Measurements of nuclear magnetic relaxation in some vinyl polymers during the conversion process

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It is well known that the N.M.R. techniques have been variously employed for studying the properties of polymers [1]. In particular some groups of researchers [2-9] have studied the line width, some [8, 10-13] have investigated the structure of the resonance line for those polymers in which amorphous and crystalline regions are present; some [3, 14-17] have studied how the line width varies when the polymer is subjected to temperature changes such as to induce transitions.

Other researchers [18] have measured the chemical shift of the resonance signal of some vinyl polymers and have been able to bring out small differences which the stereospecificity produces in the high resolution spectrum [19].

By means of spin-echo techniques it has been possible to measure the nuclear relaxation times of several polymers [20-23]; in particular the presence of more than one phase in the structure of some polymers has been demonstrated [22, 24, 25] by studying the return of the nuclear magnetization components to thermal equilibrium.

It can be seen that a great number of researchers have been concerned with the properties of polymers; very little attention has been however devoted to their formation process. We started a systematic investigation of the conversion process of some vinyl monomers into the corresponding polymers by measuring the nuclear relaxation times T_1 and T_2 with the technique of fast adiabatic passages. A study of the γ ray induced polymerization of ethyl acrylate has been performed by Shibata et al. [26] by means of line width measurements; we believe however that measurements of relaxation times are more significant and can give a clearer insight into the polymerization process.

The vinyl compounds we have hitherto studied are styrene, methyl-metacrylate and vinyl acetate. The mass polymerization of styrene and

of M.M.A. has been obtained either by keeping the sample at 90° C or by exposing it to ultraviolet light from a mercury-arc lamp, whereas the mass polymerization of vinyl acetate has been obtained without subjecting the sample to any particular treatment. It is well known that the polymers of these compounds are soluble in the corresponding monomer: the percent of polymer present in the syrup during the conversion process has been estimated from the increase of its refraction index measured using a standard sodium light refractometer [27].

The compounds we have studied have several non-equivalent protons and, in principle, should have different T_1' s. However the return of the magnetization to its equilibrium value, which we have studied with a method previously described [28], has been found exponential within experimental error. This means that the T_1' s of the various non-equivalent protons are little different from one another; we shall therefore speak of spin-lattice relaxation time T_1 of the monomer. During the polymerization process however, we have observed two spin-lattice relaxation times T_1 very different from one another. The existence of these two spin-lattice relaxation times has been revealed with the technique of adiabatic passages.

It is known [28] that if one performs two successive fast adiabatic passages through the resonance separated by an interval of time τ between them, the height of the signal due to the second passage depends on τ. It is possible to choose an interval of time τ between the two passages such that the second signal is null; this happens for $\tau = T_1 \, ln \, 2$.

If however two groups of protons having spin-lattice relaxation times T_{1l} and T_{1s} differing enough from one another are present in a sample, it is possible to choose such experimental conditions that the passage through the resonance is fast for the protons whose spin-lattice relaxation time T_{1l} is longer and it is slow for the protons whose spin-lattice relaxation time T_{1s} is shorter. Under these conditions the signal due to the second passage can never be made null. More precisely if $\tau = T_{1l} \, ln \, 2$ this signal has the shape of a dispersion signal: it is a slow passage signal due to the protons with the shorter relaxation time.

In figure 1 three recordings performed on a sample of styrene for three different values of τ are reproduced; the percent of polymer in the syrup styrene-polystyrene was 30%.

By measuring the length of the time interval τ for which the second signal is a dispersion signal it is possible to evaluate the spin-lattice relaxa-

