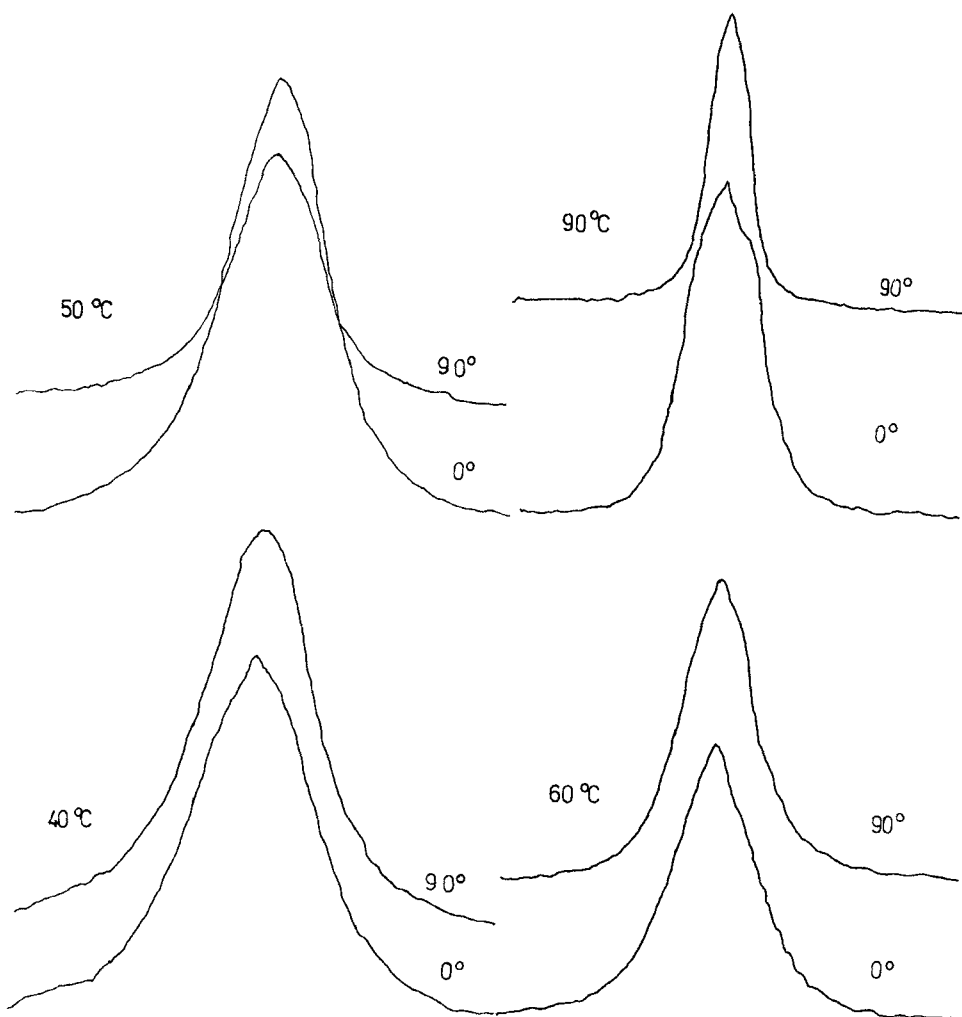


Figure 7. Proton NMR spectra at twist angles 0° and 90° as a function of temperature.

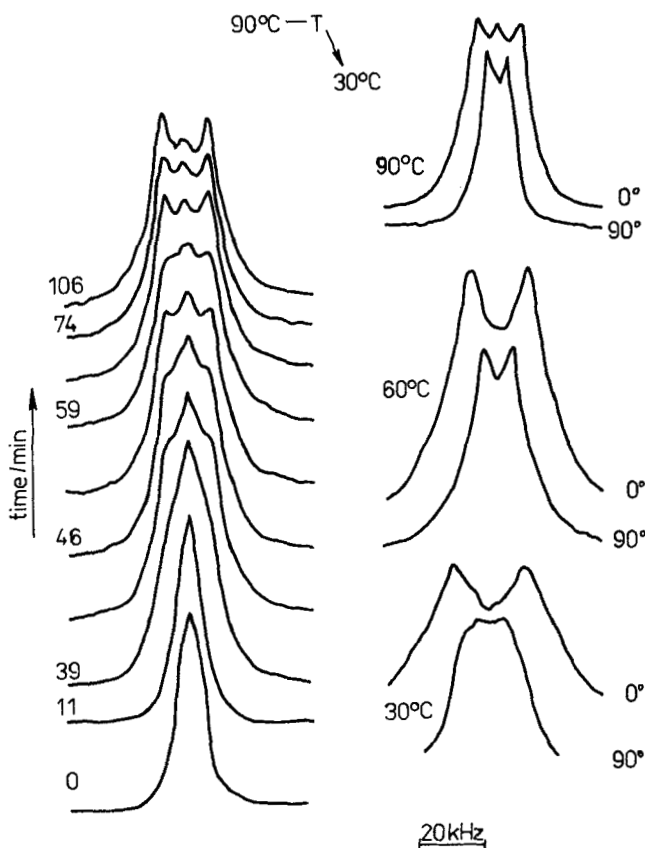


Figure 8. Proton NMR spectra (left) as a function of time at 90°C and (right) as a function of temperature at twist angles 0° and 90°.

From this we can conclude that this experiment confirms the assumption made that the reorientation process of this side chain polymer takes place in different ways according to whether the twist angle is smaller or larger than $\pi/4$. With this result obtained for the polymer investigated we cannot agree with the results of the investigations into siloxane side chain polymers published in [4].

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