Macromolecules **2002,** *35,* 5665−5669

Rescaling Approach to Molecular Orientation for NMR and Optical Properties of Polymer Networks

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Received November 26, 2001; Revised Manuscript Received April 1, 2002

ABSTRACT: A single scale invariant chain model is used to describe quantitatively the stress−optical, stress−strain, and NMR properties of polyethylene networks. The results of previous Monte Carlo simulations have been used to determine a rescaling constant for polyethylene, which enables accurate estimates of junction point densities to be made from NMR and stress−optical measurements. From the rescaling constant the stress−optical coefficient for polyethylene is calculated and is in good agreement with previous experimental values. NMR spin-echo data are used in conjunction with the rescaling constant to determine the rheological entanglement length in polyethylene melts.

Introduction

It is well-known that the development of segmental orientation in polymers is a route to producing materials with outstanding physical properties. There is consequently great interest in using a variety of physical techniques for the quantitative determination of such orientation.

A subject of especial fundamental and technological importance is the development of molecular orientation in stretched elastomer networks. The present paper addresses the key issue of providing a quantitative relationship between the segmental orientation in a stretched network and the imposed strain.

It will be shown that a rescaling approach provides the basis for the interpretation of NMR, birefringence, and spectroscopic measurements on such materials. This approach requires the calculation of average segmental orientations for unperturbed chains, from which a rescaling constant can be obtained that enables the quantitative interpretation of a wide range of experimental data. The calculation was undertaken in the present paper using the recent Monte Carlo (MC) rotational isomeric state (RIS) methods developed by Stepto, Ward, and co-workers for polyethylene, poly(ethylene terephthalate), and other polymers.[1−4] The microscopic details are then all contained in a single prefactor, the rescaling constant.

The development of optical anisotropy with strain has long been a cornerstone for understanding the behavior of stretched rubbers and, by analogy, to the development of molecular orientation during the melt extrusion and stretching of polyester fibers and films.

The classical starting point for quantitative analysis has traditionally been based on the Kuhn and Grün theory[5] of 1942 which replaces the true molecular network by an idealized network of identical chains, each of which consists of m freely jointed links of length l'.

It is found experimentally that, for strains which are not too large, both birefringence $\Delta\tilde{n}$ and true stress t for a uniaxial deformation ratio λ are proportional to $\lambda^2 - \lambda^{-1}$. Attention has therefore been focused on the experimental determination of a stress optical coefficient $\Delta\tilde{n}/t$ and on attempting to obtain a physical interpretation of this quantity from a molecular understanding.

For polyethylene, such attempts at interpretation, several due to the research of Treloar,[6] Saunders,[7] and others in the period 1945−1970, were unsatisfactory in terms of obtaining a quantitative analysis. The subject has been revisited recently by Stepto, Ward, and collaborators[1,2] using computer simulation studies based on the MC RIS modeling methods and network modeling methods developed by Stepto and Taylor.[8,9]

It has been shown that the basic thesis of the Kuhn and Grün model, where the parameters m and l' are calculated by forcing the equivalent freely jointed chain to adopt the same values of $\langle r^2 \rangle$ and $r_{\max}$ as the real chain, does not lead to a satisfactory quantitative analysis of the stress optical behavior.[1] Moreover, it is now clear that a better approach is to pursue the calculations of stress and molecular orientation quite separately. Specifically, whereas the stress relates only to the total number of chains in the network, the molecular orientation depends quite critically on the number of segments in the chains and develops more rapidly for short chains.

Scale Invariance

Techniques such as NMR, birefringence, and infrared dichroism monitor local orientation through the term $P_2(\cos \zeta)$, where $P_2(\cdots)$ is the second-order Legendre polynomial and ζ is the angle between an atomic vector and a reference direction, for example, the stretch direction.

