Topological structure and molecular mobility of linear and branched poly(meth)acrylates studied by NMR relaxation

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The method for the determination of fractions of terminal chains and chains bonded by physical or chemical knots from free induction decays (FID) and line shape was proposed on the basis of the earlier developed theory of NMR spectra in linear and cross-linked polymers. The density and topological structure of the effective polymer network and the characteristic correlation times of segmental motion of chains were determined for linear and branched poly(meth)acrylates at 130 °C from the coincidence of the theoretical and experimental FID curves and the line shape. A quantitative estimation of chain rigidity in the branched polymer with an increase in the brancher content was performed for the first time.

Key words: branched poly(meth)acrylates, topological structure, molecular mobility, NMR relaxation, correlation time.

Branched and highly branched polymers synthesized in one step by the controlled radical (co)polymerization of mono- and multifunctional monomers are polydispersed macromolecular irregular structures, whose degree of branching does not exceed 50%.[1,2] The topological structure of branched macromolecules is characterized by high concentration of terminal chains in peripheral layers and by branching knots. This structure determines unusual properties of branched polymers, such as a high solubility in various organic media, low values of intrinsic viscosity [η] compared to that of linear polymers with close molecular weight (MW), a weak sensitivity of the reduced viscosity to the change in the polymer concentration in solution, thermodynamic compatibility with polymers of different chemical nature, and high sorption capacity in combination with the capability of transporting low-molecular-weight compounds.

One of the efficient methods for studying the structure, molecular mobility, and intermolecular interaction in polymer systems is NMR spectroscopy.[3—5] For example, the dynamic properties of dendrimers, regular macromolecular structures with the degree of branching close to 100%, were studied using ^{13}C and ^{1}H spectroscopy.[6,7] It was found that the high density of functional groups does not prevent mobility of the terminal chains and the average correlation time (τ) increases substantially with an increase in the molecular size of the internal part of the macromolecules (generation number). The molecular dynamics of branched polymers, which are synthesized in one step using radical copolymerization, was not previously studied by NMR spectroscopy.

The purpose of the present work is to study the topological structure and relaxation properties of branched poly(meth)acrylates of various structure and the degree of branching by NMR spectroscopy and to obtain new data on the molecular dynamics of these polymers by the comparison of theoretical and experimental results.

Experimental

Linear and branched poly(methyl methacrylates) (PMMA) and poly(ethyl acrylate) (PEA) of the branched structure were used. Copolymers were synthesized according to a known procedure[8—10] using the radical copolymerization of methyl methacrylate (MMA) or ethyl acrylate with the multifunctional comonomer, ethylene glycol dimethacrylate (EGDM), in toluene in the presence of 1-decanethiol (DT), which restricts polymer chain growth due to the chain transfer reaction. To obtain linear PMMA with various MW, the DT concentration in the reaction mixture was varied from 0 to 5 mol.%. Branched PMMA and PEA were synthesized at the equimolar ratio brancher : DT. The content of the brancher of EGDM was 1, 5, and 15 mol.%. Linear and branched PMMA were isolated by reprecipitation into a hexane excess. (Co)polymers were dried in air to a constant weight.

Absolute molecular-weight characteristics of (co)polymers were determined by gel permeation chromatography on a Waters GPCV 2000 liquid chromatograph equipped with a differential refractometer combined with light scattering (a Wyatt Dawn Heleos II light scattering detector). The increment of the refractive index was $dn/dc = 0.114$ mL g^{-1}, THF was the eluent, the elution rate was 1 mL min^{-1}, and the measurement temperature was 35 °C.

The glass transition temperature of the linear and branched (co)polymers were measured earlier by the DSC method.[11,12]

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Relaxation measurements were carried out on an RI 23-03 NMR spectrometer. The working frequency on protons was 60 MHz. Free induction decays (FID) were recorded. The duration of the 90° radio frequency pulse was 3 μs. The time of recovery of the receiving tract after the action of a radio frequency pulse was 4—5 μs. Temperature maintaining provided temperature measurements from 0 to 130 °C, and the accuracy of the setup and temperature maintenance was 1 °C. The time of temperature establishment was 5 min. Weighed samples were 0.1—0.5 g. Free induction decays were recorded by points at an interval of 1, 2, and 4 μs, the maximum number of detection points being 2048. Before digitization, the zero line was subtracted and all FID were normalized.