tion time T_{1l}.   One can see from figure **1** that such an evaluation can be made with a fair accuracy.
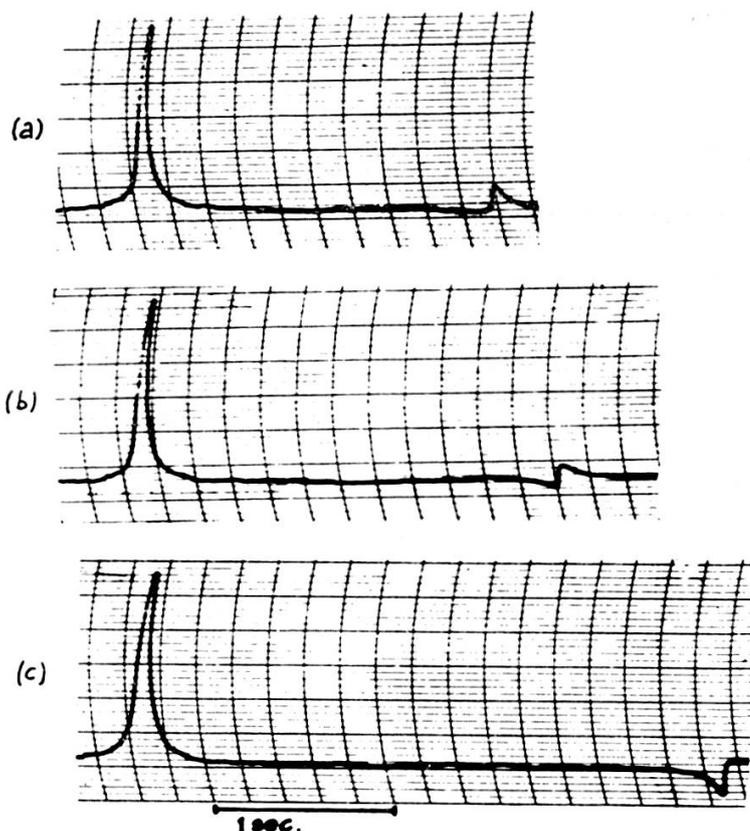

Fig. 1.

Three recordings obtained for a sample of styrene with 30% of polystyrene.   In recording *a)* the time elapsed between the two adiabatic passages is $\tau < T_{1l} \, ln \, 2$; in recording *b)* $\tau = T_{1l} \, ln \, 2$ and in recording *c)* $\tau > T_{1l} \, ln \, 2$.

An accurate enough measurement of the relaxation time T_{1s} is also possible.   We choose the experimental conditions so that the passage through the resonance is fast with respect also to this relaxation time and then we perform a succession of passages so frequent that the signals due to the protons with relaxation time T_{1l} are practically cancelled out owing to a saturation effect.   In these conditions we obtain a sequence of fast adiabatic passage signals relative to the protons with shorter relaxation time only.   From such a sequence we are able to evaluate T_{1s} [29].

Considerations of a general character and the fact that the height of the dispersion signal increases with increasing concentration of polymer in the monomer-polymer syrup lead us to believe that the relaxation time

T_{1l} is to be attributed to the monomer protons and the time T_{1l} to the polymer protons.

The experimental results we have obtained for the spin-lattice relaxation time T_{1l} of styrene during polymerization are shown in figure 2 and 3. The polymerization, both the thermal one and that induced by ultraviolet rays, as well as the measurement of the relaxation times took place in presence of oxygen.
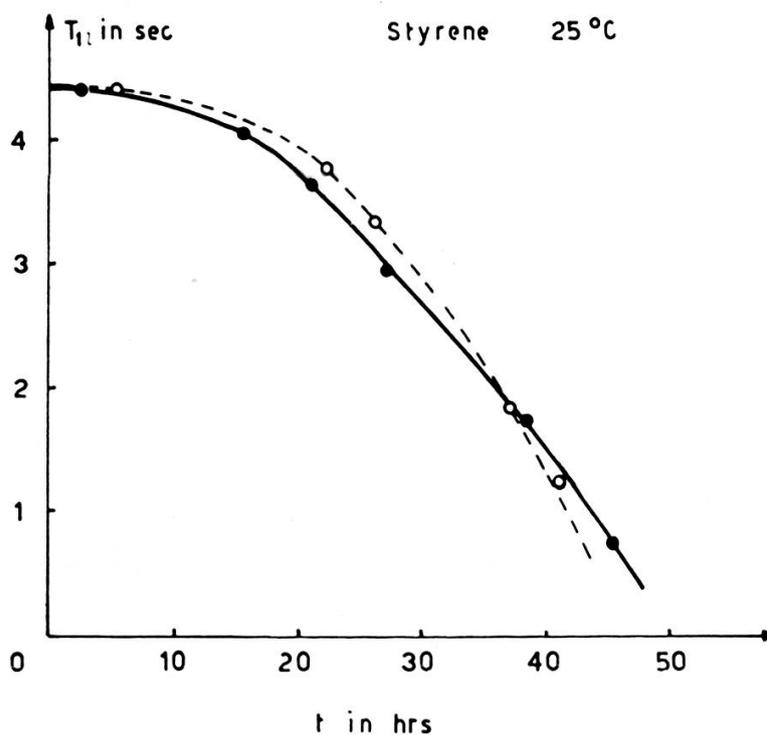

Fig. 2.