In a polymer network, the reorientation of the atomic vectors are constrained by the junction points. It is useful therefore to define a set of network vectors $\{\mathbf{r}\}$ that span consecutive junction points in the rubber. The restriction imposed by the junction points determines an average orientation of their constituent atomic

10.1021/ma0120512 CCC: $22.00

vectors $\langle P_2(\cos\zeta)\rangle_r$, where $\langle\cdots\rangle_r$ indicates an average over all available conformations subject to the end-to-end vector constraint r.

The average orientation $\langle P_2(\cos\zeta)\rangle_r$ will depend on the magnitude r of the end-to-end vector, the angle ψ between $\mathbf{r}$ and the reference direction, the number n of main chain skeletal bonds between the junction points, and the length l of these bonds. If the skeletal bonds had the properties of freely jointed rigid rods, then their average orientation would be given by[10]

$$\langle P_2(\cos\zeta)\rangle_r = \frac{3}{5}\frac{1}{n}\frac{r^2}{nl^2}P_2(\cos\psi) + 0(n^{-4}) \qquad (1)$$

To first order in n^{-1}, this result can be written as

$$\langle P_2(\cos\zeta)\rangle_r = \kappa\frac{1}{n}\frac{r^2}{\overline{r^2}}P_2(\cos\psi) \qquad (2)$$

where κ is the rescaling constant and $\overline{\cdots}$ is an average over all network vectors in the undeformed state.

For a real molecular chain, the leading term in the expansion of $\langle P_2(\cos\zeta)\rangle_r$ as a power series in n^{-1} will be the scale invariant term given in eq 2. The rescaling constant κ then incorporates all the atomistic detail and can only be determined from experiment or simulation.

An approximate value for κ can be calculated knowing a polymer's characteristic ratio C_∞ and using the relation $\langle P_2(\cos(\xi)\rangle = {}^3/_5(r/r_{\max})^2$, due to Treloar,[10] for an infinitely long freely jointed chain, where ξ is the angle between the atomic vector and the end-to-end vector $\mathbf{r}$ and $r_{\max}$ is the length of the fully extended chain. From the scaling arguments given by Flory,[11] it is easily shown that $\kappa = 3C_\infty/5$. However, in general, this formula only determines κ to the correct order of magnitude and even the use of the higher terms $(r/r_{\max})^4$ and $(r/r_{\max})^6$ in the expression for $\langle P_2(\cos(\xi)\rangle$ does not give a sufficiently accurate representation, even for polyethylene chains. Its use for other chains, e.g., poly(ethylene terephthalate)[3,4] is even less satisfactory.

Monte Carlo Simulations

Rotational-isomeric-state simulations of polyethylene chains by Taylor et al.[1] will now be used to determine the numerical value of the rescaling constant κ. The Monte Carlo algorithm was used to calculate the dimensions of polyethylene chains of n from 40 to 220 skeletal bonds. RIS parameters were obtained from Abe, Jernigan, and Flory.[12] MC sample sizes of 3×10^6 chain conformations were used. Calculated values for $\overline{r^2}$ agreed within 0.1% with exact RIS values using matrix algebra.

A segment vector was defined as a vector passing through the skeletal C atom in a direction parallel to the chain axis of an all trans chain, see Figure 2 in ref 1. The angle ξ between the chain end-to-end vector and the segment vector was monitored. This defines the reference direction to be parallel to r and in doing so sets $\psi = 0$. Equation 2 therefore simplifies to

$$\langle P_2(\cos\xi)\rangle_r = \kappa\frac{1}{n}\frac{r^2}{\overline{r^2}} \qquad (3)$$

where κ is the rescaling constant.