Results and Discussion

The chosen ratio of components of the reaction mixture vinyl monomer—brancher—DT provided a change in elements of the topological structure, the length of the primary, interknot, and terminal polymer chains of branched PMMA, in a wide range. At a low content of the brancher, the copolymer has a few branchings and is close in properties to the linear polymer.[9] As the content of the brancher increases from 1 to 15 mol.%, under the condition that [EGDM] = [DT], the length of the primary polymer chains decreases substantially and the length of the interknot and terminal chains, which determines the relaxation properties of branched polymers to a great content, also decreases.

The molecular-weight characteristics and glass transition temperatures for linear (**1—3**) and branched poly(methyl methacrylates) (**4—6**) and branched poly(ethyl acrylate) (**7**) are presented in Table 1. The data in Table 1 show that with an increase in the DT content in the reaction mixture the values of M_w and M_w/M_n of linear PMMA decrease due to the chain transfer reaction. On the contrary, with an increase in the content of the brancher and DT in the reaction mixture MMA—EGDM—DT the values of M_w and M_w/M_n of branched PMMA increases, and the polymers formed have higher degrees of branching and composition heterogeneity. The molecular-weight parameters of branched poly(ethyl acrylate) **7** are substantially lower than analogous data for branched PMMA **5** obtained from the reaction mixture of the same composition. This fact is explained by the difference in copolymerization constants of the monomers and the chain transfer coefficients of the methacrylate and acrylate radicals to DT. The different reactivities of the comonomers results in the formation of a random copolymer at the initial steps enriched in the EGDM units and at the deep steps containing predominantly the EA units for which the coefficient of chain transfer to DT is higher[8] than that for the methacrylate radical.

Differences in the segmental molecular mobility of the polymers studied are indicated by their glass transition temperatures T_g. In the series of glassy PMMA of the branched structure, T_g decreases with an increase in the brancher in them by more than 30 °C, in spite of increasing the values of M_w. This fact is considered[11] as evidence for branching of MMA copolymers and inclusion of the chain transfer agent into the chains and is explained by an increase in the number of branches (and terminal groups) in the macromolecules.

Branched PEA is characterized by the lowest T_g. The values of T_g diverge because of differences in the molecular mobility of branched PMMA and PEA and their relaxation properties. Under compared conditions, branched PEA is in the highly elastic state, which is characterized by the high mobility of all components of the macromolecule: atoms, groups, units, and segments. Under these conditions, branched PMMA exists in the glassy state, whose specific feature is the short-range order in the arrangement of molecules and a strongly restricted segmental mobility.

Thus, branched polymers differ substantially by physicochemical characteristics and properties associated with the molecular mobility and can be studied by methods of NMR spectroscopy, which are very informative for investigation of objects of this type.

According to the model proposed, the topological structure of branched macromolecules is presented as an effective polymer network formed by chains connected with knots (physical, chemical, branching knots), whose nature does not differ in the NMR spectra. The topological structure of the polymer is characterized by the average length of interknot chains N_0 and the molecular-weight chain distribution between the knots of the effective polymer network, and the chain length N between the knots is expressed in the number of statistical segments.

The method for the determination of the fraction of the effective polymer network and terminal chains from the FID and line shape was proposed on the basis of the earlier developed theory of NMR spectra for linear and cross-linked polymers.[13—15] The theory makes it possible to take into account the influence of the density of knots of the polymer network and the change in the molecular mobility in a wide temperature range on the FID. The free induction decays in the samples were presented as a sum of polarization decays from the chains with free ends $G_0(t)$ and from the chains, whose ends are fixed $G_c(t)$

$$G(t) = (1 - p)G_0(t) + \mathrm{p}G_c(t), \qquad (1)$$

where p is the fraction of the effective network; and polarization decays $G_0(t)$ and $G_c(t)$ are theoretically calculated.[13,14]

For the effective polymer network, the FID has the form[15]

$$G_c(t) = G_{\mathrm{int}}(t)G_m(t), \qquad (2)$$

where $G_{\mathrm{int}}(t)$ and $G_m(t)$ are the contributions to the FID from the interchain and intrachain dipole—dipole interactions (DDI) of spins, respectively. Contribution $G_m(t)$ is calculated by the equation[13]

$$G_m(t) = G_1(t)G_2(t)G_3(t). \qquad (3)$$

Free induction decays $G_1(t)$ and $G_2(t)$ are calculated in the Anderson—Weiss formula using the corresponding correlation functions of molecular motions $k_i(\tau)$

$$G_i(t) = \exp(-\omega_{loc}^2 \int_0^t (t-\tau)k_i(\tau)d\tau),\ i = 1, 2, \qquad (4)$$

where ω_{loc} is the average local field created on any spin by both spins belonging to the isolated segment and all other spins of the chain.

