NMR AND OTHER RELAXATION METHODS FOR THE INVESTIGATION OF DYNAMIC AND THERMODYNAMIC TRANSITION POINTS IN POLYMERS

J.Johan Lindberg [x] and Pertti Törmälä [xx]

[x]   Department of Wood and Polymer Chemistry, University of
      Helsinki, SF-00170 Helsinki 17, Finland
[xx] Institute of Materials Science, Tampere University of
      Technology, P.O.B. 527, SF-33101 Tampere 10, Finland

Abstract - Various aspects of polymer relaxation effects and their indication by NMR especially are discussed. It is concluded from the data so far published that the NMR method permits good resolution of $T \ll T_g$ relaxations but only under certain conditions between $T_{\alpha,c}$, T_g and $T < T_g$ - relaxations.

INTRODUCTION

The relaxation of a system means the time dependent return to equilibrium after a disturbance caused by an external force. A large number of important physical properties of natural and synthetic polymers have been found to be time dependent changes or relaxation phenomena. Examples of such phenomena are: mechanical properties (tensile, flexural, compressive, impact and yield strength, creep, stress relaxation and fracture phenomena), thermal properties (glass transition T_g, melt transition), electrical properties (conductivity), solid state reactivity and diffusivity, melt rheology, crystallization and solution properties (1-3).

In general, various relaxation measurements give correlative results, especially if the time scale and molecular level of the effect are taken into consideration.

GENERAL CLASSIFICATION OF FORMS OF RELAXATION IN SOLID STATE

Relaxation processes in polymers can, on the molecular level, be considered as the movement of molecular chains or segments or groups of polymer molecules. Since the definition of the phenomena are not associated with molecular mechanism there has been a lot of confusion in dealing with experimental results.

It is therefore highly desirable to designate a relaxation process by a nomenclature based on the molecular mechanism concerned, even if some ambiguity still remains. We have therefore adopted in this discussion the following nomenclature of classification which is proposed by Boyer (4):

(i) T_g-relaxation is the process occurring at the glass transition temperature in amorphous polymers. It is considered to be the primary process and referred to as the glass-rubber transition process. This relaxation process results from large-scale conformational rearrangements of the polymer chain back-bone and occur through a mechanism of hindered rotation or libration around the main-chain bonds.

(ii) $T_{\alpha,c}$ -relaxation is the process which is confined to the crystalline phase of the polymer and is caused by its motion. It is observed at high crystallinity (>60-70 %) in a temperature region which is generally higher than that of T_g-relaxation. So far it seems to be caused by distributed relaxations in which the main chain is placed under various degrees of periodic bending comprising quite long chain segments, e.g. in polyethylene about 12 CH_2-units.

(iii) $T < T_g$-relaxation is the process below T_g, and is considered to be the secondary process. It occurs in crystalline defect area and the glassy polymer phase. This relaxation process is local and results from hindered rotation of the polymer back-bone segments.

(iv) $T \ll T_g(1)$-relaxation is the process below T_g which is observed at cryogenic temperatures. It appears to be associated with locally disordered regions of the polymer, such as inner motions in polymer chain side groups.

(v) $T \ll T_g(2)$-relaxation is observed in some polymers at even lower temperatures. It can be attributed to similar reasons as for the $T \ll T_g$ (1)-relaxation.

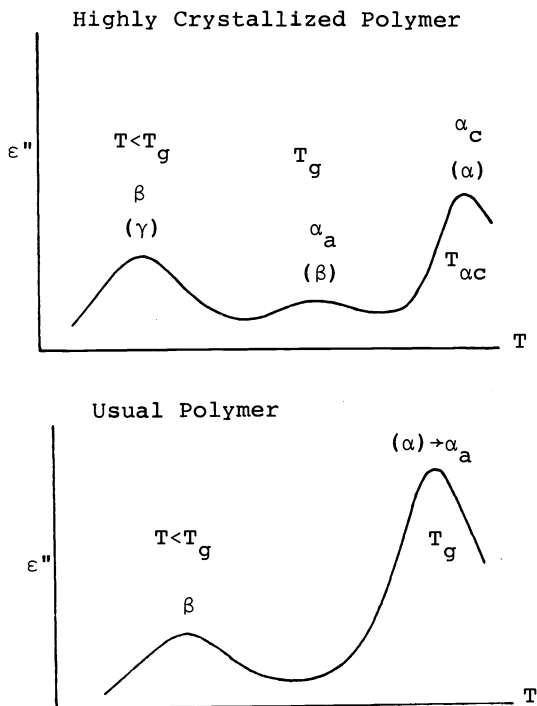A range picture of the nature of some of the above processes is given for polyethylene (5) in Figure 1.

