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C-13 Rotating Frame Relaxation of Solid Polymers

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SUMMARY

^{13}C $T_{1\rho}$ of some polymers has been measured at various temperatures. This relaxation is sensitive to other motions than those determining the proton relaxation. The $T_{1\rho}$'s of polyethylene and poly(ethylene-vinylacetate) show minima which correspond to second moments of 10^8 s^{-2} and $4 \cdot 10^8$ s^{-2}, respectively, in contrary to the theoretical value of $4 \cdot 10^9$ s^{-2}. The reason is a strongly restricted motion - e. g. torsional oscillation - which cannot average out completely the dipolar interaction. In poly(methylmethacrylate) and in poly(vinylacetate) a decrease of the restriction with increasing temperature has been observed.

INTRODUCTION

The investigation of the glass transition is of great interest in polymer research. The chain segment motion connected with this transition is relatively slow (kHz range). To study such motions we have observed the relaxation in the rotating frame ($T_{1\varrho}$) which is sensitive to this frequency range.

However, measurements of the proton relaxation have the following disadvantages:

- If there are two or more phases with different T_1's only an average value is obtainable because of spin diffusion.
- The protons are placed on the periphery of the chains. Thus, the contribution of <u>intermolecular</u> interaction is comparable with or larger than the intramolecular one.

These effects complicating the proton data analysis do not affect the ^{13}C relaxation:

- For example, the intramethylene contribution to the second moment of polyethylene carbons is about 4.0×10^9 s^{-2} ($\triangleq 0.9$ mT^2), the whole contribution from all other protons exceeds not 0.5×10^9 s^{-2} ($\triangleq 0.1$ mT^2).

  Consequently, the ^{13}C $T_{1\varrho}$ in polyethylene can be treated as three spin systems in a better approximation than the proton relaxation as a two spin problem.
- Spin diffusion is quenched completely in the ^{13}C system.

In some cases proton spin flips can reduce the ^{13}C relaxation

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time (VANDERHART and GARROWAY 1979); the measured $T_{1\rho}$ is then not relevant to the thermal motion. However, this effect occurs in noncrystalline polymers only at lower temperatures or lower rf amplitudes H_1. If $T_{1\rho}$ decreases towards higher temperatures or shows a minimum then we can assume that thermal motion rather than the proton spin dynamics determines $T_{1\rho}$. (Spin flips cause only constant $T_{1\rho}$ at low Temperature or increasing values at higher temperatures.)
The experiments were performed on a SXP (BRUKER) with a modified pulse program generator. The rf. field magnitude was 4.0 mT or in some cases 3.2 mT, at a carbon-13 Larmor frequency of 22.63 MHz.

POLYETHYLENE (PE)

To get an example for a high-crystalline-polymer $T_{1\rho}$ we have measured a sample of linear PE (fig. 1). From the minimum at 70°C we must conclude that here the influence of proton spin flips is negligible. Only at low temperature a plateau occurs which could be interpreted as a spin flip effect.
This is in contrary to a work of GARROWAY and VANDERHART who has studied ultraoriented PE with also a high degree of crystallinity. These authors concluded that spin flip dominate up to 100°C in the ^{13}C rotating frame relaxation of PE if H_1 is no larger than about 8 mT.
However, the existence of a minimum is an unambigous proof for the fact that the lattice motion essentially influences the rotating frame relaxation of the carbons.
Assuming the validity of BPP theory we take for a quantitative interpretation of our experiments the convenient formula

$$1/T_{1\rho} = M_2 \tau_c/(1 + 4\omega_1^2 \tau_c^2) \text{ with } \omega_1 = \gamma_c H_1. \qquad (1)$$

(The carbon and proton Larmor frequency should be large compared with the correlation frequency $1/\tau_c$ of the observed motion.) The minimum condition

$$\omega_1 \tau_{c\,min} = 1/2 \qquad (2)$$

yields

$$1/T_{1\rho\ min} = M_2/4\omega_1 \ . \qquad (3)$$

From this relations we estimated $\tau_{c\,min} \approx 2 \times 10^{-6}$ s and $M_2 \approx 10^8\ s^{-2}$. The high temperature slope gives an activation energy of 112 kJ/mol.
However, calculating M_2 from molecular geometry we get $M_2 \approx 4 \times 10^9\ s^{-2}$. This is by a factor of 40 larger than the

