

BROAD LINE AND PULSED NMR STUDY OF MOLECULAR MOTION IN FURFURYL ALCOHOL RESINS

BY S. GŁOWINKOWSKI AND Z. PAJĄK

Institute of Physics, A. Mickiewicz University, Poznań*

(Received November 10, 1977; Revised version received March 7, 1978)

Broad line and pulsed nuclear magnetic resonance studies are carried out on a number of furfuryl alcohol resins differentiated by viscosity. Proton NMR spectra and relaxation times T_1 and $T_{1\rho}$ are measured over a wide temperature range and the results are interpreted in terms of molecular motion. The marked decrease in second moment and existence of high temperature spin-lattice relaxation times minima are presumed to result from rotational motion of polymer chains. The relaxation processes at low temperature are believed to be due to rotational motion of methyl endgroup and paramagnetic centres.

1. Introduction

Furfuryl alcohol resins are chemically heterogeneous, low molecular weight liquid polymers, which are produced by polycondensation of the monomer, especially in the presence of an acid catalyst. They have been used for a wide variety of applications in the plastics, coating and modern casting industries and also as binder materials in the manufacture of nuclear grade graphites. Hitherto, most investigations of furfuryl alcohol resins have been concerned with the isolation and identification of their low molecular components and with the determination of the distribution of molecular weights.

Barr and Wallon [1] have separated twelve compounds, which can be arranged into four classes: polyfurfuryl alcohols, polyfurfuryl ethers, polyfurfuryl furans and methyl-substituted polyfurfuryl furans. Similar information about the higher molecular compounds are lacking because of experimental difficulties of their isolation. For that reason, the resins of furfuryl alcohol are characterised on the whole by viscosities or by distribution of their molecular weights. Wewerka [2], using gel-permeation chromatography, has shown that the molecular weights of these resins vary from the monomer weight ($n = 1$) up to about 5000 ($n \approx 60$).

It is known that the physical properties of polymers depend on the molecular motions of their chains which, in turn, are dependent on the temperature, polymer structure and composition. A useful method, widely applied to investigate the molecular motions, is

* Address: Zakład Radiospektroskopii, Instytut Fizyki, Uniwersytet A. Mickiewicza, Grunwaldzka 6, 60-780 Poznań, Poland.

nuclear magnetic resonance spectroscopy. Measurements in function of temperature of easily determined NMR parameters such as the width of the absorption line, its second moment, spin-lattice relaxation times in the laboratory and rotating frame allow often to find the microscopic parameters: molecular correlation times, and activation energies for motions characterising the polymeric systems.

This paper reports the results of broad line and pulse NMR experiments, carried on three furfuryl alcohol resins with different viscosity. The data are discussed in terms of molecular motion.

2. Experimental

Materials

Furfuryl alcohol used for this study was prepared in the Institute of Chemistry of our University by catalytic hydrogenation of furfural using Cu-Cr-Ba catalyst [3]. The product, purified by vacuum distillation, contained less than 0.05% of furfural. Furfuryl alcohol resins were obtained by polycondensation of furfuryl alcohol in the presence of hydrochloric acid as catalyst. A mixture of 100 ml furfuryl alcohol, 20 ml water and 2 ml 0.1 M hydrochloric acid cooled down to 0°C, was placed in a three-necked flask equipped with a water cooled reflux condenser, a mechanical stirrer and thermometer. The flask was ultrathermostatised at 60° or 70°C during a variable period of time. In consecutive experiments, polycondensation was terminated by cooling the products to room temperature. After separation of the aqueous phase, the polymer was washed 8 times with 150 ml of water to remove the catalyst and unreacted monomer. The residual water was subsequently stripped from the resin by heating to 40°C under reduced pressure in a rotatory evaporator.

