Depolarization of negative muons in condensed molecular media

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A correlation is established between the residual polarization of negative muons in a medium and its radiation yield. It is shown that the observed correlation can be satisfactorily explained by a formal theory involving fast reactions between the mesoradicals and the ambient medium. The chemical reaction rates for mesoradicals in different hydrocarbons are determined. The precession method has been used to determine the asymmetry coefficient for electrons from negative muon decays in aqueous solutions of hydrogen peroxide with various concentrations at room temperature. The asymmetry coefficient has been measured for a peroxide solution with a concentration of 97 wt.% at 80°K. The rates of chemical reactions involving mesic nitrogen have been determined. It is shown that the activation energy must be taken into account in the chemical reaction between the mesic nitrogen and the molecules of the hydrogen peroxide. The depolarization has been measured for a number of organic compounds as a function of temperature.

In previous papers,[1,2] we put forward a hypothesis about the depolarization of negative muons in a condensed medium as a function of macroscopic parameters of the medium, and developed a formal theory which associates the residual polarization of the muons with fast chemical reactions involving mesic radicals. In this paper, we report the results of an investigation into the connection between the depolarization and the radiation yield of the medium (see [3]), impurity concentration, temperature, and structural changes at the phase-transition point.

1. RELATION BETWEEN THE DEPOLARIZATION OF NEGATIVE MUONS AND THE RADIATION YIELD OF THE MEDIUM

One of the characteristics of a medium is its radiation yield which may be represented by the yield of radicals during the radiolysis of the medium. In radiation chemistry, the radiation yield is represented by the quantity G_R(1/100 eV) which is the yield of stabilized radicals during the absorption by the medium of 100 eV of the energy of the incident ionizing radiation.[4] To minimize recombinations of the radicals, experiments on G_R are performed at sufficiently low temperatures. It is well known [4] that radiolysis of hydrocarbons in liquid and solid phases is accompanied by the formation of radicals, mainly as a result of the breakage of the CH bond, because the hydrogen atom readily leaves the Frank-Rabinowitch cell.[5] Even at liquid nitrogen temperatures, the hydrogen atoms can enter into different chemical reactions, i.e., recombine, remove hydrogen from the original molecules, or, in the case of compounds with multiple bonds, become attached to them. Thus, experiments concerned with the determination of G_R usually involve radicals which are formed and are removed along the following channels [6]:

$$\mathrm{RH} \rightsquigarrow (\mathrm{RH})^{\cdot} \to \mathrm{R}^{\cdot} + \mathrm{H}^{\cdot}, \tag{1a}$$

$$\mathrm{RH} + \mathrm{H}^{\cdot} \to \mathrm{R}_1^{\cdot} + \mathrm{H}_2, \tag{1b}$$

$$\mathrm{RH} + \mathrm{H}^{\cdot} \to \mathrm{RH}_2^{\cdot}, \tag{1c}$$

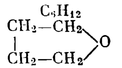
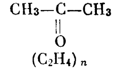
$$\mathrm{H}^{\cdot} + \mathrm{H}^{\cdot} \to \mathrm{H}_2 \tag{1d}$$

As noted in [2], the atomic capture of a muon and its cascade transition to the K shell are accompanied by the emission of a large number of Auger electrons,[7] and this may lead to strong Coulomb repulsion of the highly ionized fragments of the molecule.[8] This, in its turn, leads to the radiolysis of the medium surrounding the mesic radical. It is clear that in compounds such as hydrocarbons, the effect of the radiation on the medium at the point of formation of the mesic atom will always be the same because the muons settle mainly on the carbon atoms. In that case, the radiation yield of radicals formed by the Auger electrons and fragments of molecules determines the rate at which the mesic radical enters the chemical reaction, and hence the residual polarization of the muon.

