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Effects of Trapped Entanglements on the Chain Ordering in Strained Rubbers: A Deuterium Magnetic Resonance Investigation

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ABSTRACT: The orientational order generated in uniaxially strained rubbers is investigated as a function of the polymer concentration at which the network was formed. This study was carried out on end-linked siloxane networks synthetized from a solution of identical precursor chains at various concentrations. The average degree of order was measured by means of the deuterium NMR technique, either by using deuteriochloroform as a NMR probe or by directly observing the labeled networks. The data clearly show evidence of a strong dependence of the induced order upon the cross-linking conditions. The observed effect is discussed in terms of trapped entanglements and is analyzed as a function of the equilibrium degree of swelling, which characterizes the real network structure better than the length of the precursor chains. The results are compared with those obtained on similar samples by other local techniques (proton magnetic resonance and neutron scattering).

Introduction

Ideally, rubber elasticity is governed by the cross-linking density, i.e., the chemical mesh size of the networks. However, as soon as network imperfections (dangling chains, entanglements, ...) are present in the real structure of rubbers, the chemical mesh size is no longer a well-adapted parameter to characterize the real network topology and thus it is not sufficient to confidently account for the corresponding elastic behavior of the material. For instance, end-linked networks synthesized with identical telechelic precursor chains exhibit different elastic properties according to whether the end-linking reaction was carried out in solution or in the pure melt: the higher the polymer concentration at network formation, the higher the Young's moduli[1-3] and the equilibrium degree of swelling.[1,3] In addition, light-scattering experiments[4] provide evidence for an increase of the cooperative diffusion with concentration during the network synthesis. All of these observations are attributed to chain entanglements which are trapped inside the gel during the cross-linking reaction. Thus the chain behavior may be dependent on these additional constraints but the real effects of the latter are not yet well understood. Useful information on the local effects of trapped entanglements can be obtained from the various microscopic techniques recently developed in this field.[5]

Nuclear magnetic resonance (NMR) has emerged as a powerful technique to investigate local ordering in isotropic swollen[6] or uniaxially strained[7] rubbers. In particular, using deuterium NMR (^{2}H NMR) on elastomers under stress, we have already pointed out[8] that the orientational segment ordering is sensitive to the polymer concentration during the network synthesis. The focus of the present work is to support this initial (but restricted) observation by systematic studies of the effect quoted above.[8] More specifically, by using the ^{2}H NMR, we monitor the chain ordering in elongated end-linked poly(dimethylsiloxane) networks as a function only of the polymer concentration during the cross-linking process. The observed anisotropy of the network chains will then be related phenomenologically to the elastic properties of the samples. Finally, the results will be compared to those obtained from proton NMR[9] and neutron scattering (SANS)[2] experiments performed on the same type of materials.

Table I
Main Characteristics of the PDMS Networks[a]

	unlabeled networks PDMS[H]					labeled networks PDMS[D]			
	1	2	3	4	5	B′	B	A′	A
M_n	9300	9300	9300	9300	9300	10500	10500	25000	25000
C_c	0.9	0.8	0.7	0.6	0.5	1	0.7	1	0.7
w_d	0.10	0.11	0.18	0.17	0.20	0.10	0.12	0.15	0.23
Φ_e	0.168	0.151	0.133	0.125	0.11	0.167	0.135	0.1	0.067
p	201	163	158	128	115	42	37	28	17

[a] M_n = molecular weight of precursor PDMS chains (g/mol); V_c = volume fraction of polymer at which network was formed in toluene; w_d = weight fraction in dangling chains calculated from extractible fraction; Φ_e = volume fraction of polymer at swelling equilibrium in cyclohexane; p designates the slope of the different straight lines in Figures 2 and 3.

Experimental Results

Materials. Any study of the effect of polymer concentration during the network synthesis necessarily has to be performed on end-linked networks for which the chemical mesh size (the length of chains connecting nearest-neighbor knots) is defined by the length of the telechelic precursor chains. Therefore, our investigations employed end-linked poly(dimethylsiloxane) networks synthetized at various precursor–polymer concentrations V_c: chains, of α,ω-dihydrogenopoly(dimethylsiloxane) were reacting in toluene with tetrakis(allyloxy)ethane, as a tetrafunctional cross-link.[10,11] Some of these networks (referred to as PDMS[D]) contain a known fraction (about 10%) of perdeuteriated chains. In table I we report only the characteristics useful for the present discussion. In particular, it appears that, for a *given chemical mesh size*, the polymer fraction Φ_e at the swelling equilibrium depends on the concentration V_c. This variation in Φ_e is precisely related to the subject of our study, i.e., the influence of concentration V_c (the degree of the chains' interpenetration before the reticulation) on the network structure. Finally let us point out that the concentration V_c also affects to some extent the fraction w_d of dangling chains in the network. However, there is no simple relationship between the increase of w_d (estimated in ref 10) and the decrease of V_c.

