NMR STUDIES OF MOLECULAR MOTION OF ULTRADISPERSED POLYTETRAFLUOROETHYLENE

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Molecular motion in ultradispersed polytetrafluoroethylene obtained by special gas-phase technology has been studied experimentally and theoretically based on a temperature dependence of the second moment of ^{19}F NMR spectra and the time of spin-lattice relaxation. The results of observations are interpreted as the consequence of reorientation motion of CF_2 groups around the axis of macromolecules at low temperature and of translational motion of macromolecules in the high temperature region. Qualitative differences from the molecular motion in industrial polytetrafluoroethylene (teflon-4) were detected and parameters of dynamic processes determined.

Keywords: ultradispersed polytetrafluoroethylene, molecular motion, NMR, the second moment, spin-lattice relaxation.

INTRODUCTION

Polytetrafluroethylene (PTFE) containing a great number of ^{19}F nuclei convenient for the resonance observation provides excellent opportunities to examine the molecular dynamics by NMR techniques, especially since dynamic processes are realized in a moderate temperature range requiring no special experimental contrivances. Both the stationary ^{19}F NMR [1, 2] and spin relaxation time measuring [3-5] techniques were applied in the study of PTFE. In the temperature range 200-350 K, a considerable narrowing of the resonance line in ^{19}F NMR spectra has been observed that is the result of motion of molecular fragments. Along with common temperature behavior of NMR spectra, samples of different sorts and with different temperature history manifested special features. Hence, a study of ultradispersed polytetrafluroethylene (UPTFE) powder obtained by a thermal gas dynamic technique [6] seems reasonable. As was shown by the studies with different methods [7, 8], it has a different morphological and microscopic structure in comparison with the samples of industrial makes of teflon-4 type. Thus, in the composition of UPTFE there are groups $-CF_3$, $-CF=CF_2$ [8] not typical of PTFE. By radiographic measurements [9] it has been determined that the crystalline phase of PTFE below 292 K has a triclinic unit cell formed by spiral-like macromolecules with a period of 13 links (CF_2-groups),crystalline phase II. In the temperature range 292-303 K, the polymer has a hexagonal crystalline structure (phase IV), whose period of spirals is formed of 15 links. Above 303 K, a quasi-hexagonal structure (phase I) is observed in the absence of orientation ordering of CF_2 groups with preservation of the hexagonal packing of macromolecules. At the same time, powder X-ray diffraction studies of UPTFE [10]

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have shown that at room temperature the polymer crystallizes in a quasi-hexagonal phase; not excepting that it also remains at even lower temperatures. In a certain respect, the technology of obtaining the ultradispersed powder was hardening of the high temperature phase.

EXPERIMENT PROCEDURE

The ultradispersed powder was prepared by thermal decomposition of block polytetrafluoroethylene with subsequent nucleation and condensation of gas products of pyrolysis. Optical and electronic microscopy determined that the obtained microparticles had a spheroid shape with the average diameter 550 nm within 100 nm to 1200 nm dispersion.

^{19}F NMR spectra were recorded with simultaneous digitization on a modified RYA2301 spectrometer at a frequency of 48 MHz. The accuracy of determination of spectrum second moment was 5%, and temperature fixation 0.1 K. The time of spin-lattice relaxation (T_1) was measured on a device of a laboratory production based on a IS-3 commercial pulse spectrometer of nuclear quadruple resonance. Measurements were made at a frequency of 26 MHz. Values T_1 were determined by kinetics of regeneration of nuclear magnetization using the pulse sequence 90°–τ–90°. The accuracy of T_1 determination is about 3-5%. Temperature stabilization was performed in a cryostat by gas flow: below room temperature by vapors of liquid nitrogen, above room temperature by hot air. The error of sample temperature determination does not exceed 2-3 K; temperature stability of the gas flow during the measurement is 0.2 K and higher.

