

Rheological Properties of Acrylonitrile Terpolymer Solutions Synthesized by Different Methods

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Abstract—Series of polyacrylonitrile terpolymers with molecular weights of $(7-20) \times 10^4$ have been synthesized in dimethylsulfoxide using classical radical polymerization and reversible addition-fragmentation chain transfer (RAFT) polymerization. The effect of the synthesis method on the rheological behavior of dilute and concentrated solutions of the resulting copolymers has been analyzed. No differences have been found in the viscous properties and viscoelastic behavior of the concentrated solutions in the temperature range of 20–80°C. However, viscometry of the dilute solutions made it possible to detect a difference in the interaction between the solvent and macromolecules of the copolymers obtained by these methods. The copolymers differ in the values of the second virial coefficient, which indicates that the interaction of the solvent and polymer is specific to the synthesis method. This phenomenon seems to be caused by different branching of chains in the copolymer and/or its compositional heterogeneity. For dilute solutions, it was possible to construct a single generalized concentration dependence of reduced viscosity in the coordinates of the Martin equation. Transition to the region of concentrated solutions required an introduction of yet another parameter that describes the effective density of the mesh network, namely, the ratio of the current solution concentration to the crossover concentration. This approach made it possible to construct a generalized dependence of viscosity in the entire concentration range of solutions of polyacrylonitrile copolymers.

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INTRODUCTION

Production of high-strength industrial polyacrylonitrile yarn, which is used for obtaining carbon fiber, is a multistage process. Its first stage involves the synthesis of copolymers with the desired molecular characteristics. If the process is carried out in a solvent that is used for obtaining spinning solutions of a given concentration, then, after being purified from monomer residues and filtered, the resulting solutions are fed directly to the fiber formation stage. If, however, the process is carried out in another medium (e.g., supercritical CO₂ [1]), then PAN powder is dissolved in an aprotic solvent, after which the resulting spinning solution is used to form fibers. The next step is the finishing treatment of fibers to form precursors, which then undergo carbonization and graphitization.

The most widely known precursors are fibers based on di- and terpolymers of acrylonitrile. Strong nitrile-nitrile interactions in a homopolymer of AN [2, 3] necessitate the introduction of plasticizing comonomers (e.g., methyl acrylate (MA)) and accelerators of

thermooxidative stabilization (e.g., acrylic, methacrylic, or itaconic acids) [4, 5]. The role of the latter was analyzed in great detail in [5], where it was shown experimentally that the introduction of 0.5–1.0 mol % of itaconic acid into a copolymer of PAN leads to the formation of a large number of cyclized structures based on conjugated carbonyl and nitrile groups, a decrease in the β-aminonitrile content, and a significant acceleration of structural evolution in thermal oxidation of white fiber.

The main organic solvents in the formation of PAN are DMSO, DMF, and DMAc. These solvents are chosen because of their good dissolving power, which makes it possible to use them as a polymerization medium. The dissolution mechanism of PAN itself and its solubility in DMSO, DMF, DMAc, and dimethyl sulfone have been analyzed in a large number of experimental and theoretical studies [2–10]. It has been shown that the affinity of solvents for PAN decreases in the following order: DMSO > DMF > DMAc [11, 12]. According to the authors of the works

cited, the efficiency of the process affects the homogeneity of the solutions. The greater uniformity of PAN solutions in DMSO can be explained by the fact that the AN–DMSO interaction is stronger than the AN–DMF or AN–DMAc interactions. Using the compatibility parameters for the Hansen sphere, it has been shown that DMSO has the highest affinity for PAN.

In terms of rheological properties, solutions of PAN and DMSO exhibit a weak anomaly of viscosity at low shear rates. As the shear rate increases, the anomaly becomes significant or even turns into an unstable flow, which is sometimes interpreted as a “breakdown” or gelation [13, 14]. The latter process is especially efficient in low-concentration solutions, where specific interactions between the solvent (in particular, with DMSO) and the carboxyl and nitrile groups of AN copolymers result in the formation of a network of physical interactions that causes a gel-like behavior. Under intense strain, the solution separates into the solvent and the polymer. The phase separation effect, which is particularly pronounced when stretching solutions of different concentrations, laid the foundation for a new mechanotropic method for the formation of PAN fibers [15, 16]. The authors of the cited papers studied in detail the phase transition induced by tensile strain and proposed its mechanisms, which differ for dilute and concentrated solutions.

