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Nuclear Magnetic Resonance Study of Polymer-Low-molecular-weight Substance Systems

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The principles of the pulsed nuclear magnetic resonance method are briefly examined. A relation is demonstrated between the measured characteristics and the parameters describing molecular motion. The characteristic features of the derivation of information about molecules in the study of complex polymers-low-molecular-weight substance systems are considered. The principal results of investigations by the NMR method of solutions of polymers, plasticised polymers, polymer gels, and compositions consisting of low-molecular-weight substances adsorbed on polymers are presented. New possibilities in the application of the NMR method are indicated.
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I. INTRODUCTION

Polymer (P)–low-molecular-weight substance (LMS) systems are widely distributed in nature and technology. They include solutions of polymers, plasticised polymers, gels, and compositions consisting of small molecules adsorbed on a solid polymer. Various physical methods, one of which is NMR, are used to study such polymer systems. In many instances this method has unique possibilities. Thus it makes it possible to investigate the characteristics of the structure of complex polymeric compositions, the state of LMS molecules, the quality of the solvent, and the nature of molecular motion and helps to estimate the degree of completion of the incorporation of the LMS in the polymer, etc. However, frequently the possibilities of this method in the study of P–LMS systems are not fully appreciated and in many detailed monographs, devoted, for example, to the gel state of polymers[1] and plasticised poly(vinyl chloride) (PVC),[2] due importance is not attached to the results obtained by NMR.

The aim of the present review is (1) to describe the principal information about the pulsed NMR techniques, frequently used to investigate such compositions, (2) to examine the characteristic features of the derivation of information about molecules, (3) to describe the main results of studies on P–LMS systems, and (4) to indicate new possibilities in the application of NMR in the study of such compositions. It includes studies carried out in recent years (up to 1976) in which conclusions concerning the characteristics of the test systems have been reached from the molecular standpoint.

II. PRINCIPLES OF THE PULSED NMR METHOD

Three ways of observing NMR are used in the study of the structures and properties of matter: (1) high-resolution NMR; (2) broad-line NMR; (3) pulsed NMR. The general physical principles of the method have been described in detail in a number of monographs (for example, by Abragam[3] and Slonim and Lyubimov[4]) and will not be considered here. The characteristic features of the first method, which is one of the branches of microwave spectroscopy and makes it possible to investigate molecular structure including that of polymers, have been carefully dealt with[5,6]. The same may be said about broad-line NMR.[4,7] The most promising technique for the investigation of systems considered in this review is the pulsed NMR, the principles of which we shall describe briefly.

In order to observe the signal, the specimen is placed in a constant magnetic field H_0, at right angles to which a variable pulsed magnetic field H_1 is applied. It is generated by a pulsing microwave transmitter with a frequency $\omega_0 = \gamma H_0$, where γ is the gyromagnetic ratio of the resonating nuclei. The microwave pulse rotates the magnetisation vector $\mathbf{M}$ of the specimen by a definite angle, the magnitude of which depends on the duration of the pulse. Pulses rotating $\mathbf{M}$ by 90° ($\pi/2$ pulse) or 180° (π pulse) are usually employed. If a system of nuclei (usually protons) was at equilibrium before the application of the pulse, then $\mathbf{M}_0 \| \mathbf{H}_0$, where $\mathbf{M}_0$ is the equilibrium magnetisation of the system. After a time t has elapsed from the application of the pulse, for example, a $\pi/2$ pulse, the magnetisation vector has two components: a perpendicular component $M_\perp(t)$ and a parallel component $M_\parallel(t)$ in relation to the direction of $\mathbf{H}_0$. The nuclear relaxation process then consists in the approach of the value of $M_\perp(t)$ and of $M_\parallel(t)$ to M_0. The intensity of the signal obtained in pulsed NMR experiments as a function of the sequence and duration of the pulses is proportional to either $M_\parallel(t)$ or to $M_\perp(t)$.[8] The signal proportional to $M_\perp(t)$ is called the decrease of free induction (DFI), which is the Fourier transform of the absorption line obtained by stationary NMR methods.

Bloch suggested and it has been confirmed experimentally that

$$M_\parallel(t) = M_0[1 - \exp(-t/T_1)], \quad (1a)$$

$$M_\perp(t) = M_0 \exp(-t/T_2), \quad (1b)$$

where T_1 and T_2 are the longitudinal (spin–lattice) and transverse (spin–spin) nuclear relaxation times, which constitute additional useful information provided by the pulsed NMR method. If the NMR absorption line form is Lorentzian, then $M_\perp(t)$ is described by Eqn.(1*b*) and the line width δ is inversely proportional to T_2.

However, Eqns. (1*a*) and (1*b*) proved to be rigorously valid only for molecules containing a pair of nuclei and involved in rapid isotropic rotation. In other cases they may not hold. Thus the decreases of the values of $M_\parallel(t)$ and $M_\perp(t)$ for a three-spin anisotropically rotating system[9], four-spin systems[10], a number of polymer melts[11,12], and certain polymers in the viscoelastic state[13,14] are non-exponential, which makes it necessary to introduce effective relaxation times[11]. The spin–lattice relaxation times $T_{1\rho}$, expressed in a rotating coordinate system, are used nowadays in the study of polymer systems[8]. Studies on ^{13}C nuclear relaxation using specimens with the natural abundance of ^{13}C, have begun to develop very vigorously. The complete decoupling of the spin–spin interaction with protons, the increase of the sensitivity of pulse spectrometers, and the possibility of observing the relaxation in individual molecular fragments (CH_3–, $-CH_2-$, etc.) give rise to unique prospects for the investigation of complex polymer systems[15].

Another important characteristic of the systems, obtained with the aid of the pulsed NMR technique, is the self-diffusion coefficient D_S.[8] It is noteworthy that the method employed to measure D_S makes it possible to measure separately the translational mobility of the polymer and LMS molecules in the absence of a concentration gradient of the components.

1. Relation Between NMR Parameters and the Characteristics of Molecular Motion

The transverse and longitudinal nuclear magnetic relaxation times are magnetic parameters of the test systems and are not of independent interest in the study of polymers. However, if nuclear relaxation in polymer systems occurs as a result of the modulation of the nuclear dipole–dipole interaction of molecular motion (which occurs for the majority of polymers[4] except for polymers with conjugated bonds[16]), then it is possible to establish a relation between T_1 and T_2, on the one hand, and the characteristics of the molecular motion, on the other.

The intensity of molecular motion is characterised by the kinetic energy of the molecules E. Thus it follows from the kinetic theory that, for non-interacting molecules with a moment of inertia I', rotating about their axis with an angular velocity ω,

$$E = \frac{I'\omega^2}{2} = \frac{kT}{2}. \qquad (2)$$

If a correlation time τ_C, defined as the period of rotation of the molecule by an angle equal to one radian, widely used in NMR, is introduced in the description of molecular motion[17], then it follows from Eqn. (2) that $\tau_C^2 \propto I'/T$. Hence it is seen that, at a constant temperature, τ_C depends on the moment of inertia of the kinetic unit involved in the motion. We can therefore expect, for example, that in polymer solutions τ_C for the rotation of a segment must be greater than τ_C for the solvent molecules. If the magnetic relaxation times are related to τ_C, then there is a possibility of measuring the rate of relaxation of macromolecules and LMS molecules separately, which is in fact done in many instances.

