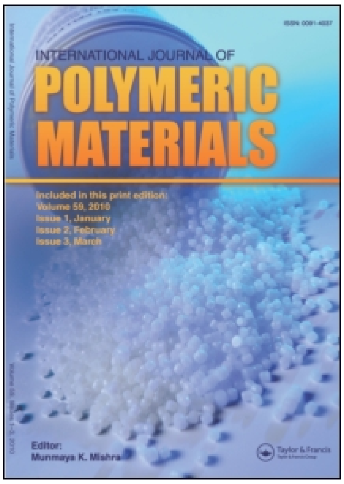

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On the Theory of NMR Line Shapes in Amorphous Regions of Uniaxially Oriented Polymers

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A theory of NMR of protons belonging to highly-stretched polymer chains with fixed ends, e.g. tie molecules of amorphous regions of oriented semicrystalline polymers, is presented. Analysis is carried out in terms of the model of freely-jointed chains. All contributions to the line shape from the intramolecular dipole-dipole interactions (DDI) are taken into account. Expressions are derived for the residual time independent component of DDI and the second moments of the fluctuating DDI. The NMR spectra are described in terms of the Anderson–Weiss approximation. A number of spectra are calculated for polyethylene. It is shown that the linewidth of high temperature spectrum rapidly grows with stretching and approaches that of crystallite polymer. It is demonstrated that the distribution function of tie molecules can, in principle, be obtained from the dependence of the spectra on the stretching ratio.

KEY WORDS NMR spectra, freely-jointed chains, molecular-weight distribution function, tie molecules, amorphous region.

INTRODUCTION

The high sensitivity to the details of the local molecular dynamics and structure has made NMR a powerful tool for polymer characterization.[1] NMR could also be applied to analyze morphology and molecular motions in oriented amorphous polymers and amorphous regions (AR) of semicrystalline polymers (SP). To work out such applications, a theoretical background must be elaborated which would relate the parameters of interest to the NMR spectra. In this article we develop such a theory for the case of ^{1}H NMR of SP. Our attention is focused exclusively on the tie molecules (TM) of AR of SP.

At temperatures above the glass transition point, when the AR are in the rubbery state, the intense molecular motions of TM strongly reduce the dipole-dipole interactions (DDI).

In contrast to simple liquids, TM are anchored by their ends to crystallites. This anchoring makes the motions of TM essentially anisotropic, due to which some part of DDI is not averaged. Thus, the DDI Hamiltonian can be split into two components: the time independent residual and the fluctuating one.

All previous attempts to derive the Hamiltonian of the residual DDI[2–8] were restricted to the case of weakly stretched Gaussian chains (exceptions were the works by Zachmann *et al.*,[9] which, however, are based on assumptions considerably limiting their utility). To treat the strongly stretched TM, the non-Gaussian chain models are necessary. In this work the Hamiltonian of the residual interactions is calculated in terms of the model of freely-jointed chains (FJC)[15] for arbitrary stretching degrees. In choosing this particular model, we take as the basis on the fact that at high degrees of stretching TM contain mainly trans isomers and can be visualized as consisting of straight rigid rods. If we assume now that the lengths of these rods are equal, we arrive at the idea of FJC. It is noteworthy, however, that the concept of FJC can be reliably applied only at intermediate and high degrees of stretching, whereas in other cases such factors as high concentration of gauche conformers (at low stretching) and the distortion of bond lengths and valence angles (at stretching ratios approaching unity) can affect the results.

At high temperatures, because of averaging out of the fluctuating components, the residual interactions fully determine the NMR spectra. At lower temperatures, however, one must calculate the contributions to the spectra from both the fluctuating and residual components of DDI.

Finally, we would like to note that the results presented in this work should not be considered as a complete theory but rather as a starting point for further studies.

Although all calculations were done for dipolar coupled protons of oriented semicrystalline linear polyethylene, the generalization to polymers of a different chemical structure and other types of nuclei and interactions presents no principal difficulties.

