Evidence for Short-Range Orientational Couplings between Chain Segments in Strained Rubbers: A Deuterium Magnetic Resonance Investigation

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ABSTRACT: Perdeuteriated linear poly(dimethylsiloxane) chains (PDMS(D)) are dissolved in a PDMS model network and used as deuterium NMR probes. The probe chain molecular weight is equal to (M_n = 10 500) or lower than that of the network chains (450 < M_n < 6100). A uniaxial deformation of the matrix induces a permanent uniaxial orientational order in the segments of the probe chains. The degree of order is independent of their molecular weight and equal to that measured on cross-linked chains. This stress-induced orientation is explained by short-range orientational couplings between chain segments. Such couplings appear to be also a dominant contribution to the segment ordering of the network chains. The introduction of these orientational couplings in a classical description of rubber allows one to account for the observations.

1. Introduction

Studies of chain segment orientation in strained rubbers may provide an information that is essential for the understanding of rubber elasticity. In particular, they give access to a more direct description of the chain deformation than macroscopic data derived from stress–strain or swelling measurements. This is one of the reasons why various techniques, sensitive to local properties, have been developed recently in this field.

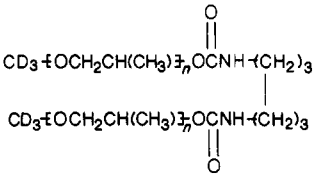
The main purpose of this work is to present an experimental approach giving better physical insights into the chain ordering process in strained rubbers. In particular, it is essential to establish clearly whether the constraints transmitted through the cross-link junctions are the only mechanism for the stress-induced chain segment orientation. To clarify this point, we have dissolved linear polymer chains inside a network made of chemically identical chains; the dissolved chains are short enough to be considered as "free", i.e., devoid of entanglements with the network structure. The basic question concerning such a system, schematized on Figure 1, is the following: is the equilibrium configuration of the free chain sensitive to a uniaxial deformation of the rubber matrix? In other words, is an orientational anisotropy induced at the segment level of the probe chain when the system is elongated? Among the techniques sensitive to the chain anisotropy, deuterium magnetic resonance (^{2}H NMR) has emerged as a powerful tool for investigating segmental ordering in strained rubber[1,2] and is used here to monitor the orientational behavior of the probe chain.

In this paper we extend our initial ^{2}H NMR experiment, performed on network chains,[2] to mobile chains dispersed inside a rubber matrix. Specifically, we report herein direct measurements of stress-induced ordering carried out on linear free chains of labeled poly(dimethylsiloxane) (PDMS(D)) and of labeled polyurethane (PU(D)) incorporated respectively into a PDMS and a PU network. In both cases the ^{2}H NMR spectra reveal an induced orientational anisotropy on the probe chain segments. In the case of PDMS the degree of anisotropy is studied as a function of the length of the probe chain and then compared with that previously obtained on cross-linked chains. Our results are discussed in terms of orientational couplings between chain segments. Finally a modified Flory–Huggins description, including the effect of these couplings, is proposed to account for our observations.

2. Experimental Section

2.1. Samples. Systematic studies were performed on linear perdeuteriated chains of poly(dimethylsiloxane) (PDMS(D)), $-(O-Si(CD_3)_2)_n-$, dissolved in an end-linked poly(dimethylsiloxane) network; a tetrafunctional network was used, prepared by an end-linking reaction in the bulk. The labeling procedure and the network synthesis are outlined in detail in ref 3 and 4. The linear chains, used as NMR probes, have either the same molecular weight as the network chains (M_n = 10 500) or a lower molecular weight (M_n = 6100, 3100, 450). In each case the molecular weight distribution M_w/M_n is about 1.7. Let us note also that the molecular weight of the linear chains is lower than the critical entanglement molecular weight M_c in the melt of such a material ($M_c \simeq$ 27 000 for PDMS[5]).