^{2}H NMR Method. The general features of ^{2}H NMR in anisotropic fluids have been largely reviewed in ref. 12, 13. The sensitivity of this technique in studying a deformed rubbery medium has been demonstrated by studies performed either on

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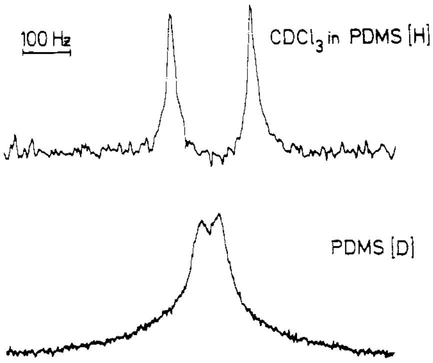

Figure 1. Comparison between the 13-MHz spectra obtained, at elongation $\lambda = 1.37$, either on a unlabeled PDMS network (sample 3) with a $CDCl_3$ probe or a labeled one (sample B) synthetized with a similar precursor ($M_n = 10\,000$) at the same polymer concentration ($V_c = 0.7$) in toluene.

labeled networks[8,14,15] or on deuteriated swelling agents used as NMR probes of unlabeled networks.[7,8,16] Deuteriochloroform has been used to probe the unlabeled networks (referred to as PDMS[H]).

We recall that in the case of rapid uniaxial molecular reorientations, the liquidlike NMR line is split into a doublet. The observed splitting $\Delta\nu$ corresponds to a residual quadrupolar interaction which may be expressed in frequency units as

$$\Delta\nu = (3/2)\nu_q P_2[\cos\Omega]\langle P_2[\cos\theta(t)]\rangle$$

where ν_q is the static quadrupolar constant (ν_q = 168 kHz for $CDCl_3$);[17] Ω designates the angle between the symmetry axis (stress axis) and the static magnetic field. Then the doublet spacing $\Delta\nu$ gives access to the order parameter $\langle P_2[\cos\theta(t)]\rangle$ of the C–D bond relative to the direction of the uniaxial constraint.

^{2}H NMR Conditions. Samples are strips approximately 1 mm thick, 6 mm wide, and 40 mm long. Both ends of the strips are gripped by means of jaws; one of these jaws is fixed while the other one can be moved along the NMR tube. A calibrated screw allows the adjustment of the sample elongation, which is controlled with a micrometer fitted on the stage of a binocular microscope. In this way, lengths are measured to within an accuracy of 0.02 mm while sliding of the sample in the jaws can be detected by measuring the spaces between the jaws and two marks on the sample.

Before any NMR experiment on PDMS[H], the weighted sample is exposed to deuteriochloroform ($CDCl_3$) vapors for about 10 min; this yields a rubber containing 15% by weight of solvent. The evaporation of the chloroform may be ignored because it is always less than 5% over the time required for one NMR experiment (about 6 h).

All ^{2}H NMR spectra were obtained by using FT NMR equipment, a CXP 90 Brucker operating at 2 T with a standard electromagnet; the static magnetic field was perpendicular to the direction of stretching.

Experimental Results

In Figure 1, we report the characteristic ^{2}H NMR spectra related to PDMS[D] and PDMS[H] + $CDCl_3$ samples strained at the same elongation ratio λ. These spectra illustrate the sensitivity of both the approaches that we used in this work. Figure 2 and 3 show the evolution of the quadrupolar splitting $\Delta\nu$ vs. ($\lambda^2 - \lambda^{-1}$) in the small deformations range. As shown earlier,[8] the data fit this strain function;[18] but the new fact here is the pronounced effect of V_c in both cases. This phenomenon is quantified in Table I, where the measured slopes $p = \Delta\nu/(\lambda^2 - \lambda^{-1})$ of the observed straight lines are given (p measures the efficiency of the constraint to induce an orientational order). For instance, in the case of PDMS[H] samples probed by $CDCl_3$, p increases by a factor 2 when V_c varies from 0.5 to 0.9.

