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Degree of polymerization and dynamics in liquid crystalline poly-(1-subst.-ethylenes)

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Dielectric relaxation measurements of two classes of liquid crystalline polymers with different degrees of polymerization were carried out. The only difference between the samples is that in the first case the liquid crystalline (LC) part is coupled to the polyethylene chain by a –COO group, whereas in the second case, an ether group (O) connect the same parts. Increasing the degree of polymerization increases the clearing temperatures and decreases the dielectric relaxation frequencies f_R of reorientation of the LC part around both its short and long molecular axes. At higher degrees of polymerization, a saturation effect of f_R is observed which is related to the chemical structure of the linking group.

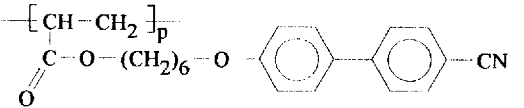
1. Introduction

Long range orientational order is a characteristic feature of liquid crystals. Whereas in nematic (N) phases only this quality exists, smectic (S) modifications additionally exhibit a layer structure. Of course, the formation of the different mesophase types [1] depends on the molecular interactions which are in competition with thermally activated translational and rotational motions. Due to these complex relations, one can observe in some cases re-entrant phases (re) for example, a polymorphism isotropic (I), N, S and N_{re} with decreasing temperature [2–4]. A restriction of the molecular dynamics can be achieved if the liquid crystalline units are connected to each other. In this way one can obtain liquid crystalline side-chain polymers and oligomers where the interaction of the different liquid crystal parts is additionally correlated via the main chain and a linking group like –COO– or –O–. Investigations of the phase behaviour and of the dielectric reorientation times resulting from variation of the degree of polymerization are the first step in studying such correlations [5].

2. Samples

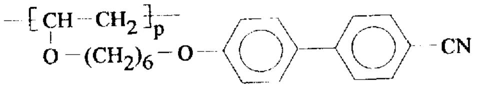
Of course, the correlation between the rod-like liquid crystalline units fixed to the same main chain depends on the chemical structure of the samples. Therefore, in both samples investigated by us, the main structural elements, a polyethylene main chain and a 4′-hexyloxy-4-cyanobiphenyl liquid crystalline unit, were kept the same. Only the linking group between them was different for the PA series, the –COO– and for the PE series, the –O– group. Phase transition temperatures, liquid crystalline phases and degrees of polymerization are given in table 1. The polyacrylates were synthesized by radical polymerization

Table 1. Phase transition temperatures in K for the oligomers and polymers investigated.



PA (Pw) [6]

P_w	P_w/P_n	g		N_{re}		S_A		N		I
11	1·12	●	287	●	—	●	—	●	349	●
15	1·08	●	293	●	—	●	339	●	366	●
23	1·09	●	301	●	323	●	366	●	382	●
30	1·39	●	313	●	333	●	378	●	391	●
60	1·15	●	313	●	352	●	396	●	401	●
130	1·19	●	313	●	355	●	402	●	406	●
380	1·32	●	313	●	357	●	406	●	409	●



PE (Pw) [7]

P_w	P_w/P_n	g		S_C		S_A		N		I
7·3	1·11	●	273	●	—	●	—	●	370	●
11	1·22	●	281	●	—	●	370	●	376	●
23	1·21	●	300	●	318	●	389	●	—	●
27	1·35	●	301	●	327	●	389	●	—	●

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[6] and the polyethers by cationic polymerization [7]; they were purified by fractional precipitation. Phase transition temperatures and phase types were obtained by hot stage microscopy, X-ray and calorimetric measurements. The temperature interval for the clearing process was less than ± 1 K; a minimal value of ± 0·2 K was detected for PA(11). Generally, an increase in the clearing temperatures with increasing degree of polymerization was detected. This increase is higher at low degrees of polymerization, indicating the strong change in physical behaviour in the oligomer range.