TABLE I

Conditions of polycondensation for furfuryl alcohol resins and their viscosities η

Resin	Polycondensation process		η [cp] at 20°C
	Temperature [°C]	Time [min]	
PFA 70/1	70	60	$1.3 \cdot 10^3$
PFA 70/2	70	120	$1.25 \cdot 10^5$
PFA 60/3	60	510	$1.4 \cdot 10^6$

The investigated resins were labelled by their viscosity value, measured at 20°C with a rotational viscometer Rheotest 2. The samples were degassed and sealed in glass tubes under vacuum to prevent contact with atmospheric oxygen.

NMR Measurements

Proton magnetic resonance spectra were recorded by means of a Bloch type spectrometer RYa 2301 (USSR) in function of temperature over the range from liquid nitrogen

temperature to about 300 K. The experimental second moments of the absorption lines M_2 were calculated as mean values from at least four spectra, at all temperatures.

The spin-lattice relaxation times of protons were measured using a pulse spectrometer constructed in this laboratory operating at a frequency of 25 MHz [4]. The rotating frame data were obtained by using a radiofrequency field $H_1 = 8.0$ gauss. The relaxation times T_1 were measured by applying $180^\circ - t - 90^\circ$ pulse sequences (null method) and $T_{1\rho}$ by spin-locking of the nuclear magnetization applying 90° pulses followed by long pulses whose phases were 90° shifted from the first pulses.

3. Results and discussion

The NMR spectrum of a solid amorphous polymer usually consists of a single broad line, the shape of which may often be approximated to gaussian. When thermal motion causes the nuclei to change their positions rapidly enough, the local fields experienced by a given nucleus tend to be averaged out. The rate of the motion necessary to produce narrowing of the absorption line is of the order $10^4 - 10^5$ Hz.

In the case of furfuryl alcohol resins, the absorption lines at the lowest temperature in this study consist of one component. At higher temperatures, above 220 K for all samples,

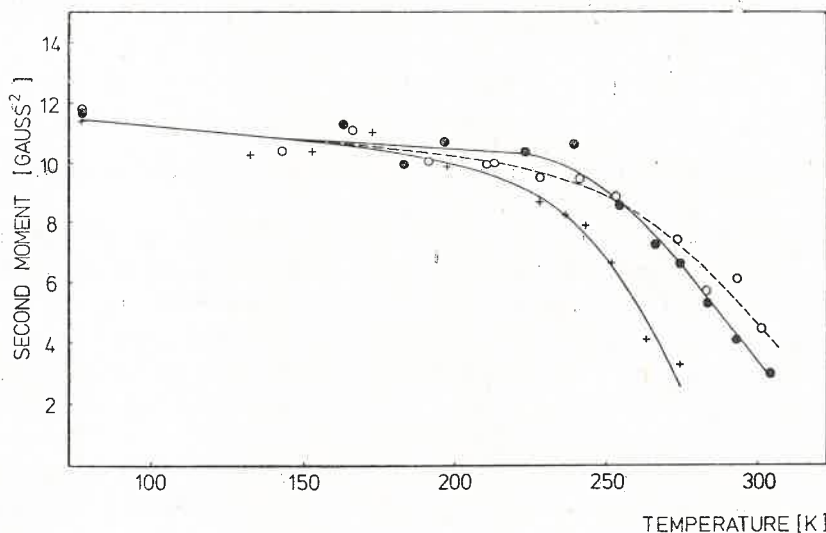


Fig. 1. Second moment (broad component) vs. temperature for furfuryl alcohol resins: + PFA 70/1, ● PFA 70/2, ○ PFA 60/3

the lines reveal two components: a broad and a narrow one pointing to the presence of two polymer phases with different mobility. The existence of two components of the NMR absorption line is characteristic for crystalline polymers where broad and narrow lines are attributable to a rigid, crystalline phase and to a mobile, amorphous one. The similar situation often observed in typical amorphous resins can be explained by the

distribution of molecular weight. Since the width of the narrow component of the absorption line is about 80 mG it seems reasonable to assume that it originates in low molecular weight compounds of the resin such as monomers or dimers having more freedom of motion than the higher ones which are rather rigid and give a broad component.

