NMR Investigation of Segmental Mobility in Chemically Cross-Linked Polypropylene

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NMR Investigation of Segmental Mobility in Chemically Cross-Linked Polypropylene

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ABSTRACT

Our previous NMR investigations of chemically cross-linked polypropylene were mainly focused on testing the relation between spin-spin and spin-lattice relaxation times as a function of cross-linking compound concentration. In our previous investigations, however, we did not consider the state of mobility of any part of the polypropylene chain, and therefore in this work we consider this problem.

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THEORETICAL INTRODUCTION

Since NMR investigations are very well known, we will not describe them here in detail. We will only focus our attention on the relaxation factors connected with the mobility of groups or segments in polymer chains which are in the solid state. One way to investigate such movements is to test the spin-lattice relaxation time T_1 as a function of temperature.

Proton NMR experiments in the solid state reveal the relaxation processes caused by the nuclear dipole-dipole interaction modulated by thermal movements. The movements are mainly characterized by the correlation time τ_c. In the case of reorientation of typical polypropylene CH_3 groups, τ_c is the time between an appropriate jump from one position of equilibrium to another in the molecular structure.

For the chaotic rotational movements of a two proton system, Bloembergen, Purcell, and Pound [4] developed an equation relating the time T_1 to the correlation time τ_c:

$$\frac{1}{T_1} = \frac{3}{10} \frac{\gamma^4 \hbar}{r^6} \left[\frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{\tau_c}{1 + 4\omega^2 \tau_c^2} \right] \tag{1}$$

where γ is the gyromagnetic ratio, r is the distance between rotating nuclei, and ω is the spectrometric frequency.

According to Arrhenius, an increase of temperature causes an increase of rotation velocity:

$$\tau_c = \tau_0 e^{E_a/RT} \tag{2}$$

where E_a is the activation energy, R is the gas constant, and T is the temperature.

The BPP equation is suitable to describe the minimal value of T_1:

$$T_{1\ min} = \frac{10}{3} \frac{r^6}{\gamma^4 \hbar^2} \frac{\omega}{1.42} \tag{3}$$

which occurs at the temperature where the product of the Larmor frequency and the correlation time τ_c are equal:

$$\omega \tau_c = 0.616 \tag{4}$$

Based on Eq. (3) and the value of $T_{1\ min}$, it is possible to evaluate the distance between pairs of nuclei. If the rotation of groups like NH_3 or CH_3 takes place in molecules or chains, then such a rotation is followed by other protons from this system according to the mechanism called spin diffusion.

The equation for such a diffusion has been given by Woessner [4]:

$$\frac{1}{T_1} = \frac{n}{N}\left(\frac{1}{T_1}\right)\begin{array}{c}rotating\\group\end{array} + \frac{N-n}{N}\left(\frac{1}{T_1}\right)\begin{array}{c}remaining\\group\end{array} \tag{5}$$

The first part of Eq. (5) takes into account the influence of side protons on the relaxation of rotating CH_3 groups containing n protons. The second part of Eq. (5) deals mainly with the rotation of side protons, i.e., in a polymer chain, and is connected with another correlation time. If the minimum of T_1 attributed to the rotation of three proton groups in the second part of Eq. (5) is neglected, we can take into account only one correlation time of this group.

For the three proton groups rotating around the C_3 axis, O'Reilly and Tsang [5] have calculated the time T_1. This equation, taking into account the spin diffusion being considered in the vicinity of $T_{1\ min}$, is

$$\frac{1}{T_1} = \frac{n}{N}\frac{9\gamma^4\hbar^2}{20}\frac{1}{r^6}\left[\frac{\tau_c}{1+\omega^2\tau_c^2} + \frac{4\tau_c}{1+4\omega^2\tau_c^2}\right] \tag{6}$$

If in the investigated polymer or chemical sample two different groups appear, like CH_3 or NH_3, then because of different kinds of structural linkage and different times of correlation, the relaxation time T_1 as a function of temperature will show two minima. A similar effect is observed when, apart from the movement around the C_3 axis, additional isotropic movement modes of molecular mobility appear. From the value of $T_{1\ min}$ we can calculate the correlation time, the distance between rotating nucleis, and the factor n/N. The factor n/N is the description of spin diffusion.