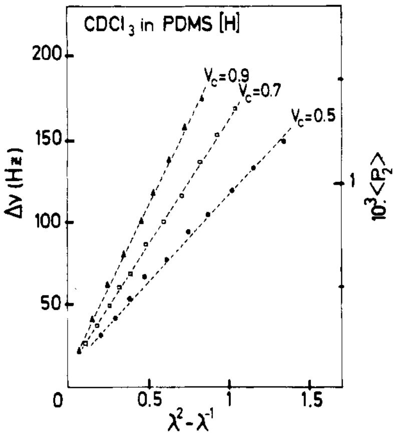

Figure 2. Quadrupolar splitting $\Delta\nu$ (left ordinate) and calculated order parameter S (right ordinate) of $CDCl_3$ (about 10%) in *unlabeled* PDMS networks vs. [$\lambda^2 - \lambda^{-1}$]. The different series of data concern networks synthetized in toluene from same precursor chains (M_n = 9300) at various polymer concentrations V_c. For reasons of clarity, all studied samples (see Table I) have not been reported in this figure.

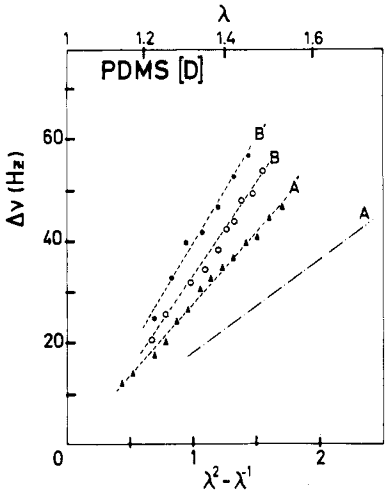

Figure 3. Quadrupolar splitting $\Delta\nu$ of the *labeled* PDMS networks (references are given in Table I) vs. [$\lambda^2 - \lambda^{-1}$]. The numerous data for sample A have already been reported in ref 14; they fall along the full line indicated.

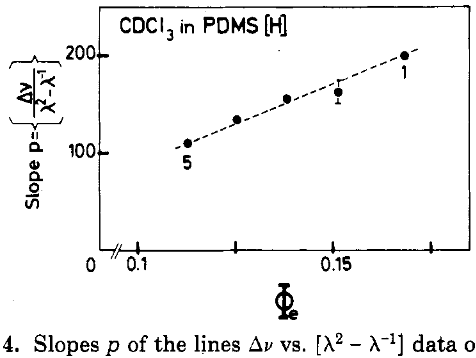

Figure 4. Slopes p of the lines $\Delta\nu$ vs. [$\lambda^2 - \lambda^{-1}$] data of Figure 2 plotted vs. the polymer fraction Φ_e at swelling equilibrium in cyclohexane for unlabeled networks (uncertainties have been estimated from several experiments).

The analysis of these data requires a relation of the slopes p to a variable sensitive to the real topological structure of the networks. We have chosen to plot these slopes vs. the polymer fraction at swelling equilibrium Φ_e just as has been done in our previous study on the effect of cross-linking density.[8] As shown in Figures 4 and 5, we obtain a linear dependence of local ordering p with Φ_e as the concentration V_c is varied. This implies that an empirical relation exists between the microscopic property $\langle P_2\rangle$ (the order parameter) and the macroscopic one Φ_e

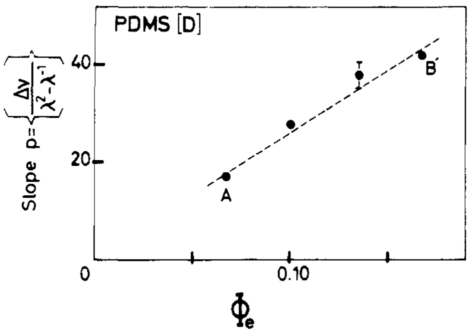

Figure 5. Slopes p of the lines $\Delta\nu$ vs. $[\lambda^2 - \lambda^{-1}]$ data of Figure 3 plotted vs. the polymer fraction Φ_e at swelling equilibrium in cyclohexane for labeled networks (uncertainties have been estimated from several experiments).