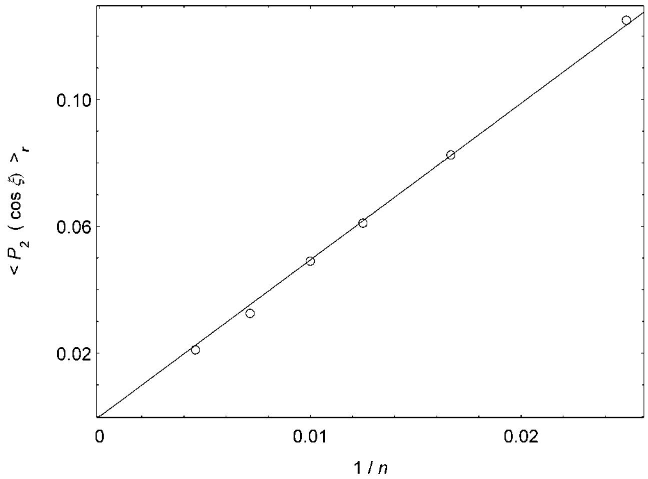

Figure 1. Average orientation of the segment vectors $\overline{\langle P_2(\cos\xi)\rangle_r}$ as a function of the number of skeletal bonds n in a polyethylene network vector r.

The average orientation $\langle P_2(\cos\xi)\rangle_r$ for each segment vector in an unperturbed chain was then calculated. This result was then averaged over all unperturbed chain end-to-end distances and all segments to give $\overline{\langle P_2(\cos\xi)\rangle_r}$. From eq 3, we have that

$$\overline{\langle P_2(\cos\xi)\rangle_r} = \kappa\frac{1}{n} \qquad (4)$$

In Figure 1 $\overline{\langle P_2(\cos\xi)\rangle_r}$ is plotted as a function of n^{-1}. The predicted linear dependence of eq 4 can be seen, supporting the use of the scale invariant term eq 2. The rescaling constant κ is found to equal 4.9.

The numerical value of κ will now be used to determine the stress–optical coefficient and the rheological entanglement length via NMR for polyethylene melts. This work shows the usefulness of the rescaling constant in determining quantitative microscopic parameters from experimental measurements.

Stress–Optical Coefficient

The stress–optical coefficient C is defined to be

$$C = \left[\frac{\Delta\tilde{n}}{t}\right]_{\lambda\to 1} \qquad (5)$$

where $\Delta\tilde{n}$ is the birefringence, t is the true stress, and λ is the deformation ratio.

The true stress depends on the molar mass between junction points M_x, density ρ, temperature T, and the gas constant R, as[6]

$$t = \frac{\rho RT}{M_x}\left(\lambda^2 - \frac{1}{\lambda}\right) \qquad (6)$$

For small uniaxial deformations birefringence measures the average orientation through[13]

$$\Delta\tilde{n} = \overline{\langle P_2(\cos\zeta)\rangle_r}\Delta\tilde{n}_{\max} \qquad (7)$$

where $\Delta\tilde{n}_{\max}$ is the maximum possible birefringence and ζ is the angle between the segment vector and the reference direction, which in this case is the strain direction.

Equation 2 can be written as

$$\langle P_2(\cos \zeta)\rangle_r = \kappa \frac{1}{n}\frac{1}{2}\frac{(2z^2 - x^2 - y^2)}{\overline{r^2}} \qquad (8)$$

where (x,y,z) are the Cartesian coordinates of the end-to-end vector $\mathbf{r}$ in the deformed rubber. These can be related to the undeformed coordinates (x_o,y_o,z_o) through the affine assumption, to give

$$\langle P_2(\cos \zeta)\rangle_r = \kappa \frac{1}{n}\frac{1}{2}\frac{(2\lambda^2 {z_o}^2 - {x_o}^2/\lambda - {y_o}^2/\lambda)}{\overline{r^2}} \qquad (9)$$

The averaging $\overline{\cdots}$ over all network vectors gives

$$\overline{\langle P_2(\cos \zeta)\rangle_r} = \frac{\kappa}{3n}(\lambda^2 - 1/\lambda) \qquad (10)$$

where the only assumption is that the distribution of end-to-end vectors in the undeformed state is isotropic.