Rheological properties of PAN solutions determine their spinnability, i.e., the ability to form liquid threads. Obviously, these properties depend not only on the nature of the solvent interacting with the polymer but also on the molecular characteristics of the polymer itself. A study on rheological properties of concentrated solutions of a high-molecular-weight PAN in DMSO has shown [17] that the elastic component of the complex elastic modulus nonlinearly increases in comparison with its dissipative component with increasing molecular weight (MW). However, there is also evidence that both viscoelastic characteristics of solutions containing mixtures of PAN copolymers with different MWs change with the strain rate in the same manner [18]. A small fraction of a high-molecular-weight PAN added to the spinning solution affects its rheological behavior by substantially increasing the spinnability. The authors of [19] believe that a fivefold difference in the reduced viscosities of dilute solutions of PAN homopolymers having similar molecular weight characteristics but obtained by methods of emulsion and solution polymerization is due to the branching of their macromolecules (the branching could not be confirmed by direct methods).

The way that the MW of AN–MA–itaconic acid ternary copolymers obtained by radical polymerization affects the viscosity properties of solutions was discussed in detail in [20]. The terpolymer was fractionated into narrow fractions having similar compositions and different MWs. Using the example of 10%

solutions, it was found that the viscosity dependence on the MW for both MW averagings is expressed by a power equation with a power exponent of 2.3. This is significantly lower than the standard value of 3.4. The authors, however, do not elaborate on the reasons for this discrepancy, although they do indicate that high-molecular-weight fractions of PAN can associate. At the same time, the dependence of viscosity on the solution concentration is described by a power equation with a power exponent of 4.6. An attempt to evaluate the role of MWD by mixing different fractions led the authors of the aforementioned work to the conclusion that low-molecular-weight fractions decrease the viscosity of concentrated solutions to a greater extent than high-molecular fractions increase it.

Synthesis and application of copolymers raise questions of monitoring the distribution of comonomer links along the chain and the compositional homogeneity of macromolecules. These questions inevitably arise when using processes of conventional radical polymerization. One of the time-consuming and complex ways of determining the compositional heterogeneity of copolymers is their fractionation by composition. The study carried out for ternary copolymers of AN, MA, and itaconic acid revealed that the distribution of monomers by fractions is irregular in the copolymer synthesized in an aqueous solution of sodium thiocyanate [21]. However, the effect of compositional heterogeneity of macromolecules on the rheological properties of their solutions has never been analyzed.

This task could be solved using another mechanism for the formation of macromolecules: namely, radical polymerization with reversible deactivation of the chain, which makes it possible to obtain copolymers that are homogeneous in their MW and composition [22]. In such processes, the reaction medium is supplied with special additives which participate in reversible reactions of chain termination or chain transfer with macroradicals. Constantly alternating periods of “sleep” and “life” of the macromolecules ensure their consistent growth during polymerization and the narrowing of their MWD. In addition, the growth of chains under identical or similar conditions leads to a significant decrease in the compositional heterogeneity of the copolymers. Naturally, the reversible deactivation of macromolecules makes it impossible to eliminate the reactions of chain transfer to the polymer, which lead to branching. However, their number and length are often lower than those in classical radical polymerization [23]. Moreover, the mechanism of reversible deactivation does not affect the elementary acts of chain growth and, consequently, the stereoregularity of macromolecules [24].

Such a study was started by the authors of [25], whose work involved two AN–MA–itaconic acid terpolymers of the same number-average MWs (2.6×10^5) and different dispersions ($D = 1.3$ and 2.0). The

Table 1. Synthesis conditions and characteristics of terpolymers

Sample	T , °C	Initiator	[M], mol/L	[DBTTC], mM	M_n , kg/mol	\bar{D}	Copolymer composition, mol %		C_{solution} , wt %
							AN	MA + itaconic acid	
B1	80	AIBN	7.3	1	57	1.60	96.2	3.8	14.4
B2	55	PSP	7.3	5	59	1.58	96.3	3.7	17.6
B3	20	Radiolysis	6.1	2	75	1.73	97.7	2.3	10.0
K1	80	AIBN	2.9	—	40	1.76	97.3	2.7	7.6
K2	45	PSP	2.9	—	59	2.06	97.6	2.4	11.2
K3	20	Radiolysis	2.9	—	69	2.99	97.5	2.5	10.0

terpolymers were obtained by reversible addition-fragmentation chain transfer (RAFT) polymerization and classical radical polymerization, respectively. Unfortunately, no data have been provided on the conversion of monomers, so it is impossible to conclude that the synthesized samples were compositionally homogeneous. A comparison of the viscosity values of 25% solutions of these terpolymers in DMSO has demonstrated that the solution viscosity is fivefold lower for a polymer with a narrow MWD than for PAN with a broad MWD. According to the authors, this is due to the different content of high-molecular-weight fractions. However, some results of dynamic tests and their interpretation raise questions. For example, the fact that the transition of terpolymer solutions with a narrow MWD to the gel state becomes slower with increasing strain frequency has not been discussed.