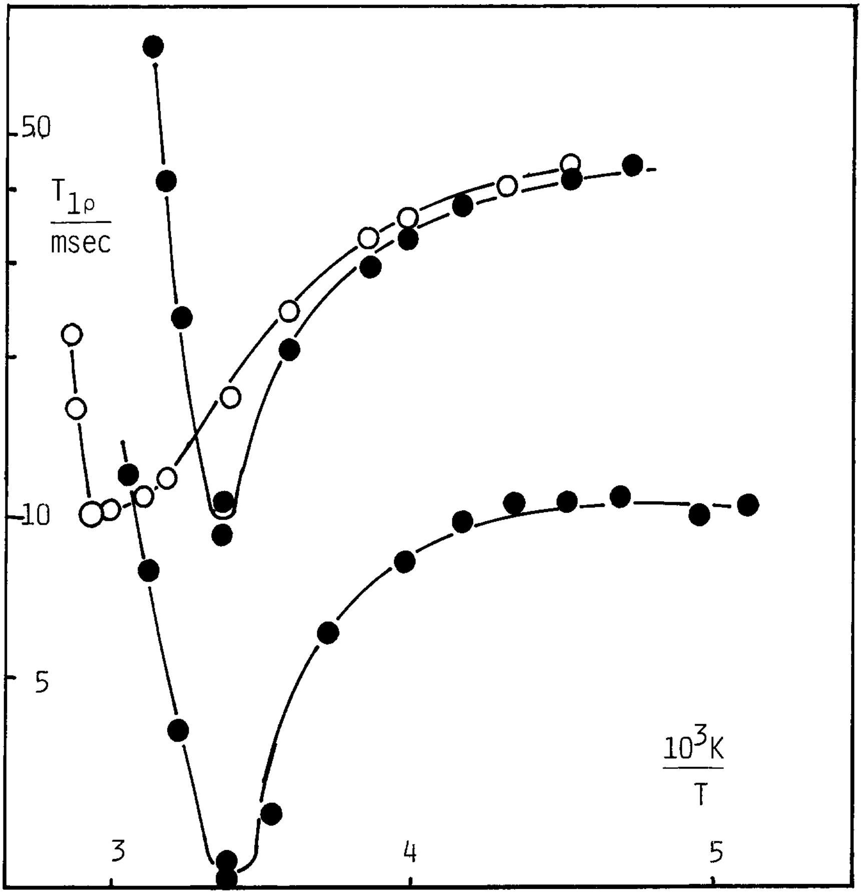

Figure 1: ^{13}C T_{1s} of PE (○) and EVA (●)

experimentally obtained second moment!
What is the reason for this discrepancy? There are some effects which cause an increasing of $T_{1s\,min}$ (e. g. anisotropic rotation, distribution of correlation times), but neither of this can generate those factor 40.

The only explanation is: The ^{13}C T_{1s} is sensitive to motions which act only on a small part of the dipolar Hamiltonian. Then in equ. (1) M_2 must be substituted by M_2' which represents only those part of ^1H-^{13}C-interaction averaged by this motion.
For example, torsional oscillation by a very small torsion angle has such an effect. Here the vector connecting proton and ^{13}C nucleus can vary his orientation only in a small range, and a large part of dipolar interaction can be assumed as statically. But only the small fluctuating part of the Hamiltonian leads to spin-lattice relaxation (fig. 2).