The temperature dependences of the second moment of the broad component for the resins investigated are shown in Fig. 1. The shape of this component was approximately gaussian making possible its separation from the experimental spectrum. It is seen in Fig. 1 that the second moment, for all resins, exhibits two distinct regions: a low temperature region where a small gradual decrease in the second moment is observed, and a high temperature region, where the decrease in second moment is larger and faster.

The change in second moment in the low temperature region is lower than 2 gauss² and can be attributed to small rotational oscillations of the polymer chains. The marked decrease in second moment in the high temperature region, greater than 6 gauss² for all samples, results from presumably more pronounced molecular motions. Information about

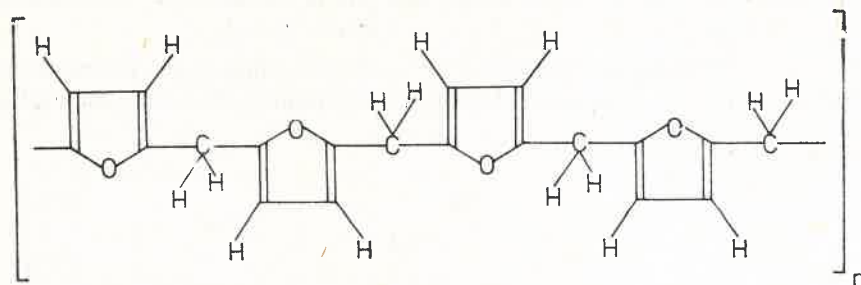


Fig. 2. Assumed schematic arrangement of furan rings and methylene groups

the type of molecular motions can be obtained by comparing the experimental and theoretical values of the second moment. In the case of the furfuryl alcohol resins, however, the lack of data concerning the detailed polymer structure makes difficult exact calculations of the second moments. Thus, such a comparison appears but of limited use in deciding what types of motion occur. Some approximate calculations of the second moment for the rigid lattice have, however, been made with the use of the Van Vleck equation [5], and also for the case in which chain rotation occurs.

The intramolecular contribution to the rigid lattice second moment was estimated assuming a planar configuration of the polymer chain and a relative arrangement of furan rings with respect to one another and to the methylene group (Fig. 2) with the following interproton distances: 1.78 Å in the methylene group and 2.95 Å in the furan ring. The value of this contribution thus obtained was 7.4 gauss².

The intermolecular contribution to the second moment cannot be theoretically calculated since the relative orientations and separations of the chains are not known. Assuming that the experimental rigid lattice value at liquid nitrogen temperature equals 11.7 ± 0.3 gauss² for all samples, the intermolecular contribution can be determined as a difference of $11.7 - 7.4$ gauss² amounting 4.3 gauss², which is a reasonable value for polymers [6-8].

Since the interproton vectors of the methylene groups giving the main contribution to the second moment are perpendicular to the axis of rotation it has been reasonable to assume that rotation of the chain about its axis reduces the intramolecular and intermolecular contributions to the second moment to 1/4 and 1/3 of the rigid lattice value [9, 10], respectively, resulting in a value of 3.3 gauss² for the second moment modulated by this motion. From a comparison of the above value with the lowest experimental second moments at higher temperatures, about 3.5 gauss², it is concluded that rotations of chains really take place. One would expect the experimental second moment to continue to decrease with increasing temperature because motions other than rotation become more important.

Further information about the molecular motions can be derived from measurements of nuclear magnetic relaxation times, which describe the approach to the thermal equilibrium between the nuclear spin system and the environment (lattice). The relaxation rate depends on the effectiveness of local, time-dependent magnetic fields, such as those arising from the motion of neighbouring spins, inducing transitions between the nuclear spin states. This process is characterized by the spin-lattice relaxation times T_1 and T_{1e} in the laboratory frame and in the rotating frame, respectively.