The form of the dependence of T_1 and T_2 on τ_C is determined by the type of molecular motion of the kinetic unit and its structure. Thus we have for the isotropic rotation of molecules containing two nuclei[3]

$$T_1^{-1} = \frac{2}{5}\frac{\gamma^4\hbar^2}{r^6} I(I+1)\left(\frac{\tau_c}{1+(\omega_0\tau_c)^2} + \frac{4\tau_c}{1+(2\omega_0\tau_c)^2}\right), \qquad (3a)$$

$$T_1^{-1} = \frac{\gamma^4\hbar^2}{r^6} I(I+1)\left(\frac{3}{5}\tau_c + \frac{\tau_c}{1+(\omega_0\tau_c)^2} + \frac{2}{5}\cdot\frac{\tau_c}{1+(2\omega_0\tau_c)^2}\right), \qquad (3b)$$

where I is the nuclear spin, h the Planck constant, and r the distance between the nuclei. Analogous relations can be formulated also for the rate of relaxation determined by the translation motion of two-spin molecules[18]. If the molecular motion is described by a spectrum of correlation times, then Eqns. (3) become somewhat more complex. Expressions for T_1 and T_2, modified taking into account the τ_C spectrum, have been published by Connor[19] and Grigor'ev and Maklakov[20] respectively. It is noteworthy that equations of type (3) for relaxation occurring as a result of the segmental motion of macromolecules have been obtained only for very dilute solutions[21,22], although such equations are used frequently in the interpretation of experimental T_1 and T_2 results for block polymers or their concentrated solutions: this leads to incorrect results in many instances[23].

If the relaxation takes place via several mechanisms, then the overall relaxation time, for example, the transverse relaxation time, is of the form

$$T_2^{-1} = \sum_i T_{2i}^{-1}, \qquad (4)$$

where T_{2i} is the relaxation time corresponding to the ith mechanism.

2. Characteristics of Nuclear Relaxation in Multiphase Systems

The above discussion refers to single-phase systems, which are characterised by unique values of T_1 and T_2. It is readily seen that the polymer–low-molecular-weight substance systems are "multiphase" from the standpoint of NMR.[24] The term "phase" in NMR is usually understood as a set of magnetic nuclei characterised by a single relaxation time. The parameters of the ith phase are the relaxation times T_{1i} and T_{2i}, the population p_i, i.e. the fraction of nuclei referring to this phase, and the residence time τ_i of the nuclei in the given phase. If the nuclei pass from one phase to another, then one speaks of the occurrence of exchange in the system; the probability of the transition from the ith phase is then equal to τ_i^{-1}.

The decreases of the transverse and longitudinal magnetisations, which carry useful information about specimens consisting of n phases, can be formulated analytically[25] as follows:

(1) For "rapid" exchange, when $\tau_i \ll T_{1i}$ or T_{2i}:

$$M_\perp(t) = \exp(-t/T_{2m}), \qquad (5a)$$

where $T_{2m}^{-1} = \sum_{i=1}^{n} p_i T_{2i}^{-1}$, i.e. the transverse magnetisation of the specimen is described by a single exponential function with an average time T_{2m}.

(2) For "slow" exchange, when $\tau_i \gg T_{1i}$ or T_{2i}:

$$M_\perp(t) \sim \sum_{i=1}^{n} p_i \exp(-t/T_{2i}), \qquad (5b)$$

i.e. the decrease of magnetisation is described by the sum of the exponential functions and times characteristic of each phase. If the $M_\perp(t)$ curve is appropriately resolved[25], it is possible to obtain the values of p_i and T_{2i} for each phase.

(3) For "intermediate" exchange, when $\tau_i \simeq T_1$ or T_{2i}, calculation is possible only in the case of two-phase systems ($i = 1$ or 2):

$$M_\perp(t) \cong \sum_{i=1}^{2} p'_i \exp(-t/T'_{2i}). \qquad (5c)$$

The measured quantities p'_i and T'_{2i} in Eqn. (5*c*) differ from the true parameters p_i, T_1, and T_2 characterising the phase. For example:

$$T'_{2i} = f(T_{2i}, p_j, \tau_j), \qquad (5)$$

where $j = 1$ or 2 and the function f has been published by Zimmerman and Britten[25] and in Chernyshev's review[26] Eqns. (5) are valid if the resonance frequencies ω_0 of the nuclei in each phase are identical; otherwise the relations between the observed and true parameters of the phases become more complex[27].

3. Derivation of Information about the Molecules in Complex Systems from NMR Data

Examination of Eqns. (3) and (5) shows that the derivation of information about the molecular characteristics of P–LMS systems is complicated and consists of several stages. In order to obtain the parameters describing the kinetic state of systems, it is usual to proceed via the following steps: (1) the magnetic parameters (T'_{1i}, T'_{2i}, p'_i, etc.), which generally speaking can differ from the true values characterising each phase, are measured; (2) a relation is established between the measured magnetic quantities and the kinetic units responsible for them (a segment of the macromolecule, its side groups, solvent molecules, etc.); (3) the true magnetic parameters of each phase (T_1, T_{2i}, p_i) are calculated from Eqns. of type (5*c*); (4) a definite relaxation mechanism, which establishes the type and characteristics of the motion of each kinetic unit, are attributed to the system; (5) the correlation times of the molecular motions of the polymer and low-molecular-weight substance are determined.

The first stage does not require explanation: it involves the measurement of the magnetic parameters, the values of which may be distorted by the exchange processes[28] occurring in the test systems (translational displacement of molecules from "phase" to "phase", spin diffusion, proton exchange, etc.). Since the systems considered are characteristic by several transverse and longitudinal relaxation times, the second stage of the treatment involves the assignment of the measured quantities to a specific kinetic unit whose motion determines a particular relaxation time. This process requires particular caution, since it can lead to an incorrect treatment of the results. For a more reliable assignment of the times to kinetic units, one of the system components (usually the solvent) is deuterated and ^1H and ^2D resonance is observed[29]. Next the true values of T_{1i}, T_{2i}, p_i, etc. are calculated from one of Eqns. (5) (third stage). After that, on the basis of general considerations or using additional information, a definite mechanism (dipole–dipole, quadrupolar, and spin–rotational interaction) is assigned to each relaxation time and the type of motion of the kinetic units and its characteristics (continuous rotation, jumps by large angles, etc., the presence of a spectrum of τ_c values) are specified. This makes it possible to select a definite relation between the correlation times of the motions and the magnetic relaxation times [see, for example, Eqn. (3)] and one can then calculate the values of τ_c (fifth stage). An example of the sequence of steps in the analysis of NMR data is provided by studies on adsorption systems[30] and polymer solutions[31].

The specific results obtained in recent years as a result of the applications of NMR to the study of systems in which we are interested are examined below.

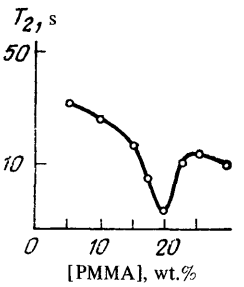


Figure 1. Concentration variation of T_2 for benzene in a solution of syndiotactic PMMA with a molecular weight of 2.2×10^6.[33]

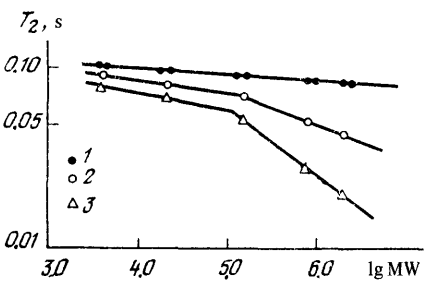


Figure 2. Variation of T_2 for the CH_3 group in the PIB–CCl_4 system with the molecular weight (MW) at 35°C; volume fraction of polymer: 1) 0.05; 2) 0.20; 3) 0.30.[34]

III. POLYMER SOLUTIONS

1. The Structure of the Solution

The measurement of the nuclear relaxation times of polymers yields information about the structure of solutions[4,32–34]. Thus the microscopic inhomogeneity of poly(methyl methacrylate) (PMM)—benzene systems has been investigated[33] and it was found that, depending on the polymer concentration, T_2 passes through a minimum (Fig. 1). The appearance of a minimum is a consequence of the diffusion of benzene molecules through the region of inhomogeneity of the solution. By means of a semiquantitative estimate of this effect, the authors found that the average size of the inhomogeneity is 200 Å, which roughly agrees with the radius of rotation of the polymer segment.