Spin-lattice relaxation time T_{1l} for styrene vs. time t of duration of the thermal treatment (full line) and of the exposition to ultraviolet light (dashed line). The sample was kept continuously at 90° C and under ultraviolet exposition respectively, except the short interruptions necessary for the measurements. The measurements were performed at 25° C.

In Table I the percent of polymer and the viscosity of the syrup during thermal polymerization of styrene are shown. For ultraviolet light induced polymerization only the percent of polymer is given: measurements of viscosity were occasionally performed and showed an increase of the viscosity of the syrup like that found during thermal polymerization.

From the results shown in Table I it is possible to see that the polymer concentration increases with time following an exponential law, in agree-

ment with the general assumptions about the polymerization kinetics one is allowed to make [30, 31], provided that a short inhibition period is taken into account. These results are consistent with those obtained by several researchers [27].
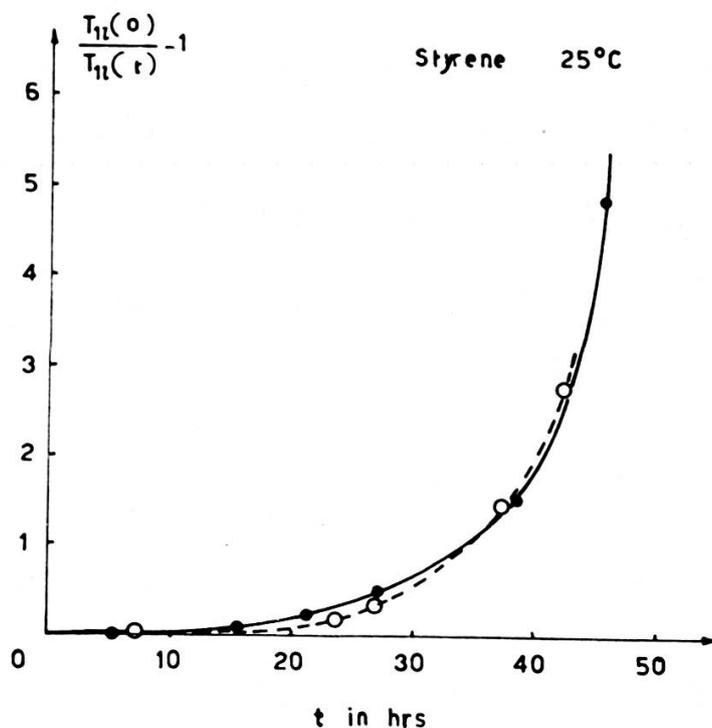
Fig. 3.

$T_{1l}(O)/T_{1l}(t) - 1$ vs. time t of duration of the thermal treatment (full line) and of the exposition to ultraviolet light (dashed line) for styrene.

TABLE I

Thermal polymerization			Ultraviolet induced polym.	
t in hrs	%	η in poises	t in hrs	%
0	0	$0.73 \ 10^{-2}$	0	0
3	0	$0.73 \ 10^{-2}$	2	0
4.5	——	$22 \ \ \ 10^{-2}$	4	0
14.5	13	32	7	3
17.5	——	≈ 60	20	15
20	23	≈ 200	23.5	22
24	32		26.5	27.5
32	50		42.5	53
63	≈ 90			

We see that, during the first twenty hours of the process, the viscoty increases of several orders of magnitude, while the spin-lattice relaxation time T_{1l} decreases only slightly. It is not possible therefore to assume that during the polymerization process the spin-lattice relaxation time T_{1l} decreases with the increasing of viscosity following a law of the form $T_{1l} \propto \dfrac{k}{\eta}$, as required by the theory of B.P.P. [32]. We may say that the monomer molecules although trapped among the polymer chains retain most of their degrees of freedom.