Therefore, the stress–optical coefficient can be written, using eqs 5–7 and 10, as

$$C = \frac{\kappa}{3n}\frac{M_x}{\rho R T}\Delta\tilde{n}_{\max} \qquad (11)$$

The molar mass between junctions M_x can be written in terms of the average molar mass M_o represented by each main chain skeletal bond as

$$M_x = M_o n \qquad (12)$$

therefore

$$C = \frac{\kappa}{3}\frac{M_o}{\rho R T}\Delta\tilde{n}_{\max} \qquad (13)$$

To calculate the stress–optical coefficient, a value for $\Delta\tilde{n}_{\max}$ is needed. For polyethylene, this has been a matter of some controversy. This is due to the difficulties of calculating it for a fully aligned structure on the basis of bond polarizabilities, because of the uncertainties as to whether simple additive schemes, which do not take into account internal field effects, are adequate. In a recent paper by Cail et al.[2] agreement was found between their simulation and experimental data when using $\Delta\tilde{n}_{\max} = 0.223$, calculated using Denbigh's[14] polarizabilities based on data for gaseous CH_4 and C_2H_6.

In a seminal paper by Saunders,[15] a range of polyethylene networks with various junction point densities at 403 K were examined. The stress–optical coefficient for the networks with $M_x > 4000$ g mol^{-1} was $(2.0 \pm 0.1) \times 10^{-9}$ Pa^{-1}. For the samples with $M_x < 4000$ g mol^{-1} the stress–optical coefficient was a function of M_x. For these networks with low molecular weights between junction points, it is expected that under deformation there will be a significant number of chains at maximum extension.

Taking $\Delta\tilde{n}_{\max} = 0.223$, $M_0 = 14$ g mol^{-1}, $\rho = 0.80$ g cm^{-3}, $T = 403$ K, and $\kappa = 4.9$ in eq 13 gives $C = 1.9 \times 10^{-9}$ Pa^{-1}, which is in excellent agreement with the experimentally determined value. This shows that a single scale invariant chain model can correctly describe both the stress–optical and stress–strain properties of the polyethylene networks.

Transverse NMR Relaxation

In this section the rescaling constant κ will enable the quantitative determination of the rheological entanglement length using NMR spin-echo data[16] from isotropic polyethylene melts.

If undeformed polyethylene melts are considered, the effect of excluded volume interactions can be ignored. In strained networks, these interactions are known to contribute to the chain segmental orientation.[17]

Dipolar intraproton pair (CH_2) interactions in polyethylene melts, above the glass transition temperature, are the dominant cause for the dephasing of the transverse nuclear magnetic components.[18] The resultant loss of net magnetization is recorded in a transverse NMR relaxation measurement. The experimental signal $G(t)$ can be determined from[19]

$$G(t) = \overline{\mathrm{Re}\exp\left[\frac{3i\gamma^2 h\mu_o}{16\pi^2 d^3}\int_0^t P_2(\cos \alpha(t'))\,\mathrm{d}t'\right]} \qquad (14)$$

where α is the instantaneous angle that an intra-proton pair vector makes with the applied magnetic field, γ ($=26.75 \times 10^7$ T^{-1} s^{-1}) is the proton gyromagnetic ratio and d ($=1.95 \times 10^{-10}$ m) is the distance between hydrogens in a CH_2 group. The $\overline{\cdots}$ indicates an averaging over all the proton pairs in the polymer melt.

In entangled melts, the transverse relaxation signal typically shows a two-component decay.[20] This has been explained in terms of the polymer chain undergoing two distinct types of dynamics.[20,21] Chain ends display fast Rouse-like motion, which generates a slowly decaying exponential that can be characterized by a time constant T_2^{end}. In contrast, the central segments undergo a more restricted reorientation through reptation within their surrounding entanglement network structure. This constrained motion produces the more rapidly decaying component.