Preliminary results have been also obtained with a polyurethane network (molecular weight M_n between junctions = 1800), lightly swollen with bis(urethane) polymer chains (M_n = 1400; M_w/M_n = 1.05) deuteriated at their extremities only (PU(D)):



The synthesis of the network and of the linear chains were respectively achieved form poly(oxypropylene) triol ($M_w/M_n \simeq$ 1.04) and from a monoalcohol obtained by a ring-opening polymerization of propylene oxide; the polymerization was initiated by KOH in deuteriated methanol.[6] Then these alcohols were coupled with hexamethylene diisocyanate (HMDI) as described in ref 7. In the present case the copolycondensation between triol and HMDI which leads to the network formation was performed in the presence of PU(D) probe chains.

2.2. ^{2}H NMR. The general features of ^{2}H NMR in anisotropic fluids have been developed in ref 8. The sensitivity of this technique for investigating rubbery media has already been shown by studies performed on labeled networks.[2,9] We recall here that when rapid molecular uniaxial reorientations take place, the observed quadrupolar interaction is not averaged to zero. The effect of this residual interaction is to split the liquidlike NMR

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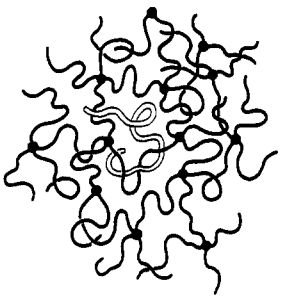

Figure 1. Schematic diagram of a probe chain dissolved into a rubber matrix. The molecular weight of the dissolved chain is supposed to be lower than the average molecular weight between entanglements M_e defined in the corresponding melt.

line into a doublet whose spacing $\Delta\nu$ may be written in frequency units as

$$\Delta\nu = {}^3/_2\nu_q|P_2(\cos\Omega)|\langle P_2(\cos\theta(t))\rangle \quad (1)$$

where ν_q designates the static quadrupolar coupling constant ($\nu_q \sim 175$ kHz for the methyl deuterons in PDMS(D)[10]). The angles in the second Legendre polynomials characterize the experimental geometry and the molecular dynamics; Ω is the angle between the steady magnetic field and the symmetry axis of the sample (i.e., the direction of the applied constraint); $\theta(t)$ is the instantaneous angle between the C–D bond and the symmetry axis. The brackets indicate an average over the rapid reorientational motions (i.e., more rapid than the characteristic time ν_q^{-1}). Then a measurement of the splitting $\Delta\nu$ gives direct access to the so-called orientational order parameter $S = \langle P_2(\cos\theta)\rangle$ of the C–D bond relative to the symmetry axis.

2.3. Experimental Conditions. A drop of liquid deuteriated linear PDMS chains ($T_g \simeq -120$ °C) is spread on the surface of a dry PDMS rubber sample (30 × 6 × 1 mm) at room temperature. The labeled chains are short enough to be perfectly compatible with the host matrix[11] and free to diffuse through the network structure[12] with a diffusion coefficient D of about 10^{-12} m^2 s^{-1};[13] after some days they have totally penetrated into the matrix and the surface of the film appears dry. The weight fraction of deuteriated chains is 9% or less. Additional neutron scattering studies, carried out on the relaxed sample, show that no phenomena of demixing and no appreciable effect of inhomogeneities occur in such a homopolymer solution.[14] On the other hand, the probe chains were incorporated in the PU sample before the cross-linking reaction, as has been mentioned previously. The corresponding weight fraction is 9%. Finally it should be pointed out that the deuteriated probe chains can be removed from the matrix: no ^{2}H NMR signal is detected after an immersion of the film in a large volume of good solvent (toluene) for 48 h. This indicates that no permanent links were created between the probe chains and the matrix.

Sample deformation is performed as described earlier.[2] Both ends of the sample are gripped by means of jaws. One is fixed while the other can be moved along the NMR tube by means of a calibrated screw. The sample elongation is controlled before and after each NMR experiment by means of a micrometer mounted on the stage of a binocular microscope; the elongation ratio λ is then measured with an accuracy of about 0.2%.