For a system of protons the relaxation rates in the laboratory and rotating frames take the form [11, 12]:

$$\frac{1}{T_1} = A \left[\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right], \quad (1)$$

$$\frac{1}{T_{1e}} = \frac{3}{2} A \left[\frac{\tau_c}{1 + 4\omega_1^2 \tau_c^2} \right], \quad (2)$$

where τ_c is an appropriate molecular correlation time, A is a constant related to the second moment, whereas ω_0 and $\omega_1 = \gamma H_1$ are Larmor frequencies in the respective reference frames.

If the motion responsible for relaxation can be described by an Arrhenius rate equation, the plot of $\ln T_1$ (or $\ln T_{1e}$) versus the inverse temperature will reveal a symmetric V-shaped minimum with slopes proportional to the activation energy for this motion. The minima of T_1 and T_{1e} occur at temperatures for which $\tau_c \approx \omega_0$ and $\tau_c \approx \omega_1$, respectively, which allows to observe the same kind of motion at different temperatures.

The temperature dependences of the proton relaxation times (in $\log T_1$ vs $1/T$ scale) for the resins investigated are shown in Fig. 3. A pronounced feature of the experimental T_1 -curves is a high-temperature minimum, which shifts to higher temperatures and increases slightly in intensity as the viscosity of the resins is increased. At lower temperatures, all resins exhibit another flat minimum at approximately the same temperature. A similar feature appears in the T_{1e} behaviour; however, at accessible low temperatures, only a small decrease in T_{1e} is observed.

The high temperature minimum can be assigned to a chain rotation, inducing a marked decrease in the second moment. Assuming validity of the Arrhenius relation $\tau_c = \tau_0 \exp(E_a/RT)$ the activation energies E_a of the rotational chain motion from T_1 , T_{1e} and M_2 measurements were calculated and are summarized in Table II. The first

and second columns contain the energies deduced from the slope of T_1 and T_{1e} , plotted against the inverse temperature. The energy in the next column was found from knowledge of correlation times at the T_1 and T_{1e} minima. Estimation of the activation energy from wide-line NMR measurement by using Gutowsky and Pake's equation [9] was impossible

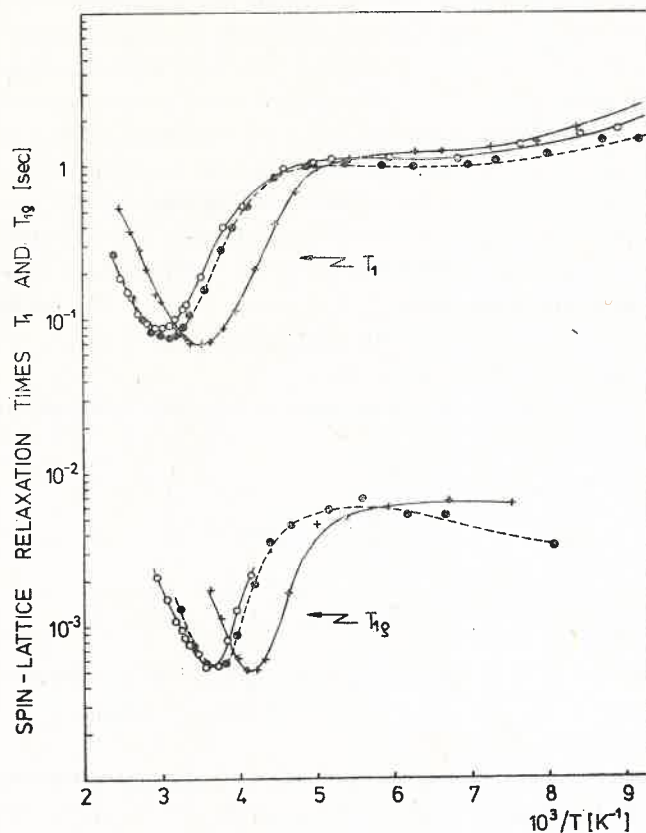


Fig. 3. Spin-lattice relaxation times vs inverse temperature for furfuryl alcohol resins: + PFA 70/1, ● PFA 70/2, ○ PFA 60/3

because of difficulties besetting the separation of the broad component from the experimental spectra, recorded above the transition region. This was done (column four) by using the simplified Waugh-Fiedin relation [13] taking arbitrary as transition temperature that