3. Dielectric measurements

Dielectric measurements were carried out using a micro-capacitor consisting of two glass plates ($A = 1\,\mathrm{cm}^2$) coated with an indium–tin oxide layer. No surface treatment was used in order not to increase the conductivity. Due to the relatively low conductivity of the ITO layer, the experiments are limited at frequencies lower than 1 MHz. Nevertheless this method was used because of the very small amounts of the samples. The plates were separated by 12·5 μm Teflon spacers. The cell was calibrated with cyclohexane or *p*-xylene and filled with the sample by capillary forces at about 15 K above the clearing temperature. In some cases, a sufficiently good planar orientation by surface interactions could be obtained and was used to measure the reorientation of the liquid crystalline part around its molecular long axis under the influence of the main chain (α-relaxation [8–11]). A homeotropic orientation was achieved partially by spontaneous orientation but in the most cases an additional electrical field was used during measurements (bias voltage 30 V) or a separate orientational process was carried out with an electric field (50 Hz, 30 V) and slow cooling at the I/N and N/S_A transitions. With external fields, the orientation was stable in the S_A phase and became disturbed in the N state, as observed by microscopic measurements. Due to the thin layer of the nematic sample, no good orientation in the magnetie field was obtained. From the literature, it is known that incomplete director orientation results only in a change of absorption intensity and not of the relaxation frequency [12, 13]. Measurements were performed with a self-made Sawyer–Tower bridge with the HP 4192A impedance analyser and a Schlumberger SI 1260 in combination with a Chelsea Dielectric Interface.

Experimental data for PA(23) with a good homeotropic and an adequate planar orientation at 321 K are given in figures 1 and 2. Using the SI 1260 bridge, an intense dielectric absorption with ε'' (max) ~ 2 could be detected for the homeotropic orientation down to frequencies of $f_R = 0{\cdot}1$ Hz (see figure 1). As shown in figure 1, the absorption can be separated into the conductivity part, important at low frequencies, and a dielectric absorption of the Cole–Cole [14] type in which the complex dielectric constant ε^* is given by

$$\varepsilon^* = \varepsilon_\infty + \Delta/(1 + i(f/f_R)^{1-h}), \qquad (1)$$

where ε_∞ = high frequency limit of ε', $\Delta = \varepsilon_0 - \varepsilon_\infty$ (dielectric increment), f_R = relaxation frequency, h = Cole–Cole distribution parameter. In this case, the molecular long axes are oriented nearly parallel to the electrical measuring field. This means that we measure the reorientation process around the short molecular axis (δ-relaxation). At frequencies about 50 times higher than the relaxation frequency f_R (frequency of the absorption maximum), stronger deviations of the fitted curve from the measured points were observed. To explain this effect, a nearly planar oriented sample was investigated (see figure 2). The director orientation was not better than 80 per cent, as estimated from microscopic observations. Here a

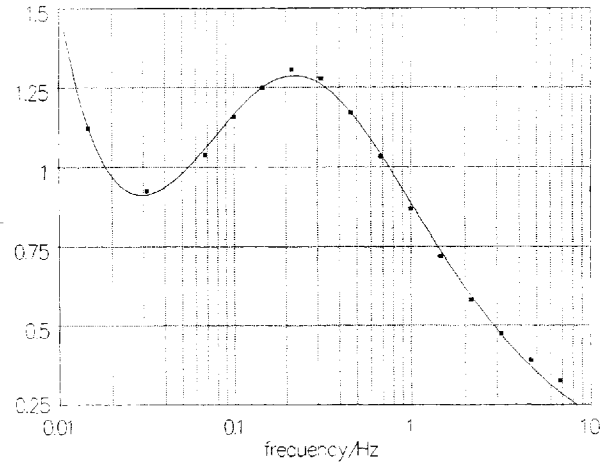

Figure 1. The dielectric absorption curve for PA(23) at $T = 309{\cdot}4$ K; nearly homeotropic alignment.