Characteristic breaks (Fig. 2), indicating the existence of a critical molecular weight or a critical concentration at which there is a sharp change in the properties of the system, have been observed in the study of polyisobutylene solutions (PIB) in CCl_4 on the curves relating T_2 to concentration or the molecular weight of the polymer [34]. According to the authors "hooked" formations are produced in the test solutions for polymer molecular weights and concentrations in excess of the critical values. It is suggested that these constitute the nodes of a fluctuation network made up of macromolecules and their supermolecular formations. The variation of local mobility, which determines T_2, with concentration is followed by observing the formation and density of this network.

The presence of empty cavities in concentrated solutions of atactic polystyrene in anisole, which are in a vitreous state, has been pointed out [35]. The LMS molecules in the cavities execute rotational and translational "jumps" at low temperatures. It has been found that LMS molecules then exhibit a tendency towards association [35,36]. The broadening of the ^{13}C NMR absorption lines in PIB solutions in CCl_4 [37] indicates a partial entanglement of the macrochains, which becomes more pronounced with increase of the molecular weight of the polymer and can be one of the causes of the formation of a three-dimensional network in solution.

The possibility of structural rearrangements in polymer solutions has been noted by Fedotov [38], who observed that the correlation time characterising the mobility of water molecules interacting with the macromolecules of poly(acrylic acid) (PAA) increases with increase of temperature from 10° to 80°C, while in a solution containing poly(methacrylic acid) (PMAA) it falls. The rearrangements are attributed to the uncoiling of the chains due to a redistribution of hydrogen bonds. It has also been found that the loose PAA macromolecule can be hydrated by twice as much water as the more rigid PMAA molecule. It is suggested that the presence of structures in macromolecules gives rise to steric hindrance to interaction between water and the macromolecule.

An attempt has been made to determine the fraction of macromolecules in helical and coiled conformations in aqueous solutions of serum albumin. [39,40] However, it is believed [41] that the information obtained in these studies [39,40] about the conformations of hydrated protein macromolecules is doubtful. Outhred and George [41] explained the same experimental results by assuming that the motion of the polymer macromolecules in solution is characterised by a spectrum of correlation times with a maximum at $\tau = 10^{-9.3}$ s.

Additional information about the structure of solutions has been obtained by studying the self-diffusion coefficient of both LMS molecules and macromolecules in aprotic solvents [42,50]. The results are usually interpreted by means of Fujita's free volume theory [51]. The parameters characterising the size of the "critical" regions for diffusional motion in solutions of natural rubber (NR), PIB, polystyrene (PS), and PMMA have been determined [42-44]. It was established that (1) in translational motion the greatest disruption of the packing of solvent molecules in the vicinity of macromolecules is observed for rigid-chain polymers and (2) that the self-diffusion of LMS molecules takes place as a result of the interchange of the kinetic units of the polymer and whole groups of solvent molecules.

A study of the self-diffusion of LMS in the PS–benzene and PS–cyclohexane systems showed [45] that the minimum free volume necessary for "jumps" by solvent molecules is greater by a factor of approximately 1.5 in the second system compared with the first. Analogous data have been obtained for PMMA solutions in benzene and acetone. [46] The temperature dependence of the free volume has been studied for these solutions and the coefficient of the expansion of the free volume in PMMA has been determined.

The study of D_S of the solvent with increasing concentration of polymers (PMMA, PS) [45,46] suggests the formation of cavities within entangled macromolecules which LMS molecules enter and are trapped. The cause of the inhibition of the translational motion of small molecules is believed to be [45,46,50] the formation of short-lived globules and small cavities in which solvent molecules are accommodated. Kosfeld and Goffloo [45] concluded that the self-diffusion of solvent molecules is determined by the motion of the macromolecules. The nature of the concentration variation of D_S for macromolecules permits a number of conclusions concerning the distribution of macromolecules in solution [42,44,47].

2. Estimation of the Quality of the Solvent

The quality of the solvent has a significant influence on the intermolecular interaction of the components in polymer solutions, which determines the molecular mobility. Since T_1, T_2, and D_S depend on the latter, the measurement of nuclear magnetic characteristics makes it possible to infer the quality of the solvent.

The first conclusions about the quality of the solvent based on the analysis of T_1 were put forward [52] in relation to the study of dilute PIB solutions in "good" (CCl_4) and "poor" (C_6D_6) solvents over a wide range of temperatures and polymer molecular weights. Comparison of the T_1 values for specimens corresponding to equal fractions of the solvent shows that relaxation in a good solvent is faster than in a poor one. It was also found that a minimum in T_1, caused by the rotation of the CH_3 group of the polymer, lies at a temperature 25°C lower in a good solvent than in a poor solvent and its value is smaller in the latter case. This finding apparently shows that the conformations of macromolecules in a good solvent are such that they give rise to less steric hindrance to the rotation of CH_3 groups.

It was later found that [53,54] the quality of the solvent has a similar influence on the intramolecular mobility also in moderately concentrated solutions. This conclusion was reached in a study of the temperature and concentration variation of the relaxation times T_1 and T_2 for PS and PMMA solutions in the aprotic solvents C_2Cl_4, C_6D_{12}, etc. Tanner et al. [47] observed that the translational motion of poly(ethylene oxide) macromolecules with a low molecular weight (approximately 1000) in a good solvent ($CDCl_3$) is more vigorous than in a poor solvent (CCl_4), while in the case of large macromolecules (with a molecular weight of approximately 870 000) the opposite relation holds. This has been explained [47] by taking into account the influence of the viscosity of the solvent and also of the solvation and shape of the macromolecules in solution.

3. The State of Solvent Molecules

The state of CH_2Cl_2 molecules in a solution of atactic PS in which the volume fraction of the solvent was 0.10 to 0.24 has been investigated [55]. The system is characterised by a weak P–LMS interaction. The calculated correlation

times of the solvent molecules surrounded by similar molecules (τ_{SS}) and in the vicinity of macromolecules (τ_{Sp}) showed that $1 \leqslant \tau_{Sp}/\tau_{SS} \leqslant 2$. According to the author[55], this showed that there is only one type of environment for LMS molecules in a PS–CH_2Cl_2 solution and that it is impossible to distinguish the "free" and "bound" solvent species. The inhibition of small molecules is more effective in a polymer with a larger molecular weight. The increased "lifetime" of the CH_2Cl_2 molecule in the "trap" with increase of the polymer concentration is caused exclusively by the influence of the macromolecular chains and not some special interactions between the π-electron system of the benzene ring and the CH_2Cl_2 molecule.

The state of solvent molecules in dilute polymer solutions has been thoroughly investigated[31,56-59]. Solutions with a strong intermolecular interaction (hydrogen bonds) were examined; the temperature and concentration variations of the nuclear spin–lattice relaxation times T_1 for protons, deuterons, and chlorine nuclei were investigated and the self-diffusion coefficients were measured. The behaviour of the solvent can be described with the aid of a simple model with two states:

$$A + M \rightleftarrows AM,$$

where the solvent molecule A can be either in a free state or in a bound state (as a solvate AM combined with the macromolecule M). It has been established for solutions of polyvinylpyrrolidinone (PVP) in chloroform, where a hydrogen bond is formed between the carbonyl group of the pyrrole ring and the deuterium atom of chloroform, that the "lifetime" of the hydrogen bond ($\sim 5 \times 10^{11}$ s) is long compared with the rotational correlation time of the molecules of pure chloroform ($\sim 10^{-12}$ s), but is very short compared with the fastest motion of the macromolecule ($\sim 10^{-9}$ s).[31] In a PVP–pyrrole solution[59] the "lifetime" of the hydrogen bond is approximately twice as long as the lifetime of the corresponding bond in the PVP–chloroform system. The reorientation of the pyrrole ring about the C–H bond in the complex with the polymer is retarded by a factor of 10 compared with the reorientation of pure pyrrole, while the rotation of chloroform molecules in the complex with PVP is retarded only by a factor of 3. According to the authors, the "lifetime" of the hydrogen bond can be regarded as the "lifetime" of the polymer–solvent solvate.

