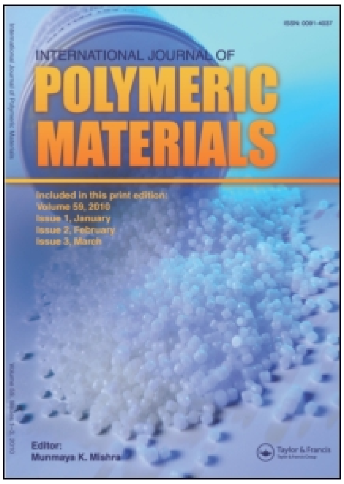

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E. R. Gasilova[a]; V. A. Shevelev[a]; L. D. Budovskaya[a]; V. N. Ivanova[a]
[a] Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg

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Local Anisotropy of the Side Group Motion in the Melts and Swollen Gels of Cross-Linked Comb-Like Polymers

E. R. GASILOVA, V. A. SHEVELEV, L. D. BUDOVSKAYA and V. N. IVANOVA
Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, 199004

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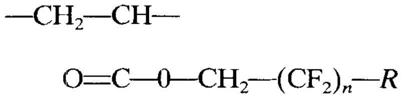
We have investigated the ^{1}H and ^{19}F spin-spin relaxation behavior in the melts and swollen gels of cross-linked polyfluoroalkyl acrylates PFA-nR where n is the number of CF_2 groups in the side chain ($n = 2, 3, 4$). It was found that in the strands the anisotropic motion of the main chain units and the side groups lead to the non-zero degree of averaging of magnetic dipole-dipole interactions (Q). Q of side groups was estimated to depend on the degree of cross-linking $Q \approx b/x$, where x is the number of persistent lengths in the strand. b was found to decrease with increasing n. In opposite to PFA-3F and PFA-2H networks, the dangling ends in PFA-4R network were shown to influence the relaxation behavior, indicating the growth of motional anisotropy of dangling ends with chain diameter.

KEY WORDS Networks, gels, side groups, transversal magnetization

It has been recognized for more than 10 years, that the dependence of the transversal magnetization decay (TMD) on temperature in the swollen networks demonstrates a region of high-temperature plateau (HTP).[1] This region was found also in the melts of the networks obtained by emulsion polymerization.[2] The appearance of HTP in these networks reflects the solid-like character of TMD, which is due to the presence of residual magnetic dipole-dipole interactions.[3,4] They are governed by the anisotropic character of small-scale motions of polymer chains anchored by the cross-links, and therefore depend on the degree of cross-linking. However, very often a complex form of TMD is observed, which can be ascribed to the distribution of the network cell dimensions, or to chain structure defects (namely, dangling ends), or to the motion of the cross-links, and/or to intermolecular contacts.[3–6] The role of these contacts in swollen gels may be diminished.[2]

If the monomer unit of the cross-linked polymer contains side groups, then the question of the side-group contribution to TMD arises. In this work we investigated the role of the side groups in the HTP region of the TMD of cross-linked comb-like polymers. Another goal was to study the influence of dangling ends, taking into account, that the side group can serve to some extent as a model of dangling end.

The investigated polymers are polyfluoroalkyl acrylates (PFA-*nR*) with the repeating unit:



$$\begin{array}{l} -CH_2-CH- \\ \quad\;\; | \\ O{=}C-O-CH_2-(CF_2)_n-R \end{array}$$

namely, PFA-2H, PFA-3F, PFA-4H. Since the fluorine nuclei are located in the side groups, and protons are in the main chain, the ^{19}F- and ^{1}H-TMD were compared.

The preparation of the investigated polymers by emulsion polymerization with a water-soluble initiator has been described previously.[7] The weight percents of the curing agents (ethylene glycole dimethacrylate for PFA-2H and allyl methacrylate for PFA-3F and PFA-4H), m_0 are listed in Table I. Swollen gels containing 30 wt.% of the polymer were prepared by adding the solvent (hexafluorobenzene) and storing the gels for a week at room temperature for making them homogeneous. It should be mentioned, that the PFA-4H and PFA-2H gels were transparent, but the PFA-3F gel was not.

The measurements of TMD were performed on a magnetic pulse relaxometer RRP-1 (resonance frequency 16 MHz, dead time 10 mcs, 90° pulse—2.7 mcs). A 90° pulse was used to measure TMD in the glassy state, a 90°-*t*-180° sequence (*t* is the time interval between the pulses) in the melts or swollen gels. The accuracy of evaluating the rate of simple TMD, described by the exponential or Gaussian functions, was within 3%. In the case of the bicomponent TMD, it was within 10% in the melt and 15% in the swollen gel.