RESIDUAL AND FLUCTUATING PARTS OF DIPOLAR INTERACTIONS BETWEEN PROTONS OF STRETCHED MACROMOLECULES

Consider a molecule two ends of which are immobile. The molecule is characterized by a set of parameters $\Omega = \Omega(\boldsymbol{R}_e, N_m)$, where $\boldsymbol{R}_e$ is the end-to-end vector of the chain, N_m is the chain length (number of monomer units between the ends). For a pair of protons i and j, the DDI is characterized by the lattice coefficients[13,14]

$$b_{ij}(\boldsymbol{r}_{ij}) = \frac{\gamma^2 \hbar}{r_{ij}^3} P_2(\cos\theta_{ij}), \tag{1}$$

where $\boldsymbol{r}_{ij}$ is the vector connecting the i-th and j-th nuclei, γ is the gyromagnetic ratio of protons, θ_{ij} is the angle between the vector $\boldsymbol{r}_{ij}$ and the magnetic field, $P_l(x)$ is a Legendre polynomial of l-th rank. Because of the molecular motions, the coefficients b_{ij} are functions of time and can be presented in the form

$$b_{ij}(t) = b_{ij}^{(r)} + b_{ij}^{(f)}(t). \tag{2}$$

The constants

$$b_{ij}^{(r)} = \langle b_{ij} \rangle_{\text{conf}} = \int \mathrm{d}\Gamma\, b_{ij}[\boldsymbol{r}_{ij}(\Gamma)] P_l(\Gamma), \tag{3}$$

where the averaging is carried out over the conformations Γ of TM, determine the residual DDI. The fluctuating component constants are given by

$$b_{ij}^{(f)}(t) = b_{ij}(t) - \langle b_{ij}(t)\rangle_{\text{conf}}. \tag{4}$$

The calculation of the spectrum can be made more accurate if the interactions are further classified; three components can be considered: (i) interactions between the protons of the same methylene group ("intragroup interactions"), (ii) interactions between the protons of closely spaced methylene groups of the same molecule (intrasegment), and (iii) interactions between the protons of distanced methylene groups (intersegment). In this work, we assume that the second group comprises protons belonging to the same Kuhn segment. The Hamiltonian of DDI has now the form

$$\hat{H}_d^z(t) = \hat{H}_g^{(r)} + \hat{H}_k^{(r)} + \hat{H}_c^{(r)} + \hat{H}_g^{(f)}(t) + \hat{H}_k^{(f)}(t) + \hat{H}_c^{(f)}(t). \tag{5}$$

Here the superscripts r and f designate the residual and fluctuating components; subscripts g, k, and c stand for intragroup, intrasegment, and intersegment interactions, respectively.

To simplify the analysis, we ignore DDI between protons of different molecules (intermolecular interaction). This assumption is based on the facts that (i) dipolar interactions are short range and (ii) relative motions of protons of different chains strongly reduce the residual intermolecular interactions. With the intermolecular interactions ignored, we can describe the NMR spectrum as a superposition of the spectra of separate TM.

The second moments of the residual $M_i^{(r)}$ and the fluctuating $M_i^{(f)}$ components (on the i-th proton) are defined by the equation

$$M_i^{(\eta)} = \frac{9}{4}\sum_{\{j\}_\delta}\left(b_{ij}^{(\eta)}\right)^2. \tag{6}$$