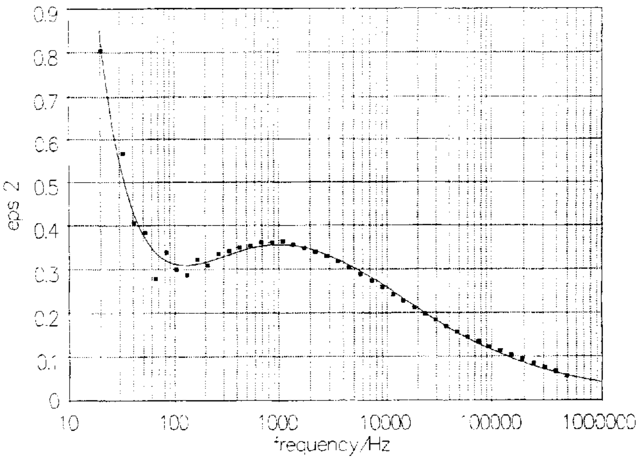

Figure 2. The dielectric absorption curve for PA(23) at $T = 322{\cdot}0$ K; nearly planar alignment.

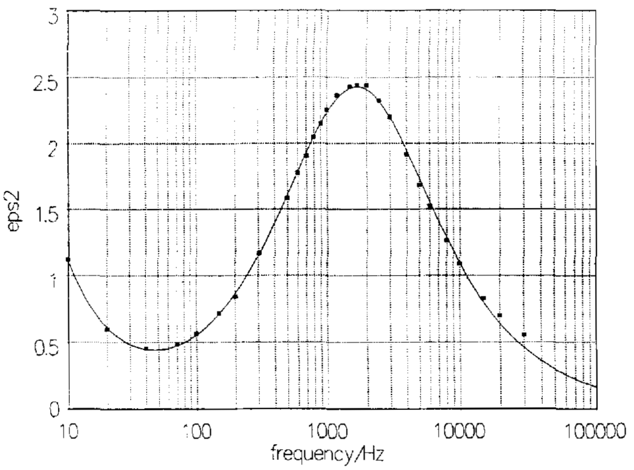

Figure 3. The frequency dependence of ε'' for PA(60) at $T = 356{\cdot}6$ K; nearly homeotropic orientation.

conductivity part and an absorption range could be separated. This high frequency process should be related to the α-process. A dielectric absorption curve for homeotropically oriented PA(60) is given in figure 3. The Cole–Cole distribution parameter $h = 0{\cdot}127$ is nearly the same as that observed for sample PA(30) with $h = 0{\cdot}114$. comparing this with the difference in the distribution of the molecular weights, symbolized by the ratio of P_w/P_n, one can conclude that this does not play an important role with respect to the distribution parameter h. This result is confirmed if we consider all the experimental data and the respective h-values; no systematic change of h with the degree of polymerization could be detected.

A dielectric absorption curve for PE(7·3) is presented in figure 4. In this case we could detect a distribution parameter $h = 0{\cdot}02$. It should be pointed out here that the data of figure 4 are originally measured values without any correction due to the conductivity. In contradiction to the samples of the PA series, we have found here higher relaxation frequencies of the δ-process and no α-relaxation, because we could not obtain a planar orientation.

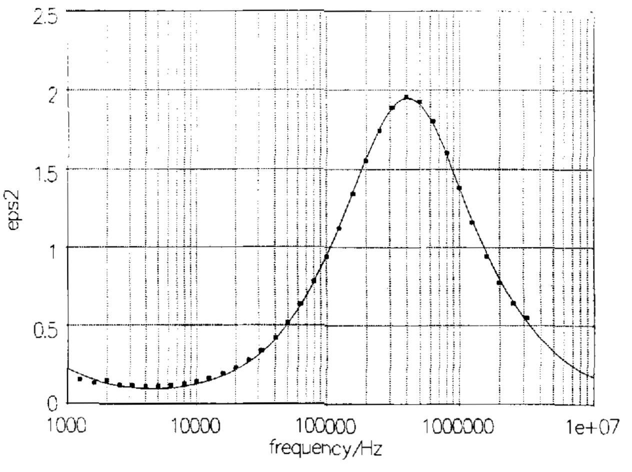

Figure 4. The frequency dependence of ε'' for PE(7·3) at $T = 356{\cdot}5$ K; nearly homeotropic orientation.