EXPERIMENTAL

In the melts TMD was found to be exponential for both types of nuclei in PFA-2H and PFA-3F, and in PFA-4H it was exponential only for fluorine nuclei

$$A(t)/A_0 = \exp(-t/T_2) \tag{1}$$

TABLE I

Polymer and network characterization

	$\langle\delta\omega_0^2\rangle 10^{-9}$, c^{-2}					
Polymer	^{1}H	^{19}F	2α	m_0 wt. %	x	m/m_0
PFA-2H	13.6		11.6	0		
				2	4.6	0.13
PFA-4H	13.6	5.5	14.2	0		
				1	6.1	0.52
				3	2.0	0.53
				5	1.2	0.55
PFA-3F	15.5	4.5	15.0	0		
				1	19.0	0.18
				2	2.9	0.58
				3	1.2	0.53

where $A(t)$ and A_0 are the amplitudes of the current and initial magnetizations, respectively, and T_2 is the spin-spin relaxation time. In the melts of PFA-4H the ^{1}H-TMD was found to be biexponential:

$$A(t)/A_0 = p \exp(-t/T_{2r}) + (1 - p)\exp(-t/T_{2s}) \tag{2}$$

where the subscripts r and s denote the rapidly and slowly decaying components of TMD, and p is the fraction of the rigid (rapidly decaying) component. Figure 1 shows an example of ^{19}F- and ^{1}H-TMD of PFA-4H.

Figures 2–4 demonstrate some characteristic temperature dependences of spin-spin relaxation times in the melts of cross-linked and uncross-linked polymers. The region of HTP is observed only in the networks of PFA-4H ($m_0 \geqslant 3$ wt.%) and PFA-3F ($m_0 \geqslant 1$ wt.%). In the uncross-linked polymers and slightly cross-linked networks of PFA-4H ($m_0 = 1\%$) and PFA-2H ($m_0 = 2\%$) the slope of the temperature dependence of T_2 only decreases with temperature. The curves in Figures 2–4 clearly show that the values of T_2 decrease with the content of the curing agent.

Figure 5 shows the temperature dependence of p, obtained from the ^{1}H-TMD of PFA-4H. In the uncross-linked PFA-4H p monotonically diminishes with temperature tending to zero. In the cross-linked PFA-4H Figure 5 exhibits the region of HTP, where p increases with the content of the curing agent.

Figure 6 shows the temperature dependences of the proton spin-spin relaxation times T_{2r} and T_{2s} of the swollen gels of PFA-4H and PFA-2H. The curve for the uncross-linked PFA-4H displays a single T_2, monotonically increasing with temperature. In the gels of the cross-linked PFA-4H and PFA-2H the temperature dependences of T_{2s} and T_{2r} demonstrate the region of HTP. As for PFA-3F, it was shown that T_2 (gel) << T_2 (melt). It is probably due to association that takes place in hexafluorobenzene.

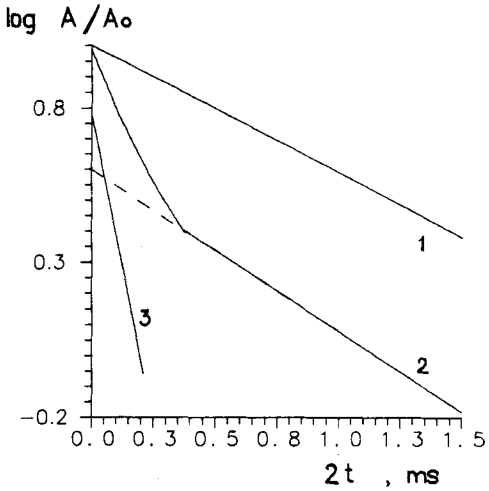


FIGURE 1 Transversal magnetization decay (TMD) at 100°C in PFA-4H: (1) ^{19}F, (2) ^{1}H, (3) calculated rapidly decaying component of ^{1}H-TMD, using a linear extrapolation of the TMD tail (dashed line).