Comparison of the results of studies on PS solutions in methylene dichloride[55] and of PVP in $CDCl_3$ [31] showed that the state of solvent molecules is determined to a large extent by the extent of the interaction between the polymer and LMS molecules. In systems with a strong interaction between the components there is a possibility of the subdivision of molecules into "bound" and "free".

The study of proton and deuteron relaxation in PMMA–benzene solutions[57] showed that, in the absence of a strong polymer–solvent interaction, the "lifetime" of the bond between the components is of the same order of magnitude as the rotational correlation time of the benzene molecule. At the same time the translational correlation time of benzene ($\sim 10^{-10}$ s) is longer almost by two orders of magnitude than the rotational correlation time.

As was to be expected, an increase of the polymer concentration in the solution leads to a decrease of the rotational and translational mobilities of the LMS molecules.[43,44] It is striking that the inhibition of the molecules, characterised by the ratio D_S/D_{S0}, depends very little on the nature of the polymer or on the type of LMS (Fig. 3). Nevertheless it is claimed[43] on the basis of a study of D_S for H_2O, CH_3COOH, CH_3OH, and CH_2Cl_2 molecules in PVP solutions that the stronger the polymer–solvent interaction the greater the inhibition of the [mobilities of the] latter.

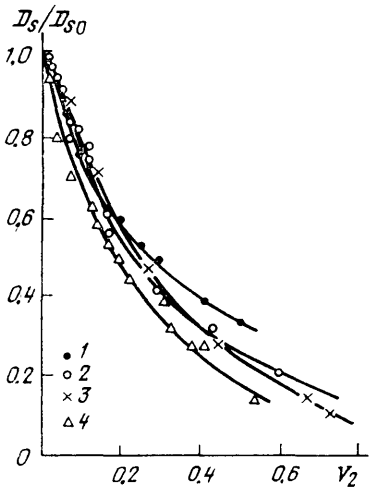


Figure 3, Dependence of the ratio of the self-diffusion coefficient of the solvent D_S in solution to the self-diffusion coefficient of the pure solvent D_{S0} on the volume fraction of the polymer in different systems: 1) natural rubber–benzene; 2) PIB–benzene; 3) PIB–toluene; 4) PMMA–toluene.[44]

The inhibition of [mobilities of] acetone molecules in solutions containing between zero and 20 wt.% PMMA has been studied over a wide temperature range[60] by the method of ^1H and ^{13}C spin–lattice relaxation. It was observed that the introduction of up to 10 wt.% of the polymer does not affect the translational and rotational diffusion of acetone molecules, but in the presence of 20 wt.% of the polymer the mobility decreases sharply. The sharp inhibition [of mobilities] of the solvent molecules over a narrow concentration range can be explained by the formation of an entangled network of macromolecules.

4. The Study of Selective Solvation

An independent field of research on complex formation in polymer solutions by NMR involves the study of the selective solvation by the polymer of one of the components in a mixture of two solvents[29,61-64]. The mixtures are chosen so that one component is a good solvent and the other a poor one. Liu observed for the first time[61] in a study of T_1 for the PIB + CCl_4 (C_6H_{12}) + CH_2Cl_2 and PMMA + CCl_4 + CH_3COCH_3 (CH_2Cl_2) systems that the spin–lattice relaxation time of one of the components of the mixture of solvents depends strongly on the type of added polymer, i.e. that the interaction of the polymer with this solution component is stronger than with the other one. In the systems indicated above CH_2Cl_2 is a good solvent for PMA but a poor one for PIB.

The study of the spin–lattice relaxation of C_6H_6 + C_6H_{12} + PS, C_6H_6 + CCl_4 + PMMA, $CHCl_3$ + CCl_4 + PMMA, and C_6H_6 + $CHCl_3$ + PMMA mixtures[62] with different ratios of the LMS components at a constant polymer concentration established that in mixtures with PS benzene (a good solvent) is solvated preferentially and that the polymer monomer unit combines with four C_6H_6 molecules. The numbers of benzene and chloroform molecules adsorbed on the PMMA monomer unit are respectively 5 and 4.

In solutions of PVP [29] in a mixture of solvents consisting of $CHCl_3$ (a good solvent) and C_6H_{12} (a poor solvent) the inhibition of the rotation of $CHCl_3$ molecules was observed as the polymer content was increased, while the mobility of C_6H_{12} remained unchanged. This finding can be explained by the preferential solvation of PVP by $CHCl_3$. Anallgous preferential solvation of PS by $CHCl_3$ had been observed in PS + $CHCl_3$ + CH_3COCH_3 mixtures[29].

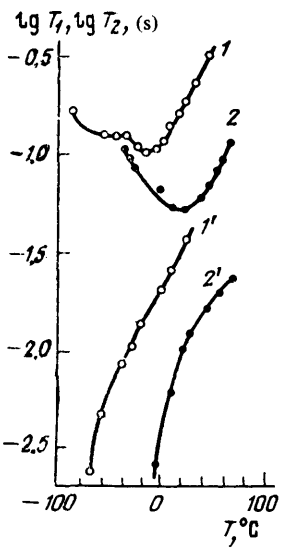


Figure 4. Temperature variation of lg T_1 (curves *1* and *2*) and lg T_2 (curves *1'* and *2'*) for solutions of PS in $C_6D_6CD_3$ at concentrations of 5 wt.% (curves *1* and *1'*) and 40 wt.% (curves *2* and *2'*).[53]

A novel approach to the study of the solvation equilibrium in a system with a mixed solvent, namely CCl_4 + PMMA + C_6H_6, at 31°C in the polymer concentration range from 0 to 100 g litre^{-1} has been described[63,64]. The author introduced the equilibrium constant K for the exchange of solvent molecules, which depends on the concentrations of molecules of both solvents—free and involved in solvate complexes with the polymer. In order to determine K, use was made of the measured T_1 for benzene protons at different polymer concentrations. It was found that in the system indicated above the exchange equilibrium constant obtained is $K = 2.5 \pm 0.5$; on the other hand, $K = 0$ in the C_6O_6 + PMMA + C_6H_6 system, where there is no selective solvation. Thus K is a convenient measure of the preferential solvation of one component (C_6H_6).

5. Phase Separation in Solutions

Information about the intermolecular interactions under conditions preceding the separation of the solution into layers has been obtained[53] in a study of PS solutions in aprotic solvents (CCl_4, $CDCl_3$, $C_6D_5CD_3$, and C_6D_{12}) at different concentrations. The amount of polymer was varied from 5 to 40 mole % and its molecular weight was varied from 10^4 to 10^6. The temperature variation of T_1 and T_2 for PS solutions in $C_6D_5CD_3$ is illustrated in Fig.4. The authors suggest that the stepwise variation of T_1 reflects the change in the state of the macromolecules, which involves the appearance of long-lived polymer–polymer contacts (associated species, aggregates), i.e. the separation of the solution into layers. Under these conditions, the observed relaxation time T_1 is a weight-average quantity referring to protons, highly mobile macromolecules, and macromolecules inhibited by the appearance of long-lived interchain contacts.