To analyze the influence of molecular motions of the chains between the knots of the effective network on the FID signal, we used the correlation functions characterizing three types of motions of a particular chain in various temperature ranges[13] at temperature higher than the glass transition temperature T_g

$$k(\tau) = (1-\alpha)\,k_1(\tau) + \alpha k_2(\tau) + k_3(\theta,\mathrm{N}). \qquad (5)$$

Function $k_1(\tau)$ is the Bloembergen—Purcell—Pound correlation function that characterizes small-scale motions of the polymer chains in the low-temperature range ($T_g < T < T_g + 50°$)

$$k_1(t) = e^{-\tau/\tau_c}, \qquad (6)$$

where τ_c is the characteristic correlation time of molecular motions. Function $k_2(\tau)$ is the Kargin—Slonimskii—Rause correlation function that characterizes large-scale motions of segments of the polymer chains in the medium-temperature range ($T_g + 50° < T < T_g + 100°$) and is determined by Eq. (7)

$$k_2(\tau) = N_0^{-1}\sum_{p=1}^{N} e^{-p^2\pi^2\tau/\tau_c N_0^2}. \qquad (7)$$

Coefficient α is the fraction of large-scale motion, *viz.*, empirical coefficient (for the cross-linked structure and chains with free ends, $\alpha = 0.05$). Function $k_3(\theta,N)$ is the correlation function in the high-temperature range ($T > T_g + 100°$) that characterizes motion of the chain as a whole, $k_3(\theta,N) = (3\cos^2\theta - 1)^2\ln N/N^2$, where θ is the angle between the direction of the magnetic field and the radius-vector of the chain with fixed ends.

It was shown[13] that the FID for a particular chain can be described by the following function:

$$g(N,\theta,t) \sim \exp[-\omega_{loc}^2(3\cos^2\theta - 1)^2 t^2(\ln N/N^2)]. \qquad (8)$$

To calculate the FID for the whole sample, function (8) should averaged by the distribution $P(N)$ of all chains over the lengths between knots and over angles

$$G_3(t) = \int_1^{N}\int_0^{\pi/2} g(N,\theta,t)P(N)\mathrm{d}\cos\theta\mathrm{d}N. \qquad (9)$$

For the non-oriented polymer, the distribution over angle θ is isotropic. The distribution over the chain lengths between knots $P(N)$ is an analog of the molecular-weight distribution (MWD) in polymer networks. Note that at $t/N_0 >> 1$ the slowly decaying component, whose amplitude is asymptotically proportional to t^{-1}, appears in the FID $G_m(t)$. The main contribution to the FID signal is made by the DDI of spins of the chains arranged at a magic angle to the magnetic field.[13]

The contribution of the interchain DDI of spins[15] $G_{int}(t)$ is calculated by formula (10)

$$G_{int}(t) = \exp(\beta t/N_0^{3/2}), \qquad (10)$$

where β is the parameters dependent on the nature of the substance.

For the description of motion of chains with free ends, the correlation function [14] was used

$$k_0(\tau) = (1-\alpha)k_1(\tau) + \alpha k_2(\tau), \qquad (11)$$

where functions $k_1(\tau)$ and $k_2(\tau)$ are determined by formulas (6) and (7), respectively, at the correlation time of molecular motions τ_{c_1} and the average chain length N_{0_1}. The corresponding FID $G_{0_1}(t)$ and $G_{0_2}(t)$ are calculated by formula (4). The free induction decay for chains with free ends has the form

$$G_0(t) = G_{0_1}(t)G_{0_2}(t). \qquad (12)$$

The line shape $f(\omega)$ is calculated from the FID using the Fourier transform

$$f(\omega) = \sqrt{\frac{2}{\pi}}\int_0^{\infty} G(t)\cos(\omega t)\mathrm{d}t. \qquad (13)$$

It was shown[13] that the most full information about the topological structure in polymer networks is provided by the NMR spectra obtained at high temperature ($T > T_g + 100$ °C) and, hence, in the present work experiments were carried out at maximally possible instrumental temperature maintenance (130 °C).