Here $\delta = g, k, c$ and $\eta = r, f$. The summation defined as $\{j\}_\delta$ is carried out over the protons belonging to the corresponding group δ. Using the results of Reference 8 we find that the constant of residual part of dipolar intragroup interactions is given by

$$b^{(r,g)}(\Omega) = -\frac{1}{2}\frac{\gamma^2\hbar}{d_0^3}P_2\{\cos[\beta(\Omega)]\}g_2[\alpha(\Omega)], \tag{7}$$

where $d_0 = 1.78$ Å is the distance between the protons of methylene group, $\beta(\Omega)$ is the angle between $\boldsymbol{R}_e$ and the magnetic field, $\alpha(\Omega) = |\boldsymbol{R}_e|/N_m b$ is the stretching ratio, and $b = 1.554\sin(\xi/2)$, where ξ is the valence angle,

$$g(\alpha) = 1 - \frac{3\alpha}{L^*(\alpha)}, \tag{8}$$

and $L(x) = \coth x - x^{-1}$ is the Langevin function, $L^*(x)$ is the inverse Langevin function.

The constant of the residual part of intrasegment interactions $b_{ij}^{(r,k)}$ differs from $b^{(r,g)}$ by a numerical factor

$$b_{ij}^{(r,k)}(\Omega) = \frac{\gamma^2\hbar}{|\boldsymbol{r}_{ij}|^3}P_2\{\cos[\beta(\Omega)]\}P_2(\cos\theta_{ij})g_2[\alpha(\Omega)], \tag{9}$$

where θ_{ij} is the angle between $\boldsymbol{r}_{ij}$ and the segment axis.

Calculation of the residual intersegment interactions is more difficult because the interproton vector can in this case change both its orientation and length. The calculation of the average, however, is possible if we assume that the chain is described by the Gaussian statistics. For a pair of protons i, j separated by S monomers, the distribution of the interproton vector $\boldsymbol{r}_{ij}$ is then given by

$$P(\boldsymbol{r}_{ij}) \propto \exp\left[-\mu\left(\boldsymbol{r}_{ij} - \frac{S}{N_\mathrm{s}}\boldsymbol{R}_\mathrm{e}\right)^2\right], \tag{10}$$

where

$$\mu = \frac{3N_\mathrm{s}}{2C^2S(N_\mathrm{s} - S)}, \tag{11}$$

$N_\mathrm{m}b = N_\mathrm{s}C$, C is the segment length, and N_s is the number of segments in the chain. The distribution (10) is very convenient for our purposes as it enables one to calculate the average (3) analytically. Unfortunately, it can be used only at $|\boldsymbol{R}_\mathrm{e}| \ll CN_\mathrm{s}$, whereas for moderately and highly stretched TM numerical averaging, based on a non-Gaussian model, should be performed. To use the advantages of distribution (10), we modify the parameter μ in (10) so that it should give correct results in two limiting cases: for weakly and highly stretched chains. This can be achieved if we put

$$\mu = \frac{3N_\mathrm{s}^2(N_\mathrm{s}+1)}{2S(N_\mathrm{s} - S)(N_\mathrm{s}C - |\boldsymbol{R}_\mathrm{e}|)^2}. \tag{12}$$

Substituting distribution (10) with (12) into Equation (3) we find

$$b_{ij}^{(r,c)} = \frac{\gamma^2\hbar}{\left(|\boldsymbol{R}_\mathrm{e}|SN_\mathrm{s}^{-1}\right)^3} P_2(\cos\beta)g_1\left(|\boldsymbol{R}_\mathrm{e}|S\mu^{1/2}N_\mathrm{s}^{-1}\right), \tag{13}$$

where

$$g_1(x) = \operatorname{erf}(x) - \frac{1}{\sqrt{\pi}}\left(\frac{4}{3}x + 2x\right)\exp\left(-x^2\right), \tag{14}$$

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x \exp\left(-z^2\right)\mathrm{d}z. \tag{15}$$

