N.m.r. study of molecular dynamics in chemically crosslinked polyethylene

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Results of measurements of the proton spin-lattice relaxation time T_1 in chemically crosslinked low-pressure polyethylene are presented. The dicumyl peroxide used for crosslinking changed the α-process dynamics without disturbing the β-process or the motion of the methyl groups. Classical relaxation processes (which are analogous to the case of pure polyethylene) have been observed for samples with 0.5–2.5 wt% crosslinking.

INTRODUCTION

Polyethylene has been widely studied, and its dielectric properties, relaxation rates, n.m.r. spectra and mechanical parameters are well known. In this work we investigated the properties of polyethylene which had been chemically crosslinked with dicumyl peroxide. Since the temperature dependence of the spin-lattice relaxation time T_1 of pure polyethylene at low pressure have been already studied, we compared observable relaxation parameters of both pure and chemically crosslinked polyethylene. The occurrence of complex molecular motions which are responsible for the observable relaxation rates, makes the qualitative analysis of oscillatory modes and kinds of motions rather difficult. In such a case it makes sense to search for parameters which do not raise any uncertainty when compared to analogous parameters from pure polyethylene.

Spin-lattice relaxation of protons in polymers under investigation is caused by dipolar interactions between neighbouring nuclei, modulated by thermal motions. The theory, describing these phenomena is well established[1], therefore we shall limit our description here to basic features of this effect.

Hindered rotation of a three-proton group (e.g. CH_3, NH_3) about C_3 axis in powdered samples determines the relaxation time T_1, as calculated by O'Reilly and Tsung[2], who modified the Bloemberger–Purcell–Pound (BPP) theory[3] which describes the interaction between two dipoles:

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

where γ is the proton magnetogyric ratio, $\hbar$ Planck's constant divided by 2π, r is the internuclear distance within the rotating group, ω is the Larmor frequency, τ_c is the correlation time.

For the motion being described τ_c is the time between subsequent jumps by 120° among potential wells, separated by potential barrier E_a. Often it is assumed that the temperature dependence of τ_c is given by the Arrhenius formula:

$$\tau_c = \tau_0\exp\left(\frac{E_a}{RT}\right) \qquad (2)$$

with τ_0 being a preexponential factor, R is the gas constant. On lowering the temperature in solids a change of τ_c by a few orders of magnitude (10^{-12}–10^{-6} s) is observed with a characteristic minimum of T_1. At the temperature, where $\omega_0\tau_c = 0.616$ T_1 is given simply by:

$$T_1^{\min} = \frac{20r^6\omega}{9\gamma^4\hbar^2 1.42} \qquad (3)$$

from which, using the experimental data, the interproton distance r can easily be deduced. The above reasoning holds for isolated three-proton groups.

In polymers (often below glassy temperatures) the relaxation is made possible by rotations of CH_3 groups, which are a small portion of macromolecules. As can be shown experimentally, the remaining protons relax by spin-diffusion processes, when the relaxation time T_1 is given by Gutovsky–Woessner formula (4):

$$\frac{1}{T_1} = \frac{3n}{N}\left(\frac{1}{T_1}\right)_{\substack{\text{rotating}\\\text{group}}} + \frac{N-3n}{N}\left(\frac{1}{T_1}\right)_{\substack{\text{remaining}\\\text{group}}} \qquad (4)$$

where N is the number of all relaxing protons in a macromolecule, n is the number of CH_3 groups. The factor 'n' is important in determining the structure of the polymer. It can be deduced close to the minimum value of T_1, where the second term of equation (4) (resulting from the rotation of CH_3 groups whose geometry is known) is negligible.

For unknown dynamical processes, near to the minimum value of T_1 the analysis becomes more complicated. At temperatures close to the minimum value of T_1, and with the spin-diffusion process being effective, the