There is a large number of papers in the literature on the determination of the radiation yield of radicals per 100 eV absorbed by the medium. The review given in [6] quotes the most important papers and lists the values of G_R(1/100 eV) for a large number of organic compounds. These values of G_R(1/100 eV) were obtained as a result of radiolysis by a beam of approximately 1.6 MeV electrons in specimens between −180° and −150°C. Such low temperatures were chosen to prevent secondary reactions involving radicals in the solid. Of course, at such temperatures, only sufficiently heavy radicals with relatively low diffusion coefficients are stabilized.

Table I gives a selection of experimental data taken from the literature (see, for example, [6,9,10]) on the

TABLE I. Summary of data on radiation yield (G_R) and residual polarization of muons (a/a_C) for organic compounds

No.	Medium	Structure	a/a_C	Reference	G_R	Refenrence
1	Diphenyl	Ph—Ph	0.14±0.03	Present work	0.045±0.009	[6]
2	Toluene	Ph—CH_3	0.30±0.06	[11]	0.08±0.02	»
3	Phenol	Ph—OH	0.30±0.05	Present work	0.10±0.02	»
4	Anisole	Ph—O—CH_3	0.58±0.02	»	0.10±0.02	»
5	Benzene	Ph	0.35±0.07	[9]	0.16±0.03	»
6	Chlorobenzene	Ph—Cl	0.32±0.07	Present work	0.20±0.04	»
7	Styrene	Ph—CH=CH_2	0.45±0.04	[9]	0.30±0.06	»
8	Phenylcyclohexane	Ph—C_6H_{11}	0.43±0.04	[11]	0.30±0.06	»
9	Cyclohexane	C_6H_{12}	0.51±0.04	»	1.6±0.3	»
10	Tetrahydrofuran		0.64±0.05	Present work	1.7±0.3	»
11	Acetone	 $CH_3-C(=O)-CH_3$	0.63±0.05	»	1.8±0.9	[9]
12	Polyethylene	$(C_2H_4)_n$	0.51±0.05	[11]	3.0±1.5	[10]
13	Methanol	CH_3OH	0.75±0.05	[9]	5.5±2.7	[9]
14	Ethanol	C_2H_5OH	0.67±0.05	»	6.0±3.0	»

radiation yield of radicals $G_R(1/100\ \text{eV})$ for which measurements are available on the relative (against a graphite target) asymmetry coefficients for electrons from negative-muon decays in units of a/a_C,[11-13] where a_C is the asymmetry coefficient for graphite. The various compounds listed in the table clearly divide into two groups, depending on the magnitude of $G_R(1/100\ \text{eV})$. One group contains the aromatic compounds with $G_R < 1$, and the other contains saturated compounds with $G_R > 1$. According to some workers (see, for example, [14]), this difference in the radiation yield is due to the difference between the positions of the first excited states of the molecules. In compounds with multiple bonds, the first excited state lies below the C–H bond energy and, consequently, the probability of dissociation from the longest-lived first excited state is substantially reduced.

Table I shows a clear correlation between the radiation yield of radicals and the residual polarization of muons in the various media. The residual polarization increases with increasing G_R. This correlation is determined by the relationship between the residual polarization of muons and the rate of chemical reactions involving the mesoradical, which is proportional to the radiation yield of the radical.

In a previous paper,[2] we gave a relationship between the residual polarization of negative muons and the rate at which the mesoradicals entered into chemical reactions. This result was obtained on the assumption that the rate ν of hyperfine interaction between the magnetic moment of the paramagnetic electron shell, on the one hand, and the magnetic moment of the muon in the K shell, on the other, was much greater than the precession frequency Ω of the resultant magnetic moment in the external magnetic field. For the boron mesoradical (mean values for the ground and metastable states of the electron shell $\bar{\nu} = 2.5\times10^9\ \text{sec}^{-1}$ and $\Omega_{50\ \text{gauss}} \approx 10^9$ rad sec^{-1}) one must simultaneously take into account the effect of both interactions. In that case, the asymmetry coefficient for the decay electrons is given as an average over the probabilities of entering the chemical reaction:

$$x(t_1) = FB_C\cos(\omega t+\Omega t_1) + (1-F)B_0\cos(\omega t+\Omega t_1+\pi f(t_1\nu)). \tag{2}$$