The polymerization of M.M.A. was induced by ultraviolet light and took place in vacuo: in fact oxygen strongly inhibits this polymerization. The spin-lattice relaxation time of the M.M.A. monomer at the beginning of the conversion process was 7,2 sec.; after a 120 hour exposition to ultraviolet light it had decreased to 0,5 sec.

The dependence of $T_{1l}(O)/T_{1l}(t)-1$ on the exposition time is similar to that already discussed for styrene.

As regards the vinyl acetate we have so far studied only its polymerization at room conditions and in the absence of atmospheric oxygen. The time necessary for this polymerization has been several months: the plot of T_{1l} vs. t is shown in figure 4.

Measurements of spin-spin relaxation time T_2 [33] were occasionally performed for all three the compounds only at low percentages of polymer: the T_2 we measured is relative to the protons with longer T_1 only and was found to be in general little different from the corresponding T_{1l}.

As regards the shorter spin-lattice relaxation time, which we attributed to the polymer protons, accurate enough measurements were possible only for high concentrations of polymer. Because of the experimental error, which is still very large, the values we have obtained are only indicative.

For a sample of styrene with 60% of polymer we found $T_{1s} = 3.10^{-2}$ sec. For a sample of M.M.A. with 50% of polymer we obtained $T_{1s} = 1,8.10^{-2}$ sec. As the polymerization proceeded these values have been decreasing slightly.

As to the vinyl acetate we found $T_{1s} = 19.10^{-2}$ sec. 117 days after the beginning of the polymerization; after 8 more days we found $T_{1s} = 5.10^{-2}$ sec.

These values we found for T_{1s} seem to us to be larger than those one would expect from considering the size of the polymer chains and the very high values of the viscosity. It must therefore be admitted that also at very high polymer concentrations some hindered motions of the chains are possible.

The results hitherto obtained seem to point out that measurements of nuclear relaxation can give new information for a microscopic interpretation of the polymerization process.   Besides the measurement of the nuclear relaxation times seems to be more effective than the measurement of the line width of the resonance signal.
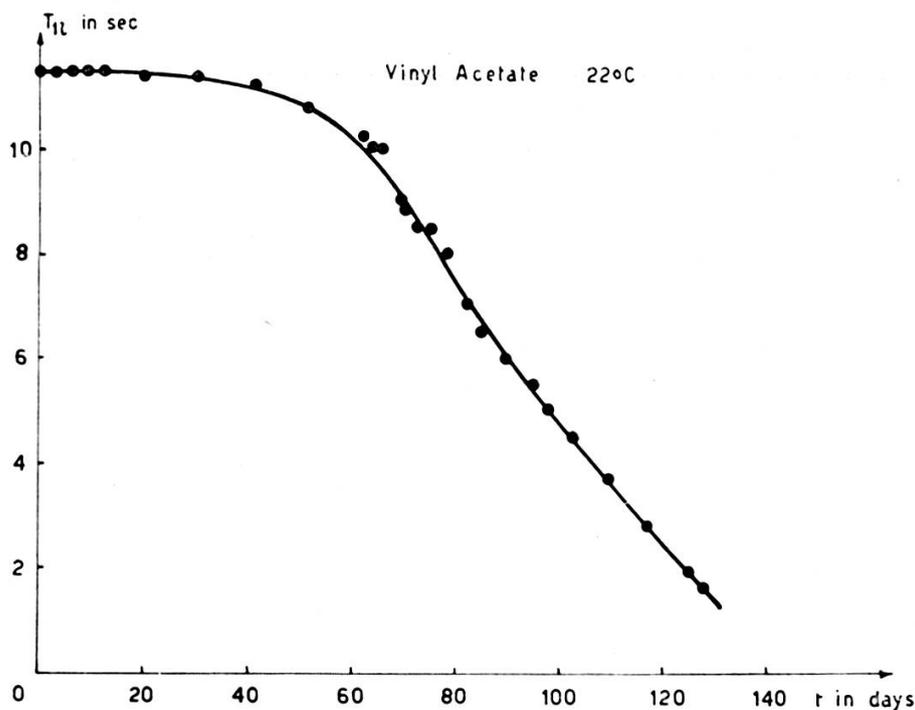

Fig. 4.

Spin-lattice relaxation time T_{1l} for oxygen-free vinyl acetate vs. time t elapsed from the beginning of the polymerization process.

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