

^2H n.m.r. study of a deformed poly(dimethylsiloxane) rubber network below and above the crystallization temperature

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Abstract

Deuterium n.m.r. is used to observe the change in segmental dynamics and orientation at the crystallization temperature T_c in a uniaxially stretched poly(dimethylsiloxane) (PDMS) network. Experiments are performed over a wide temperature range (235–294 K). The amorphous parts of the chains are probed via perdeuterated *n*-octane probe molecules dissolved in the network. ^2H n.m.r. spectra change drastically within a small temperature interval of 4 K in the vicinity of T_c . Above T_c , the spectra reflect the uniaxial dynamics of the octane probes. In the vicinity of T_c , the spectra are sensitive to the internal dynamics of the octane probe and indicate a heterogeneity in the mobility of the network chains. The isotropic lines obtained for $T \leq T_c$ confirm that the local constraints introduced by the external deformation disappear in the amorphous part of the sample in the presence of the crystalline phase. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: ^2H n.m.r.; Crystallization; PDMS

1. Introduction

Deuterium nuclear magnetic resonance (^2H n.m.r.) has been extensively used to study the molecular dynamics in anisotropic fluid media such as strained polymer networks [1], liquid crystals [2] and polymer liquid crystals [3–5]. A very simple and relevant approach consists of using molecules of deuterated diluents as ^2H n.m.r. probes. For instance, various ^2H n.m.r. investigations have shown that some swelling agents are suitable probes for studying orientational molecular order of the anisotropic matrix itself [6–10]. In the case of rubber networks the molecular order is induced by the applied stress only. Then by varying the temperature while keeping the macroscopic deformation constant, it is possible (contrary to liquid crystals) to change the molecular mobility and to maintain the source of the anisotropy. In this work we propose to use this probe method to observe how the temperature affects the chain dynamics of a polymer network under constraint.

In particular, it is known that crystallization of a pre-stretched polymer allows constraints in the chains to relax to a great extent, in the molten, amorphous parts of the sample. To investigate this problem, we have studied ^2H n.m.r. spectra of a uniaxially stretched poly(dimethylsiloxane)

(PDMS) network in a wide temperature range. However, the large broadening of the spectra which occurs during crystallization precludes a detailed analysis of the molten, amorphous parts of the chains. Free chains introduced as probes in the network show essentially the same broadening, which means that they participate as well in the crystallization process. Thus, we have introduced perdeuterated octane molecules in the uniaxially stretched PDMS network, to be used as selective probes of the amorphous (molten) part of the chains in the semicrystalline sample. We report herein some characteristic spectra of perdeuterated octane, observed between 235 and 294 K. Clearly, the dynamics is greatly affected in a small temperature range, ($\Delta T \approx 4$ K), around the crystallization temperature T_c of the system. This effect, related to changes in molecular mobility and structure of the polymer matrix, is due to the modification of local constraints as the crystalline phase disappears, in the vicinity of T_c . The spectra are also affected by differences in the internal dynamics of the octane probe molecules.

2. ^2H n.m.r. background

The analysis of ^2H n.m.r. spectra depends on how the quadrupolar hamiltonian is averaged by molecular motions [11]. In the presence of fast, anisotropic molecular motions,

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the quadrupolar interaction is averaged to a non-zero value, which results in a doublet of Lorentzian lines characterized by a splitting $\bar{\Delta}$. In the very general case of fast uniaxial motions around a local symmetry axis denoted by \vec{n} the splitting is given by:

$$\bar{\Delta} = 2\nu_Q \overline{P_2(\theta)} P_2(\Omega) \quad (1)$$

in which $P_2(\theta)$ is the second-order Legendre polynomial:

$$P_2(\theta) = \frac{3 \cos^2 \theta - 1}{2} \quad (2)$$

$\theta(t)$ is the instantaneous angle between the C–D bond and the local axis \vec{n} , Ω is the angle between \vec{n} and the steady magnetic field \vec{B}_0 [12]. The overbar denotes a time average over motions faster than the characteristic time ν_Q^{-1} . The factor $\overline{P_2(\theta)}$ is the local order parameter which describes the degree of orientational order (that is, the degree of motional anisotropy) of the C–D bond with respect to the symmetry axis. For C–D bonds in $-\text{CD}_2-$ or $-\text{CD}_3$ groups, $\nu_Q \approx 125$ kHz. In the fast motion limit the linewidth of each component of the doublet depends on the relaxation time T_2 and is generally small with respect to the value of the splitting, which leads to resolved spectra. In a disordered system, the resulting spectrum is the superposition of such doublets, and the resulting lineshape is thus directly related to the distribution of residual interactions in the system[13]. In a macroscopically oriented system, the spectrum is a doublet, which gives a direct measurement of the macroscopic order parameter.