In this expression, t_1 is the time at which the mesic atom enters the reaction,

$$F = \frac{1}{3}\left[1+\frac{2}{(2J+1)^2}\right], \tag{3}$$

J is the angular momentum of the paramagnetic electron shell of the mesic radical, B_0 is the asymmetry coefficient of the decay electrons which would correspond to the polarization of the muon at the end of the cascade,

$$f(t_1\nu) = \begin{cases} 0 \text{ if integral part of } (t_1\nu) \text{ even} \\ 1 \text{ if integral part of } (t_1\nu) \text{ odd} \end{cases} \tag{4}$$

and ω is the precession frequency of the free muon spin, observed experimentally.

Equation (2) leads to the following relation between the residual polarization and the rate at which the mesic radical enters the chemical reaction:

$$\frac{a}{a_C} = \frac{a_0}{a_C}\frac{\lambda}{\lambda_0}\left\{\frac{\lambda_0^2}{\lambda_0^2+\Omega^2}\left[F^2+(1-F)^2\left(\operatorname{ch}\frac{\lambda_0}{\nu}-\cos\frac{\Omega}{\nu}\right)\Big/\left(\operatorname{ch}\frac{\lambda_0}{\nu}+\cos\frac{\Omega}{\nu}\right)\right.\right.$$
$$\left.\left.+2F(1-F)\operatorname{sh}\frac{\lambda_0}{\nu}\Big/\left(\operatorname{ch}\frac{\lambda_0}{\nu}+\cos\frac{\Omega}{\nu}\right)\right]\right\}^{1/2}. \tag{5}$$

When $\nu \gg \Omega$ and $\lambda_0 \gg \Omega$ this formula takes the form

$$\frac{a}{a_C} = \frac{a_0}{a_C}\frac{\lambda}{\lambda_0}\left[F+(1-F)\operatorname{th}\frac{\lambda_0}{2\nu}\right], \tag{6}$$

which is, in fact, the relation given in [2].

We used (6) in [11] to analyze experimental data on the temperature dependence of the residual polarization in styrene and benzene. In [15] a similar analysis was given for water and a solution of hydrogen peroxide with a concentration of 7.5 wt.%. Table II (second row for each material) gives the results based on (5) on the assumption that the ratio $a_0\lambda/a_C\lambda_0$ is independent of temperature and

$$\lambda_0 = \Lambda\frac{T}{300}e^{-E/RT}, \tag{7}$$

where Λ is the pre-exponential factor in the rate of chemical reaction involving the mesic radical at $T = 300$°K, E is the activation energy for the chemical reaction involving the mesic radical with the formation of a diamagnetic product, and R is Boltzmann's constant. The factor proportional to the first power of the temperature T/300 is introduced into the expression for λ_0 because the chemical reactions of the mesic radical with radicals formed in the medium must be described in terms of reactions whose rate is controlled by diffusion.[16] The analysis was carried out by the method of least squares in the parameters $a_0\lambda/a_C\lambda_0$, E, and Λ. We note the very low values of the activation energy E which confirm the radical-radical nature of the reactions of the mesic atom. The first row gives for each material the data obtained in [11,15] with λ_0 recalculated using the more accurate values of $\bar{\nu}$ ($2.5\times10^9\ \text{sec}^{-1}$ for mesic boron and $7\times10^9\ \text{sec}^{-1}$ for mesic nitrogen). The last column in Table II gives the rates of chemical reactions of mesic radicals at room temperature.