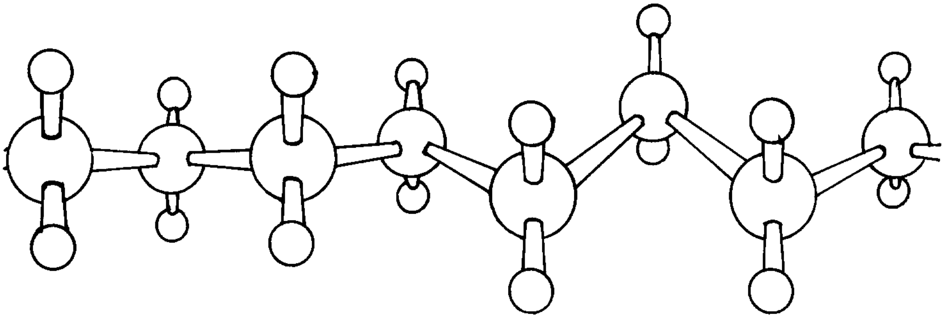

Figure 2: Chain torsion oscillation as an example of a strongly restricted motion

Why does not occur this motion in proton relaxation? Here the protons from neighbouring methylene groups contribute essentially to M_2. Because of the greater distance the oscillation amplitude of the proton-proton vector is smaller than that of the C-H vector (fig. 3).

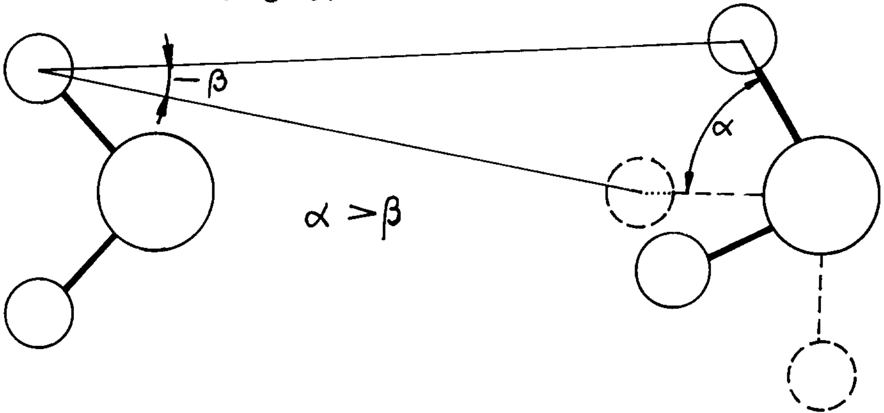

Figure 3: The vector connecting protons of different methylene groups has a smaller amplitude due to torsional oscillation than the C-H- vector.

So the relative part of dipolar interaction effective to this relaxation is much smaller than in the ^{13}C relaxation. Thus, often another relaxation mechanism will be stronger and makes the former negligible.

POLY(ETHYLENE-VINYLACETATE) (EVA)

Here the relaxation passes biexponentially. The two components have equal intensity and show a nearly constant ratio of short to long T_{1s} (1 : 4) (fig. 1). Comparing these curves with that from PE we must point out:

- The minima (for both components at the same temperature !) are shifted to lower temperature.

- The long $T_{1\rho}$ component has the same $T_{1\rho\,min}$ as PE.

Because of its low vinylacetate content (18.8. weight-%) the signal is caused only by methylene carbons; the contributions of the other carbons are neglected.
Using the model mentioned above we must conclude:

- There exist two phases in EVA which differs from another in amplitude of torsional oscillation, i. e. in the degree of motional restrictions. The shorter $T_{1\rho}$ component caused by a larger part of averaged C-H interaction is related to the phase of lower restriction.
- The correlation frequency is the same in both phases though the restrictions are different. The latter only influence the the motional amplitude.

Thus, with $T_{1\rho}$ measurements it is possible to distinguish phases of different oscillations. These phases could be identified with ranges of high order (large motion restrictions, i. e. long $T_{1\rho}$) and of low order. But it is not clear yet whether we can relate this to crystalline or amorphous phases discussed elsewhere.

POLY(METHYLMETHACRYLATE (PMMA), POLY(VINYLACETATE (PVAc)

Here also the influence of proton spin flips can be neglected: $T_{1\rho}$ decreases up to temperatures that are higher than the glass transition (fig. 4). Is there a slow motion which shows the minimum at temperatures far above the glass transition? This seems unlikely: If such a motion exists the minimum related to this must be not more than 30 ... 50 K higher than the highest temperature of this plot (120°C). Extrapolating the PMMA curve to this temperatures we see that the theoretically calculated value of 0.25 ms cannot be reached. The assumption of restricted oscillations used above seems unlikely at such high temperatures.
What is the reason for the measured $T_{1\rho}$ if we exclude

$\omega_1\tau_c = 1/2$ at higher temperatures than 120°C?