^{2}H NMR spectra are obtained with a CXP-90 Bruker spectrometer operating at 2 T with a conventional electromagnet; the steady magnetic field is normal to the principal strain direction of the uniaxially elongated sample. Before an NMR experiment, the sample is held at least 10^2 s in a given state of elongation. This time is much larger than the maximum relaxation time of the free chains. The temperature is regulated to 293 K (±1 K). Data are acquired after a $\pi/2$ pulse of 8 μs. The repetition delay is 1.2 s or more, since the longitudinal relaxation time T_1 in the system is of the order 250 ms. Absorption spectra are obtained by Fourier transforming the free induction decay, without any data manipulation (line broadening, trapezoidal multiplication, ...).

3. Results

3.1. Induced Orientational Order. Figures 2 and 3 show the transformations in the ^{2}H NMR spectra of the probe chains (PDMS(D) and PU(D)) on deforming the samples. In the relaxed state the spectrum is a single line (motionally narrowed) characteristic of a liquid: rapid isotropic motions (chain isomerizations and larger scale chain reorientations) totally average the quadrupolar interactions. Surprisingly, as in the case of network chains studied earlier,[2] well-defined doublets appear when the sample is either uniaxially compressed ($\lambda < 1$) or elongated ($\lambda > 1$); for instance the splitting magnitude $\Delta\nu$ observed on the PDMS(D) chains (M_n = 10 500) increases from 26 Hz at λ = 1.22 to 72 Hz at λ = 1.55. As quoted above, the time of an experiment is much larger than any characteristic relaxation time of such short linear chains (maximum Rouse time < 10^{-5} s). Moreover, for a given deformation rate $\lambda \neq 1$, the splitting $\Delta\nu$ remains constant over a time span larger than a few 10^5 s. So we may consider the system to be in a quasi-equilibrium state. Last, from additional experiments performed at various angles Ω for a fixed λ, the variation of the splitting $\Delta\nu(\Omega)$ reproduces exactly the $|P_2(\cos\Omega)|$ curve given by relation 1 as shown on Figure 4; typical spectra for Ω = 0°, 90° and

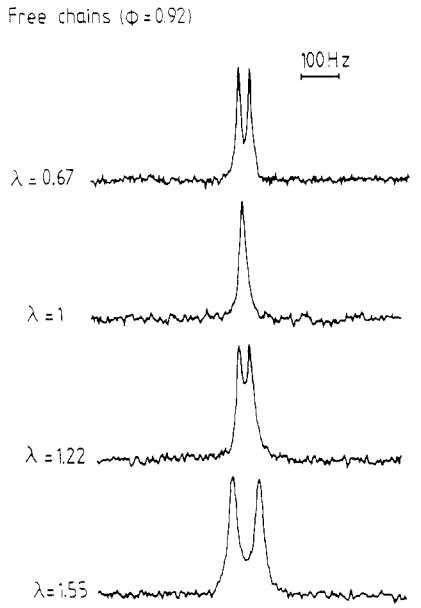

Figure 2. ^{2}H NMR spectra, 13 MHz, of perdeuteriated free chains of poly(dimethylsiloxane) (PDMS) dispersed in a PDMS network which is uniaxially compressed ($\lambda < 1$) or elongated ($\lambda > 1$) along a direction perpendicular to the spectrometer magnetic field (Ω = 90° in eq 1 of the text). Both probe chains and cross-linked chains have the same size (M_n = 10 500). The volume fraction of free chains is 9%. The number of accumulations is 10 for λ = 1 and 100 for λ = 1.55.

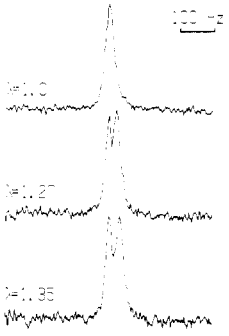

Figure 3. ^{2}H NMR spectra, 12 MHz, of bis(urethane) polymer chains (M_n = 1400), deuteriated at their extremities only, dissolved in a polyurethane network (molecular weight M_n between junction = 1800) uniaxially elongated along a direction perpendicular to the spectrometer magnetic field. The volume fraction of free chains is 9%. The number of accumulations is 1000 for λ = 1 and 3000 for λ = 1.35.