However, on approaching the glass transition temperature or in semicrystalline polymers, the system is no longer in the fast motion limit and the lineshape depends both on the geometry and on the correlation times of (slow) motions. Spectra become much broader and are not resolved in disordered systems. The detailed analysis of ^2H n.m.r. spectra in this regime essentially requires multidimensional n.m.r. techniques [14].

3. Experimental

This study makes use of end-linked tetrafunctional poly(dimethylsiloxane) (PDMS) networks whose synthesis was outlined in references [15] and [16]. The number-average molecular weight of the precursor chains is $M_n \approx 9700$; the polydispersity is about 1.5. The fraction of dangling chains is estimated to be of the order 15% to 18%. The crystallization temperature of this material, $T_c = 242$ K, was obtained by d.s.c. measurements.

Two networks with similar characteristics were used: one has a fraction of its chains perdeuterated, which allows observation of network chains themselves, the other one has no deuterium labelling and was studied in conjunction with deuterated probe molecules. The non-deuterated network was slightly swollen with perdeuterated octane (*n*-octane- d_{18}). A preweighed sample of dry PDMS ($25 \times 4 \times 1$ mm) was exposed to the solvent vapour; the solvent

weight fraction was about 7%. It should be noted here that unlabelled *n*-octane is liquid for $T > T_m = 216$ K. A sample was also swollen with linear, perdeuterated PDMS chains of number-average molecular weight $M_n \approx 3000$. The weight fraction of free chains was 10%.

Sample elongation was performed as described earlier [1]. The elongation ratio $\lambda = L/L_0$ (L and L_0 being the lengths of the swollen network respectively elongated and relaxed, measured at room temperature) was maintained constant, equal to 1.350 ± 0.003 during the experiments. All n.m.r. measurements were done at $\Omega = 90^\circ$ (see Eq. (1)).

A Bruker CXP 90 spectrometer operating at 13 MHz with a 2 T electromagnet was used. The radiofrequency coil was situated around the middle of the sample, which corresponds to its uniformly stretched part. Temperature was controlled by a Bruker VT1000 variable temperature unit with a uncertainty $\Delta T = \pm 0.5$ K. The spectra were recorded by slowly increasing the temperature (1 K every 20 min), starting from 235 K.

4. Results and discussion

4.1. Network chains

Fig. 1 shows the evolution of the spectra obtained in the deuterated PDMS network, as the temperature increases from 240 to 294 K. First, for spectra $T \geq 245$ K, the spectra exhibit the characteristic features which are obtained in such a system at room temperature. The resolved doublet is related to the fast, uniaxial dynamics of chain segments.

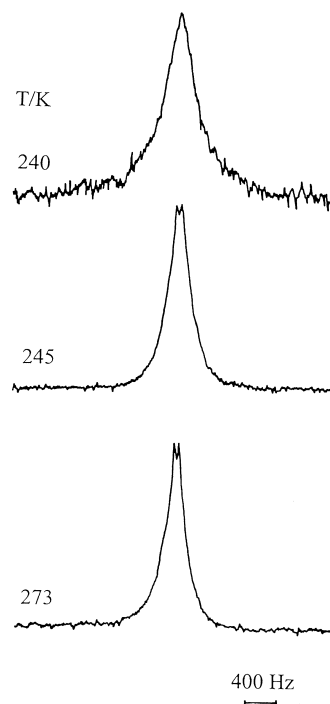


Fig. 1. ^2H n.m.r. spectra of deuterated PDMS network versus temperature. The extension ratio λ (relative to the unstrained state) is 1.35.

This has already been studied extensively and related to the effect of an orientational field, originating from short-range interactions between chain segments. In this temperature range (245 to 293 K), the value of the splitting seems to be only slightly affected by temperature. This indicates clearly that the doublet is of a statistical (entropic) origin, as interpreted previously [17].