Table I can be used to select compounds which, as a result of radiolysis, will yield radicals which react with mesic radicals (mesic boron) in the same way. These are the aromatic compounds [with the exception of arrisole for which we obtain an anomalously high value (≳30%) for the capture of muons by the OCH_3 group], cyclohexane, and polyethylene. Phenol also belongs to this group since capture by oxygen amounts to ≲7%. In all these compounds, with the exception of atomic hydrogen, the resulting radicals have linear dimensions which impede their migration from the chemical activity zone of the mesic radical.[17]

Figure 1 shows the empirical relationship between the experimental data on the asymmetry factor a/a_C and the radiation yield of radicals for the compounds taken from Table I (the uncertainty in G_R is not shown in Fig. 1). The solid curve describes adequately ($\chi^2 = 3.1$) the experimental points and agrees with (5) provided

TABLE II. Results of an analysis of the residual polarization of muons as a function of the temperature of the material

Material	$a_0\lambda/a_C\lambda_0$	E, cal	m	$\Lambda\cdot10^{-10}$, sec^{-1}	$\lambda_0\cdot10^{-10}$, sec^{-1}
Water	0.39±0.02	—	2.3±1.1	—	3.2±2.4
	0.40±0.02	232±176	—	5.2±4.0	3.5±2.7
H_2O_2 (7,5 %)	0.59±0.07	—	1.4±0.4	—	2.4±1.5
	0.60±0.02	197±29	—	5.3±4.0	3.8±1.8
Styrene	0.49±0.05	—	3.7±1.3	—	0.60±0.25
	0.60±0.34	345±135	—	0.55±0.16	0.31±0.09
Benzene	0.36±0.03	—	1.9±0.6	—	0.60±0.40
	0.54±0.16	0±275	—	0.18±0.09	0.18±0.09

$$\lambda_0 = \Lambda G_R. \tag{8}$$

The following values of the parameters were found: $a_0\lambda/a_C\lambda_0 = 0.51 \pm 0.03$ and $\Lambda = (1.7 \pm 0.3) \times 10^{10}$ sec^{-1} for $G_R = 1$; the uncertainties in G_R were not taken into account in these calculations.

Figure 1 enables us to estimate the rate at which the mesic radical enters into chemical reactions with radicals produced during the stopage and capture of the muon in different compounds at room temperature. The systematic uncertainty in the rate of chemical reactions is due to the formalism used to describe this dependence and does not exceed 30%, and the 20% uncertainty in G_R [6] leads to a 20% uncertainty in λ_0. Consequently, the uncertainty in the rate at which the mesic radical enters the chemical reactions in Fig. 1 is 27%. The rates at which the mesic radicals enter the chemical reactions at room temperature, obtained from (8) with allowances for the uncertainties in G_R for benzene and styrene are, respectively, $(2.7 \pm 0.7) \times 10^9$ and $(5.1 \pm 1.4) \times 10^9$ sec^{-1}, and agree to within experimental and systematic uncertainties with the rates obtained from the temperature dependence of the residual polarization in the same media. This can also be noted for the values of the parameter $a_0\lambda/a_C\lambda_0$ (see Table II). The fact that there is a correlation between the residual polarization of negative muons and the radiation yield of radicals in a given material may be regarded as confirmation of the hypothesis of fast (as compared with the rates of hyperfine splitting) chemical reactions between the mesic radicals of boron and the radiolysis products of the medium.

Since the mean time of entry of the mesic boron into chemical reactions with the surrounding medium is of the order of 2×10^{-10}–3×10^{-10} sec, one would expect that a/a_C would, in contrast to G_R, be sensitive not only to radicals formed along channel (1) but also to radicals formed as a result of the breaking of the C–C bond because mesic boron can be an acceptor of such radicals in the Frank-Rabinowitch cell.[6] The probability of chemical reactions between mesic boron and atomic hydrogen appears to be small because of the high mobility of the latter which reduces the hydrogen concentration in the chemical reaction zone of mesic boron. From the correlation between a/a_C and G_R, we may conclude that radicals formed along channels (1b) and (1c) lie within the radius of chemical action of the mesic radical of boron.