The theoretical and experimental FID and line shapes of all polymers were compared (see Table 1). The theoretical spectra were calculated by formulas (1)—(13) with the variation of parameters N_0, N_{0_1}, τ_c, and τ_{c_1} to the best correspondence of the experimental signals, and the calculated parameters are presented in Table 2. The calculated and experimental spectra for samples **1** and **6** are compared in Figs 1 and 2. The comparative analysis showed that the effective network was formed in PMMA and the function of chain distribution over lengths between knots $P(N)$ was exponential

$$P(N) = N_0^{-1}\exp(-N/N_0). \qquad (14)$$

The average chain length and the network fraction depend on the polymer, the segmental motion is developed,

Table 1. Composition and characteristics of the linear and branched (co)polymers **1—7**

Polymer	Composition of mixtures* monomer : EGDM : DT (mol.%)	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	M_w/M_n	T_g/°C
1	100 : 0 : 0	11.8	22.0	1.9	108.0
2	100 : 0 : 2	5.6	8.9	1.6	—
3	100 : 0 : 5	3.4	4.6	1.4	70.0
4	100 : 1 : 1	9.6	33.0	3.4	103.0
5	100 : 5 : 5	7.2	40.0	5.6	78.0
6	100 : 15 : 15	15.0	95.0	6.3	67.0
7	100 : 5 : 5	3.5	8.0	2.3	−35.6

* In case of polymers **1—6**, monomer is methyl methacrylate; and in case of polymer **7**, it is ethyl acrylate.

and the correlation time is $\tau_c \approx 10^{-3}$ s. Under the same conditions, the polymer network was also formed in PEA (Fig. 3): the network fraction is 50% ($p = 0.5$), function $P(N)$ is exponential and described by formula (14), the average chain length is $N_0 = 49$, the segmental motion is developed, and the correlation time is $\tau_c = 10^{-4}$ s.

The parameters of the topological structure of the polymer network and the characteristic correlation times of segmental motion of the chains were determined for all samples at 130 °C from the comparison of the theoretical and experimental FID and the line shape $f(\omega)$ (see Table 2).

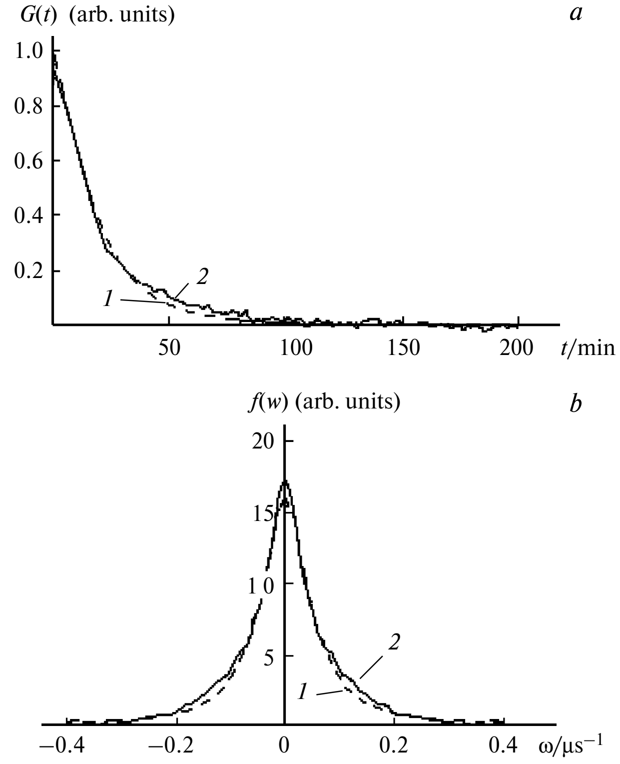

Fig. 1. Free induction decay (*a*) and the NMR spectrum (*b*) of polymer **1** at 130 °C: *1*, calculation; and *2*, experiment.

The number of units of monomer z in the statistical segments was estimated by the formula

$$z = pM_n/N_0M_{mon}, \tag{15}$$

where $M_{mon} = 100$ g mol^{-1} is the molecular weight of the MMA monomer. The value of z can serve as a characteristic of chain rigidity: the chain becomes less flexible with an increase in z. The data in Table 2 show that the chain rigidity is maximum in polymer **6** with a high content of