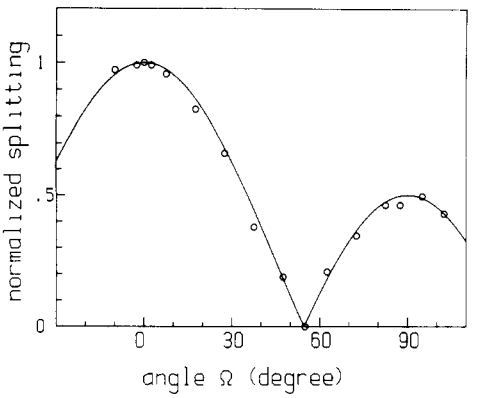

Figure 4. Variation of the normalized splitting as a function of the angle Ω between the applied uniaxial constraint and the spectrometer magnetic field. The continuous line represents the function $|P_2(\cos \Omega)|$.

the magic angle Ω = 55° are reported in the ref 15.

The appearance of resolved splittings for λ = 1, together with the angular dependence $\Delta\nu(\Omega)$, prove that the quadrupolar interactions are no longer averaged by the rapid molecular motions and that the direction of the stress axis is a symmetry axis for the observed residual interactions. This means that as the probe chain diffuses through the deformed network, its segments undergo uniaxial reorientational motions on the NMR time scale; more precisely, the orientation of one segment, averaged over times longer than $\Delta\nu^{-1}$, is along the strain axis.

It is worth noting that the averaging process observed on the perdeuteriated probe chains (PDMS(D)) gives rise to one single doublet in the low deformation range investigated here.[16] This implies that, within the line-width limit of the doublet structure, the various methyl groups are equivalent on the time scale of the ^{2}H NMR spectrum and that the degree of induced segmental orientation is quasi-uniform along the probe chains, whatever their molecular weight is ($450 < M_n < 10\,500$). The corresponding orientational order parameter $\langle P_2(\cos\theta)\rangle$ can be easily deduced from eq 1, exactly as it has been done in ref 17: for instance, in the PDMS chain (M_n = 10 500), at λ = 1.22 ($\Delta\nu \sim 26$ Hz), the order parameter of the methyl symmetry axis (i.e., the Si–CD_3 bond) is $\simeq 0.9 \times 10^{-3}$ and that of the segment connecting two adjacent oxygen atoms along the chain skeleton is $\simeq 1.8 \times 10^{-3}$.[18]

3.2. Effect of the Chain Length. In the low deformation limit (λ < 2) the splittings $\Delta\nu(\lambda)$ are a linear function of $(\lambda^2 - \lambda^{-1})$ as observed earlier, either on network chains[2] or on solvent probes.[1,19] However, the experimental fact that we want to point out here is that no particular effect occurs on this strain dependence when the molecular weight M_n of the PDMS probe chain decreases from 10 500 to 450: as shown in Figure 5, the slope $p = \Delta\nu/(\lambda^2 - \lambda^{-1})$, which describes the efficiency of the stress-induced orientation process, remains practically constant in this range of chain dimensions. The reported values of the slope p have been extrapolated to zero probe content in order to avoid any effect of probe concentration and so to make relevant the comparison between the various free chains.

Finally, we consider useful for the following discussion to include, in Figure 6, some ^{2}H NMR spectra previously obtained on linked chains of PDMS network under stress.[2]

4. Discussion

4.1. Orientational Couplings. The main result of these experiments is that the segments of the probe chains acquire a permanent *nonzero orientational order*, although the extremities of the chains are not linked to the network. This unexpected result attenuates the role of the cross-link

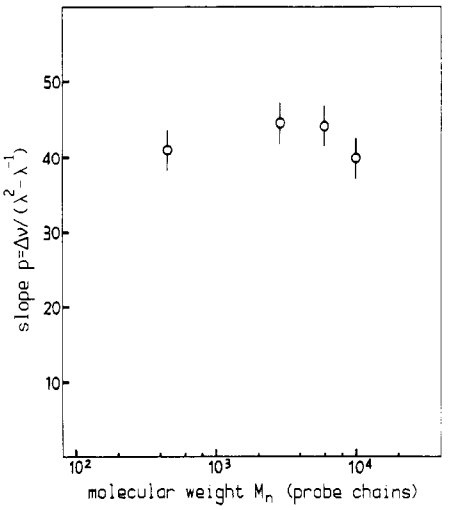

Figure 5. Slopes $p = \Delta\nu/\lambda^2 - \lambda^{-1}$ plotted against the molecular weight M_n of the probe chains (PDMS(D)). The reported values of p correspond to an extrapolation to zero probe concentration.