Additionally, from the slope of log T_1 vs the reciprocal temperature it is possible to calculate the energy of activation of particular molecular movements from Eqs. (2), (5), and (6).

Investigation of T_1 times could also be used to observe first- and second-order phase transitions in polymers.
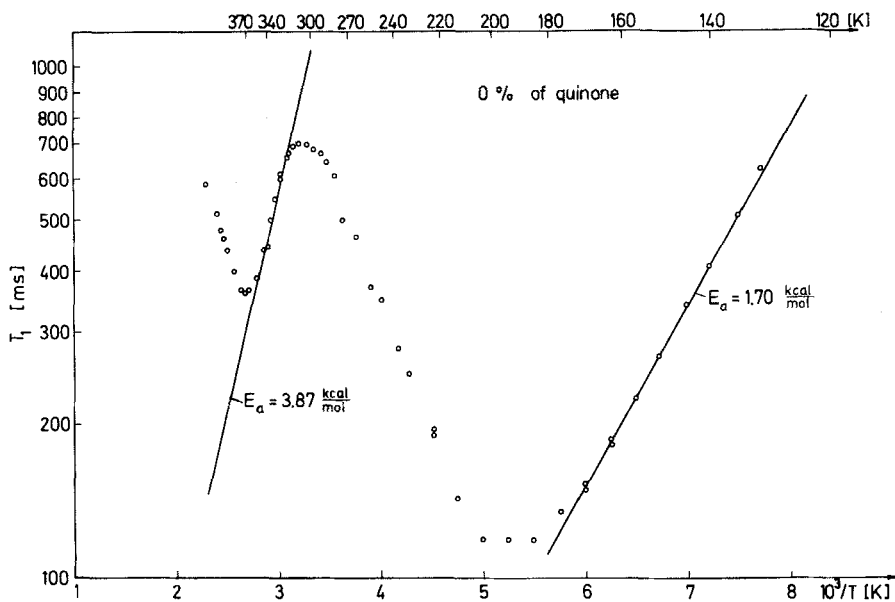
FIG. 1. The relation between spin-lattice relaxation time T_1 and the temperature for uncross-linked polypropylene.

EXPERIMENTAL

Measurements have been performed by means of the Bruker SXP 4-100 pulse NMR spectrometer. We have evaluated the spin-lattice relaxation time T_1 as a function of temperature from 125 to 450 K at a testing frequency of 90 MHz. From these data we calculated the energy of activation as a function of the cross-linking compound concentration.

The cross-linked polypropylene was prepared by using the polymer with a molecular weight of 200,000, 1,4-(tertbutylperoxy)-diisopropyl benzene as a peroxide at a constant concentration of 2 wt%, and varying concentrations of quinone as a coagent. The amounts of quinone in polypropylene were 0.5, 1.0, 1.5, 2.0, and 3.0. The preparation of the cross-linked polypropylene has been described recently [1-3]. A gel fraction between 70 and 90% [1, 2] was obtained using the cross-linking compound mentioned above. To measure the T_1 time, we used the $\pi - \tau - \pi/2$ pulse method.