It is clear from the data in Table I that the relative asymmetry coefficient for oxygen-containing media (with the exception of phenol for the reasons indicated above) is substantially greater than in hydrocarbons. This fact can also be readily explained in terms of the hypothesis of fast chemical reactions of mesic radicals. The point is that the mesic radical of nitrogen, which is produced during the atomic capture of the muon by oxygen, very rapidly enters chemical reactions not only with radicals but also with neutral molecules of organic materials with the formation of mainly the diamagnetic cyanide $\text{H}-\text{C}\equiv\mu\text{N}$.[18]

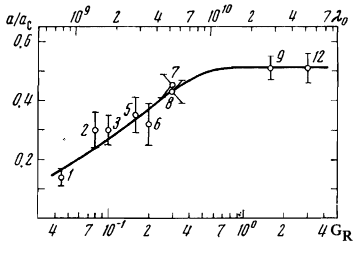


FIG. 1. Relative asymmetry coefficient as a function of the radiation yield of radicals. The numeration corresponds to Table I.

2. DEPOLARIZATION IN AN AQUEOUS SOLUTION OF HYDROGEN PEROXIDE

We have shown in [15] that the relative asymmetry coefficient in the case of an aqueous solution of hydrogen peroxide is much higher than for other aqueous solutions and we gave data on the dependence of the residual polarization of muons on the concentration of the hydrogen peroxide solution. The limiting concentration was 33 wt.%. The absence of experimental data at higher concentrations prevented us from determining with good accuracy the character of the chemical reactions between the mesic nitrogen and the molecules of hydrogen peroxide, and of the parameters of the equation describing the dependence of the residual polarization of the negative muons on the concentration of nitrogen peroxide.

In the present paper, we report experimental data on the depolarization of negative muons in high-concentration solutions of H_2O_2 (up to 97%) at two temperatures. Even for water (see [3,13,15]) the temperature dependence of the residual polarization of the muons reaches a plateau, beginning with roughly 0°C. In the hydrogen peroxide solution, there are new channels for chemical reactions involving the mesic radical of nitrogen, and this enables us to conclude that in (6)

$$F + (1-F)\,\text{th}\,(\lambda_0/2\nu) \approx 1. \tag{9}$$

In that case, assuming that a_0 for oxygen in water and in hydrogen peroxide is the same, we find for the two-component solution the following concentration dependence of the residual polarization:

$$\frac{a}{a_C} = \frac{a_0}{a_C}\frac{\lambda}{\lambda_0} = \frac{\lambda'(1-R') + lR'}{\lambda_0'(1-R') + l_0R'}. \tag{10}$$

where λ_0' and l_0 are the rates of chemical reactions between the mesic nitrogen, on the one hand, and pure water and pure hydrogen peroxide, on the other; λ' and l are the same quantities for the formation of diamagnetic compounds, and

$$R' = [H_2O_2] \Big/ \left\{\left(1 - \frac{M_{H_2O_2}}{dM_{H_2O}}\right)[H_2O_2] + \frac{A}{M_{H_2O_2}}\right\}, \tag{11}$$

where $[H_2O_2]$ is the absolute concentration of hydrogen peroxide molecules in cm^{-3}, M is the molecular weight of the material. A is Avogadro's number, and $d = 1.462$ g/cm^3 is the density of pure hydrogen peroxide. Using (11) and the numerical values for A, M, and d, we can rewrite (10) in the form of a function of the absolute concentration of hydrogen peroxide in solution

$$\frac{a}{a_C} = \frac{a_0\lambda}{a_C\lambda_0}\,\frac{1 + (0.30l/\lambda' - 0.39)[H_2O_2]}{1 + (0.30l_0/\lambda_0' - 0.39)[H_2O_2]}. \tag{12}$$

In this expression, the concentration of hydrogen peroxide is given in units of 10^{22} cm^{-3}.