TABLE II

Activation energies E_a [kcal/mol] and distribution parameters β for furfuryl alcohol resins

Resin	$E_a(T_1)$	$E_a(T_{1e})$	$E_a(\tau_c)$	$E_a(M_2)$	β
PFA 70/1	5.5	5.9	19.6	9.4	0.28
PFA 70/2	6.1	6.3	20.6	10.3	0.30
PFA 60/3	4.7	6.7	21.6	10.5	0.22

for which the second moment equals a half of its value observed at liquid nitrogen temperature. The large difference between the value of the activation energy calculated from the known correlation times and the other values (Table II) can be explained as usually for polymeric systems [14-16] by assuming the existence of a wide distribution of correlation times for the rotational motion considered. This seems reasonable for chemically heterogeneous resins having a wide distribution of molecular weights.

Connor [14] showed that, for a motion described by a correlations time distribution, the activation energy value estimated from the slope of $\ln T_1$ (or $\ln T_{1e}$) versus the inverse temperature dependence is lower than the energy really required to activate the motion. It depends on the width of the distribution according to the relation [15]

$$E_a = \pm \frac{R}{\beta} \frac{\partial(\ln T_1)}{\partial(1/T)}, \quad (3)$$

where the parameter characterizing the width of the distribution is $0 < \beta < 1$. For a correlation time distribution described by a symmetric density function the minimum of T_1 does not change its position in the temperature scale. Therefore one can assume that the energy

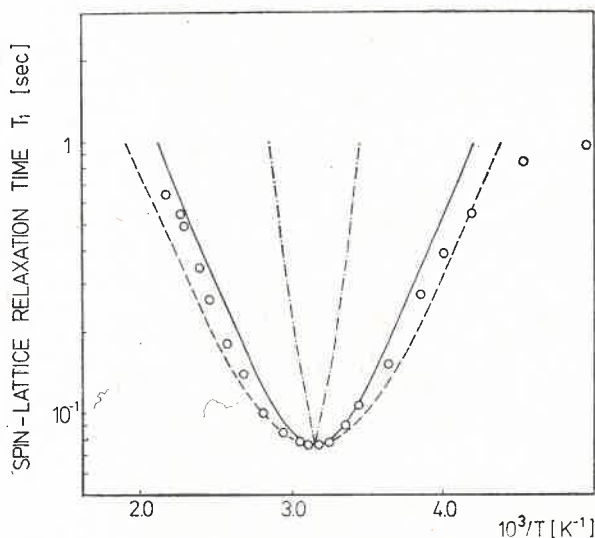


Fig. 4. Theoretical fits of high temperature T_1 results for furfuryl alcohol resin PFA 70/2: \circ experimental, - - - - BPP, ——— Fuoss-Kirkwood distribution, - · - · - Cole-Cole distribution

calculated from correlation times at T_1 and T_{1e} minima correctly characterizes the motion considered. The widths of the distribution functions for all resins were found and are given in Table II.