The result of these tests are shown in Figs. 1 and 2. In Fig. 1 the relation between T_1 and the temperature for uncross-linked polypropylene shows two distinct minima. We see the same phenomenon for cross-linked polypropylene with 3% quinone in Fig. 2. For all
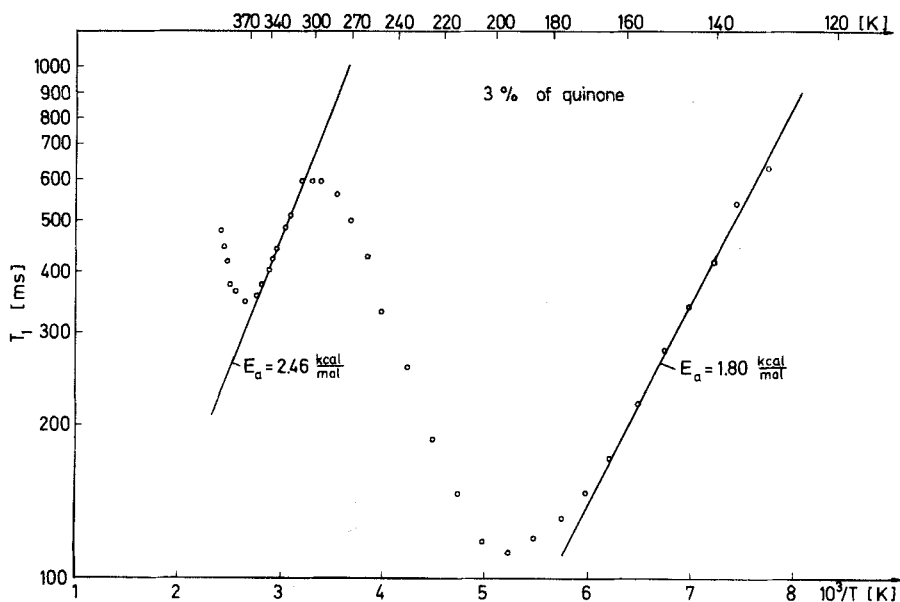
FIG. 2. The relation between spin-lattice relaxation time T_1 and the temperature for polypropylene cross-linked with 3% of quinone.

other concentrations of quinone the situation is the same, so we do not show these relations here.

The maximum on these figures does not have any theoretical interpretation, but in this temperature range the so-called second-order liquid-liquid transition in polypropylene usually appears [6].

The first minimum in the 210 K temperature range is attributed to the rotation of CH_3 groups on the polypropylene chain. This rotation, as we can see, takes place below the glass transition temperature of polypropylene which is at 253-268 K. The glass transition temperatures of these polymers are evidenced by little bending of the curves near the maximum in both drawings.

The second minimum, in the vicinity of 385 K, is probably related to the rotation or dynamic movement of polypropylene segments. This phenomenon takes place at a temperature higher than the glass transition temperature of this polymer. A more precise measurement of the first maximum is shown in Fig. 3 where we can see two little maxima at temperatures of about 293 and 313 K.

DISCUSSION

We think the rotation of the CH_3 groups takes place around the C_3 axis which is created by the chemical bond $C-CH_3$. The exponential
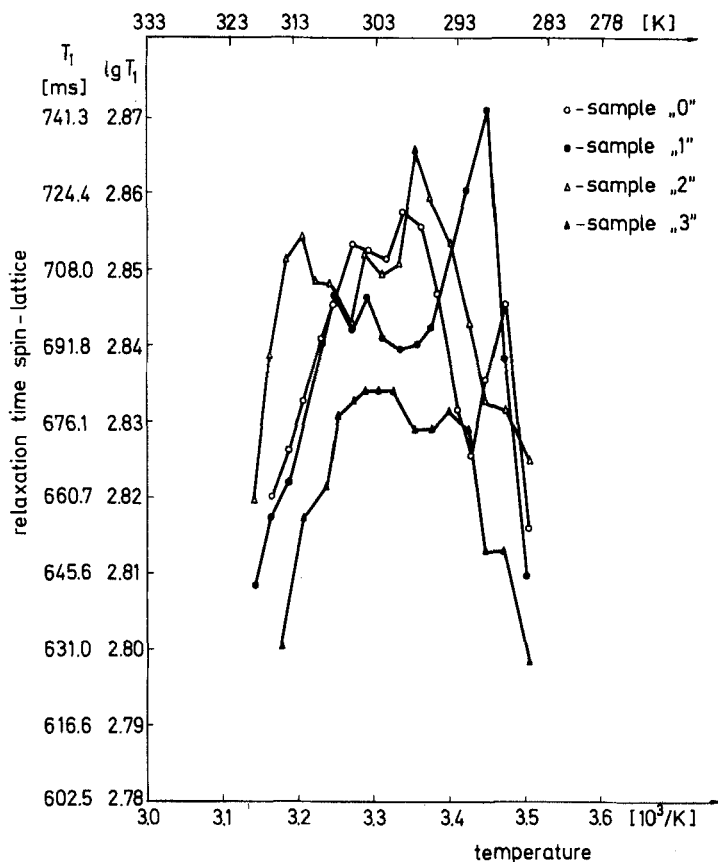
FIG. 3.   The relation between spin-lattice relaxation time T_1 and
the temperature for cross-linked polypropylene (very accurate
measurements of the first maximum from Fig. 2).