We can get an explanation if we take the concept of restricted motions for temperatures that are not toll high: If there exist such oscillations at room temperature we must expect that by increasing the temperature the amplitude of the oscillation increases, and at the melting point a more isotropic motion is observed. That means: The part of Hamiltonian not influenced by the oscillation decreases, and M_2' (substituted for M_2 in eq. (1)) increases. Thus, the growth of $T_{1\rho}$ as a consequence of decreased τ_c is overcome by a faster growth of M_2' and so $T_{1\rho}$ decreases. If anywhere M_2' reaches M_2 a minimum occurs that not relates to a $\omega_1\tau_c = 1/2$ condition, and $T_{1\rho}$ increases at still higher temperatures "normally".
This discussion for PMMA can be made analogous for PVAc.
In conclusion, it can be stated:

The $T_{1\rho}$ of ^{13}C nuclei is determined by trosional oscillations (or other strongly restricted motions).

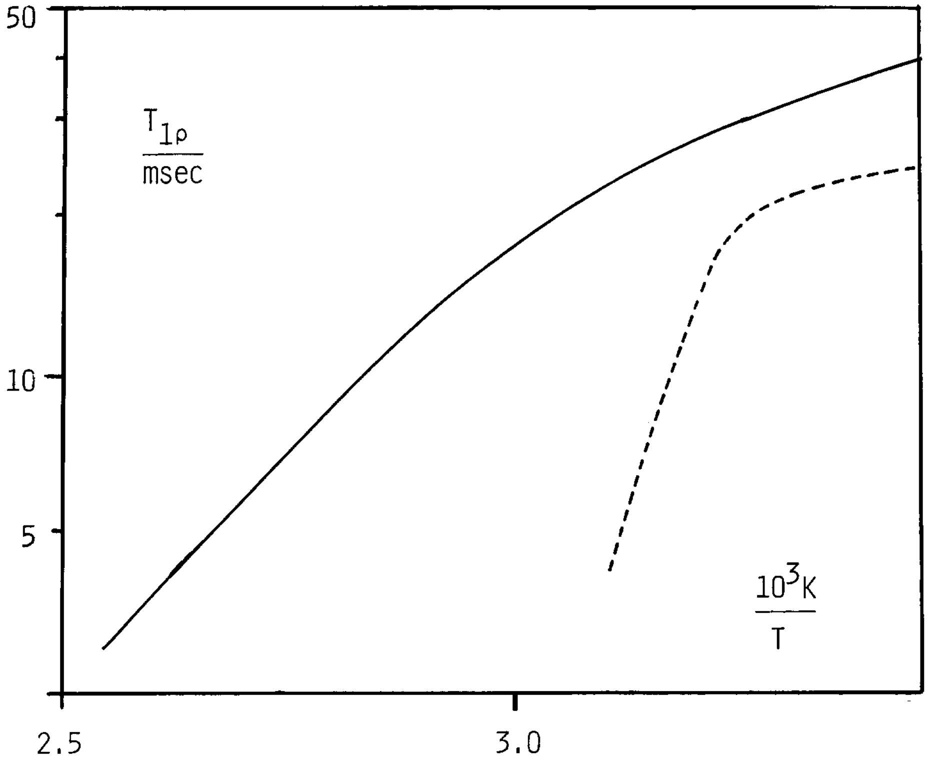

Fig. 4. ^{13}C $T_{1\rho}$ of PMMA (—) and PVAc (---)

Beyond the frequency also the amplitude of torsion determines $T_{1\rho}$ of ^{13}C. It is not clear, how this motions are related to those observed otherwise (proton relaxation or other methods), but it is an interesting field and a possibility to get more information about thermal motion in polymers.

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