Fig. 1. Temperature dependence (schematic) of loss tangent for highly crystallized polyethylene. The old classification (α_c, α_a, β, etc.) is indicated in addition to the new classification of relaxations proposed by Boyer (4).

THERMODYNAMICS AND RELAXATION BEHAVIOUR

An attempt to describe the relaxation behaviour in terms of thermodynamics is a far from easy task. Thus, for instance, an intensive debate has been conducted during the past few years to explain the relationship between thermodynamic and dynamic behaviour in the glass transition region. Thus, in the case of polymers an attempt has been made to explain the nature of the amorphous glassy polymer in terms of a first order thermodynamic transition (6), kinetically in terms of a two state system (7), in terms of the hole theory (8) and in terms of an intrinsic temperature (9), etc.

It is evident from experimental data that polymer glasses in the transition region exhibit a type of behaviour which partially resembles that of a first order thermodynamic transition. Thus, when annealed glassy polymers are heated through the transition region, an abrupt, almost discontinuous increase takes place in volume V and enthalpy ΔH before approaching the steady state conditions above T_g. The thermal expansion coefficient, α, and the specific heat, C_p, also pass through discontinuities before reaching, at higher temperatures, a value characteristic of the supercooled liquid state (10) (cf. Fig. 2).
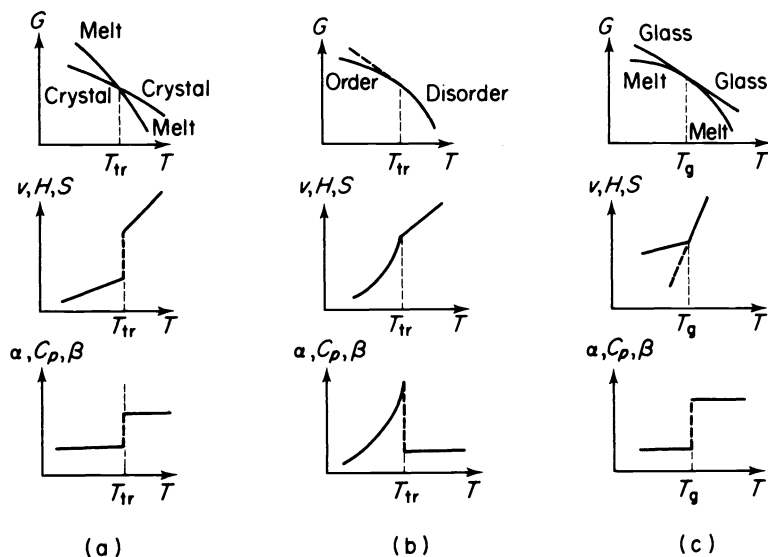
Fig. 2. A comparison of different types of transition processes:
(a) first-order, (b) second-order, and (c) vitrification pro-
cess. Notation: G is the free energy, H is the enthalpy, S is
the entropy, α is the coefficient of expansion, β is the com-
pressibility, C_p is   the specific heat, T_g is the glass transi-
tion temperature, T_{tr} is the transition process temperature.

RELAXATION INVESTIGATIONS WITH NMR (11)

In magnetic resonance spectroscopy the interaction of electron or nuclear
spin systems with an external static magnetic field is measured. Therefore
these techniques are also sensitive to relaxation processes. The return of
the spin system to the equilibrium with the magnetic field is conventionally
characterized by three relaxation times: the spin-lattice relaxation time
T_1, which describes the radiationless transition from an excited spin level
to the ground state - the excess energy being transferred to the surroundings
(lattice), i.e. to the phonon field. The polarization of an excited spin
system in the direction of the external field decays in this process at a
rate described by T_1.