RESULTS AND DISCUSSION

Fig. 1 shows the temperature dependence of the second moment (M_2) of the ^{19}F NMR spectrum of ultradispersed powder. A two-step decrease of M_2 with temperature rise is observed, that is quantitatively different from the data for industrial samples of PTFE [1, 2]. The value of M_2 for the UPTFE sample (11.8 E^2) in the region of a low temperature plateau (Fig. 1, below 150 K) is slightly higher than 11.4 E^2 [1] and 10.8 E^2 [2] in industrial samples from different producers. We can assume several reasons for the observed difference: the difference in crystalline structures of ultradispersed and industrial polymers at low temperatures; different microscopic structures of macromolecules of polymers; different ratios between the portions of crystalline and amorphous phases. However, the absence of reliable data on interatomic spaces in crystalline phases, the number of CF$_3$ groups in UPTFE samples, the ratio of amorphous and crystalline phases does not allow us to make sufficiently rigorous calculations. The qualitative estimations show that the noticed mechanisms rather well allow for the observed differences.
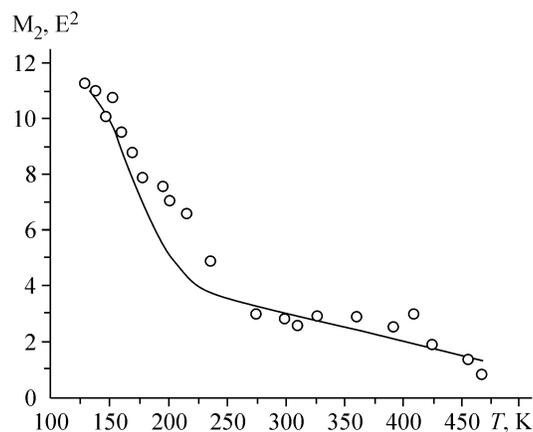
Fig. 1. Temperature dependence of the second moment of the ^{19}F NMR spectrum of the polytetrafluroethylene ultradispersed powder: o — experimental data, the solid line is the fitting curve.
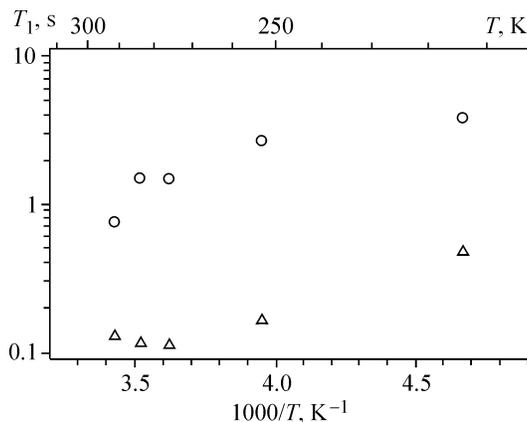
Fig. 2. Time of nuclear spin-lattice relaxation in the industrial teflon (the mean for several samples); △ — fast relaxing phase, ○ — slowly relaxing phase.

Another difference in $M_2(T)$ dependence is that the temperature of the beginning of transformation of the UPTFE NMR spectra is substantially lower (~150 K) than in industrial samples (200-250 K). Lower temperature of the spectrum narrowing reflects higher orientation mobility of CF_2 groups in the ultradispersed sample. The latter can be the result of their disordering in crystalline phase I, which creates more favorable conditions for reorientation or rotational motion of these groups.

Note also that the transition region from the first to the second plateau in the ultradispersed sample is extended along the temperature axis almost by 120 K, while in industrial samples it takes no more than 50 K. The broad transition region may evidence a great dispersion of parameters of reorientation motion of CF_2 groups in UPTFE. It should be noted that extended transition regions hamper the determination of numerical parameters of the internal motion of molecules from the temperature dependence of the line width and the second moment of spectra.

As to the beginning of the second plateau decrease for the ultradispersed sample, it is displayed in the region of 400 K typical also of both industrial samples. At these temperatures, total averaging of dipole-dipole interaction of nuclei occurs due to diffusive motion of macromolecules or of their separate moieties with a corresponding change in the shape of the resonance line. Above 423 K, a spectrum of high resolution is observed in the UPTFE sample, which makes it possible to fix a low-intensive line shifted by 40 ppm to the weak field with respect to the main signal. This component is absent in PTFE spectra. Its origin, judging by quantum chemical calculations of chemical shifts [11], belongs to the signal from CF_3 groups, which are produced in the process of PTFE dispersion by thermal gas dynamic technique.

Theoretical calculations based the on the molecule structure computed with Desktop Molecular Modeler (Oxford Electronics) software give for intra- and intermolecular contributions to M_2 of the spectrum averaged by reorientation motion the values of 2.67 E^2 and 0.625 E^2, respectively [8].

Studies of relaxation times of nuclear magnetization (T_1, T_2, $T_{1\rho}$) [3, 4] and decay of free induction [5] have detected in PTFE industrial samples two types of fluorine atoms with highly different mobility [3]. The time of spin-lattice relaxation for different types of atoms differs 5-10 times. More mobile molecular groups were traditionally correlated with the amorphous component of the polymer. But as it has been shown by the studies of crystalline samples (97% crystallinity) [4], in this case also subsystems with different mobility are observed. Therefore, the cause for the existence of subsystems of fluorine atoms with different mobility in polytetrafluoroethylene remains obscure.