It has been observed[52] that the time T_2 in dilute solutions also changes when phase separation begins.

6. Characteristics of the Motion of Macromolecules

The mechanisms of the motion of PIB macromolecules in aprotic solvents have been investigated[52] and two forms of macromolecular motion have been found: (1) the low-temperature form involving the reorientation of the CH_3 groups and (2) the high-temperature form involving segmental motion. The addition of a low-molecular-weight substance facilitates the rotation of the CH_3 groups, whose motion is not free in the pure polymer.

The analogous problem of the study of the local forms of motion (rotation of CH_3 groups and reorientation of the Si–C bond) of macromolecules has been solved[65] in relation to solutions of PDMS [polydimethylsiloxane] having different molecular weights in protic (C_6H_6, C_6H_5Cl) and aprotic (C_6D_6, C_6D_{12}, CCl_4) solvents. The polymer concentration in solution varied from 1 to 20 g in 100 ml of the solvent. It is assumed that the inhibition of the rotation of the CH_3 groups increases with increasing molecular weight of the polymer at fairly high concentrations of the latter owing to steric hindrance.

In solutions of poly(ethylene oxide) in HCl, H_2O, D_2O, and DCl and pentachloroethane ($CHCL_2CCl_3$) the motions associated with conformational transitions around C–C bonds were investigated[66]. It was noted that the rotation of the molecule as a whole influences the relaxation in low-molecular-weight oligomers only, i.e. the mechanism of the motion of macromolecules changes from segmental to the rotation of the molecule as a whole as the molecular weight decreases.

The influence of the molecular weight of the polymer on the degree of inhibition of the translational motion of solvent molecules has been demonstrated[42,44,49]. New possibilities for the study of macromolecular motion arise in connection with the ^{13}C NMR method[37,67–73]. It has been observed that the motion of the carbon chain is almost isotropic in a 20% solution of PIB in $CDCl_3$.[37] The study of PS–tetrachloroethylene solutions at the same concentration showed that the rotation of the phenyl groups of the polymer is subject to a considerable steric inhibition, because their correlation time is appreciably longer than the effective correlation time for segmental motion[67]. It has been established that macromolecules with low molecular weights move as a whole and that these motions determine the observed T_1, while macromolecules with

high molecular weights exhibit predominantly an internal (segmental) motion of the polymer chain, which is fairly rapid[64-73].

Comparison of the activation energies for segmental motion in polyethylene (PE), polypropylene, and PIB solutions in *o*-dichlorobenzene showed[37] that the activation energy E increases on passing from PE to PIB. This is due to steric hindrance to the motion of methyl groups when the latter are introduced into the polymer as side units. The study of the relaxation of ^{13}C nuclei showed[73] that the motion of poly(propylene oxide) (PPO) molecules and PIB with a molecular weight of 2500 in $CDCl_3$ depends on the frictional forces acting from the side of the immediate environment. According to the author[73], the immediate environment consists of the first solvation shell, which is believed to be formed when the ratio of the number of $CDCl_3$ molecules to the number of monomer units is 5. It was established that the motion of CH_3 groups of PIB is strongly inhibited and that their orientation takes place co-operatively with neighbouring methyl groups. It is claimed that in PPO and PIB solutions, where the ratio of the number of solvent molecules to the number of monomer units exceeds 5, the correlation of the motion of the main chain disappears over a distance equal to 2–3 monomer units.

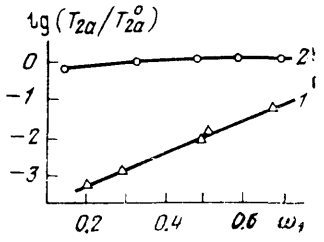


Figure 5. Dependence of $\lg (T_{2a}/T_{2a}^0)$ on the weight fraction ω_1 of the plasticiser in different systems: 1) PVC–DBP; 2) PVC–glycerol (at room temperature) [24].

IV. PLASTICISED POLYMERS

Plasticised polymer systems differ from solutions by the high content of the polymer and the consequent very high viscosity. The difficulty of the study of such objects by NMR is due to the fact that the plasticisers usually employed are high-boiling liquids whose molecules are bulky, have a complex structure, and possess a large number of internal degrees of freedom; the deuteration of such molecules is usually difficult. However, a series of results have been obtained recently showing the usefulness of NMR, particularly its pulsed version, in the study of such systems.

It has been established[24] that, from the standpoint of NMR, plasticised polymers are multiphase systems where exchange between the phases as a rule does not occur or is fairly slow. In this case the study of the decrease of transverse magnetisation[74], from which the nuclear relaxation time T_1 is determined by Eqn.5*b*, is most informative. Specimens with a moderate content of the plasticiser (up to 80 wt.%) are described by two times T_2 over a wide range of temperatures: a long time T_{2a} and a shorter time T_{2b}. The former characterises mainly the plasticiser protons and the latter the polymer protons[75].

1. Assessment of the Nature of the Plasticisation of Polymers

In the first studies[76,77] on plasticised PVC by the pulsed method it was shown that at room temperature T_{2a} for a molecular plasticiser introduced into the polymer is smaller by 2–3 orders of magnitude than T_{2a}^0 for the pure plasticiser, while in a polymer plasticised by a structural plasticiser $T_{2a} \simeq T_{2a}^0$. This feature makes it possible to deduce the type of plasticiser directly from the measured transverse relaxation time.

The concentration variation of $\lg (T_{2a}/T_{2a}^0)$ for a molecular plasticiser (Fig. 5) is described by the equation[24]

$$\lg [T_{2a}/T_{2a}^0] = A\omega_1 + B$$

where ω_1 is the weight fraction of the plasticiser and A and B are constants which depend on the nature of the polymer–plasticiser interaction (high values of A and low values of B correspond to a strong interaction and low values of A and high values of B correspond to a weak interaction). In many systems (for example, in PVC plasticised with glycerol, ethyl stearate, castor oil, phthalates, and sebacates) the form and positions of the curves corresponding to this relation make it possible to determine the limits of the compatibility of the polymer and plasticiser and to introduce criteria for subdividing plasticisers into molecular and structural[78,79].

Analogous results were obtained for plasticised PS and polyvinylbutyral[80], which demonstrates the applicability of the parameter T_{2a}/T_{2a}^0 to the estimation of the nature of the plasticisation for a wide range of polymers. The characteristics of the plasticisation of vinyl chloride–vinyl acetate copolymers by phthalates have been investigated[81,82]. Thus dioctyl phthalate (DOP) is a molecular plasticiser for PVC and a structural plasticiser for poly(vinyl acetate). Examination of the concentration variation of T_{2a} made it possible to assess the compatibility of DOP with copolymers and to observe an inversion of the action of the plasticiser (a transition, depending on the content of vinyl acetate groups, from the molecular to the structural mechanism of plasticisation).

A broad-line NMR study of the nature of the polymer–plasticiser interaction in relation to rubbers plasticised by phthalates and sebacates has been undertaken[83]. The difference between the second moments of the absorption lines of the plasticised specimen, on the one hand, and the pure polymer and plasticiser taken in appropriate proportions, on the other, served as a characteristic of the interaction.

2. The Introduction of the Plasticiser into the Polymer

Measurements of T_{2a} make it possible to investigate the processes involved in the combination of the plasticiser with the polymer in the mixing and rolling stage, i.e. pulsed NMR can be used for purely technological purposes[80,84]. Thus the optimum time t_m for the mixing of PVC with phthalates and sebacates at 98°C in order to obtain a homogeneous mixture has been estimated (Fig. 6). The time t_m was determined from the point of intersection of the tangents to the sharply descending and horizontal sections of the T_{2a}—mixing time curves. The mixing time

t_m increases for all plasticisers with increase of their concentration. It is a minimum for systems which are highly compatible. An analogous approach has been used to estimate the optimum rolling time for films of plasticised PVC. It was established [84] that, with increase of the temperature of the operation, the rolling time required for the preparation of homogeneous films diminishes. Analogous results have obtained in the study of the pressing of PVC specimens [80].

