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STATE OF DIBUTYL PHTHALATE MOLECULES IN PLASTICIZED POLY(VINYL CHLORIDE)*

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It was found that the rotational motion of plasticizer molecules in the polymer matrix is hindered, the degree of hindrance differing for different molecules. With use of the data on the dibutyl phthalate (DBP) autodiffusion it was possible to evaluate the lifetime of the PVC–plasticizer solvates. This lifetime is a function of the amount of small molecules and of temperature. The solvatation in these systems is of the dynamic type. The "free" plasticizer is absent in samples containing 30–52 wt.% DBP. The measurements were made by the pulse NMR method.

Several investigations have been reported in connection with the state of plasticizer molecules introduced into polymer [1]. However, the problem has yet to be fully resolved. In some cases use of the NMR method allows separate evaluation of the mobility of macromolecules and molecules of a low molecular substance and it appears that the use of NMR may provide additional information on the mode of behaviour of molecules of components forming part of plasticized systems.

Our aim in the present work was to shed light on the state of dibutyl phthalate (DBP) molecules in PVC, using a pulse NMR method.

Samples were prepared by press moulding at 180° from C-70 grade PVC with $\sim 7\%$ crystallinity determined by the X-ray method, and DBP of chemically pure grade. The weight concentrations of plasticizer in the samples $\omega_1 = 30$, 42 and 52%.

Measurement of the nuclear transverse magnetic relaxation times T_2 was based either on the free nuclear induction decay, when $T_2 < 500$ μsec, or on the Carr–Purcell–Mayboom–Hill method [2] with 250 μsec spacings between π-pulses.

Spin-echo or free induction decay $A(t)$ envelopes of the samples are complex in character, and were approximated over a wide range of T as the sum of two curves

$$A(t) = A_{0a} \exp(-t/T_{2a}) + A_{0b} f_b(t), \tag{1}$$

where T_{2a} is the longest transverse relaxation time derived from the $A(t)$ curve, $f_b(t)$ is a decreasing function normally differing the exponent [3]. The decay rate of $f_b(t)$ was characterized as the effective transverse relaxation time T_{2b}, in which the latter function was reduced by a factor of ε. Reasons for subdividing the $A(t)$ curve into two sections are given below. The number of protons having time T_{2a} was defined as $P_a = A_{0a}/A_{0a} + A_{0b}$.

Coefficients of autodiffusion D of the phthalate in the samples were as previously determined in [4]. Measurements of $T_{2a,b}$ were made on a laboratory pulse NMR relaxometer at 22 Mc/s on protons in the temperature range -50–$+120°$.

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