In a network the mean position of the junction points is fixed, forming the static Gaussian distribution of $\{\mathbf{r}\}$ vectors. The idea in this work is that the polyethylene melts can be viewed as temporary networks formed by the presence of entanglements. The relaxation signals will be fitted to the expression $G(t)$ given by where f is

$$G(t) = (1 - f)G_{\mathrm{network}}(t) + f\exp\left(-\frac{t}{T_2^{\mathrm{end}}}\right) \qquad (15)$$

the fraction of chain considered to be loose ends and $G_{\mathrm{network}}(t)$ is the signal from the central entangled segments.

The signal from the central entangled segments $G_{\mathrm{network}}(t)$ can be derived from eq 14. The fast local reorientation of the proton pairs constrained between entanglement points will generate their average value $\langle P_2(\cos \alpha)\rangle_r$ in the integral of eq 14,[22] as

$$G_{\mathrm{network}}(t) = \overline{\mathrm{Re}\exp\left[\frac{3i\gamma^2 h\mu_o}{16\pi^2 d^3}t\langle P_2(\cos \alpha)\rangle_r\right]} \qquad (16)$$

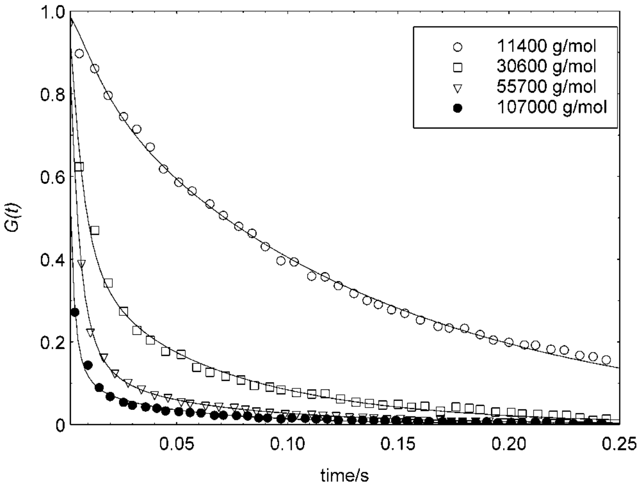

Figure 2. Transverse NMR relaxation data from linear monodisperse polyethylene melts at 422 K taken from ref 16. The solid lines are fits to eqs 15 + 18. The fitting parameters are displayed in Table 1.

Table 1. Parameters Obtained from the Analysis of the Transverse NMR Relaxation Signals from Polyethylene Melts in Figure 2 Using Eqs 15 + 18

M_n/g mol^{-1}	f	T_2^{end}/ms	n
11 400	0.81	140	2500
30 600	0.31	73	910
55 700	0.088	73	650
107 000	0.078	55	270

To accomplish the averaging in eq 16 we make use of the scaling procedures through eq 2, thus

$$G_{\mathrm{network}}(t) = \mathrm{Re}\ \overline{\exp\left[\frac{3i\gamma^2 h\mu_{\mathrm{o}}}{16\pi^2 d^3} t \frac{1}{2}\frac{\kappa}{n}\frac{r^2}{r^2} P_2(\cos\psi)\right]} \qquad (17)$$

where ψ is the angle between a vector $\mathbf{r}$ and the reference direction, which in this case is the applied magnetic field. The extra factor of $^1/_2$ arises because the intraproton pair vector is rigidly at right angles to the segment vector as defined in the simulation work above. Therefore, from the Legendre addition theorem,[23] we have that the average orientation of the intra-proton pair vector will be $-^1/_2$ of that of the segment vector, because $P_2(\cos \pi/2) = -^1/_2$. For neatness in eq 17, the minus sign has been discarded as this does not affect the measured real part.

To carry out the explicit integration in eq 17, the network vectors $\{\mathbf{r}\}$, which span entanglement points, are assumed to have orientations and lengths given by the Gaussian distribution. This makes the averaging required in eq 17 straightforward and produces the result[24]

$$G_{\mathrm{network}}(t) = \mathrm{Re}\left\{\left[1 - i\frac{\kappa}{n}\frac{\gamma^2 h\mu_{\mathrm{o}}}{16\pi^2 d^3}t\right]^{-1/2}\left[1 + i\frac{\kappa}{n}\frac{\gamma^2 h\mu_{\mathrm{o}}}{32\pi^2 d^3}t\right]^{-1}\right\} \qquad (18)$$

Equation 18 has been successfully employed[17] on networks to measure inverse junction point density through the parameter n.