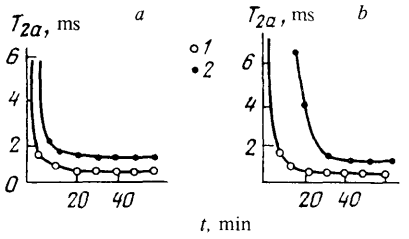


Figure 6. Dependence of T_2 on the mixing time of the components at 98°C for PVC–DBP (*a*) and PVC–DOP (*b*) systems containing 40 wt.% (curves *1*) and 50 wt.% (curves *2*) of the plasticiser [84].

3. The State of Plasticiser Molecules Introduced into the Polymer

The main aim of the plasticisation of polymers is to create the maximum molecular mobility in the polymer–plasticiser system [85]. It is therefore of interest to investigate the nature of the motion of small molecules introduced into the polymer, particularly since plasticiser molecules constitute a kind of "label" characterising the system as a whole[24].

(a) Plasticised PVC. The PVC–phthalate system with a low polymer content (< 10 wt.%) belongs to gels of type 1B.[1] However, at high PVC concentrations (> 50 wt.%) they can be treated as ordinary plasticised systems.

Measurements of the spin–lattice relaxation times in PVC plasticised by various phthalates and nitrophthalates in the range from −150°C to +70°C [86,87] made it possible to determine the nature of the motion executed by small molecules: the methyl groups are seen to rotate between −150°C and −120°C, while at approximately −50°C alkyl groups rotate as a whole at a frequency of approximately 10^7 Hz regardless of the concentration of the added plasticiser. However, a complete interpretation of the temperature variation of T_1 in such systems is difficult, since the measured quantities are as a rule distorted by exchange [74]. The study of the temperature variation of the transverse relaxation times proved to be more informative in this respect.

In the region of moderate plasticiser concentrations (≤ 60 wt.%) the PVC–DMF and PVC–DOP systems [74,75] are characterised, as mentioned above, by two relaxation times (Fig. 7). It was established that T_{2a} is determined by the rotational motion of the plasticiser molecules. The decrease of T_{2a} with increasing content of the polymer in the system relative to T_{2a}^0 over the entire experimental temperature and concentration ranges indicates a reduction of the rotational mobility of the phthalate molecules introduced into PVC. It has been noted that in the specimens investigated there is a distribution of correlation times for the reorientation of molecules. This makes it possible to regard the entire plasticiser introduced into the polymer as "bound" to different extents, provided that the degree of "binding" is estimated in terms of the degree of retardation of the rotational motion. The most probable correlation times for the rotational (τ_{r_0}) and translational (τ_t) motions of DMF molecules have been estimated.

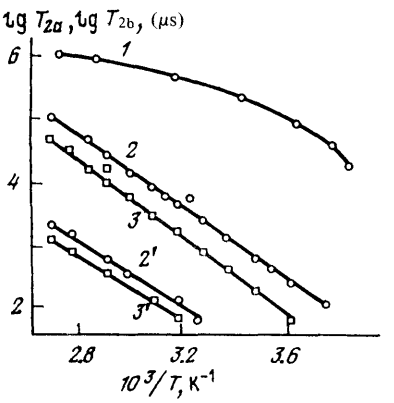


Figure 7. Temperature variation of lg T_{2a} (curves *2* and *3*) and lg T_{2b} (curves *2'* and *3'*) for PVC–DMF systems containing 24.2 mole % DMF (curves *2* and *2'*) and 13.3 mole % DMF (curves *3* and *3'*). Curve *1*—pure DMF. [75]

The NMR method permits a sounder approach to the determination of the lifetime of the polymer–plasticiser solvate. Thus in the PVC–DMF system it is most useful to select as the lifetime the correlation time τ_{r_0} for the rotational motion as the shortest time parameter characterising the system. However, since the correlation times for reorientations are characterised by a spectrum of values, one must assume that the lifetimes of various solvates present are different and have a wide range of values, which depend on the content of the plasticiser and the temperature of the measurement.

It has been established that the phthalate molecule interacts with the polar group of PVC, undergoes a reorientation during a period $\tau_t \geq \tau_r$, and then "jumps" to another site where it begins to rotate, etc. The PVC–dioctyl sebacate system has been investigated [88].

(b) Plasticised nitrocellulose. A study of the characteristics of the molecular motion of trinitroglycerol (TNG) plasticising nitrocellulose (NC) has been described [89]. Only T_{2a} was measured by high-resolution NMR. Various nitrocelluloses with nitrogen contents varying from 10.9 to 13.9 wt.% were investigated; the TNG concentration was in the range 30–60 wt.%. The solvation limit, which depends on the nitrogen content in NC, was estimated. The degree of nitration of cellulose was shown to influence the mobility of the plasticiser molecules. The linear relation between lg T_{2a} and $1/T$ makes it possible to determine the activation energies for

the motion of TNG. The values of E proved to be independent of the plasticiser content.

The analogous NC–TNG systems have been investigated[75,90] by pulsed NMR. Like the PVC–phthalates specimens, the above systems are characterised by two transverse relaxation times. The presence of a spectrum of correlation times for the motion of TNG molecules at $T < 60$°C was demonstrated. The pressure of a plateau on the $\lg T_{2a} = f(1/T)$ curves in the region of $T \geqslant 60$°C (Fig. 8) indicates the occurrence of exchange between the "quasi-free" and "bound" plasticiser species under these conditions. The rate of molecular exchange was estimated as ~10–10^2 Hz. The molecular motion in polystyrene plasticised by dibutyl phthalate has been investigated[91].

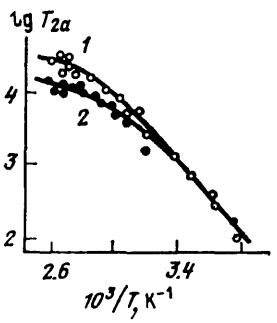


Figure 8. Temperature variation of lg T_{2a} for low-nitrogen (curve *1*) and high-nitrogen (curve *2*) nitrocellulose containing 50 wt.% of trinitroglycerol.[90]

The dynamic picture of the state of phthalate molecules introduced into PVC makes it possible to represent the overall picture of the transition of the plasticised system from the vitreous to the viscoelastic state. This transition is accompanied by a kind of "accelerated rocking" of the polymeric skeleton under the influence of the intense rotational and translational motion of the plasticiser molecules. The efficiency of this rocking depends on the number of internal degrees of freedom f of the plasticiser molecules and the amount of plasticiser. The condition for vitrification can be formulated as follows in this case:

$$\alpha f T_g \frac{Nm}{1-N} = E_p,$$

where N is the molar percentage of the plasticiser, m the number of monomeric units in the segment, E_p the minimum energy required to initiate segmental motion, α the proportionality coefficient, and T_g the glass point.

Ideas concerning the mobility of nitrocellulose macromolecules in plasticised specimens have been put forward[93].

V. THE GEL STATE OF POLYMERS

In the study of gels NMR has been used recently mainly to investigate aqueous polymer gels (agarose, gelatin, starch, carboxymethylcellulose, etc.). With some exceptions, the term LMS will therefore be understood below to imply water.

The majority of studies were carried out by pulsed NMR, gels containing a small amount of the polymer (2–3 wt.%) being characterised by unique values of T_1 and T_2 [94,95] or a one-component NMR absorption curve[96]. For a polymer content exceeding the above limit, there is a two-component absorption line. The broad component ($\delta \simeq 9$ Oe) is attributed to the polymer protons and the narrow component to the water protons[97].