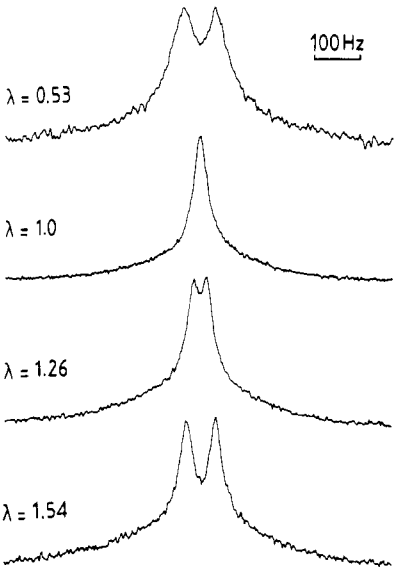

Figure 6. ^{2}H NMR spectra, 13 MHz, of perdeuteriated cross-linked chains of a dry PDMS network (molecular weight between junction = 10 500), uniaxially compressed (λ < 1) or elongated (λ > 1) along a direction perpendicular to the spectrometer magnetic field (Ω = 90°). The number of accumulation is 20 for λ = 1 and 200 for λ = 1.54.

junctions in stress-induced orientation and is contrary to the various classical descriptions of rubber elasticity, wherein the segmental orientation is presumed to arise solely from deformed independent chains. More precisely, such descriptions lead to a segmental anisotropy along the end-to-end vector of each chain, which is fixed to the network; accordingly, the macroscopic uniaxiality arises from a uniaxial distribution of these end-to-end vectors relative to the strain direction.[20,21]

A very different process emerges from this work. Indeed the induced uniaxial order observed on free chain segments necessarily involves orientational couplings between chains. These interchain effects are strong enough to prevent the free chain from relaxing to an isotropic equilibrium configuration in the deformed network. Steric interactions probably dominate these segmental couplings. Nevertheless they are not related to the transient effect of chain entanglements, because otherwise the induced order would not be permanent, as it has been observed. Moreover, Figure 5, where the induced segment ordering appears to be independent of the probe chain length, suggests that

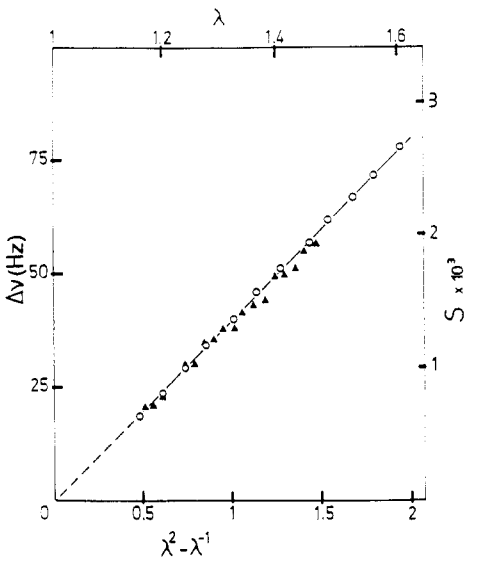

Figure 7. Probe chain (○) and network chain (▲) quadrupolar splittings as functions of $(\lambda^2 - \lambda^{-1})$. The free chain volume fraction is 9%. On the right vertical ordinate is reported the calculated order parameter S for the Si–CD_3 bonds of the PDMS chains. The samples break at about $\lambda = 1.7$.

these couplings are short range, i.e., that the range is intermediate between a molecular distance (a) and the dimension (R) of the shortest chain used here ($M_n = 450$). In fact the observation of a splitting in the case of the methyl end groups of PU(D) chains may be another relevant illustration of the local character of these couplings. So, one segment interacts with its spatial neighbors, which can be either segments of neighboring chains or "remote" segments within the same chain. Obviously these intersegmental couplings have to be distinguished from the purely intramolecular correlations among nearest-neighbor chain segments dictated by dihedral angle energetics, which are the ones currently introduced.[22]