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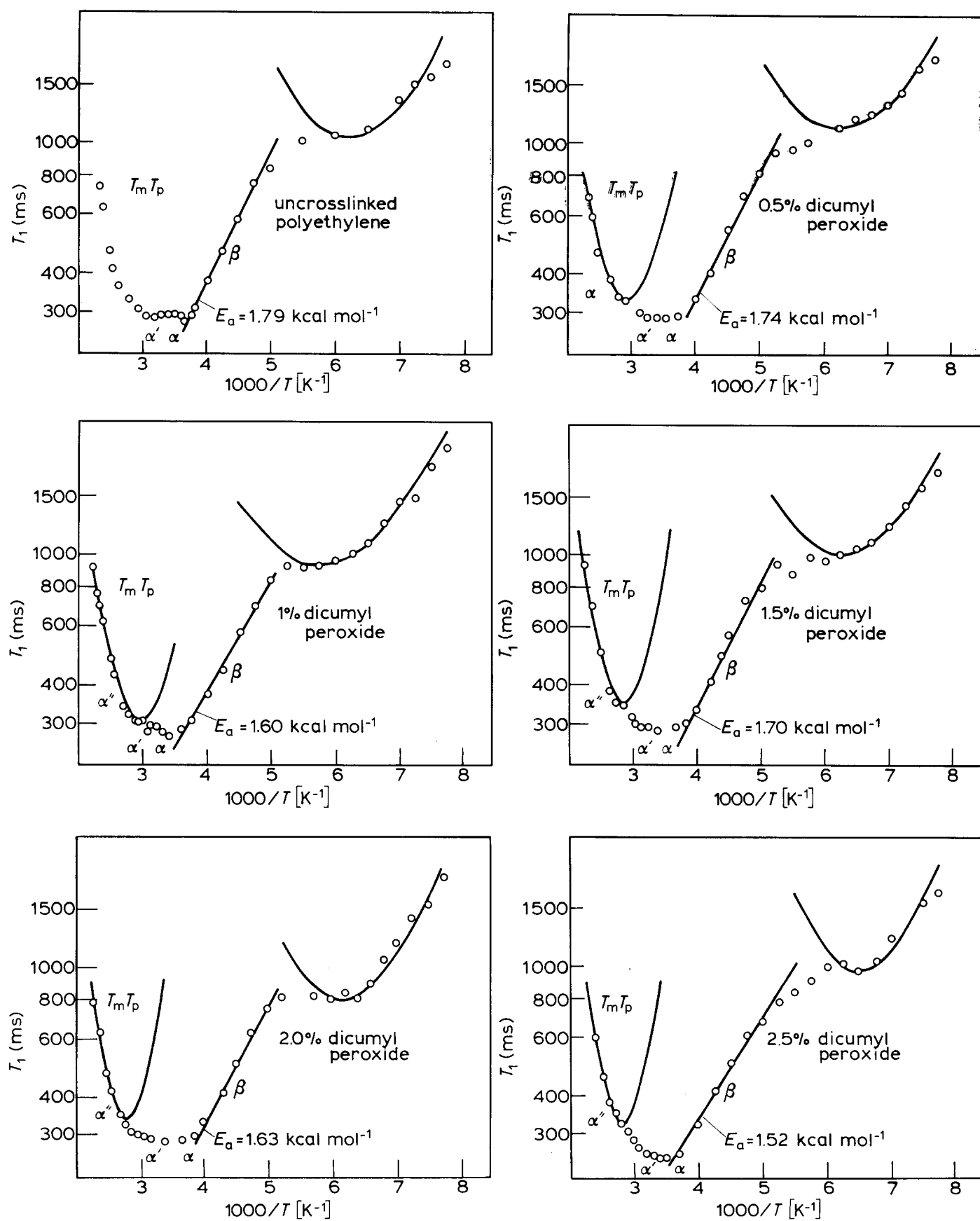** Burgaska 3/9, 02-757 Warszawa, Poland.

Figure 1 Temperature dependence of the spin-lattice relaxation time T_1 for pure polyethylene and cross-linked samples. T_p-temperature of start of melting. T_m-maximal melting temperature

experimental results will only allow the determination of C from the formula:

$$\frac{1}{T_1} = C\left[\frac{\tau_c}{1+\omega^2\tau_c^2} + \frac{4\tau_c}{1+4\omega^2\tau_c^2}\right] \quad (5)$$

since the type of oscillations remains unknown. Temperature dependence yields an activation energy of these unknown motions as well as the preexponential factor τ_0.

Discontinuities in the temperature dependence of T_1 indicate phase transitions. These phenomena in polymers are not as distinctive as in monocrystals.