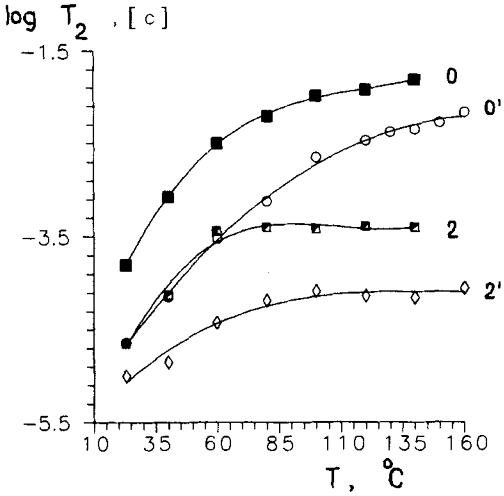


FIGURE 2 T_2 temperature behavior in PFA-3F, cross-linked by 0, 2 wt.% of allyl methacrylate. Parameters: wt.% of curing agent. Prime: ^1H data, without prime: ^{19}F data.

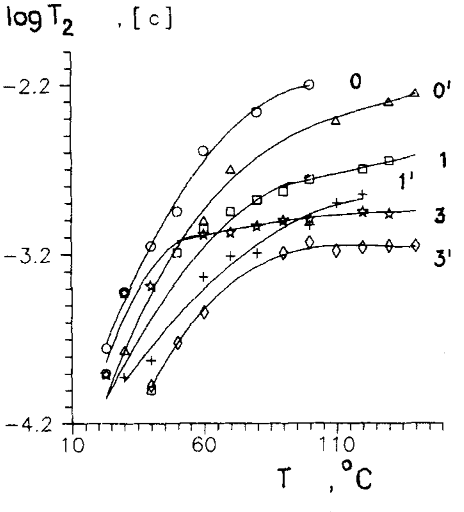


FIGURE 3 Temperature dependence of T_2 (^{19}F) and T_{2s} (^1H) in cross-linked PFA-4H. The other networks are ommited for clarity. Parameters: wt.% of curing agent. Prime: ^1H data, without prime: ^{19} F data. The other networks are ommited for clarity.

DISCUSSION

According to Reference 8, the observed exponential form of ^1H-TMD of the lower homologues of PFA-*nR* ($n = 2, 3$) are probably due to the influence of the random distribution of the cross-links along the chain. The differences in the mobilities of the side groups and the adjoining parts of the main chain do not seem to influence the ^1H-TMD. The exponential form of ^1H-TMD of PFA-3F shows that T_2 of CH_2-group in the side chain is indistinguishable from that of the main chain unit. Therefore, these groups are moving cooperatively with the main chain. The ap-

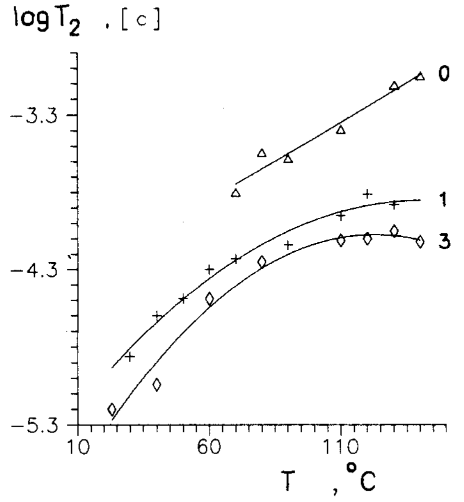


FIGURE 4 T_{2r} temperature behavior in PFA-4H (^{1}H data). Parameters: wt.% of curing agent. The other networks are ommited for clarity.

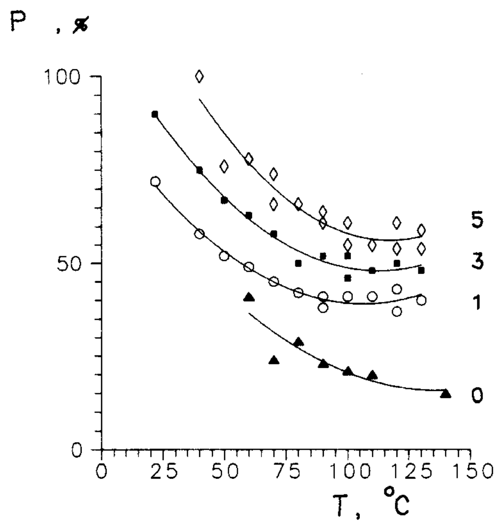


FIGURE 5 Temperature behavior of the rigid component fraction p (^{1}H-TMD) in PFA-4H. Parameters: wt.% of curing agent.

pearance of the slowly decaying component of ^{1}H-TMD in PFA-4H can be attributed to the first approximation to an increase in the mobility of the end CF_2H group with the side chain length.