Melting of the crystallites occurs between 240 and 245 K and is manifested through a rapid and large narrowing of the spectrum on raising the temperature. It is not the purpose of this work to study this process in details, which has already been done extensively [18–21]. The narrowing is due to the disappearance of the strong topological constraints introduced by the presence of crystallites, as the temperature is raised. Large-scale, fast motions appear as the crystallites melt.

4.2. Free PDMS chains

We have also introduced short deuterated free PDMS chains ($M_n = 3000$) in the network. Fig. 2 shows the spectra obtained on free chains as a function of temperature, from 241 to 294 K. For $T \geq 245$ K, the spectra consist of well-resolved doublets. The splitting is roughly independent of temperature and has the same value as that obtained on the deuterated network (referred to the same elongation ratio), as already observed [22]. On raising the temperature, the resolved doublet appears suddenly between 244 K and 245 K. For $T \leq 245$ K, the line is much broader and is not

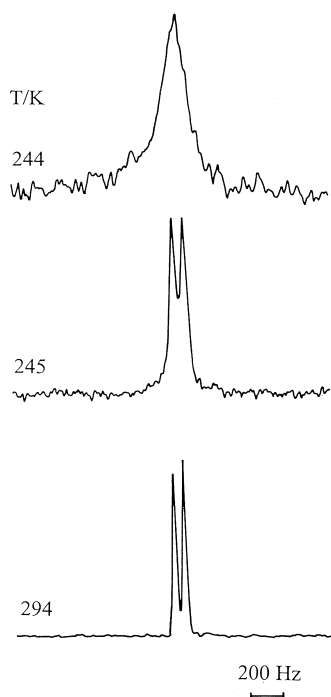


Fig. 2. ^2H n.m.r. spectra of perdeuterated PDMS free chains ($M_n = 3000$) dissolved in a PDMS network *versus* temperature. The extension ratio λ (relative to the unstrained state) is 1.35. The volume fraction of free chains is 10%.

resolved. This indicates that the dynamics of the free chains is sensitive to the presence of crystallites. Indeed, it is likely that parts of the free chains crystallize, that is, are embedded in the crystalline phase. Even though the linewidth is much larger in this case, the lineshape suggests that no uniaxial order is present in the amorphous phase, since no doublet appears.

The line broadening observed on labelled polymer chains is difficult to analyse. Indeed, the appearance of crystallites has two effects on the chain dynamics, as perceived from ^2H n.m.r. First, statistical properties of chains are modified: since crystallites introduce strong topological constraints, the broadening may result from a distribution of local anisotropy directions for the motions, in contrast to the uniaxial case which is observed at high temperature. On the other hand, the dynamics may also become slower (and probably heterogeneous), which would result in much broader lines as well. In other words, it is impossible to determine at this point whether the doublet related to the uniaxial dynamics in the molten, amorphous parts of the sample is still present. Thus, introducing solvent molecules may provide a way to clarify this problem.

4.3. Spectra of *n*-octane- d_{18}

Fig. 3 shows the evolution of the ^2H n.m.r. spectra of

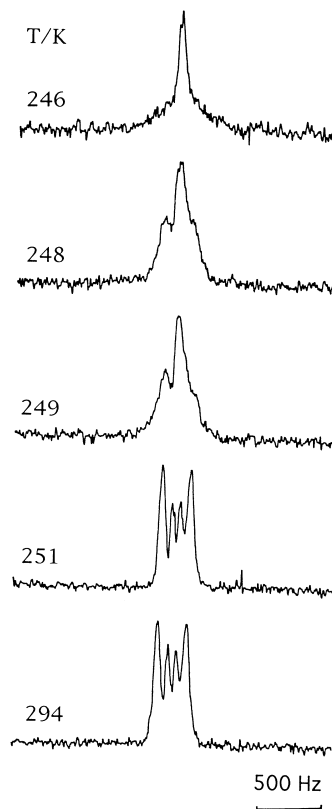


Fig. 3. ^2H n.m.r. spectra of *n*-octane- d_{18} dissolved in a uniaxially strained PDMS network *versus* temperature. The solvent volume fraction is about 7%; the extension ratio λ (relative to the swollen, unstrained state) is 1.35.