The transverse NMR relaxation data from linear monodisperse polyethylene melts at 422 K can be found in Figure 2 and are taken from ref 16. The solid lines are fits to eqs 15 + 18. The fitting parameters are displayed in Table 1.

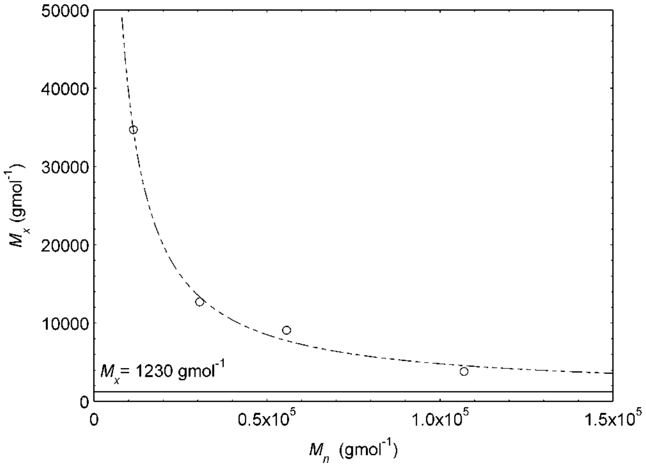

Figure 3. Apparent cross-link density M_x as a function of the chain molar mass M_n. The dashed line corresponds to a fit to eq 19.

The number of main chain skeletal bonds n can be more usefully turned into a molar mass between junction points M_x using eq 12. In Figure 3 the apparent molar mass between junction points M_x has been plotted as a function of chain molar mass M_n.

As the molar mass of the polymer chains increase their tube renewal times will rise as $M_n^{3.3}$. Eventually the reptation times will be longer than that of the NMR experiment. This technique will then observe a network formed by entanglement points. In this limit the inverse of the junction point density M_x deduced using eq 18 will equal that of the entanglement density.

In Figure 3 the dashed line is a fit to the parameter M_x as a function of M_n using a phenomenological expression

$$M_x/\mathrm{g\ mol}^{-1} = \left(\frac{a}{M_n}\right)^b + c \qquad (19)$$

where a, b, and c are fitting constants. The best fit was found for $a = 2.8 \times 10^8$ g mol^{-1}, $b = 1.03$, and $c = 1230$. The parameter c is the one of interest as it reveals the asymptotic value of M_x as M_n tends to infinity. As argued above this limiting value is close to the entanglement density of 1150 g/mol for polyethylene melts, as found by rheological experiments.[25] The rescaling constant κ is essential in obtaining the correct numerical value of M_x.

Conclusions

A methodology for quantifying the relationship between orientation and imposed strain for a scale invariant chain model was presented. Computer simulations[1] of polyethylene were used to evaluate a rescaling constant κ. This parameter enabled a quantitative determination of microscopic parameters from both NMR and stress–optical measurements of polyethylene networks.

The stress–optical coefficient for polyethylene was calculated using κ to be 1.9×10^{-9} Pa^{-1} and is in good agreement with previous experimental values.[15] This shows that a single scale invariant chain can quantitatively describe both the stress–optical and stress–strain properties of polyethylene networks.

NMR spin-echo data[16] from linear entangled polyethylene melts were analyzed using the scale invariant chain model. From κ and the transverse relaxation signals the entanglement molar mass was determined to be 1230 g/mol. This is remarkably close to the accepted rheological value of 1150 g/mol,[25] showing the usefulness of this rescaling approach for quantitative analysis of orientation in polymer networks.

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