The other relaxation time referred to as spin-spin or transversal relaxation
time, T_2, describes the mutual interaction between individual spins; it go-
verns the decay of the magnetization components perpendicular to the direc-
tion of the polarizing field. T_1 and T_2 can be measured e.g. by the pulse
technique.

In the case of dipolar relaxation when log T_1 is plotted against reciprocal
temperature, a V-shaped curve is obtained with a minimum at

$$\omega_L \tau_c \approx 0.68 \tag{1}$$

where τ_c is the correlation time of the system, and ω_L is the Larmor
frequency.

For the rotating frame spin-lattice relaxation time we have (12)

$$\frac{1}{T_{1\rho}} = K(\frac{3}{2}\frac{\tau_c}{1+4\omega_{eff}^2\tau_c^2} + \frac{5}{2}\frac{\tau_c}{1+\omega_{eff}^2\tau_c^2} + \frac{\tau_c}{1+4\omega_{eff}^2\tau_c^2}) \qquad (2)$$

where K is a constant for a given nucleus. At the minimum of the log $T_{1\rho}$ versus 1/T curve we have

$$\tau_c \approx 1/\omega_{eff} \qquad (3)$$

$T_{1\rho}$ is the spin-lattice relaxation time in a frame rotating at resonance frequency, thus giving information regarding processes leading to correlation times reduced by a factor of 10^7-10^8. A typical temperature dependence of T_1, T_2 and $T_{1\rho}$ for natural rubber are given in Figure 3 (13).
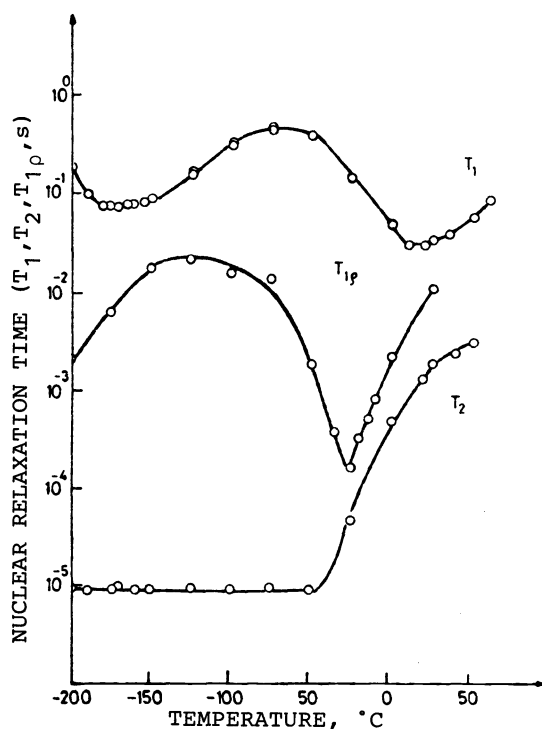

Fig. 3. Typical temperature dependence of (T_1), spin-spin (T_2) and rotating frame spin-lattice ($T_{1\rho}$) relaxation times of natural rubber.

The principles discussed so far may be applied to various nuclear as well as to electron spin systems. Most experiments on polymers are done by proton resonance. However ^{13}C, ^{19}F, ^{15}N and ^{29}Si nuclei also have magnetic moments. This makes NMR useful for distinguishing between different chemical groups and studying their motion separately. The pulse techniques in NMR are rather well developed and extend to a great extent the usefulness of the instruments. It is possible, using the same instrument for instance, to measure T_1 and $T_{1\rho}$ from the same sample with the nuclei ^{13}C and ^1H.