(the equilibrium swelling). Such a relation is observed for various molecular weights of the precursor chain whatever V_c may be; the double linear dependence is clearly illustrated when we compare the samples B and A′ (or B′ and A) for which *both* M_n and V_c are different. Finally, let us note that this phenomenological relation ($\langle P_2 \rangle \sim \Phi_e$) is obtained from independent measurements performed on different states of the rubber (dry and swollen). This is rather surprising because excluded volume interactions are not the same in both states.

Discussion

The first point which has to be elucidated is the reason why, for a given elongation, the segmental order $\langle P_2 \rangle$ diminishes with decreasing values of the concentration V_c as shown in Figures 2 and 3. It may be tempting to relate this effect to an increase of the fraction w_d of dangling chains since, according to Table I, the latter increases by a factor 2 when V_c decreases from 0.9 to 0.5. However, two arguments are opposed to this viewpoint. First, it seems improbable that such a variation of the proportion of dangling chains can lead to such a large effect on the local ordering whereas no significant variation of the Young's modulus[19] is detected (the property directly related to the density of the elastic chains). Second, it has been experimentally proved that free polymer chains dissolved in a strained network are as well oriented as the elastic chains;[20] then it is obvious to infer that the dangling chains are also well oriented and that they contribute to the orientational correlations between constrained chains. Consequently, the presence of pendant chains is not expected to significantly affect the orientational anisotropy of the polymeric medium. Under these conditions, it is more realistic to attribute the observed variation in $\langle P_2 \rangle$ to trapped entanglements, which decrease in number when the cross-linking reaction is carried out in a more and more dilute solution. Thus, the polymer concentration Φ_e in the equilibrium swollen system appears now as a variable well suited for an analysis of our data since we know from the investigation mentioned in ref 19 that Φ_e is almost independent of the presence of dangling chains. In other words, the plots reported in Figures 4 and 5 strongly support the fact emphasized in our previous work[8] according to which the induced order $\langle P_2 \rangle$ is related to the network structure in the same way as Φ_e.

Quantitatively, it is striking that the increase of the slope p observed for the samples A′ and B′ (V_c unchanged) is about the same as that for the samples A and A′ (M_n unchanged). This means that the effect of the physical constraints on the segmental ordering might be as efficient as the chemical junctions. Moreover, the comparison of the slopes corresponding to the samples (A,A′) and B,B′) shows that the influence of V_c is more pronounced for a large chemical mesh size. This is consistent with the fact that the larger the size of the precursor chains (the lower the cross-linking density) the larger the probability to trap entanglements. Thus, the ratio of the density of physical constraints to cross-linking density is more important for rubbers A and A′, which have the larger chemical mesh.

Now, to go further into the understanding of the role of trapped entanglements, it may be instructive to compare the present results to those obtained on the same type of PDMS samples by other techniques sensitive to the local behavior of chains, i.e., proton magnetic resonance (^{1}H NMR) and neutron scattering (SANS). Concerning the ^{1}H NMR, let us first recall that, in the case of swollen networks, Cohen-Addad et al.[6] succeeded in relating the residual dipolar energy (a quantity similar to the residual quadrupolar energy of deuterons reported here) to the order of the monomeric units of one elementary chain. For a given swelling ratio the authors[9] that the local order scales as $V_c^{-5/3}$ whereas, as for the plot p vs. Φ_e (cf. Figure 4), a linear dependence is also obtained in plotting our slopes p vs. V_c.[21] Obviously, it is not surprising that the scaling laws in V_c are not identical in both cases since the segmental ordering induced by isotropic dilation and by uniaxial elongation is not necessary equivalent. Nevertheless, from Cohen-Addad's analysis it is clear that the ^{1}H NMR results are also consistent with the picture of trapped entanglements acting somewhat as supplementary chemical junctions. Finally, from these NMR studies, the role of trapped entanglements is mainly to reduce the chemical mesh size.

Such a similarity between the physical and chemical constraints does not hold with respect to the mechanical experiments. For instance, in order to explain the Mooney–Rivlin plots, it has been proposed that trapped entanglements behave as "rings" able to slip along the chains[22-24] and thus appear as nonlocalized constraints. This distinction between physical and chemical constraints is also apparent in measurements of spatial anisotropy performed by SANS on PDMS networks identical with those studied here,[2] i.e., obtained from the same synthesis. The component $R_{\parallel}$ of the radius of gyration along the stress axis depends on the chemical mesh size M_n but remains constant with the concentration V_c. In fact, the concept of sliplinks quoted above may be relevant to understanding why SANS does not exhibit the same sensitivity to the two kinds of constraints, in contrast to NMR. Indeed, according to the crude analysis developed in ref 25, the component $R_{\parallel}$ of one chain of N statistical segments may be simply expressed as a function of both $\langle \cos\theta \rangle^2$ and $\langle \cos^2\theta \rangle$