The second moments of the fluctuating components of the dipolar interactions are given by (6). Performing the averaging we find

$$\begin{aligned} M_\delta^{(f)} = 2.25\gamma^4\hbar^2 \sum_{\{j\}_\delta} |\boldsymbol{r}_{ij}|^{-6}\bigg\{ & \frac{1}{5} + \frac{2}{7}P_2\{\cos[\theta(\boldsymbol{n}_R,\boldsymbol{H})]\}P_2\{\cos[\theta(\boldsymbol{r}_{ij},\boldsymbol{n}_C)]\}g_2(\lambda) \\ & + \frac{18}{35}P_4\{\cos[\theta(\boldsymbol{n}_R,\boldsymbol{H})]\}P_4\{\cos[\theta(\boldsymbol{r}_{ij},\boldsymbol{n}_C)]\}g_4(\lambda) \\ & - [P_2\{\cos[\theta(\boldsymbol{n}_R,\boldsymbol{H})]\}P_2\{\cos[\theta(\boldsymbol{r}_{ij},\boldsymbol{n}_C)]\}g_2(\lambda)]^2\bigg\}, \end{aligned} \tag{16}$$

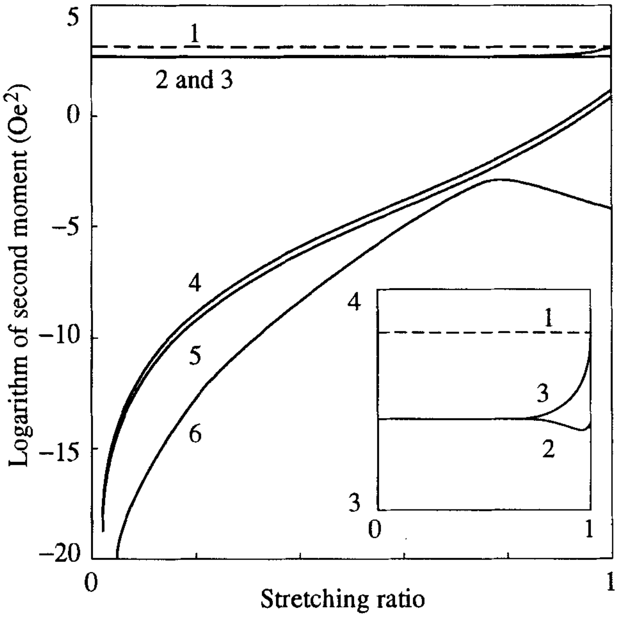

FIGURE 1 Experimental dependence of the second moments of DDI components on the stretching ratio for polyethylene (dashed curve 1) and theoretical ones (solid curves) for polyethylene chains with $N_m = 100$, $N_s = 10$. The value of $\beta = 90°$ corresponds to the geometry of typical NMR experiment. Fluctuating part of the dipolar interactions (curve 2), total second moment (curve 3), intragroup dipolar interactions (curve 4), intrasegment residual dipolar interactions (curve 5), intersegment residual interactions (curve 6). Details of the behavior of second moments of the total and fluctuating components at large stretching is shown in the inset.

where $\delta = g$ for intragroup and k for intrasegment interactions, and

$$g_4 = 1 + \frac{35}{L^*(\alpha)} - \frac{5\alpha}{L^*(\alpha)}\left(2 + \frac{21}{[L^*(\alpha)]^2}\right). \tag{17}$$

According to the data[15] at ambient temperatures and in an ideal solution, the Kuhn segment consists of about 10 monomer units. Neutron scattering data[16] show that the flexibility of polyethylene in melts is approximately the same as in ideal solution. Proceeding from this fact, we put $N_s = N_m/10$.

The second moments of different components of DDI calculated for a polymer chain are plotted in Figure 1 as functions of α. It can be seen that virtually at all values of α the residual components are much smaller than the fluctuating ones. The intrasegment and intragroup components are generally larger than the intersegment one.