Let us now estimate the degree of the cross-linking of these networks using its dependence on the degree of non-averaging of the magnetic dipole-dipole interactions (Q) of the main-chain nuclei. The value of Q^2 is determined by

$$Q^2 = \langle \delta\omega^2 \rangle / \langle \delta\omega_0^2 \rangle \tag{3}$$

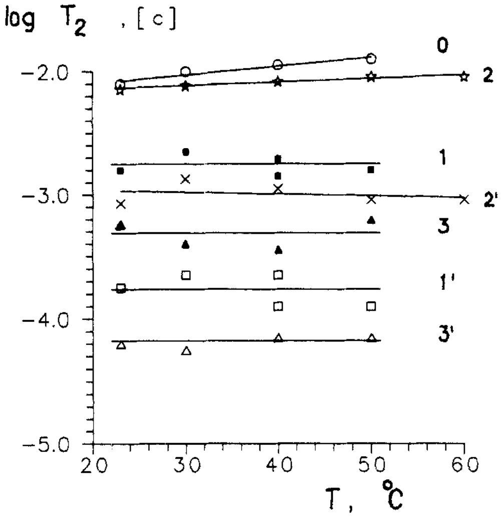


FIGURE 6 T_{2s} (0, 1, 2, 3) and T_{2r} (1', 2', 3') temperature behavior in the swollen gels of PFA-4H and PFA-2H. Parameters: wt.% of curing agent. The other networks are ommited for clarity.

where $\langle \delta\omega^2 \rangle$ and $\langle \delta\omega_0^2 \rangle$ are the second moments of the resonance line of NMR absorption in HTP region and in the solid state, respectively. According to Reference 1 we can write

$$Q = \langle 3 \cos^2\gamma_{ik}/2 - 1/2 \rangle \tag{4}$$

where γ_{ik} is the angle between the internuclear vector and the vector **L**, connecting the chain ends of the strand. This formula resembles the definition of the order parameter (here it reflects the intramolecular order). In fact, Equation (4) displays the degree of the anisotropy of small-scale motion with respect to **L**. Let us use the result of the averaging of $\langle \cos^2\gamma \rangle$ on chain configurations derived in the theory of optical anisotropy for a persistent chain model.[9]

$$Q = \frac{[15x - 26 + (9x + 27)\exp(-x)][x - 1 + \exp(-x)]}{9x[5x^2/3 - 52x/9 + 214/27 - 2(4 + x)\exp(-x) + 2\exp(-3x)/27]} \tag{5}$$

where x is the chain length expressed in the number of persistent lengths. In cross-linked polymers $x = \mathbf{L}/\alpha$, where **L** and α are the numbers of monomer units in the strand and in the persistent length, respectively.

Figure 7 shows the log-log plot of $Q(x)$. In highly cross-linked systems from Equation (5) it follows that when $x \Rightarrow 0$ $Q \Rightarrow 1$ (case of ideal intramolecular order). When x is large enough ($x > 5$) Equation (5) transfers to $Q = 1/x$. This result agrees with the well-known dependence derived by Kuhn and Grün for freely jointed chains of a fixed length. The change in the slope of the $Q(x)$ in Figure 7 in the region $x \cong 3$ describes the change in the width of the $\cos^2\gamma$ distribution from that in the highly cross-linked networks to moderately cross-linked ones.

Since the second moment of the experimentally observed Lorentzian line (which

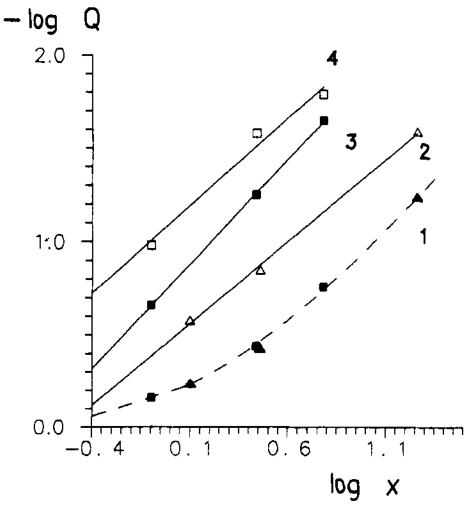


FIGURE 7 Log-log plot of the reciprocal of intramolecular order parameter Q vs the number of persistent lengths in the strand (x) for the backbone (1); side groups in PFA-3F (2) and PFA-4H (4)—^{19}F data; the ^{1}H-TMD tail in PFA-4H (3). Dashed line: calculated $Q(x)$ using Equation 5.