$$R_{\parallel}^2 \sim [\langle \cos^2\theta \rangle + (N/2)\langle \cos\theta \rangle^2]$$

where θ is the angle between the statistical segment and the fixed end-to-end vector. From this expression, $R_{\parallel}$ depends mainly of the dipolar contribution due to the front factor ($N/2$). Then, a possible interpretation of the reported observations would be that, due to their ability to slip along the chain under stress, entanglements do not contribute to the dipolar term related to the chain end-to-end stretching, on the contrary, they would affect the local orientational correlations between chains which are measured through the $\langle \cos^2\theta \rangle$ term. However, this distinction between physical and chemical constraints as perceived by the SANS technique at the scale of the chain dimension R may be no more valid at shorter scales; so a complete determination of the form factor at various concentration V_c would be very interesting to better compare how the two kinds of constraints are probed through NMR and SANS.

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Conclusion

This work demonstrates that the segmental ordering induced in strained networks depends largely on the conditions of the network synthesis. For instance, a variation of only 10% in the polymer fraction during the cross-linking process has a noticeable effect on the induced orientational anisotropy. Quantitatively, we find that the degree of order $\langle P_2 \rangle$ goes like the degree of equilibrium swelling Φ_e. Since this phenomenological scaling law is the same as that obtained by varying the cross-linking density, the present study strongly supports our previous conclusion:[8] Φ_e is the thermodynamical variable well adapted to precisely define the real topological structure of the network, with respect to the orientational chain ordering.

In contrast, neutron scattering measurements show that the physical constraints have no noticeable effect on the mesh size. Therefore, a better understanding of the difference between the response obtained from the NMR and the SANS experiments could provide useful information. Particularly, it is important to determine whether the concept of sliplinks is compatible with trapped entanglements acting on the molecular ordering only but without changing the overall dimensions of the distorted chains.

Finally, concerning the experimental approach, let us notice that the present work emphasizes the reliability and the sensitivity of the solvent-probe method for testing orientational order in rubbers; indeed it leads to the same result as those obtained from direct investigation of the polymer chain. Thus, this probe method appears to be a very attractive tool since it allows us to obviate the perturbations of conventional probe techniques (electron spin resonance, fluorescence) while providing reliable information on local chain behavior.

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(18) This representation $\Delta\nu$ vs. $(\lambda^2 - \lambda^{-1})$ is well adapted here for two reasons: (i) the investigation is limited to the low-deformation regime; (ii) in the case of PDMS, a Mooney–Rivlin-like plot for the local ordering $(\Delta\nu/(\lambda^2 - \lambda^{-1}) = D_1 + D_2/\lambda)$ is not useful since we always obtained $D_2 = 0$; this is consistent with the fact that the constant C_2 for the Young's modulus is known to be small for these materials (see, for instance: Valles, E.M.; Macosko, C. W. *Macromolecules* **1979**, *12*, 673).
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Molecular Orientation and Structure in Solid Polymers with ^{13}C NMR: A Study of Biaxial Films of Poly(ethylene terephthalate)

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ABSTRACT: Two- and three-dimensional experiments greatly expand the applicability of ^{13}C NMR to measurement of molecular orientation in samples of synthetic polymers. For biaxially oriented films of poly(ethylene terephthalate) (PET) it has been possible to measure all orientation moments for which $l = 2$. There is a highly oriented component of the film for which the planes of the aromatic rings lie close to, but not in the plane of, the film. The protons in this component relax slowly in the rotating frame, suggesting that it largely comprises the crystalline portion of the film. The observed chemical shifts of the carbons in the film are adequately explained in terms of the known crystal structure of PET. A component of the sample whose protons relax rapidly in the rotating frame is much less oriented relative to the plane of the ring than is the crystalline portion. This component may be considered amorphous because the short proton relaxation time indicates that the polymer chains are relatively mobile.

I. Introduction

Industrial processing of polymeric materials often induces a high degree of molecular orientation in the individual polymer chains.[1] This orientation can have both positive and negative effects on the quality of the product.

For example, extrusion to produce fibers tends to orient the polymer chains along the extrusion direction. Much of the strength of extruded fibers is derived from the

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