HIGH RESOLUTION ^{13}C NMR IN SOLIDS

It is impossible in this short review to give a comprehensive description of such a broad topic as the current developments in the techniques of NMR spectroscopy which are of relevance to the polymer chemist. The reader is referred
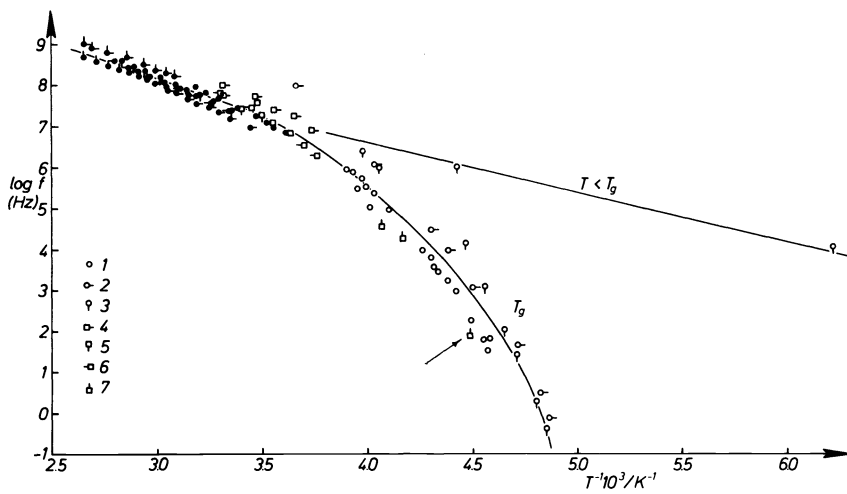
Fig. 4. Relaxation map of natural rubber: dielectric, mech-
nical, ESR and NMR (□-, ⊡,-□,⊔) data (20).

Fig. 5. Relaxation map of isotactic polypropene: dielectric,
mechanical, ESR and NMR (△,⊿,⋀,⋊) data (20).

to critical reviews on the subject (14)(15)(16).

The line broadening caused by the dipole-dipole interaction, e.g. in the solid state, may be removed by high power spin decoupling and the magic angle rotation technique. Magic angle rotation means mechanically spinning the sample at an angle of 54.7° to the polarizing field with an angular frequency of 1-6 kHz depending on the magnitude of the field.

Of the various techniques available at the present time the following seem to be of particular value to polymer chemistry:

(i)   dipolar decoupling cross-polarization magic angle rotation experiments on solids
(ii)   multinuclear studies
(iii)   high field operation

From the point of view of the present problem, the proton relaxation parameters T_1 and $T_{1\rho}$ are very valuable information sources and should be obtained prior to attempting ^{13}C NMR work. However, the above techniques have also made it possible to obtain high-resolution data of natural abundance ^{13}C NMR in solids with a sufficiently detailed structure to permit the relaxation behaviour of individual carbon lines to be studied. In particular there are several relaxation processes which can occur in cross-polarization NMR experiments with the potential to yield information about molecular motions and interactions.

A typical example of this is the work of Steiskal and co-workers (17), who found that $T_{1\rho}$ (C) values for some crystalline and amorphous polymers are dominated by spin-lattice effects, while crystalline polymers relax through a spin-spin mechanism. Thus, the T_1 relaxation is seldom solely determined by a single motion of a single intermolecular interaction. Nevertheless, if the dominant source of relaxation is known, T_1 can provide useful information. Similarly, $T_{1\rho}$ (C) can be used to provide information about those classes of systems in which its dominant source is clear, even if a full theoretical analysis has not yet been carried out.

It seems clear, however, that NMR only at relatively low molecular weights tells us something about chain end relaxations owing to the generally low concentration of these elements in the polymer structure (18).

The above statements mainly refer to high resolution NMR, but they are also valid when we consider broad line NMR spectrometry, where second moment measurements provide information especially regarding molecular motions in the solid state, intermolecular distances and crystalline parameters.

        THE RELAXATION MAP (1)(19)

The comparison of dynamic and thermodynamic data of polymers over wide temperature range with the ones obtained in NMR and ESR measurements illustrates the applicability of the analytical methods. The above comparison of dynamic data may be conveniently carried out by means of Arrhenius plots, i.e. plots of frequency of relaxation, log f, versus reciprocal temperature, 1/T (20). As correlation time τ_c and frequency values f are interrelated by the equation, $f = (2\pi \tau_c)^{-1}$, it is possible to establish correlations between a large number of methods. The usefulness of the above principle is easily seen from the following examples.

The relaxation map of dielectric and mechanical data, NMR data and ESR spin probe data of natural rubber are summarized in Figure 4. The NMR data sofar reported are generally located over the range log f = 4 to 8, where it is possible to draw a distinction between T_g and $T < T_g$ transitions especially in the low frequency range. The $T_{1\rho}$-data of McCall and Falcone (13) at log f about 2 are of special interest. They indicate a rather low relaxation time measured by NMR and a high resolution in identification of type of relaxation correspondingly.