Our calculations for T_1 of several teflon-4 samples have supported the said about the presence of dynamic heterogeneity of fluorine atoms in the polymer. Fig. 2 illustrates averaged results for room and below room temperatures.
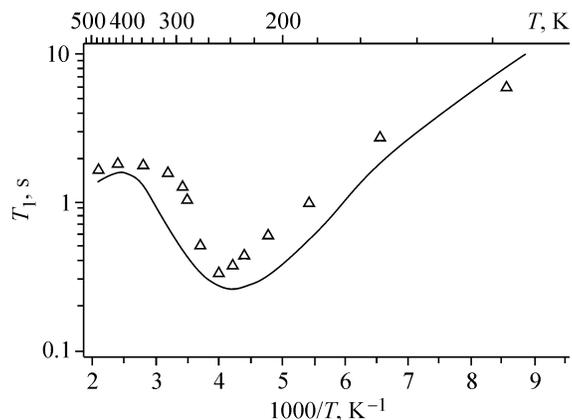
Fig. 3. Time of nuclear spin-lattice relaxation in polytetrafluroethylene powder; △ — experimental data, solid line is a fitting curve.

According to our data, short and long times of relaxation differ by an order. The ratio of rapidly and slowly relaxing phases was estimated as 1:1-1:1.5*.

In the sample of ultradispersed PTFE, an unexpected signal described only by one time of spin-lattice relaxation T_1 was observed. Fig. 3 illustrates the T_1 dependence on the inverse temperature. The presence of one time of relaxation shows that in the ultradispersed sample, unlike the teflon-4 samples, there is no division of fluorine atoms into two subsystems. Therefore, we observe the appearance of a certain dynamic homogeneity inside the fluorine system with the maintenance of the distribution of relaxation parameters. Below 300 K, the temperature dependence is a V-shaped curve with a minimum value of 330 ms near 250 K. The comparison with the data for teflon-4 samples shows that the value T_1 observed in the ultradispersed polymer has an intermediate value between the values for crystalline and amorphous phases. For example, near 273 K the value T_1 for ultradispersed phase is ~500 ms (Fig. 3), and in the crystalline and amorphous phases according to the data from [3] and our (Fig. 2)** ~1500 ms and ~100 ms, respectively. At the same time, the minimum of T_1 UPTFE is situated in the same temperature region as the minima of both phases of PTFE [3].

Unlike the usually used Bloembergern–Purcell–Pound model curve [12], the observed T_1 dependence is asymmetric to the temperature minimum. The low temperature branch has an essentially lower incline comparing to high temperature one, and the extreme point (region 120 K) does not lie on the line at all, thus having an explicitly underestimated value. The traditionally used quantitative determination of activation energy of motion along the incline of branches [12] is in this case incorrect. This is likely to be the reason why the numerical parameters of fluorine motion in PTFE samples investigated in [3] were not determined. The observed shape of the relaxation curve indicates a wide set of parameters of reorientation motion of CF_2 groups in UPTFE. Such a behavior of T_1 is consistent with the above noticed extension of the transition region between the first and second plateaus in the diagram of the temperature dependence of the second moment of spectra.

The small value of T_1 near 120 K may be associated with the presence of paramagnetic centers in UPTFE observed by EPR data [13]. Indeed, the plateau with the level of tens of seconds on the temperature dependence T_1 are not rare in the systems where the dominant mechanism of relaxation turns out to be interaction with paramagnetic admixtures.

The observed decrease of T_1 above 400 K is explained by intensification of the second type of motion (translational). The narrowing of spectra caused by this motion and its beginning in 400 K region has been already mentioned. The

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* It should be noted that experimentally observed processes of nuclear magnetization regeneration do not quite well agree with the approximation of two times of relaxation which was used due to its relative simplicity and lack of information on the functions of distribution of relaxation times. Therefore, the data of Fig. 2 on industrial teflons should be taken as qualitative.

**This comparison is quite normal because our and [3] frequencies of resonance observation do not differ much, and 273°C point is above the temperature minimum.

TABLE 1. Parameters of Reorientation and Translational Motion Used in the Curve Building

Type of motion	M_2	τ_0	$\overline{E}_a$	σ_{E_a}	$\overline{M}_2$	$\overline{\overline{M}}_2 = \langle M_2 \rangle$
Reorientation	12.5	10^{14}	25	3.75	4.5	—
Translational	12.5	10^{14}	62.5	28	—	0

respective minimum on the curve $T_1(T)$ would be still more pronounced at yet higher temperature, at which the sample starts destroying.