magnetization recovery in the temperature range tested indicates
very fast spin diffusion.

Taking into account the values of the T_1 minima and knowledge of
the geometry of the CH_3 group, we can calculate the n/N factor from
Eq. (5). The results of these calculations show that for uncross-
linked PP this factor is 0.46 and for PP cross-linked with 3% quinone
it is about 0.487.

It can be concluded that the value of n/N is close to the value
coming from the chemical structure of two polypropylene mers.
The independence of these values from the concentration of a cross-
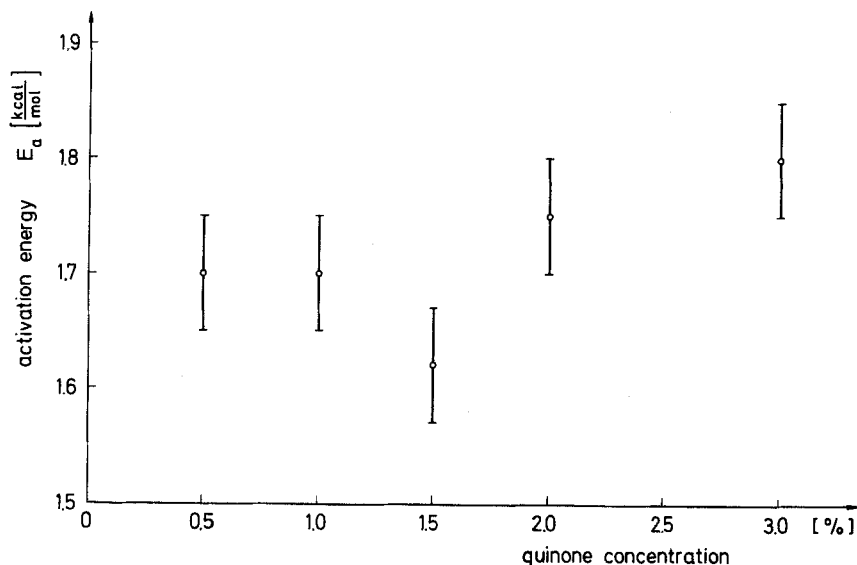linking compound is obvious because the number of protons in

FIG. 4. The relation between the activation energy of CH₃ groups
and the concentration of quinone.