Finally a simple way to visualize the observed behavior is to consider that the reorientational diffusion of the unattached chains takes place through an anisotropic fluid medium made of the partially aligned network chains. Such effects of polymer chain confinement are quite similar to those already observed on short n-alkanes[1] or on polybutadiene oligomers[23] dissolved in a rubber matrix under stress.[24]

4.2. Comparison with Linked Chains. It is quite reasonable to infer that the orientational couplings quoted above also play a role in the orientation process of cross-linked chains. A comparison of the order induced on cross-linked and uncross-linked chains would enable us to appreciate their relative contribution to the segmental orientation in the network chains. In order to establish a relevant comparison, we have used two identical PDMS networks, i.e., according to the work of Dubault and al.,[25] PDMS networks characterized by the same equilibrium swelling Φ_e (here $\Phi_e = 0.165$ as measured in cyclohexane). One network contains a known fraction (~20%) of perdeuteriated cross-linked chains while the other is unlabeled. These two samples were swollen with unlabeled and labeled free PDMS chains, respectively; the contour lengths of the two kinds of probe chains are identical ($M_n = 10\,500$) and the volume fractions Φ of the network chains are the same in both cases ($\Phi = 9\%$). Figure 7 shows the quadrupolar splittings of the cross-linked ($\Delta\nu_c$) and uncross-linked ($\Delta\nu_u$) chains, measured at maximum signal height, vs. $(\lambda^2 - \lambda^{-1})$. Both $\Delta\nu_c$ and $\Delta\nu_u$ are linear in this strain function; moreover, at the same λ, the observed ratio $\Delta\nu_c/\Delta\nu_u$ is close to one, as anticipated in ref 17. The fact

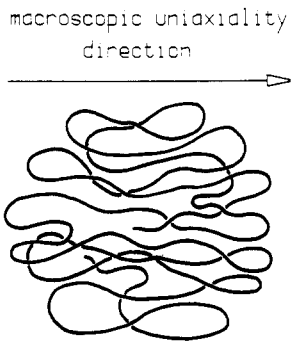

Figure 8. Scheme of a polymer chain exhibiting a nonzero degree of orientational order at the segment level together with a very low degree of spatial anisotropy at larger scale.

that both the host matrix and the guest probe exhibit the same strain dependence and reflect the same degrees of order is striking. This indicates that orientational couplings between the segments of both polymer chains, uncross-linked and cross-linked, contributes predominantly to their orientational behavior. In particular this means that most of the anisotropy of the cross-linked chains, as manifested by the splitting in the ^2H NMR line, is related to intersegmental effects rather than to the conventional end-to-end stretching of isolated chains. From that point of view, a given segment may ignore its exact relationship with the system, i.e., whether it belongs to a free chain or a linked one.

Despite the similarities quoted above, some differences between the two kinds of chains are noticeable. By contrasting the spectra of Figures 2 and 6, it is apparent that those corresponding to the network chains are broadened and exhibit spectral wings spreading out with increasing λ. These wings are mainly attributed to an anisotropy of local motions giving rise to residual interactions, even in the relaxed state.[26] Moreover these wings do not disappear totally at the magic angle $\Omega = 55°$ for $\lambda \neq 1$. This emphasizes the fact that they may be related to deuterons whose dynamical behavior is different from that of deuterons associated with the doublet structure (in particular a behavior nonuniaxial along the stress axis on the ^2H NMR time scale).

In addition, small-angle neutron scattering (SANS) experiments performed on the same PDMS samples reveal also a very different spatial behavior for the two kinds of chains. No definite evidence for an anisotropy of the radius of gyration of the free chains can be detected when the sample is elongated up to $\lambda = 1.4$, whereas an anisotropy is observable on linked chains.[14]