A survey of the relaxation frequencies as a function of temperature is given for the PA derivatives in figures 5 and 6 and for the PEs in figure 7. In order not to confuse the reader, not all the data obtained at low frequencies are presented. Furthermore we have to point out that some irregularities at high temperatures, for example, at 10^5 Hz for PA(11), can be seen which are related to the phase transition N/I. Generally, we could detect a WLF behaviour for the relaxation maps of PA samples for both the δ- and the α-mechanisms. In the case of samples PA(11) and PA(23), the low frequency absorption data could not be calculated with high accuracy, because of the high conductivity of the samples. Therefore, stronger deviations of T_0 were found. The measured relaxation frequencies f_R in the S_A and N_{re} phases do not show a step at the phase transition N_{re}/S_A; therefore, the data—excluding the values near to the N/I transition—were connected by one line. the fitted parameter to the Vogel–Fulcher equation

$$\ln f_R = A - \frac{B}{T - T_0} \qquad (2)$$

are listed in table 2. The experimental points for PE(7·3) were also fitted to equation (2) (see table 2). For the other fractions, we had not enough points at low frequencies due to the conductivity and phase transitions are indicated by broken lines. Therefore, the relaxation frequencies of these samples are connected in one phase by a straight line. For the fitting procedure, all measured points for one sample were used, without taking into account the phase transitions. This procedure is justified by the experiments, because no steps in f_R were detected at the phase transitions N/S_A and S_A/N_{re}. On the other hand, the relaxation frequencies increase by a step at the $N(S_A)/I$ transition (figure 5). Therefore, values for the isotropic phase were not used for the fit. The T_0-values of the δ-relaxation were found to be about 240 K and for the α-process, t_0 was generally higher. In order to decide whether the T_0-data belongs to the same or different glass processes, experimental f_R-values down to about 10^{-3} Hz are necessary but these could not be obtained due to the conductivity of the sample.

3. Discussion

The main point of our studies is the change in the dynamics with respect to differences in the degrees of polymerization and in the linking group. For the discussion, we have replotted in figure 8 the dependence of $\ln f_R$ versus P_w at constant temperature. In this case f_R-values were calculated from the fit parameters of