1. The Formation, Fusion, and Ageing of Gels

Gels are known[98] to be characterised by gel (T_{gel}) and melting (T_m) points. The dependence of T_2 on the age of an aqueous agarose solution for T less than the gel melting point (Fig. 9) makes it possible to follow the gel formation process[95]. The curves illustrated in Fig. 9 suggest that an increase of the agarose content increases the rate of gel formation; the authors attribute this to the intensification of the nucleation stage. The decrease of T_2 in the course of the formation of the gel (Fig. 9) is accounted for by the decrease of the mobility of the macromolecules and of bound water. The T_2–agarose concentration curves indicate the formation of a macromolecular network. The temperature variation of T_2, measured in the course of the cooling of the specimen (curve *2'*, Fig. 10), shows a sharp break in the region of $T \simeq T_{gel}$ due to the loss of molecular mobility in the system. It is noteworthy that the $T_1(T)$ relations do not exhibit such anomalies. The decrease of T_2 with the duration of storage of the gel suggests the "ageing" of the system. Even a 3% solution of agarose at 40°C, i.e. above T_{gel}, "ages" in the course of 6 h without any visible signs of the formation of a network (T_2 diminishes).

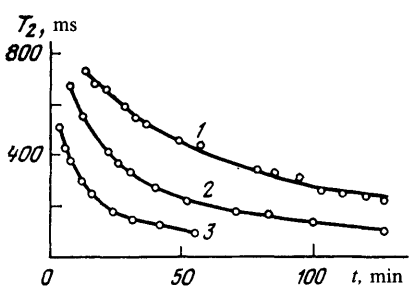


Figure 9. Dependence of T_2 on the gel formation time t at 34.7°C for different concentrations of agarose in solution (%) [95]: 1) 1.6; 2) 2; 3) 3.

The formation of the gel in a 0.5% solution of monodisperse α-gelatin with a molecular weight of 110 000 has been investigated[99]. The integral intensities J of lecithinyl, alanyl, prolyl, and arginyl lines were determined by high-resolution NMR in the course of the formation of the gel at 15°C. The form and positions of all the observed lines remain unchanged during the process, but the values of J diminish in accordance with the law

$$\frac{dJ}{J} = -K\,dt$$

with the same constant K for all the lines.

The decrease of J_- is attributed to the formation of helical molecules in which there is a sharp retardation of molecular motion, which entails a broadening of the line, precluding the possibility of its observation by high-resolution NMR. The same view has been expressed by Rouse and Gross[100]. This enabled Finer et al.[99] to reach conclusions about the possible conformational changes undergone by α-gelatin on formation of the gel. It is believed that gel formation is a multistage process in which the slow stage is described by the equation quoted above and involves the formation of the nuclei of the helix from the coil.

Gel formation in the poly(hexadecyl acrylate)–n-decane system has been investigated[101] with a polymer concentration varied from 1 to 100%. It was shown that at the temperature T_{gel} there are anomalies in the behaviour of T_1, the effective T_2, and the self-diffusion coefficient D_S. It was established that the formation of the gel is accompanied by a decrease of the mobility of the polymer molecules — the retardation of the rotational and translational motion of the molecules of the bound and non-solvated solvent.

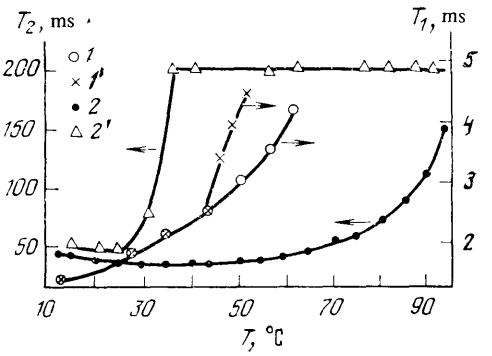


Figure 10. Temperature variation of T_1 obtained on heating (*1*) and cooling (*1'*) a 5% agarose gel and temperature variation of T_2 on heating (*2*) and cooling (*2'*) a 2% agarose gel.[95]

2. Hysteresis Phenomena in Gels

Hysteresis in agarose gels[94,95] consists in different positions of the curves representing the temperature variation of T_1 and particularly T_2 measured during the cooling and heating of the system (curves *1* and *1'* and *2* and *2'* in Fig. 10). It has been shown[95] that the form of the hysteresis loop depends on the maximum temperature to which the test specimen was heated during the measurement. The causes of the hysteresis have not been discussed, but presumably this effect is associated with the kinetic nature of the curves obtained. Another type of hysteresis is observed in the measurement of T_2 in a 3% agarose solution with alternation of the specimen heating and cooling cycles (Fig. 11).[95] The authors suggest that, with increase of temperature, the existing nodes break down and the mobility of the chains increases; however, on cooling to 60°C the nodes are restored to a different extent in each case, which leads to hysteresis.

3. The State of Water in Gels

Earlier studies (without the use of NMR) of the behaviour of water in gels led to the conclusion that the majority of water molecules are in a state intermediate between that of ordinary water and ice[102,103]. However, systematic study of the agarose–water system by NMR showed[94,104] that "free" water, having the mobility of ordinary bulk-phase water and "bound" water predominate in the gels. The degree of "binding" of water can be different and Sterling and Masuzawa[96] divided bound water into two parts: (1) simply "bound" water whose molecules exhibit a limited mobility and (2) "solid" water. Aizawa et al.[97], who investigated agarose gels in which the polymer content was varied within wide limits (from zero to 100%), suggest that the form of the curve for the concentration variation of the NMR absorption line width δ (Fig. 12) makes it possible to differentiate, apart from "free" and "bound" water, also a third type, namely "intermediate" water. Point *A* (Fig. 12) permits the determination of the amount of "bound" water. The independence of δ of polymer concentration along section *AB* indicates the existence of "intermediate" water, whose introduction is particularly necessary in the treatment of dilatometric and electrochemical data in such systems[105]. The sharp increase of δ in the region of 0°C indicates the existence of free water. Whereas bound water consists of molecules strongly interacting with the OH groups of agarose, the nature of the intermediate water is not clear.

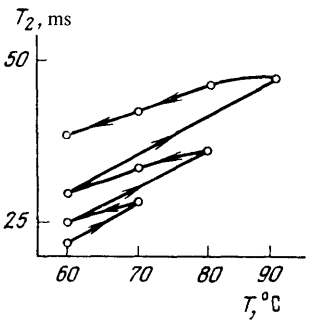


Figure 11. Temperature variation of T_2 for a 3% agarose solution recorded in the course of heating–cooling cycles.[95]

The use of pulsed NMR made it possible to determine the fraction of free water in gels (on the assumption that free and bound water exist in the system). Thus, a study of agarose gels containing 1–8 wt.% of the polymer showed[94] that more than two-thirds of the entire water is present in the free state. This is indicated by the closeness of the values of D_S for the water in gels ($D_S = 1.95 \times 10^{-5}$ cm^2 s^{-1}) and for pure water ($D_S = 2.25 \times 10^{-5}$ cm^2 s^{-1}) at room temperature. In the next study by the same authors[104], where a mixture of H_2O and D_2O with different component ratios was used as the solvent for agarose, it was shown that only 1% of the entire water is present in the bound state, in the gel containing 7–8 wt.% of agarose, while the remaining 99% is ordinary free water. With increase of polymer concentration, the fraction of bound water increases. Attention has been drawn to the small

difference between the values of D_S determined by NMR and the tracer atom method, which apparently indicates the existence in gels of "barriers" (various macromolecular structures) distributed at comparatively long distances from one another. A later study[106] established that 1 g of agarose retains 0.59 g of water, which is several times more than the amount of bound water determined by Woessner and Snowden[104]. However, the scheme proposed by Derbyshire and Duff[106] for the interpretation of relaxation data yields many anomalous results, which are difficult to explain from a physically significant standpoint.