Equation (12) can be reduced by the equalization method to the form

$$Y = A' + B'[H_2O_2], \qquad Y = [H_2O_2] \Big/ \left(\frac{a}{a_C} - \frac{a(R'=0)}{a_C}\right). \tag{13}$$

The rate of chemical reactions between the mesic radical of nitrogen and pure hydrogen peroxide is given by

$$l_0 = \frac{\lambda_0}{0.30}\left(\frac{B'}{A'} - 0.39\right). \tag{14}$$

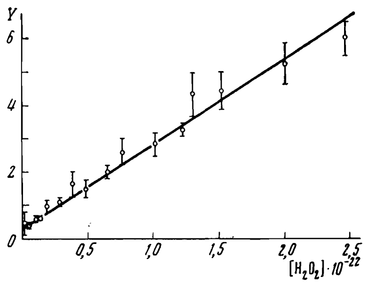


FIG. 2. The function $Y([H_2O_2])$ and experimental points.

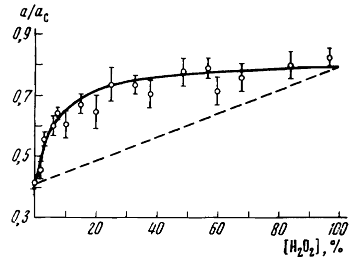


FIG. 3. Residual polarization of negative muons as a function of concentration in aqueous solution of hydrogen peroxide.

A least-squares analysis of the experimental data in the form given by (13) yields the following values for the parameters in (14): $A' = 0.30 \pm 0.04$ and $B' = 2.5 \pm 0.1$. The form of the smoothed function $Y([H_2O_2])$ and the experimental points are shown in Fig. 2. It is clear that, with these parameters, the chosen function satisfactorily describes ($\chi^2 = 8$) the experimental data. Figure 3 shows the relative asymmetry coefficient for electrons from negative muon decays as a function of the hydrogen peroxide concentration. The broken line in this figure shows the relative asymmetry coefficient without taking into account the chemical reactions of the mesic radical formed in one of the components with the other component. For this system

$$\frac{a}{a_C} = \left(\frac{a}{a_C}\right)_{H_2O}(1-x) + \left(\frac{a}{a_C}\right)_{H_2O_2} x. \qquad (15)$$

In this expression $(a/a_C)_{H_2O} = 0.415 \pm 0.015$ is the relative asymmetry coefficient for electrons from negative muon decays obtained for pure water, and $(a/a_C)_{H_2O_2} \simeq 0.8$ is the same factor for pure hydrogen peroxide. It is assumed that the muon capture in H_2O and H_2O_2 molecules is proportional to the electron fractions of the solution components:

$$x = \frac{R'\bar{Z}_{H_2O_2}}{\bar{Z}_{H_2O} + (\bar{Z}_{H_2O_2} - \bar{Z}_{H_2O})R'}, \qquad (16)$$

where $\bar{Z}$ is the mean charge of the molecule. It is clear that (15) does not agree with experimental data. This fact unambiguously confirms the existence of chemical interactions between the μN radical and the ambient medium.

The above values of A' and B', and the mean value $\bar{\lambda}_0 = (2.8 \pm 1.5) \times 10^{10}$ sec^{-1} found from the temperature dependence in water and in the 7.5% (by weight) solution of hydrogen peroxide,[3] can be used to determine the rate at which the nitrogen mesoradical enters into chemical reactions with the hydrogen peroxide molecules: $l_0 = (6.9 \pm 5.0) \times 10^{11}$ sec^{-1}. It is important to note that the main uncertainty in l_0 is connected with the high uncertainty in $\bar{\lambda}_0$. Since l_0 corresponds to the reaction rate for the nitrogen mesoradical in pure hydrogen peroxide, it is possible to determine the rate constant for the chemical reaction between the mesic nitrogen and the hydrogen peroxide molecule: $K = (2.7 \pm 1.9) \times 10^{-11}$ sec^{-1} cm^3. This result is more accurate than the figure given earlier,[15] and agrees to within an order of magnitude with the constants for chemical reactions limited by diffusion.[16]