corresponds to exponential TMD) is not determined, we evaluated $\langle\delta\omega^2\rangle$ for the Lorentzian line with wings cut off on the level of 2% intensity

$$Q = (11.2/\langle\delta\omega_0^2\rangle)^{1/2}/T_2 \tag{6}$$

The second moments $\langle\delta\omega_0^2\rangle$ were determined from the TMD at the temperatures lower than – 140°C, where the solid-like plateau of TMD is observed. The obtained values of $\langle\delta\omega_0^2\rangle$ are presented in Table I. The values of x were determined graphically for the Q values for the main chain protons. The efficiency of cross-linking was estimated

$$\beta = m/m_0 \tag{7}$$

where m and m_0 are the molar fractions of the cross-links and the cross-linking agent, respectively. The values of m was calculated according to

$$m = 1/4x\alpha \tag{8}$$

where α was evaluated from the additive rule for the cohesion energies of individual groups. (The experimental value of $2\alpha = 19.8$ for polyfluoroamyl methacrylate, obtained from the hydrodynamics data[12] was used). The calculated values of β are listed in Table I. It can be seen that they are rather high. Therefore, as a result of high thermodynamic rigidity of PFA-nR and the high efficiency of cross-linking these networks belong to highly cross-linked ones, i.e., their properties are described by the persistent chain model.

Figure 7 displays the $Q(x)$ log-log dependences for the side groups (the ^{19}F data).

It can be seen that these dependences are linear and therefore $Q(x)$ can be roughly approximated by the function $Q \cong b/x$ ($Q = 0.34/x^{0.78}$ for PFA-3F, $Q = 0.80/x^{0.94}$ for PFA-4H). The values of b decrease with the side group length from 0.3 for PFA-3F to 0.1 for PFA-4H (the ^{19}F data). Thus, in the networks of the comb-like polymers the intramolecular anisotropy decreases with the side group length.

Note, that the dependences $Q(x)$ in PFA-4H for ^{19}F and for the slowly decaying component of ^{1}H-TMD ($Q = 0.17/x^{1.12}$) do not coincide. The next fact that we must take into consideration while interpreting the slow component data of ^{1}H-TMD is the dependence $p(m_0)$. If the slow component reflects only the mobility of CF_2H group then p should not depend on the network structure.

A way to interpret this situation is to assume the influence of dangling ends on the slow component of ^{1}H-TMD of PFA-4H. Let us consider that the system of spins consists of 4 components:

I. Main chain units in the strands;
II. Side chains in the strands;
III. Main chain units in the dangling ends;
IV. Side chains in the dangling ends.

We assume that only the systems with $\langle \delta\omega^2 \rangle \neq 0$ contribute to TMD in the region of HTP. Therefore, the absence of the second component in ^{19}F-TMD of PFA-*nR* is attributed to the averaging of the dipole-dipole interactions of the side groups in the dangling ends ($\langle \delta\omega^2_{\mathrm{IV}} \rangle = 0$), so that only $\langle \delta\omega^2_{\mathrm{III}} \rangle \neq 0$. The single-component ^{1}H-TMD of PFA-3F is therefore due to the averaging of $\langle \delta\omega^2_{\mathrm{III}} \rangle$. The reason for the increase of the number of components in ^{1}H-TMD with the side group length is twofold: the mobility of CF_2H group becomes independent of that of the main chain, and the mobility of the dangling end decreases with increasing diameter, so that $\langle \delta\omega^2_{\mathrm{III}} \rangle$ becomes different from zero. The absence of the third component in the ^{1}H-TMD of PFA-4H shows that we cannot distinguish between systems II and III. However, the fact that the value of Q for the slowly decaying component of ^{1}H-TMD is greater than that for the side groups only (^{19}F-TMD) proves our assumption.

Let us consider from this point of view the temperature behavior of p in the uncross-linked PFA-4H. The appearance of the two-component ^{1}H-TMD at temperatures below 100°C is due to the influence of long-living intermolecular contacts, which play the role of the temporal cross-links, i.e., those contacts, the life time of which τ is greater than the observation time T_2. With increasing temperature τ diminishes and T_2 increases. Hence, the number of long-living contacts decreases, therefore $p \Rightarrow 0$.

Note also that the equality of the T_{2r} and T_{2s} values of melts and gels of PFA-4H networks with $m_0 \geq 3$ wt.% in the region of HTP. It means that the role of the long-living contacts is diminished equally well by heating or upon swelling in hexafluorobenzene, unlike the networks of flexible polybutyl acrylate,[2] where in the region of HTP T_2 (melt) $<<$ T_2 (gel). This behavior of PFA-4H is probably caused by the low number of intermolecular contacts in the highly cross linked thermodynamically rigid polymers.

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