From these data it is clear that some aspects of the average conformation of a chain depend on its connection to the network structure. Indeed the extremities of a free chain are not submitted to the network deformation, so that no condition is imposed on the end-to-end vector. Then a uniform degree of segmental quadrupolar order, due only to local confinement, may coexist with a spatial isotropy of the overall coil dimension, as it is schematized in Figure 8. On the other hand, the constraints imposed on network chains by the cross-link junctions involve a dipolar effect which may contribute to the anisotropy detected in SANS experiments. Such a dipolar contribution is the one considered in the conventional end-to-end stretching process.[20,21] In other words, the orientational distribution function of the free chain segments (relative to the uniaxial constraint axis) would depend on terms of quadrupolar symmetry only ($\cos^2\theta \neq 0$; orientations θ and $\pi - \theta$ equivalent), whereas both quadrupolar *and* dipolar terms ($\cos\theta \neq 0$, orientations θ and $\pi - \theta$ unequivalent)

have to be considered when chains are also submitted to the topological constraints associated with cross-link junctions and trapped entanglements.

4.3. Free Energy. The experimental results of this paper support the crude phenomenological approach of Deloche and Samulski[1] for describing the solvent orientation in a lightly swollen rubber under elongation. We recall that to account for the segment–solvent couplings these authors included the effect of an orientational field coupled to the deformation tensor in the expression for the network free energy. This analysis is still relevant here and, in that respect, the observed orientation of the probe chain clearly illustrates the effect of the so-called nematic-like field generated in the deformed rubber. Under these conditions we propose to extend such an approach to the present case, i.e., to networks swollen with polymer chains.

According to eq 7 in ref 1 the free energy may be written as

$$\frac{1}{kT}F/\text{site} = \frac{1}{P}(1-\Phi)\log(1-\Phi) + \Phi\frac{AS^2}{2} + (1-\Phi)\frac{AS^2}{2} + \frac{1}{2}\frac{\Phi}{N}r^2\left[\lambda^2(1-ES+\ldots) + \frac{2}{\lambda}\left(1+\frac{ES}{2}+\ldots\right)\right] + \frac{3}{20}\frac{\Phi}{N^2}r^4\left(\lambda^4+\frac{2}{\lambda^2}\right) \quad (2)$$

where T is the temperature, Φ the volume fraction of network chain segments, and λ the elongation ratio. P and N are the number of segments of the free chains and the network chains respectively; $r^2 = R^2/R_0^2$ is the ratio of the mean-square end-to-end distance of a network chain to its mean-square value in the absence of constraints.

The first term in eq 2 is the translational entropy of the free chains obtained in the framework of a Flory lattice model. The following terms involve the effect of an orientational field experienced by the segments of the two kinds of chains. The magnitude of such a field is coupled to the applied (uniaxial) strain and is characterized by the mean degree of order $S = \langle P_2(\cos\theta)\rangle$, where θ is the angle between the constraint axis and the anisotropy axis of the segment; uniaxial symmetry is assumed for the latter. The two terms quadratic in S represent the self-energy of one segment of a network chain and a free chain, respectively, in the orientational field. In the analysis reported in ref 1 these terms were assumed to be the same (the same coupling coefficient A and the same degree of order S). Of course such approximations appear much more valid here since the swelling agent (probe chains) is now chemically identical with the cross-linked chains and the order S observed on the two kinds of chains is the same (see Figure 7). The next term in eq 2 is the standard form of the Gaussian entropy of an elongated elastic chain modified by the coupling between the order S and the end-to-end chain deformation. In this term we include only the first-order correction to the entropy: $-ES\lambda^2$ ($E > 0$) is the decrement caused by the enhanced chain segment propensity to align in the direction of the uniaxial field S; $ES/2\lambda$ is the corresponding effect in each of the two perpendicular directions. We have also included in eq 2 a non-Gaussian contribution to the chain entropy which may be of the same order of magnitude as the coupling term $ES\lambda^2$. More details on all these terms are given in the ref 1 and 27. Finally, for such a polymeric solvent of the same chemical nature as the network chains, the Flory interaction parameter χ_0 is zero. In brief, except that property ($\chi_0 = 0$) and the factor $1/P$ in the mixing entropy, the basic structure of this free energy is analogous to that written previously.[1] Such a similitude comes from the fact that we have neglected the connectivity between free chain segments, which are therefore treated as the molecules of an usual solvent. This is a consequence of the local character of the orientational interchain couplings under consideration.