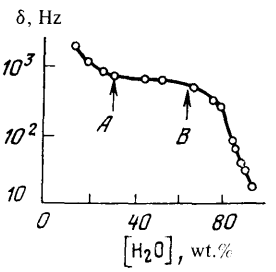


Figure 12. Dependence of the NMR absorption line width δ on the water content in agarose gels at 25°C.[97]

Ideas concerning the state of bound water have been put forward. In particular, it has been shown[104] that the rotational motion of its molecules should be anisotropic. At $T > 75$°C the bound molecules begin to rotate more vigorously, which can lead to the disruption of the water–agarose hydroxyls solvate. Agarose gels have been investigated[107] in the temperature range from −10° to −80°C, where free bulk phase water is frozen and the bound water exhibits some mobility (down to −80°C). The form of the temperature and concentration variations of T_1 permits the conclusion that the molecules of bound water have a different mobility and that their behaviour requires the introduction of a logarithmic normal distribution of the correlation times[108] for molecular motion.

VI. LOW-MOLECULAR-WEIGHT SUBSTANCES ADSORBED ON POLYMERS

1. The Interaction of Adsorbed Molecules with the Polymer

A few studies have been devoted to the NMR investigation of the adsorption of LMS by polymers. In most of them the substance adsorbed by the polymer was water. Thus a study has been made[109] of the interaction of H_2O molecules with oriented nylon 6,6 macromolecules. It was noted that the narrow component in the spectrum, corresponding to the molecules of adsorbed water, appears for a water content in excess of 1.4 wt.% and that its form is independent of the angle between the axis of the fibre and the direction of the magnetic field. For higher percentage moisture contents, water molecules decrease by 20–30°C the temperature of the transition associated with the motion in the crystalline regions of the polymer and lead to the appearance of a water phase with an intermediate mobility, due to motion in the amorphous parts of the polymer, and the "free" water phase. A study of the temperature variation of T_1 and T_2 in a polystyrene latex showed[110] that the presence of water decreases T_g for the polymer particles approximately by 10° and that its influence is somewhat greater in the presence of a concentrated electrolyte (0.1 M manganese sulphate). It has also been found that the penetration of the electrolyte into the polystyrene particles is restricted by a thin layer having a thickness of approximately 1 nm.

The interaction of adsorbed molecules with the polymer depends appreciably on its crystallinity[111]. The same conclusion was arrived at by the analysis of the temperature variations of the relaxation times for various celluloses. It has been found that the barrier to the diffusion of water molecules in cellulose of low crystallinity and based on cotton fibres is lower than in highly crystalline specimens.

The influence of ionic salts on the interaction of water molecules with collagen has been examined[112] on the basis of a ^2H NMR study. The decrease of the deuteron quadrupole splitting due to adsorbed water molecules in the presence of salts indicates a decrease of the fraction of water molecules bound to collagen fibres by hydrogen bonds. It is suggested that ions should either block certain sections of the chain, suitable for the formation of hydrogen bonds, or should alter slightly the conformation of the collagen molecules, hindering the binding of water.

Analysis of the NMR data for hydrated and oriented collagen fibres [113,114] suggests that water molecules diffuse rapidly between the polymer fibres. This motion is slightly anisotropic.

The study of the relaxation behaviour of water molecules adsorbed on keratin led to the hypothesis[115] that water molecules form clusters, whose number increases with increasing water content in the specimens. It has been established that water molecules have a continuous spectrum of correlation times for their motion and that, with increase in the amount of moisture in the specimens, the width of the spectrum diminishes.

In hydrated collagen only some of the adsorbed water molecules are linked to the collagen triple helix and are oriented. The remaining ("free") molecules are in a state of rapid reorientation. There is rapid exchange between the bound and free molecules. Examination of the NMR spectra led Fung and Traumann[112] to the same conclusion. It is believed that, in the presence of high water contents, excess water appears and is distributed on the surface of the specimen where it does not participate in exchange with water within the bulk of the specimen.

It has been reported[116] that 0.05–0.3 of all the cellulose protons are involved in exchange with water protons in celluloses or purified paper fabrics, silk yarn, and artificial silk in the presence of 7% of water.

The study of water adsorbed by specimens of cellulose acetate with different degrees of substitution at 20°C and a water concentration of approximately 10% showed[117] that the mobility of water molecules passes through a maximum for degrees of substitution in the range 0.5–0.6. The change in the mobility of water molecules is caused by redistribution of hydrogen bonds.

The NMR method makes it possible to determine the amount of water bound to the polymer. Thus it has been found[118] from ^2H NMR spectra that in oriented collagen fibres 1 g of the polymer binds 0.6 g of heavy water. The amount of water in celluloses of different types has been

determined[119] from measurements of spin–spin relaxation. Assuming that the bound water is distributed in a monomolecular layer, the authors[119] estimated the surface area of the specimens, the results agreeing satisfactorily with data obtained by other methods.

The relaxation analysis of ^1H NMR data for water adsorbed by lyophilized methaemoglobin crystals[120] showed that 1 g of the protein binds 16 mg of water. For a high moisture content in the compositions (up to 350 mg per g of the polymer) at −40°C a water phase is observed with correlation times intermediate between the values of τ_c for bound and ordinary liquid water.

However, despite the successful application of the NMR method to the determination of the number of bound water molecules by polymers and to the investigation of certain characteristics of their motion, it has been shown[121] for the relaxation of PAA in D_2O and H_2O that the difference between the rates of relaxation of the water associated by the polymer and unassociated water is small and yields no information about the behaviour of hydrated water molecules.

2. The "Freezing" of Adsorbed Water

A reduction of the temperature of the adsorbed mixture below 0°C does not lead to the appearance of breaks on the curves for the temperature variation of T_1 and T_2.[111] The signal amplitude is also constant and indicates a fairly high mobility of the adsorbed water molecules. On the other hand, the T_2–temperature plots for cotton cellulose show an inflexion in the region of 0°C. It has been suggested[111] that a certain amount of water on cotton cellulose behaves analogously to bulk-phase water. Below 243 K, the "freezing" of adsorbed water is observed in both systems and the NMR signal amplitude falls almost to zero at 223 K. The "freezing" process observed at low temperatures is not an indication of the formation of the ice lattice. A similar conclusion was arrived at[115] in a study of the relaxation times of keratin hydrates containing between 12 and 34 wt.% of water and in a study[122] of the relaxation of the water adsorbed in an amount of 33% by the walls of *Bacillus megaterium*.

It has also been discovered[115] that the correlation times of the water molecules adsorbed on keratin are approximately 10^3 times shorter at 270 K than in ice and that in the temperature range 273–240 K the above time is smaller by a factor of 100 than in the bulk-phase water. The authors believe[115] that the ice lattice is formed at high concentrations because some of the water molecules have "moved away" somewhat from the polymer surface and interact only slightly with the latter.

At high water concentrations, for example, in highly hydrated collagen containing more than 0.8 g of D_2O per g of the polymer, it was found that approximately 0.2 g of water is frozen at 0°C.[118]

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The data presented show that the NMR method leads to extensive possibilities for the investigation of polymer–low-molecular-weight substance systems. These possibilities can be greatly expanded by employing ^{13}C NMR spectra and relaxation properties. The application of NMR to the study of such systems is based on the fact that the method makes it possible to assess the molecular mobility, which depends on the concentration of the components, their interaction, the phase state of the specimens, and other factors which determine the macroparameters of the system.

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