n-octane-*d*₁₈ dissolved in a uniaxially stretched PDMS network as the temperature is raised. Let us first comment on the spectrum obtained at room temperature ($T = 294$ K). It consists of two resolved quadrupolar doublets ($\bar{\Delta} \neq 0$): the central doublet ($\bar{\Delta} = 60$ Hz) corresponds to the n.m.r. signal of methyl ($-\text{CD}_3$) groups, whereas the signals associated with the various methylene ($-\text{CD}_2-$) groups are superposed within the larger outer doublet ($\bar{\Delta} = 222$ Hz). The slight asymmetry of the spectrum is related to the small difference in chemical shifts between methyl and methylene deuterons. The spectrum shows that octane molecules exhibit anisotropic reorientational motions around the applied tension direction as they diffuse through the deformed rubber matrix. The dynamics is characterized by a well-defined uniaxial orientational order, the doublet spacing $\bar{\Delta}$ being larger than the linewidths of the doublet components.

This phenomenon of solvent orientation has already been observed for various solvents and is related to orientational couplings between solvent molecules and chain segments of the polymer network [8,10]. The observed splitting reflects the segmental order of the polymer matrix [23,24]. It is interesting to compare the magnitude of the splittings for the different groups in the system. Fast rotation of terminal $-\text{CD}_3$ groups in the octane molecules averages the quadrupolar tensor along the $-\text{CD}_3$ group axis and divides it by a factor 3. The factor observed experimentally is of the order 3.7, which indicates that the $-\text{CD}_3$ group axis has essentially the same conformational (dynamic) behaviour as C–D bonds in $-\text{CD}_2-$ groups, but with a slightly smaller order parameter. Then, for the same elongation ratio ($\lambda = 1.350$), the splitting of $-\text{CD}_3$ groups in octane molecules ($\bar{\Delta} = 60$ Hz) is almost the same as that of $-\text{CD}_3$ groups in the PDMS chains, measured in the deuterated network ($\bar{\Delta} = 68$ Hz). This suggests that octane molecules, and specifically $-\text{CD}_3$ groups, are quite strongly coupled to PDMS chains in the molten, amorphous phase. This is certainly related to the fact that octane is a good solvent for PDMS.

Fig. 3 shows that the spectra remain essentially unchanged above 251 K. In this regime, the degree of order is independent of temperature, in the measuring range ($\Delta T = 40$ K).

The modifications in the spectra observed at lower temperature indicate that the swollen, stretched PDMS network crystallizes at $T = T_c = 247$ K. The small difference between the crystallization temperatures measured by n.m.r. and by d.s.c. might be due both to the external force and to the presence of solvent; this point would need more specific investigation and is left aside here.

In a small temperature range immediately above T_c (247 K $< T < 250$ K), the spectra indicate that the dynamics of the octane probe molecules is affected quite abruptly. This is manifested in broader, less structured n.m.r. lines. The value of the quadrupolar splitting in the outer doublet is the same as at room temperature ($\bar{\Delta} = 222$ Hz), though its resolution is much lower. However, the central doublet disappears and the observed spectra therefore consists of a

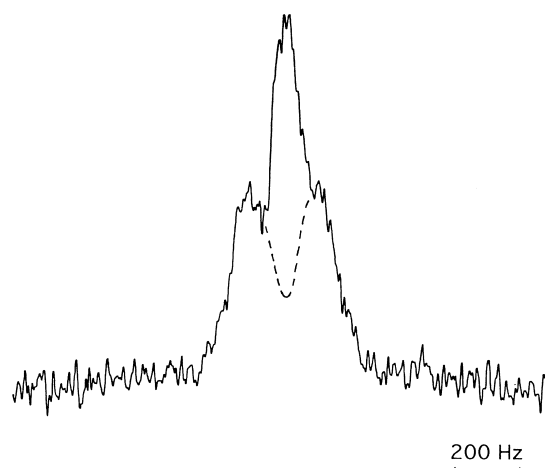


Fig. 4. Rough analysis of the lineshape observed at $T = 248$ K, indicating the presence of an outer doublet structure.

superposition of the outer doublet with an intense central line, as suggested in the rough analysis given in Fig. 4. The probe dynamics (which reflects the dynamics of network chain segments) is restricted by the local constraints due to the presence of crystallites. These local constraints, without a preferential direction, are still weaker than (or comparable to) the constraints introduced by the macroscopic deformation, since the overall linewidth does not increase significantly. The line broadening may also be associated with a slowing down of the probe dynamics in this small temperature range. Note that the polymer matrix still exhibits an orientational anisotropy in this regime (see Fig. 1): amorphous polymer chains are already sensitive to the uniaxial deformation just above crystallization.