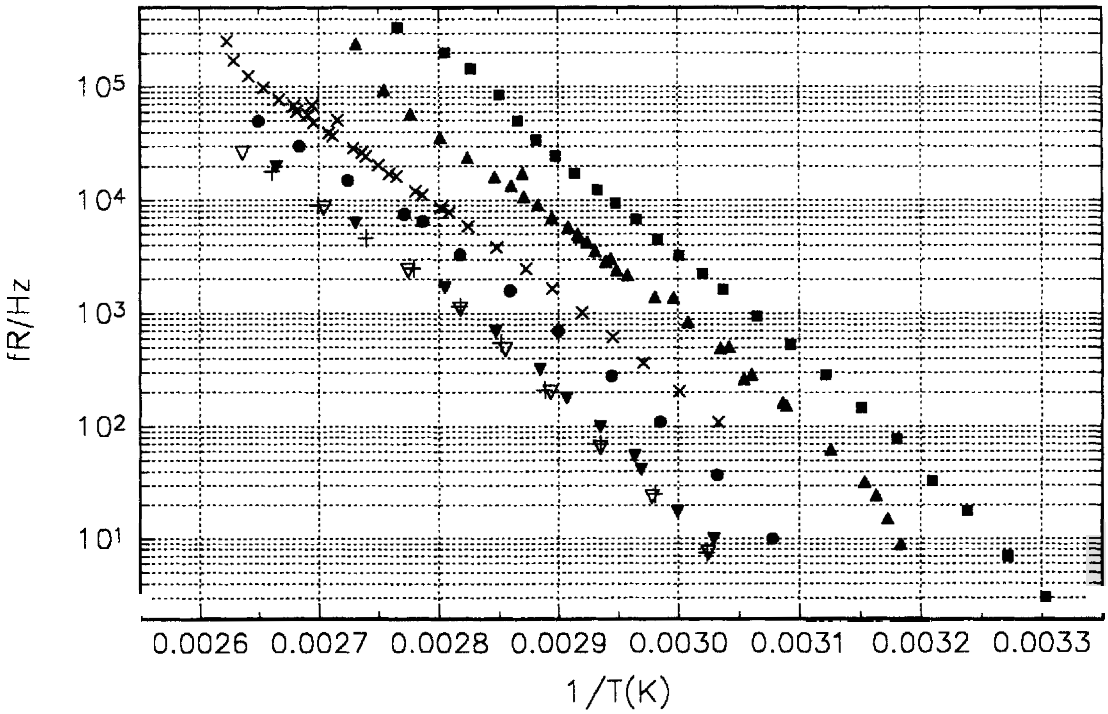

Figure 5. Arrhenius plots for PA polymers (δ-relaxation): [■]PA(11); (▲)PA(15); (×)PA(23); (●)PA(30); (▼)PA(60); (▽)PA(130); (+)PA(380).

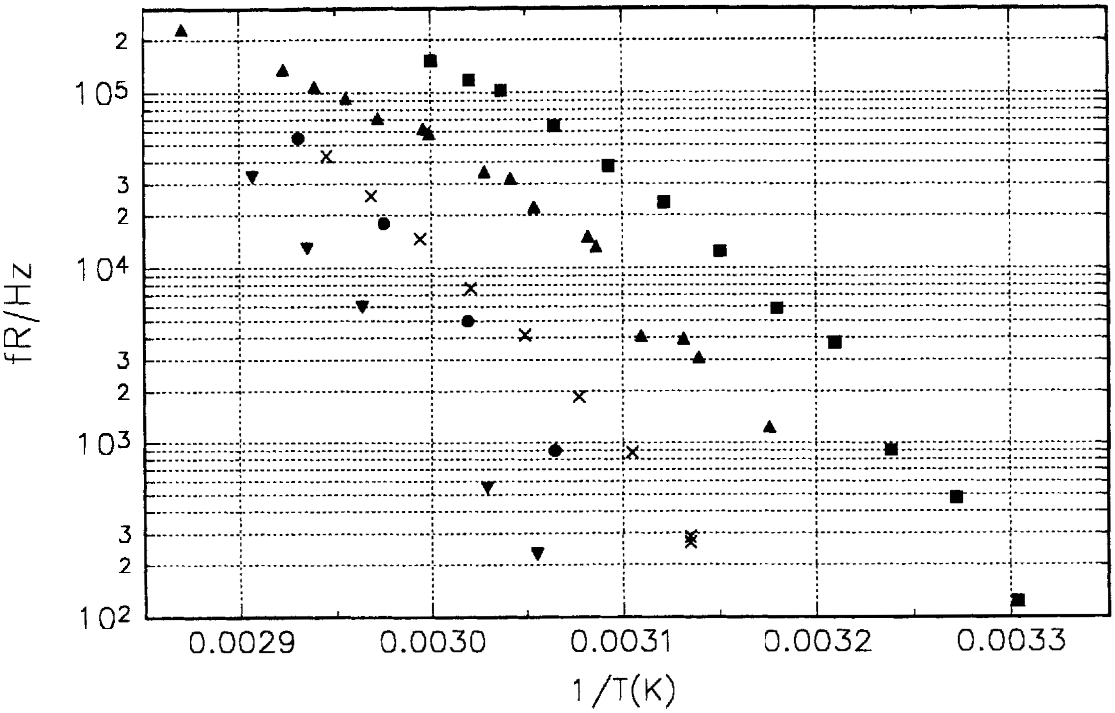

Figure 6. Arrhenius plots for PA polymers (α-relaxation). The symbols are the same as in figure 5.