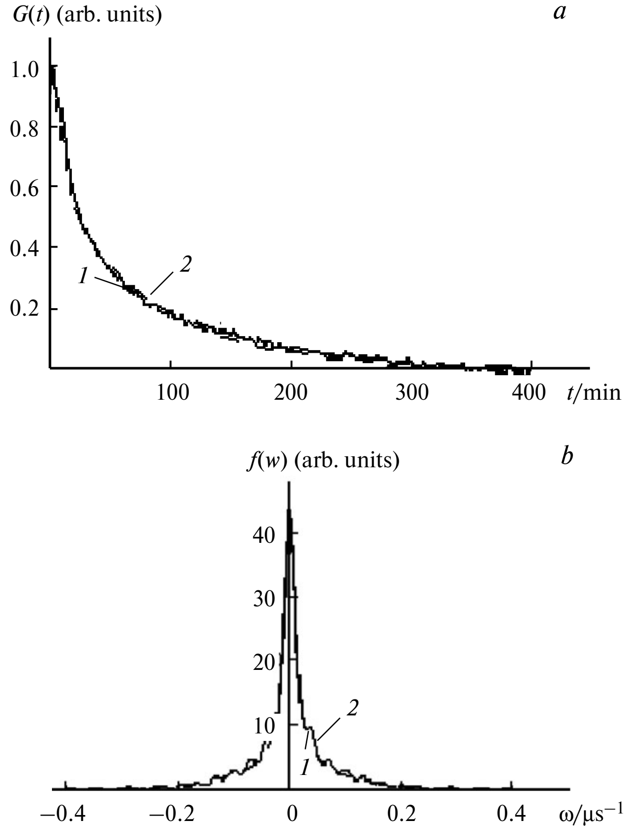

Fig. 2. Free induction decay (*a*) and the NMR spectrum (*b*) of polymer **6** at 130 °C: *1*, calculation; and *2*, experiment.

Table 2. Topological structure and molecular mobility

Polymer	$T-T_g$[a]	p[b]	N_0	$\tau_c \cdot 10^2$ /s	N_{0_1} /s	$\tau_{c_1} \cdot 10^3$	z
1	22	0.70	49	3.0	49	8.5	3
2	—	0.50	29	1.0	21	6.0	2
3	60	0.30	21	0.9	21	9.0	1
4	27	0.70	40	2.0	49	8.5	3
5	52	0.60	21	1.0	47	3.0	4
6	63	0.45	17	1.0	49	2.0	7
7	55	0.50	49	0.5	49	0.6	1

[a] T is the temperature of the thermostat (130 °C).

[b] p is the fraction of the effective network.

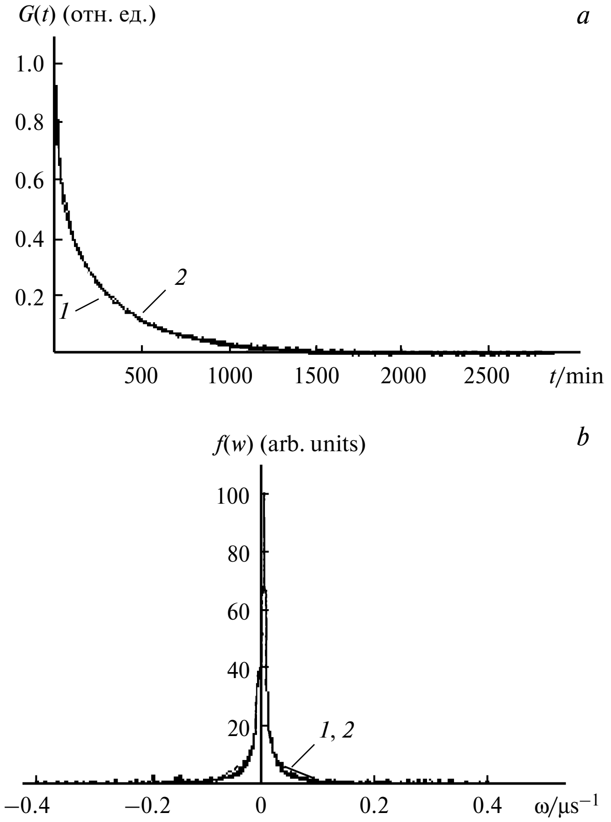

Fig. 3. Free induction decay (*a*) the NMR spectrum (*b*) of polymer **7** at 130 °C: *1*, calculation; and *2*, experiment.

decanethiol and the brancher. A comparison of the spectra of polymers **5** and **7** showed that the molecular mobility in PEA is higher than that in PMMA and the number of monomer units z in the statistical segment is lower, which confirms the higher mobility of PEA.

Thus, the proposed theory of NMR relaxation spectra makes it possible to model experimental signals in branched polymers and estimate the molecular mobility and parameters of the topological structure: density of branching knots, their distribution, and the average length of interknot and terminal chains. The proposed method of NMR study makes it possible to analyze the structure of the obtained materials during synthesis and predict their properties associated with the molecular mobility.

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