CALCULATION OF SPECTRA

Consider the free induction decay (FID) from a single polymer chain $G(t, \Omega)$ with a given set of parameters $\Omega(\boldsymbol{R}_e, N_m)$. To simplify the analysis, we assume all protons on the chain to be magnetically equivalent and calculate the FID from one proton. The contribution of the residual interactions into the line shape can be approximately presented as convolution of a doublet[18] resulting from the intragroup interactions with a Gaussian line

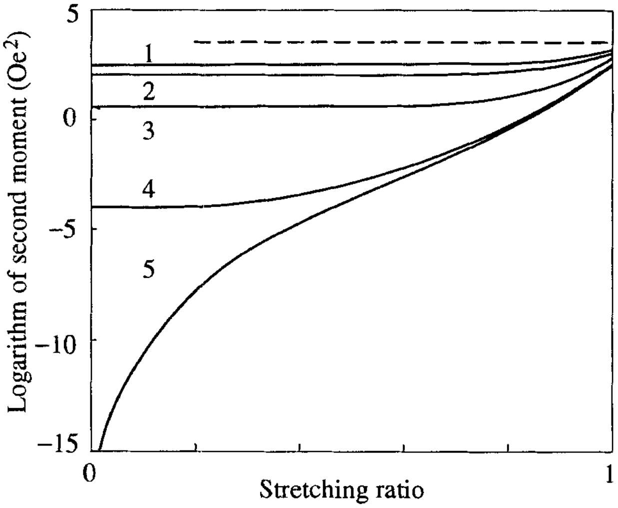

FIGURE 2 Experimental halfwidth of the absorption spectrum of TM versus stretching ratio for polycrystalline polyethylene (dashed curve) and theoretical ones for unimodal distribution of chain lengths with $N_m = 100$, $N_s = 10$, $\beta = 90°$ (solid curves). End-to-end vectors of chains are parallel to the stretching direction. $T = 270\,\mathrm{K}$, $\tau_c = 11\,\mu\mathrm{s}$ (curve 1); $T = 330\,\mathrm{K}$, $\tau_c = 7.2\,\mu\mathrm{s}$ (curve 2); $T = 350\,\mathrm{K}$, $\tau_c = 2.8\,\mu\mathrm{s}$ (curve 3); $T = 414\,\mathrm{K}$, $\tau_c = 0.28\,\mu\mathrm{s}$ (curve 4); $T \to \infty$, $\tau_c = 0\,\mu\mathrm{s}$ (curve 5).

with second moment $M_k^{(r)}$. Taking as the basis the small amplitude of the intersegment residual interactions (see Figure 1), we ignore its contribution into the relaxation. It seems reasonable to make further approximation. We restrict ourselves to a qualitative description and calculate the contribution from the fluctuating components in terms of the Anderson–Weiss model.[17] The resulting expression for the FID is

$$G(t,\Omega) = \cos\left(1.5b_g^{(r)}(\Omega)t\right)\exp\left(-0.5M_k^{(r)}(\Omega)t^2\right)$$
$$\times\exp\left(-\int_0^t\left[M_g^{(f)}(\Omega)+M_k^{(f)}(\Omega)\right]K_f(\tau)(t-\tau)\mathrm{d}\tau\right). \quad (18)$$

$K_f(\tau)$ is the normalized correlation function of the sum of local dipolar fields due to the fluctuating intragroup and intrasegment components

$$K_f(t) = \sum_{\{j\}_{g+k}} \frac{1}{K_f(0)}\left\langle b_{ij}^{(f)}(t)b_{ij}^{(f)}(0)\right\rangle. \quad (19)$$

The FID of the whole sample is found by averaging (18) over the distribution of the parameters Ω of polymer chains. In the simplest case where all TM are parallel to the stretching direction and have equal end-to-end distance