quinone is very small in comparison to the number of protons in the
polypropylene chain.
    The position of the low temperature minimum as measured by the
value of time T_1 vs temperature does not change with a variation of
quinone concentration.
    This means the cross-linking process or the variation of cross-
linking density do not influence the dynamic movement of CH₃ groups.
Additional proof of this is the stable activation energy value in all
of the cross-linked polypropylene samples tested. This energy was
calculated from the low temperature minimum and is presented in
Fig. 4.
    The high temperature minimum located above the glass transition
temperature of polypropylene in the viscoelastic range of this poly-
mer seems to be connected with the segmental mobility around the
axis of minimal momentum of inertia parallel to the direction of
chain growth. The activation energy of this moment, calculated in the
vicinity of the T_1 minimum as a function of quinone concentration in
Fig. 5, is approximately two times higher than the energy of activation
of CH₃ groups.
    In this case, however, the energy of activation depends very strongly
on the quinone concentration and diminishes proportionally to an in-
crease of quinone concentration. The energy of activation for uncross-
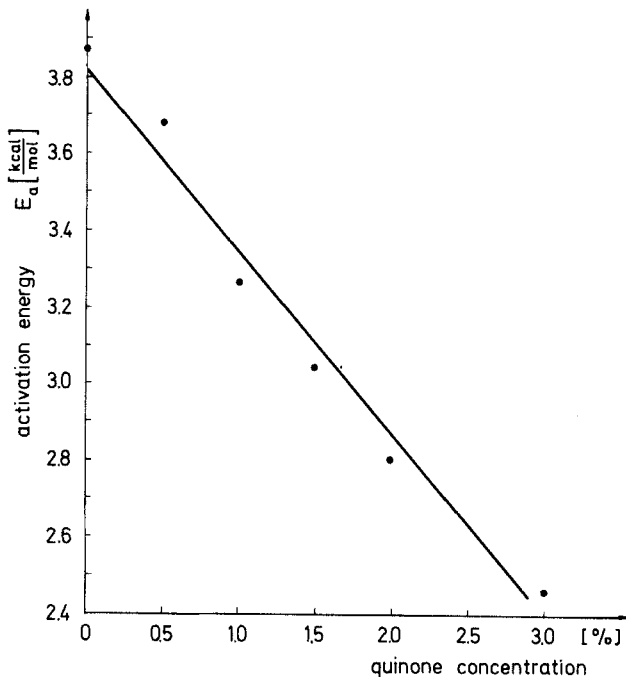linked polypropylene is 3.85 kcal/mol, and for polypropylene cross-linked

FIG. 5. The relation between the activation energy of polypropyl-
ene segments and the concentration of quinone.

with 3% of quinone this energy has a value of 2.45 kcal/mol. This
probably means that when the number of quinone bridges as cross-
links increases, the distance between neighboring chains also in-
creases, and this provides more space for segmental dynamic
movements. It can be simply described as a plastification effect
of quinone cross-links in polypropylene. The relation of activation
energy and quinone concentration can also be used as a proof of that.
Chodak [8] was right saying that in this case the polypropylene is
cross-linked by quinone links.

Moreover, from the relationship in Fig. 5 we can assume that the
density of cross-links in polypropylene is a linear function of quinone
concentration. Thus our previous interpretation of the physico-
mechanical properties of cross-linked polypropylene as a function of
quinone concentration seems to be correct. Very accurate measure-
ments of time T_1 as a function of temperature reveals two instead of
one maximum (Fig. 3). The first maximum is in the vicinity of 293 K,
the second is in the vicinity of 313 K, and both change with the varia-
tion of quinone concentration used for cross-linking. The positions

of these maxima on the temperature scale correlate very well with the second-order transition called liquid-liquid transition in poly-propylene. According to Takahara [6] and others [7], these transitions can be attributed to the phase transitions semectic-amorphous and amorphous-monoclinic, respectively.

CONCLUSIONS

1. Investigations of T_1 have shown that in cross-linked poly-propylene we are facing two distinct dynamic movements. One is connected with the rotation of CH_3 groups and the other with the mobility of polypropylene segments.

2. The energy of activation of CH_3 groups does not depend on cross-link density. However, the energy of activation of polypropylene segments is very much dependent on cross-link density.

3. The linear decrease of activation energy when the concentration of quinone increases may be proof that the concentration of quinone is a good approximation of cross-linking density in cross-linked polypropylene.

ACKNOWLEDGMENT

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