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ABSTRACTS

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NMR STUDY OF ULTRAFINE POLYTETRAFLUOROETHYLENE

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Introduction:

Polytetrafluoroethylene (PTFE) – $(CF_2)_n$ –, obtained by thermal gas dynamic method [1], has a number of unique properties due to which it has found wide application in many areas (see [2] and references therein). The physical essence of this method is the preparation of an aerosol mixture of monomers and oligomers; in definite thermodynamic conditions, the mixture polymerizes into ultrafine powder (UPTFE) possessing improved adhesion to metal surfaces while retaining its protective and friction characteristics. In spite of broad practical application of UPTFE powder, the mechanism of its destruction, the microscopic and supramolecular structure, the internal mobility remain unknown. In the present work we report our interpretation of ^{19}F NMR data obtained in [2,3].

Experimental Results and Discussion

The experimental temperature dependence of the second moment of ^{19}F NMR spectrum and of the spin-lattice relaxation time (T_1) obtained in [2,3], are shown in Figs.1 and 2.

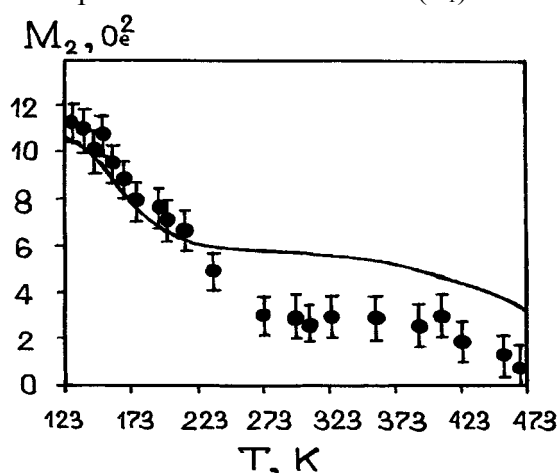


Fig. 1. Temperature dependence of the second moment M_2 (Oe^2) of ^{19}F NMR spectrum of UPTFE. (•) – experimental data and the solid line is the theoretical curve.

PTFE is a partially crystalline polymer, which has been extensively studied by different physical methods. The IR and NMR spectroscopic investigations of UPTFE demonstrated that thermal gas dynamic dispersing changes the structure of polytetrafluoroethylene macromolecules and leads to the formation of oligomers with terminal $-CF_3$ and $-C=CF_2$ groups [2]. From these investigations it follows also that the crystallinity and the formation of macromolecular packing possessing in UPTFE are higher compared to PTFE samples.

The temperature dependence of the second moment (Fig.1) clearly shows that in the temperature range 270-400K, it is observed one more plateau, which may be ascribed to reorientations of both individual CF_2 groups and macromolecules. The experimental value of the second moment on this plateau ($3 Oe^2$) is close to the theoretical value of $2.67 Oe^2$, obtained for the macromolecule reorienting along the longitudinal axis [2,3]. From

In the low-temperature region ($T < 140K$), the second moment of UPTFE is independent on temperature and close to the theoretical value ($M_2 = 9.89 Oe^2$ [2]). This fact indicates that the fluoride subsystem is rigid in this temperature range. At elevated temperatures (150-400K), the resonance signal is narrowed. The transformation is the result of the motion of fluorine atoms with a frequency higher than the width of the NMR spectral line.

In the low-temperature region ($T < 293K$), the shape of the experimental temperature dependence of T_1 is similar to \cup curve with minimal value equals to 425 ms. At $T > 295K$ the shape of the experimental temperature dependence of T_1 is similar to \cap curve with maximal value equals to 1 s.

comparison of the NMR spectra narrowing of PTFE and UPTFE it follows that the motions of fluorine atoms in UPTFE start at lower temperatures than in PTFE [2,3]. This agrees with the assumption concerning the low-molecular composition of UPTFE. Above 400K, the NMR spectrum of UPTFE is narrowed into a narrow line. This transformation of NMR spectrum in this temperature range is result of the diffusion of macromolecule or its segments with a frequency higher than the width of the NMR spectral line.

In order to interpret the experimental results, obtained in [2,3] we have used the theory developed in [4]. The calculated theoretical dependences of $M_2(T)$ and $T_1(T)$ are shown in Figs. 1 and 2. It is well known, that the specific of majority of polymer is its dynamic inhomogeneous. The dynamical inhomogeneous leads to the distribution of the activation energy and the correlation time of molecular motion. So we assumed that the dynamic processes are described by the normal distributions of the activation energies

$$p(E_{ai}) = \frac{1}{\sqrt{2\pi\sigma_{Ei}}} \exp\left\{-\frac{E_{ai} - \bar{E}_{ai}}{2\sigma_{Ei}^2}\right\}. \quad (1)$$

For the first dynamical process (the reorientations of molecular segments about the longitudinal axis of the macromolecule) we used the following parameters in Eq.(1): $\sigma_{E_1} = 5,6$ kJ/mol and $\bar{E}_{a1} = 25$ kJ/mol. For the second dynamical process (the diffusion of the molecular segments) we used the following parameters in Eq.(1): $\sigma_{E_2} = 16.6$ kJ/mol and $\bar{E}_{a2} = 83$ kJ/mol.

From Figs.1 and 2 we see that developed in [4] theory describes rather well the observed temperature dependences of the second moment $M_2(T)$ and spin-lattice relaxation rate ($T_1^{-1}(T)$) of ^{19}F nuclei in UPTFE. This confirms also that the proposed model of two independent type of molecular motions (reorientation and diffusion) may be considered as a preferable model for molecular mobility of fluorine nuclei in UPTFE.

References:

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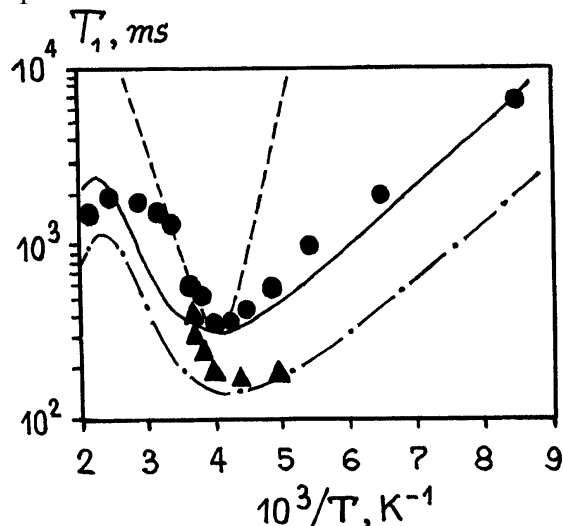


Fig. 2. Temperature dependence of the spin-lattice relaxation time T_1 of ^{19}F in UPTFE. (●) – experimental data and (—) - theoretical curve obtained for $\nu_0 = \omega_0 / 2\pi = 38$ MHz; (▲) – experimental data and (- · - · -) - theoretical curve obtained for $\nu_0 = \omega_0 / 2\pi = 15$ MHz; (---) – theoretical curve calculated using classical BPP theory. This curve was obtained with correlation time $\tau_c = (3,4 \pm 0,6) \cdot 10^{-14} \exp(28,8 \pm 0,4 \text{ kJ/mol/kT})$ s.