EXPERIMENTAL

The polyethylene used was Petrolen WJG-47 (from I.C.I.). This polyethylene formed at low pressure has a molecular weight of 32 000, with 30 short branches and 1000 carbon atoms. Chemical crosslinking was performed using di-

Figure 2 Dependence of the activation energy (●), number of CH_3 groups per 1000 carbon atoms (■) and temperature of T_1^{min} (⊚) on the concentration of dicumyl peroxide

Figure 3 Dependence of the activation energy of the β -process on the concentration of dicumyl peroxide

cumyl peroxide in following weight concentrations: 0.5%, 1%, 1.5%, 2% and 2.5%. The efficiency of the process has been verified by determining the gel contents[5]. The efficiency increased from 81.9 to 89.4%, reflecting the amount of the crosslinking compound used. The relaxation times T_1 have been measured on a pulsed n.m.r. spectrometer Brukre SXP 4-100 in the temperature range 120–400 K. The temperatures were set and stabilized with accuracy of ± 1 K using a nitrogen gas flow unit. The free induction decay signal, observed at 90 MHz, measured by a boxcar utilizing a digital voltmeter, was simple. Single-exponential decays of the magnetizations at all temperatures used allowed unambiguous determination of T_1 (see *Figure 1*).

A broad minimum can be seen around 160 K, a linear decrease of log T_1 vs. $1/T$ and a second, complex minimum below 350 K.

Moreover, in crosslinked polyethylene a small jump of T_1 can be seen just before the second minimum.

DISCUSSION

Rotation of CH_3 groups

As the temperature increased from 120 K to temperatures where the polymer was glassy there was a shortening of the relaxation times T_1 from 1.7 s to the value, determined as T_1^{min} (dependent on the type of sample). Following McCall and Douglas[7], as well as Buckley Crist and Peterlin[8], we associated these changes with rotations of CH_3 groups. Numerical fitting to the temperature dependence of T_1 permitted the determination of the activation energy E_a of this motion about C_3 axis assuming $r = 1.80$ Å and the number n of methyl groups/ 1000 carbon atoms. Data for the samples under investigation are shown in *Table 1*. *Figure 2* presents the dependence of E_a, n and T_1^{min} with the concentration of dicumyl peroxide used for crosslinking. As can be seen from the graphs, the activation energy of the motion of the CH_3 groups, and the temperature (at T_1^{min}), does not change with increasing crosslinking. The value of n is in the range 30–45 and does not differ from data of ICI.

β process

Above the T_g the relaxation times T_1 changes exponentially with $1/T$. This process, denoted as β results from chaotic motions in the amorphic part of polymer[7,9,10]. The activation energy (*Figure 3*) slightly diminishes with increases in the degree of crosslinking, what might prove that crosslinking causes spreading of polymer chains, thus allowing motion.

α processes

Increases in the temperature above 273 K causes the appearance of a broad and inhomogeneous T_1 min. These processes (denoted as α processes) are associated with motions within the crystalline part of the polymer[9-12]. Description of the α processes are complicated and ambiguous. In our crosslinked samples, after completion of α'-processes occurs a discontinuity of T_1 thus indicating the existence of a phase transition. At temperatures above the transition region, the motions inside the crystalline phase cause relaxation, which can be described by equation (5).

Numerical analyses of experimental results yielded the coefficient C, activation energy E_a, T_1^{min} and the pre-
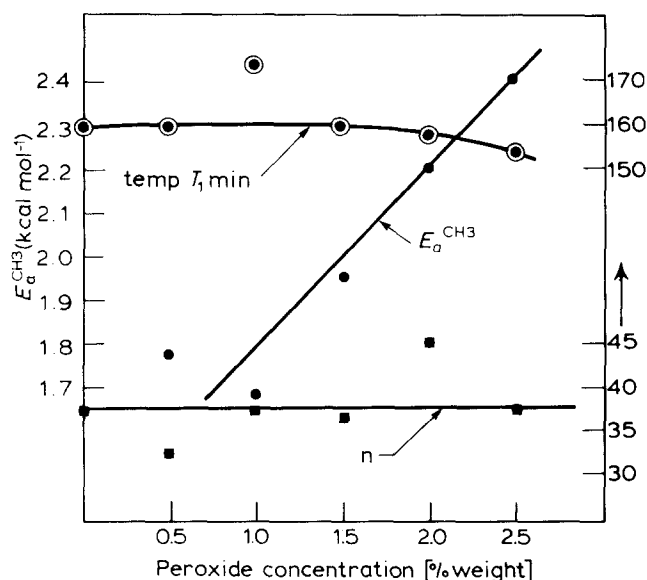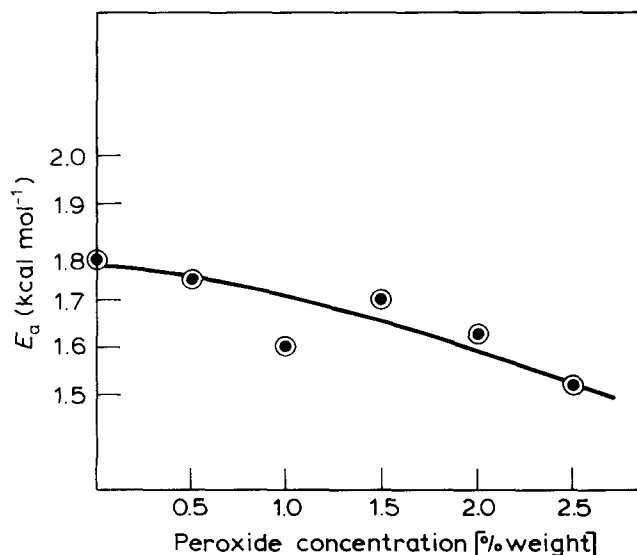
Table 1