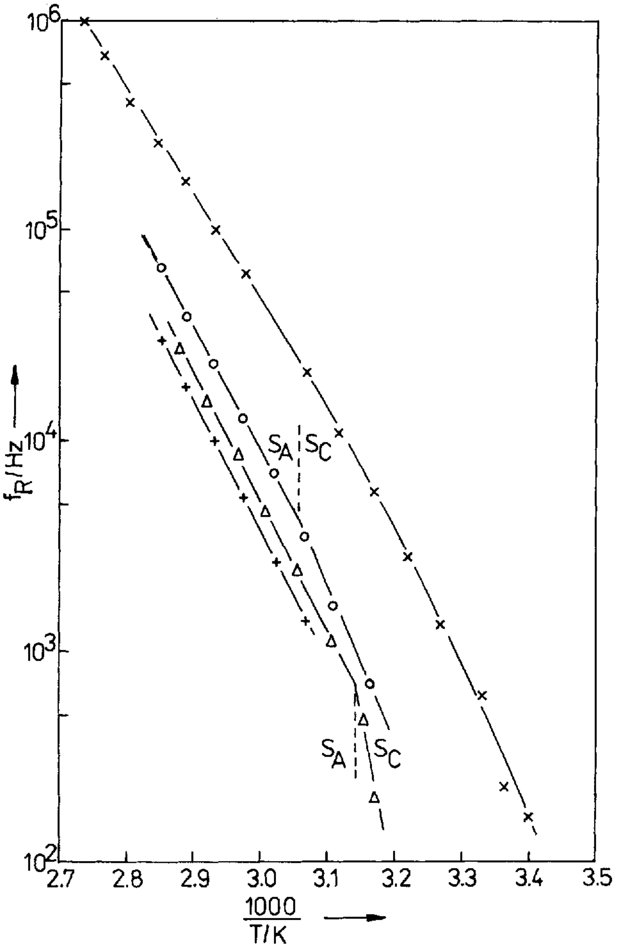

Figure 7. Arrhenius plots for PE polymers (δ-relaxation): (×)PE(7·3); (○)PE(11); (△)PE(23); (+)PE(27).

Table 2. Constants of the fit to equation (2).

	δ-Relaxation			α-Relaxation		
Sample	A	B/K	T_0/K	A	B/K	T_0/K
PA(11)	31·59	3107·8	200·7	19·54	473·6	270·6
PA(15)	30·15	2969·0	205·7	17·22	307·8	284·8
PA(23)	31·21	3642·6	192·4	21·53	715·1	273·9
PA(30)	23·88	1750·5	243·7	20·27	457·9	292·3
PA(60)	26·38	2339·9	233·3	37·26	2868·2	237·3
PA(130)	24·85	1984·7	243·9	—	—	—
PA(380)	25·69	2174·8	239·0	—	—	—
PE(7·3)	26·16	2213·4	189·3	—	—	—

table 2. The temperature of 338 K was chosen because it is in the middle of the investigated temperature range. As one might expect, the strongest changes in f_R with degree of polymerization occur in the oligomer range. A saturation effect can be assumed for the δ-relaxation of PA; therefore the experimental data were fitted to the equation

$$P_w = \frac{D}{(\lg f_R + \lg f_{R\infty})^c}. \tag{3}$$

A saturation value of the relaxation frequency $f_{R\infty} = 44\cdot6\,\mathrm{Hz}$ was obtained ($D = 22\cdot248$, $c = 0\cdot5679$). For the α-relaxation of PA and the δ-relaxation of PE, such a fitting procedure is not justified, because there are not enough experimental points. But from the data for the δ-relaxation, it is clear that a saturation can be expected at about 3×10^3 Hz. Furthermore, we can see that for PE, change in the degree of polymerization at about $P_w > 30$ does not strongly influence the relaxation frequency, whereas this situation is observed at about $P_w > 100$ for PA. This statement is confirmed by the phase transition temperatures shown in figure 1.

From the experimental fact that $f_{R\infty}(\mathrm{PE}) \sim 100\, f_{R\infty}(\mathrm{PA})$, it can be concluded that the coupling between the motions of the side and the main chain decreases if oxygen is the linking group. The weaker coupling also results in a shorter correlation length between the liquid crystalline units, indicated by the saturation effect at lower P_w-values discussed before. The main result of these investigations is the direct connection between the correlation of the liquid crystalline units via the main chain and the hindrance of the dipolar reorientation in general, as well as the influence of the linking group on this.