At temperatures below T_c , (235 K $< T < 246$ K) the outer doublet structure also disappears and the n.m.r. spectra are completely different: bimodal spectra, composed of a superposition of a narrow and a broad line are observed. While the lineshape remains essentially the same, the linewidths of both components decrease on increasing the temperature. To measure the linewidths, we analysed the spectra as a superposition of two Lorentzian lines with different widths. Linewidths resulting from a best fit are plotted in Fig. 5. The fraction of the narrow component is about 18% and does not depend on temperature in the measuring range. Since the

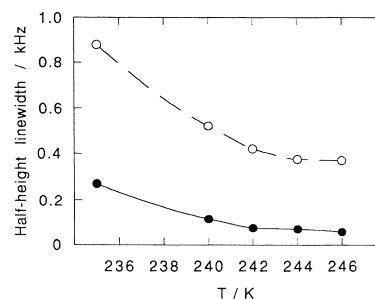


Fig. 5. Variation of the half-height linewidth of the rapid and slow spectral components versus temperature.

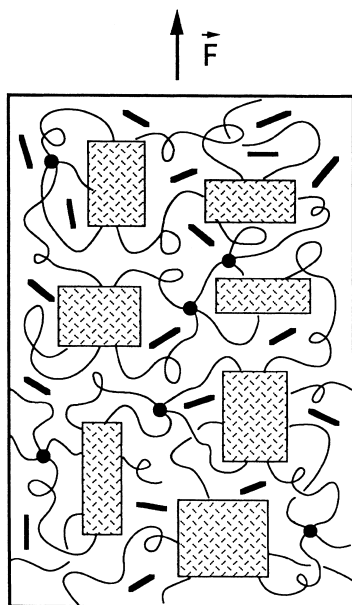


Fig. 6. Schematic representation of the semicrystalline phase of the strained network. Dark rods represent the alkane diffusing through the amorphous domains.

integrated intensity of the spectrum is similar to that of spectra observed at high temperatures, it is reasonable to consider that most of the octane molecules are ejected from the crystallites and probe the amorphous parts only, as has been observed in a PS–PDMS diblock copolymer [25].

The main observation here is the disappearance of the doublet in the fast (narrow) component of the spectrum, in the semicrystalline phase. The narrow component comes from octane molecules which have the fastest dynamics. This component is thus a probe for the part in the sample which remains molten, amorphous. No orientational order is observable in this part; significantly, the linewidth in this component remains comparable to the width of the doublet components above T_c . This is direct proof that the presence of crystallites allows the anisotropy induced by the external stress to relax, as represented schematically in Fig. 6. In this situation, the macroscopic strain is accommodated at a microscopic level, essentially via the orientation of the crystallites themselves.

This bimodal character of the spectrum, related to two motionally different regions in the amorphous phase, seems to be characteristic of the semicrystalline phase under deformation since it has been already observed for toluene- d_3 dissolved in the same PDMS network [26], and directly on oriented poly(ethylene terephthalate) chains [27,28]. Such dynamic heterogeneity, sensitive to the temperature as suggested by the data of Fig. 3, may be due to the distribution of the polymer chain length between crystallites, or to the gradient of mobility in chain segments close to crystallites. Also the morphology of crystallites, which may also influence the n.m.r. probe behaviour, is not well known in semicrystalline crosslinked materials.

5. Conclusions

The present observations emphasize the sensitivity of the deuterated probe method for investigating the motional behaviour in amorphous polymer networks, in the presence or absence of a crystalline phase. The approach—complementary to the e.p.r. spin probe method used as well in this field—[29,30] allows one to probe the dynamics of the amorphous matrix. Such information is essential for a better physical understanding of the properties of crosslinked and/or semicrystalline polymer systems. The problem of crystalline phase formation in PDMS and of constraints introduced by the presence of crystallites was studied earlier by n.m.r. [31]. Here, we demonstrate clearly that the formation of crystallites influences the local constraints in the amorphous phase, introduced by an external force [32].

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