The equilibrium value of the order parameter S which is experienced by the probe chains is obtained by minimizing the free energy at fixed λ and Φ, $\partial F/\partial S = 0$. This yields in the low deformation limit

$$S = \frac{\Phi E}{NA}(\lambda^2 - \lambda^{-1})r^2 \quad (3)$$

Then, for a given host matrix, characterized by N, the prediction of eq 3 concerning the λ-dependence and the independence of the probe chain size is in agreement with our observations (see Figures 7 and 5).

5. Concluding Remarks

These results show unequivocally that stress-induced orientation in a rubber is not a single-chain process but involves cooperative orientational couplings between chain segments. Under these conditions this work is in contrast to various theoretical descriptions wherein the physical effects of the chains are mainly restricted to their actions on the cross-link junctions, the chains being otherwise devoid of any material properties.

Orientational couplings may strongly affect macroscopic network properties and so must be taken into account in order to interpret these properties at the macroscopic level. For instance optoelastic properties are a case wherein short-range couplings of both the guest probe and the elastomeric host matrix must be considered.[1] In fact, recent interpretations of strain-birefringence data on swollen PDMS networks have suggested that such coupling effects may dominate the classical contribution,[28] namely, the segmental orientation due to chain elongation. Let us note also that the segment polarizability (relative to the network chains or to the diluent chains), as currently derived from the stress–optical coefficient,[29] may not be representative of the intrinsic properties of isolated chains.

An extrapolation of our results to the case of dangling chains leads us to consider that they may exhibit the same orientational behavior as the free chains when the network is elongated. This property of dangling chains has already been suggested in the framework of NMR studies of polybutadiene networks[9] and also has been deduced from fluorescence polarization investigations in polyisoprene networks.[30]

Finally the present work emphasizes the reliability of the probe method for testing orientational phenomena in rubbers; in particular the labeled polymer chains used herein appear to be ideal nonpertubative NMR probes to investigate local properties in strained elastomers.

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Local Molecular Motion of Polystyrene Model Compounds Measured by Using Picosecond Pulse Radiolysis. 1. Diastereoisomeric Styrene Dimers: Multicomponent Fluorescence Decay Curves, Concentration Dependence, and Alkyl End-Group Effect on Excimer Formation

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ABSTRACT: The dynamic process of intramolecular excimer formation in meso and racemic 4,6-diphenylnonanes (PS2(propyl)), diastereoisomeric dimer models of polystyrene, was investigated by using a picosecond pulse radiolysis technique. In dilute cyclohexane solution, the monomeric fluorescence of racemic PS2(propyl) decays single exponentially with a time constant of 11 ns, while that of meso PS2(propyl) was found to decay dual exponentially with time constants of 6 and 0.5 ns. These multicomponent fluorescence decays were found to be explicable by the local motion of conformational change. In conclusion, each time required for the conformational change (g^+t/tg^-) → tt, (g^+t/tg^-) → g^+g^-, and g^+g^- → (g^+t/tg^-) in meso PS2(propyl) is estimated to be 0.7, 2.5 and 6 ns, respectively, at room temperature. The proposition that fluorescence decay of diastereoisomeric dimers is influenced by molecular motion (conformational change) is also valid for explaining the profile of the transient fluorescence spectra of racemic PS2(propyl). The present result is an indication that multicomponent fluorescence decay observed in some polymer systems may be mainly due to the conformational change motion in meso dyads. The concentration dependence of the time constants of meso and racemic PS2(propyl) was also measured. In addition, an alkyl end-group effect on intramolecular excimer formation in styrene dimers is found to exist by comparing time constants of styrene dimers with methyl ends, propyl ends, and pentyl ends.

Introduction

Recently many investigators have published papers concerning intramolecular excimer formation in aromatic dimers compounds.[1-15] There are three main reasons for studying dimeric compounds: (1) to understand the photophysical interaction between chromophores in excited states since the encounter probability of rings increases greatly in dimeric compound such as diarylpropanes,[1-3] (2) to clarify complex photophysical processes in polymer systems because the structure of these dimeric compounds are identical with those of polymer dyands,[4-11] and (3) to investigate the end-to-end cyclization rate of polymer molecules in terms of the theory of polymer so-

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