Furthermore, the dielectric relaxation frequency of the monomer (C (312 N) 328 I) has been measured in the temperature range from 332 to 321 K. There could also be detected an intense dielectric absorption effect in the isotropic state. For a comparison between the data for the polymer and the oligomer one has to consider also, in this case, data for the isotropic phase. From the activation energy of 61 kJ mol, we could calculate the relaxation frequency of the monomer at 333 K ($f_R = 31\cdot5$ MHz). Therefore, we tried to extrapolate measured values for PA(11) in the isotropic phase ($E_a = 116\,\mathrm{kJ\,mol^{-1}}$) down to a temperature of 333 K. For PA(15), we used the same activation energy and the measured point in the isotropic phase. A problem was the estimation of the relaxation frequencies of the polymers PA(23), (30), (60), (130) and (380). Using the fitted data of table 2, we could calculate the relaxation frequency in the LC state at the clearing temperature. By adding a step of $\ln f_R(\mathrm{I})/f_R(\mathrm{N}) = 0\cdot59$ (experimental value for PA(11)), we could estimate the expected relaxation frequency in the isotropic phase which was taken for the estimation of f_R at $T = 333\mathrm{K}$. Data estimated in this way are presented in figure 9, from which one can recognize an increase of f_R for the δ-relaxation of about five decades. This result is important, because it demonstrates the influence of the main chain on the dynamics for the reorientation of the LC part around its short molecular axis without any influence from different