Relaxation data for isotactic polypropene, PP(i), with a crystallinity of about 60 %, are presented in Figure 5. It is evident that a good resolution between $T_{\alpha,c}$, T_g and $T<T_g$ transitions are obtainable only at frequencies log $f<4$. The NMR data sofar presented permit a distinction to be drawn between high temperature (T_g, $T_{\alpha,c}$, $T<T_g$) and low temperature effects ($T \ll T_g$). A similar behaviour is also observed for other polymer systems (20).

CONCLUSIONS

The above results indicate that NMR spectroscopy may be used as an indicator of relaxation regions in polymer solids. Being a typical medium frequency method between ESR spin probe or label methods (log $f>6$) and low frequency dielectric and mechanical and calorimetric methods (log $f<5$) it permits at least a straight distinction to be made between $T<T_g$ and $T \ll T$ realaxations, but only partially between $T_{\alpha,c}$, T_g and $T<T_g$ relaxation effects depending on the polymer structure in question. The new NMR techniques which have been developed do not seem to alter the above statements, although they permit a more exact determination of relaxation data.

REFERENCES

1. N.G. McCrum, B.E. Read and G. Williams, Anelastic and Dielectric Effects in Polymer Solids, Wiley, Bristol (1967).
2. P.I. Vincent, Polymer, 15, 111 (1974).
3. P. Törmälä, G. Weber and J.J. Lindberg, Rheol. Acta, 17, 201 (1978).
4. R.F. Boyer, J. Polymer Sci., Symposium No. 50, 189 (1975).
5. Y. Ishida, J. Polymer Sci., A2, 7, 1835 (1969).
6. J.H. Gibbs and E.A. Dimarzio, J. Chem. Phys., 28, 373 (1958).
7. M.V. Volkenshtein and O.B. Ptitsyn, Sov. Phys. Tech. Phys.,1,2138 (1957).
8. B. Wunderlich, D.M. Bodily and M.H. Kaplan, J. Appl. Phys., 35, 95 (1964).
9. C.L. Choy and K. Yong, Polymer, 19, 1001 (1978).
10. J.F. Rabek, Experimental Methods in Polymer Chemistry, Wiley, Chichester (1980).
11. G.C. Levy, R.L. Lichter and G.L. Nelson, Carbon-13 Nuclear Magnetic Resonance Spectroscopy, Wiley, New York (1980). J. Schaefer and E.O. Steiskal, Topics in Carbon-13 NMR Spectroscopy, Vol. 3 (G.C. Levy, ed.) Wiley-Interscience, New York (1979).
12. G.P. Jones, Phys. Rev., 148, 332 (1966).
13. D.W. McCall and D.R. Falcone, Trans. Faraday Soc., 66, 262 (1970).
14. P. Hedvig, Macromolecular Reviews, 15, 375 (1980).
15. E.L. Hahn, Faraday Symposia, 13, 7 (1978).
16. F.A. Bovey, in Encyclopedia of Polymer Science and Technology, Vol.9 p. 356 (H.F. Mark, N.G. Gaylord and N.M. Bikales, eds.), Wiley-Interscience, New York (1968).
17. E.O. Steiskal, J. Schaefer and T.R. Steger, Faraday Symposia, 13, 56 (1978).
18. A.T. Bullock and J. Sohma, Spin Labels vs. Spin Probes vs. ^{1}H, ^{13}C, ^{19}F), in Molecular Motion in Polymers by ESR, p. 295 (R.F. Boyer and S.E. Keinath, eds.) Harwood Academic Publishers, Chur (1980).
19. P. Törmälä, Spin Labelling Studies on Segmental Relaxation in Linear Polymers, Ph.D.Dissertation, Department of Wood and Polymer Chemistry, Helsinki University, Helsinki (1973).
20. P. Törmälä, G. Weber and J.J. Lindberg, Spin Label and Spin Probe Studies of Relaxations and Phase Transitions in Polymeric Solids and Melts, in Molecular Motion in Polymers by ESR, p. 81 (R.F. Boyer and S.E. Keinath, eds.), Harwood Academic Publishers, Chur (1980).