Since $\lambda_0 \sim [H_2O_2]$, the increase in λ_0 in the case of the concentrated solution of H_2O_2 should lead to a weaker temperature dependence of the depolarization. Bearing in mind the fact that, in the aqueous solution of H_2O_2 with a concentration of 75% by weight, the contribution to λ_0 of reactions between the mesic nitrogen and H_2O_2 and the radicals due to the radiolysis of water are roughly the same, one would expect that, as the concentration of H_2O_2 is increased to 97%, the value of λ_0 will increase by a factor of, say, 5–10. This means that the ratio a/a_C should reach its plateau at temperatures as low as 30–60°K if λ_0 is assumed to be proportional to the first power of the temperature, and if we neglect the activation energy for the $\mu N + H_2O_2$ reactions.

To verify this assumption, we have determined the asymmetry of the decay electrons in an aqueous solution of hydrogen peroxide with a concentration of 97 wt.% at ≈80°K. The relative asymmetry coefficient at this temperature is found to be 0.603 ± 0.026. According to,[15] the ratio of residual polarizations at room (≈300°K) and nitrogen (≈80°K) temperatures for the 7.5% solution of hydrogen peroxide is $P_{300}/P_{80} = 1.85 \pm 0.15$, whilst for the 97 wt.% concentration the result is $P_{300}/P_{80} = 1.39 \pm 0.08$.

The existence of a temperature dependence of the residual polarization in pure hydrogen peroxide shows that the activation energy E for chemical reaction between the nitrogen mesoradical and the hydrogen peroxide molecule must be taken into account (see Table II). The addition of the exponential factor to the expression for λ_0 for this value of E leads to a reduction in λ_0 (when the temperature is reduced from 300°K to liquid nitrogen temperature) by a factor of about 5–6, which is to be compared with the reduction by a factor of roughly 4 when only the linear dependence or temperature is taken into account, and this leads to the observed temperature dependence.

3. TEMPERATURE DEPENDENCE OF DEPOLARIZATION IN ORGANIC COMPOUNDS

When the temperature dependence of the depolarization of muons in hydrocarbons [11] was analyzed, no account was taken of the possible discontinuity in a/a_C at the phase transition point. We have carried out a special experiment to detect this discontinuity in styrene. The temperature of the target was monitored by a number of thermocouples and, since the target was in a container made of foamed plastic with 25 mm thick walls, the rate of change in temperature was very low. To produce the solid styrene near the phase transition point (≈−31°C), the target was first frozen down to a much lower temperature and then slowly heated. Measurements in the beam were carried out when the temperature varied within an interval of a few degrees below the phase transition point. The procedure used in measurements with liquid styrene was identical. Two identical targets were used in turn in the measurements. For the ratio of the asymmetry coefficients in liquid and solid styrene, we found $a_l/a_S = 0.93 \pm 0.08$, which suggests the absence of a large phase discontinuity. Using the explanation (see [2]) of the fact that residual polarization in monomers is higher than in polymers,[19] one would expect a slower temperature dependence of the depolarization in polymers, as compared with low-molecular compounds. In fact, if the density of the radicals near the mesic atom in polymers is reduced (as a result of the migration of some of the energy along the molecular chains), this must lead to a shift of the temperature dependence to the region of lower λ_0, well away from the point $\lambda_0 = \nu$, and is characterized by a slower dependence of a/a_C on λ_0 and, consequently, on T.[3]

Our measurements of the ratio of the asymmetry coefficients at 300 and 80°K gave the following values: for polymers 1.57 ± 0.13 (polybutylmethacrylate) and 1.33 ± 0.31 (polystyrene). For monomers the results were 3.6 ± 0.8 (styrene [9]) and 2.72 ± 0.40 (n-butyl alcohol). Comparison of these data clearly shows that the temperature dependence in polymers is, in fact, slower.

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