$$G(t) = \int N_m P_N(N_m)G(t,N_m,\boldsymbol{R}_e)\mathrm{d}N. \quad (20)$$

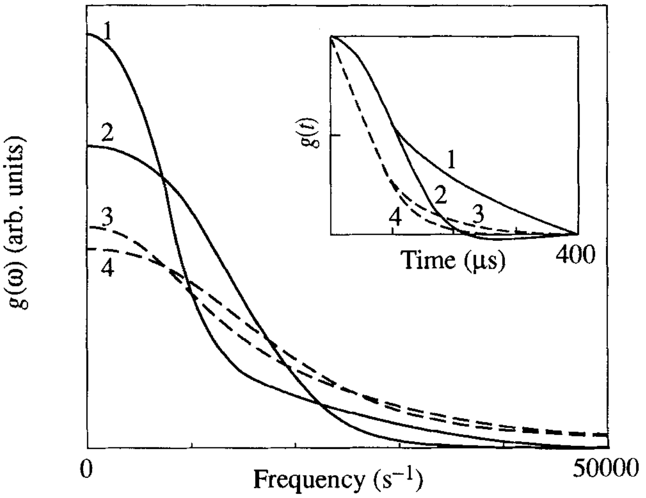

FIGURE 3 Absorption spectra for the unimodal and bimodal distributions at $T \to \infty$ and $T = 400$ K. End-to-end vectors of all chains oriented parallel to the stretching direction, $N_s = 10$, $\beta = 90°$, end-to-end distance $R_e = 76.2$ Å. The chain lengths were chosen to make the average order parameters equal in both cases at the given end-to-end distance. Unimodal distribution, $N_m = 83$: $\tau_c = 0$ μs (curve 1), $\tau_c = 2.8$ μs (curve 3). Bimodal distribution, equal numbers of $N_m = 75$ and $N_m = 100$: $\tau_c = 0$ μs (curve 2), $\tau_c = 2.8$ μs (curve 4). The corresponding free induction decays are shown in the inset.

RESULTS

Figure 2 presents the dependence of the halfwidth Δ of the absorption spectrum on α at various temperatures. The curves were calculated for unimodal distribution of TM lengths, $N_m = 100$, $\beta = 90°$. The absorption spectra were found by numerically Fourier transforming the free induction decays calculated by equations (18), (20). The contribution to the decay from the fluctuating components was calculated by substituting into (18) one-exponential correlation function with the correlation time found from the experimental data of Fedotov.[1] It can be seen from Figure 2 that at low temperatures the halfwidth is primarily determined by the fluctuating components and is not very sensitive to α. In contrast, at higher temperatures the spectra are dominated by the residual components of DDI and show a remarkable dependence on the parameters of the amorphous region. In particular, as $\alpha \to 1$, the halfwidth approaches the experimental value for semicrystalline PE.[1]

An important problem in polymer characterization is the analysis of the distribution of TM lengths. Considerable progress in this field has been achieved by Egorov and Zhizhenkov[20] who proposed to derive the TM distribution function from the dependence of second moment of the absorption spectrum on the stretching degree. A similar technique was proposed in References 11, 12 to measure the distribution of lengths of interjunction chains in polymer networks. The "cornerstone" assumption[20] was that upon stretching the TM molecules undergo a step-like transition from the amorphous (unstretched) to the fully-stretched state. The results obtained in this work support this assumption. Indeed, as can be seen from Figure 2, the dependence $\Delta(\alpha)$ is fairly steep at large stretching, and the interval of values α over which the halfwidth changes, say, by two orders of magnitude is very narrow. This means that one can, in principle, obtain quite detailed information on the distribution of chain lengths by analyzing the $\Delta(\alpha)$ dependence.

The effect of the distribution of TM lengths is demonstrated in Figure 3, where we present the absorption spectra calculated for unimodal ($N_m = 83$) and bimodal ($N_m = 75$ and 100) distributions at $T = 400$ K ($\tau_c = 0.8\,\mu$s) and infinitely high temperature ($\tau_c = 0\,\mu$s). It can be seen that the high-temperature spectra (solid curves) for unimodal and bimodal distributions differ noticeably.

CONCLUSION

Our results show that the NMR spectra of TM of oriented PE depend essentially on the parameters of the amorphous region, and, above all, on the distribution of chain lengths. This enables one to develop a method for analysis of chain length distributions.

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