Calculation of motion parameters. In [14] analytical expressions for temperature dependences T_1 and M_2 were obtained with the presence of two independent types of motion: reorientation and translational with times of correlation satisfying the Arrenius equation: $\tau_{Ci} = \tau_0 \exp(E_{ai}/kT)$, where $i = 1, 2$; E_{ai} is the activation energy of the appropriate motion.

$$M_2(T) = \langle M_2 \rangle + \left(\overline{\overline{M}}_2 - \langle M_2 \rangle \right) \cdot \frac{2}{\pi} \mathrm{arctg}(\delta\omega \cdot \tau_{c1}) + \left(\overline{M}_2 - \langle M_2 \rangle \right) \cdot \frac{2}{\pi} \mathrm{arctg}(\delta\omega \cdot \tau_{c2}) +$$

$$\left(M_2 + \langle M_2 \rangle - \overline{M}_2 - \overline{\overline{M}}_2 \right) \cdot \frac{2}{\pi} \mathrm{arctg}(\delta\omega \cdot \tau_{c3}),$$

$$T_1^{-1} = \frac{1}{6} \left(\overline{\overline{M}}_2 - \langle M_2 \rangle \right) \left[\frac{\tau_{c1}}{1 + (\omega_0 \tau_{c1})^2} + \frac{4\tau_{c1}}{1 + (2\omega_0 \tau_{c1})^2} \right] + \frac{1}{6} \left(\overline{M}_2 - \langle M_2 \rangle \right) \left[\frac{\tau_{c2}}{1 + (\omega_0 \tau_{c2})^2} + \frac{4\tau_{c2}}{1 + (2\omega_0 \tau_{c2})^2} \right] +$$

$$\frac{1}{6} \left(M_2 + \langle M_2 \rangle - \overline{M}_2 - \overline{\overline{M}}_2 \right) \left[\frac{\tau_{c3}}{1 + (\omega_0 \tau_{c3})^2} + \frac{4\tau_{c3}}{1 + (2\omega_0 \tau_{c3})^2} \right],$$

where M_2 is the second moment of the line corresponding to the rigid lattice; $\overline{M}_2$ and $\overline{\overline{M}}_2$ are the second moments of the line narrowed by the first and the second motions, respectively; $\langle M_2 \rangle$ is the moment after the averaging of dipole-dipole interaction of nuclei by two motions with $\tau_{c3}^{-1} = \tau_{c1}^{-1} + \tau_{c2}^{-1}$. There being dynamic inhomogeneity of molecules in the polymer under study, it is necessary to take account the spread of the motion parameters. We used the normal distribution of activation energies with the normalized density function

$$\rho(E_{ai}) = \frac{1}{\sqrt{2\pi}\sigma_i} \exp\left\{ \frac{(E_{ai} - \overline{E}_{ai})^2}{2\sigma_i^2} \right\},$$

where σ_i is the dispersion of the distribution function E_{ai}.

This approach has allowed us to determine quantitative parameters concurrently of reorientation and diffusion motion. The values that best of all describe the experimental data on the second moments and the relaxation time are summarized in the Table 1. Figs. 1 and 3 illustrate, along with experimental points, the calculation diagrams M_2 and T_1. As is seen, the fitting curves quite well reproduce the experimental dependencies. In description of spin-lattice relaxation, a less accurate agreement with experiment can be attributed to the difference in actual and model distributions of the activation energy and, as a consequence, of the relaxation time. Also it may be important that the contribution to relaxation made by interaction with paramagnetic centers is not considered. Moreover, the use of a traditional procedure of averaging over the powder seems not quite correct in the presence of the relaxation time spectrum, which also may remarkably affect the shape of the theoretical curve.

CONCLUSIONS

From the temperature dependence the second moment of ^{19}F NMR spectra and the time of spin-lattice relaxation, the difference in internal mobility of molecules between the industrial samples of PTFE and unltradispersed powder of

polytetrafluoroethylene obtained by the thermal gas dynamic procedure has been determined. Two types of motion in the ultradispersed sample interpreted as orientation and diffusive are observed, but there is a higher mobility exhibited, in particular, in spectrum transformation at lower temperatures. The underlying reason is the different reorientation motion of molecules in different crystalline phases of polytetrafluroethylene. In the temperature interval of the study, UPTFE has a crystalline phase with higher reorientation mobility, which in the industrial samples occurs at above 303 K. Molecular groups in UPTFE display, according to relaxation measurements, dynamic homogeneity — the motion parameters of molecules are similar, though there is a dispersion among them, while in the industrial samples of PTFE there are two groups of molecules with highly different parameters of the reorientation motion. As for the diffusive motion of macromolecules, it is, judging by the temperature of spectra narrowing, identical in samples of ultradispersed and industrial PTFE. On the basis of the theoretical calculation of the temperature dependence of the second moment and the time of spin-lattice relaxation, the quantitative characteristics of the molecular motion distribution have been determined.

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