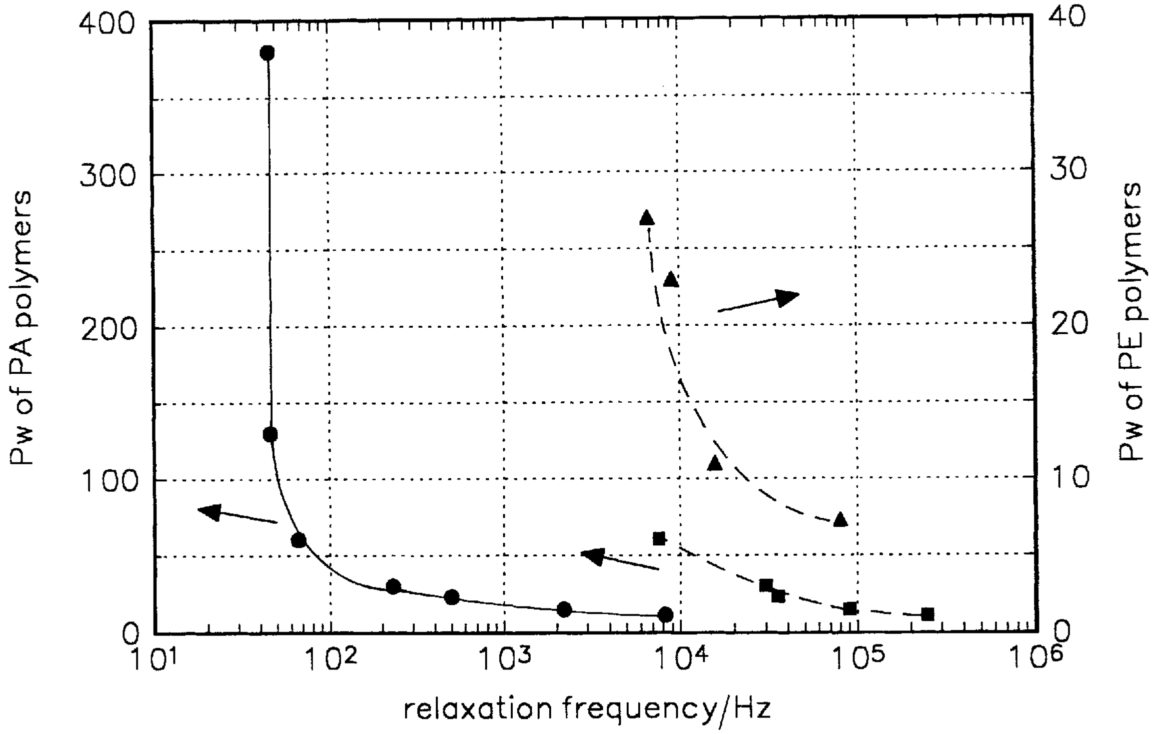

Figure 8. The dependence of the relation frequency f_R on the polymerization degree P_w (average by weight) in the liquid crystalline phase at 338 K: (●) δ-mechanism of PA polymers: (▲) δ-mechanism of PE polymers: (■) α-mechanism of PA polymers.

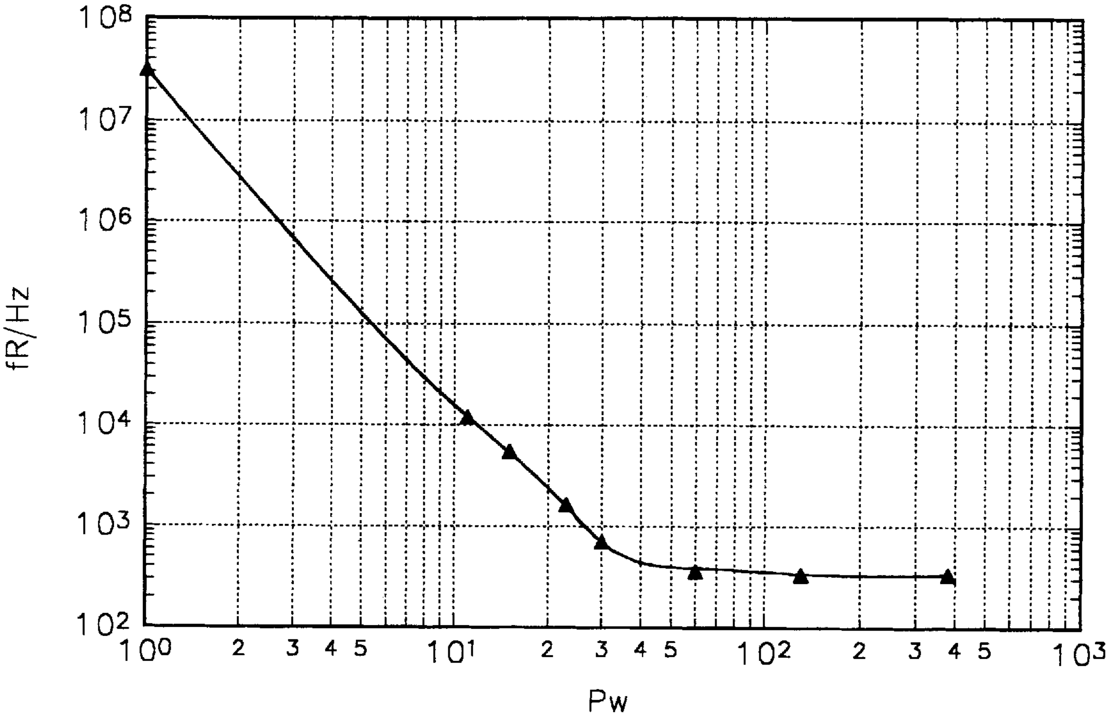

Figure 9. The dependence of the relaxation frequency f_R on the polymerization degree P_w in the isotropic phase (PA polymers and PA monomer) at 333 K.

clearing temperatures. The last effect could simulate the data presented in figure 5, if we consider the different activation energies in the isotropic and LC phases.

In the light of these results, all earlier data should be regarded as typical for the particular samples under investigation, but not for the polymer. In every case, for example, by variation of the main chain [15], the spacer length [16, 17] and the linking group, it seems to be necessary to measure data on samples with P_w-values in the saturation range in order to obtain a correct f_R. On the other hand, the results presented also show that the oligomer range of materials presents excellent possibilities for optimizing physical parameters.

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