Sample	Melting temp.		α^* process			β process			CH$_3$ rotation			
	T_p [K]	T_m [K]	Temperature T_1 min [K]	C [10^8 S^{-2}]	E_a kcal mol^{-1}	$\bar{\tau}_0$ [10^{-13} s]	E_a (kcal mol^{-1})	Glassy temp. [K]	E_a (kcal mol^{-1})	Temperature T_1 min [K]	T_1 min [K]	n
Pure polyethylene	343	378	—	—	...	—	1.79	193	2.0	160	1.023	35.5
0.5% peroxide	338	376	338	12.05	4.5	13.3	1.74	193	1.78	160	1.122	32.5
1% peroxide	335	372	345	13	4.8	8.49	1.60	193	1.68	174	0.9120	37.3
1.5% peroxide	338	371	352	11.57	5.4	4.58	1.70	193	1.95	160	1.000	36.4
2.0% peroxide	334	358	354	11.70	5.85	2.15	1.63	193	2.2	160	0.831	45.0
2.5% peroxide	333	371	357	12.15	6.3	1.47	1.52	193	2.4	153	0.977	37.2
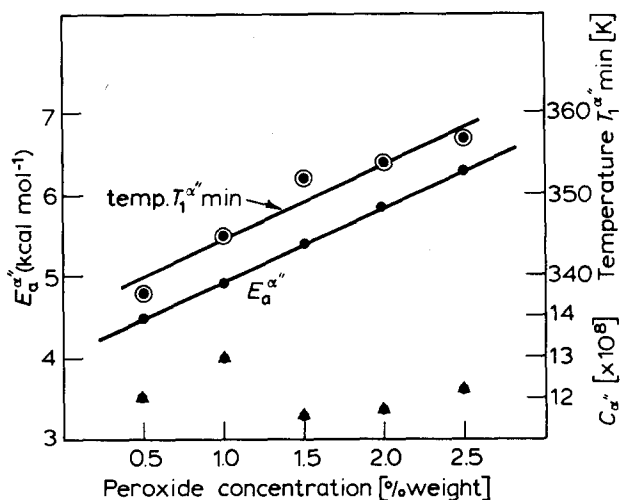
Figure 4 Dependence of the activation energy ($\bullet$), temperature of $T_1{}^{min}$ ($\circledcirc$) and C ($\blacktriangle$) of the α'' process on the concentration of dicumyl peroxide

CONCLUSION

Studies of temperature dependence of relaxation times enables the determination of the ratio between the number of CH$_3$ groups to 1000 carbon atoms in polymers; the activation energies of the motion of CH$_3$ groups; the motion of macromolecular fragments in amorphic parts of polymers, and the analysis of complex α processes. In a chemically crosslinked polyethylene we have observed the process α'' (not found in literature), which is preceded by a stepwise change of T_1.

The collected data on molecular dynamics along with the melting and glassy temperatures (*Table 1*) complement the mechanical and dielectric studies of chemically crosslinked polyethylene.

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exponential factor τ_0 (*Table 1*). *Figure 4* shows values of T_1^{min} and activation energies of thermal motions in the α'' phase, evidences existing correlations between them. Increases in the crosslinking compound causes increases of both the activation energy and the temperature of occurrence of T_1^{min} which shows the higher degree of hindering the motions within this phase.

A constant value of C suggests that the kind of motion and amount of phase do not depend on contents of the crosslinking compound. If the α'' phase is regarded as a polymer which had been heated above the melting temperature, we may consider that the α'' processes are the motion of liquid macromolecules of great viscosity, but with preserved areas of order resembling a liquid-crystalline phase.

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