An attempt was made to fit the theoretical calculations to the experimental data in the region of the high-temperature minimum. Results of fitting by means of various theoretical expressions are shown in Fig. 4 for PFA 70/2 resin. Theoretical values of T_1

were derived from the BPP expression (Eq. (1)) and its modified forms which include the effect of distribution of correlation times [14]:

$$\frac{1}{T_1} = A' \frac{\beta}{\omega_0} \left[\frac{(\omega_0 \tau_c)^\beta}{1 + (\omega_0 \tau_c)^{2\beta}} + 2 \frac{(2\omega_0 \tau_c)^\beta}{1 + (2\omega_0 \tau_c)^{2\beta}} \right] \quad (4)$$

for the Fuoss-Kirkwood function, and

$$\frac{1}{T_1} = \frac{A''}{\omega_0} \left[\frac{\cos \left[\frac{\pi}{2} (1 - \beta) \right]}{\cosh(\beta \ln \omega_0 \tau_c) + \sin \left[\frac{\pi}{2} (1 - \beta) \right]} + 2 \frac{\cos \left[\frac{\pi}{2} (1 - \beta) \right]}{\cosh(\beta \ln 2\omega_0 \tau_c) + \sin \left[\frac{\pi}{2} (1 - \beta) \right]} \right] \quad (5)$$

for the Cole-Cole function. Above, A' and A'' as well as A in equation (1) are treated as fitting parameters at T_1 minimum. It can be seen that both theoretical curves derived from the expression including the effect of a distribution of correlation times fit much better experimental results than the curve obtained according to the expression without a distribution of correlation times. Similar results of fitting were obtained for other investigated resins.

The origin of the flat low temperature minimum is not obvious but a tentative assignment in terms of methyl endgroup rotation seems to be reasonable taking into account the temperature at which the minimum occurs and Barr's and Wallon's [1] study, which points to the presence of such groups in furfuryl alcohol resins.

The insignificant slope of the low temperature side of this minimum is thought to result from the presence of a small amount of paramagnetic centres, giving a temperature independent contribution to the relaxation rate. It seems likely that a spin-diffusion mechanism is operative. Magnetization is thus transferred along the polymer chains to the methyl endgroups or paramagnetic centres which have good thermal contact to the lattice.

The authors thank Mr. Z. Szuba for carrying out the polycondensation process, Dr. K. Jurga for assistance with relaxation times measurements and Professor Z. Dudzik for valuable discussions.

REFERENCES

- [1] J. B. Barr, S. B. Wallon, *J. Appl. Polym. Sci.* **15**, 1079 (1971).
- [2] E. M. Wewerka, *J. Appl. Polym. Sci.* **12**, 1671 (1968).
- [3] Z. Dudzik, L. Górski, L. Trzasański, W. Mitura, R. Maliński, F. Puchalski, Z. Duda, J. Charpula, Cz. Szlakowski, *Pol. Pat.* 67.674 (1969).
- [4] Z. Pająk, K. Jurga, S. Jurga, *Acta Phys. Pol.* **A45**, 837 (1974).
- [5] J. H. Van Vleck, *Phys. Rev.* **74**, 1164 (1948).
- [6] D. W. McCall, W. P. Slichter, *J. Polym. Sci.* **26**, 171 (1957).
- [7] W. P. Slichter, E. R. Mandell, *J. Appl. Phys.* **29**, 1438 (1958).
- [8] K. M. Sinnott, *J. Polym. Sci.* **42**, 3 (1960).
- [9] H. S. Gutowsky, G. E. Pake, *J. Chem. Phys.* **18**, 162 (1950).

- [10] E. R. Andrew, *J. Chem. Phys.* **18**, 607 (1950).
- [11] N. Bloembergen, E. M. Purcell, R. W. Pound, *Phys. Rev.* **73**, 679 (1948).
- [12] G. P. Jones, *Phys. Rev.* **148**, 332 (1966).
- [13] J. S. Waugh, E. I. Fiedin, *Fiz. Tverd. Tela* **4**, 2233 (1962).
- [14] T. M. Connor, *Trans. Faraday Soc.* **60**, 1574 (1964).
- [15] T. M. Connor, in *NMR Basic Principles and Progress*, Vol. 4, Springer-Verlag, Berlin 1971, p. 247.
- [16] T. M. Connor, *J. Polym. Sci.* **A2**, **8**, 191 (1970).