Analysis of the published data makes it possible for us to conclude that there is a demand for a systematic study and a comparison of the properties of solutions obtained using copolymers of different macromolecular homogeneity and composition. For this, it is natural to use terpolymers prepared in the same solvent under the conditions of classical radical and RAFT polymerization mechanisms.

This study aims to elucidate the rheological properties of dilute and concentrated solutions of ternary AN, MA, and itaconic acid copolymers obtained in DMSO using different methods.

EXPERIMENTAL

In the present work, acrylonitrile and methyl acrylate were purified by distillation at atmospheric pressure, whereas itaconic acid was used without further purification. As for the initiators, AIBN was purified by recrystallization from ethanol, whereas anhydrous potassium persulfate (PSP) was not subjected to additional purification. The RAFT agent, dibenzyl trithiocarbonate ($\text{C}_6\text{H}_5\text{CH}_2\text{—S—C(=S)—S—CH}_2\text{C}_6\text{H}_5$, DBTTC), was synthesized and characterized according to the standard procedure [26]. The conversion of

monomers was 60–80%. The solvents DMSO and DMF were distilled in vacuum before use.

The procedure for the synthesis and isolation of terpolymers was described in [27]. All terpolymers were prepared by polymerizing a mixture of AN, MA, and itaconic acid of the same composition using different initiators and methods of synthesis (Table 1). Samples of series **B1–B3** were synthesized under RAFT conditions, whereas samples **K1–K3** were obtained by traditional radical polymerization. Within the framework of these two synthesis strategies, samples B3 and K3 were synthesized by radiation initiation. For comparison, we used an industrial terpolymer CS synthesized in a water–rhodanide solution ($M_n = 45$ kg/mol; $\bar{D} = 2.1$; the AN–MA–itaconic acid molar content in the mixture was 93.0, 5.7, and 1.3% monomers, respectively; and the concentration of the copolymer in a DMSO solution was 15 wt %).

Viscometric measurements of dilute solutions were carried out at $30 \pm 0.1^\circ\text{C}$ on an Ubbelohde viscometer in accordance with GOST 25438-82. The rheological behavior of concentrated solutions was investigated in continuous and oscillation modes on Anton Paar MCR 301 and Thermo Haake RheoStress RS600 rotational rheometers at 25°C . Thus, we obtained flow curves in the shear range of 10^{-3} – 10^4 s^{-1} , the amplitude dependences of the complex elastic modulus in the deformation range of 10^{-3} – $10^3\%$, and the frequency dependences of the shear storage and loss moduli in the linear viscoelasticity region at frequencies ranging from 10^{-3} to 10^3 s^{-1} .

RESULTS AND DISCUSSION

Figure 1 exemplifies the flow curves of solutions obtained from terpolymer samples synthesized by classical and RAFT polymerization.

All solutions have a wide range of shear rate in which the flow is characterized by the highest Newtonian viscosity, which differs by two and a half orders of

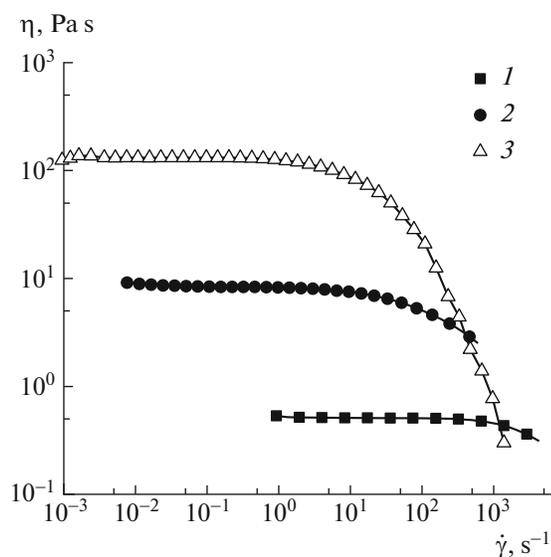


Fig. 1. Flow curves of solutions of polymers synthesized by classical and RAFT polymerization: samples K1 7.6% (1), K2 11.2% (2), and B1 14.4% (3).

magnitude. This is due to differences in the concentrations of solutions and the MWs of polymers.

The shear rate that characterizes the transition to non-Newtonian flow decreases with increasing viscosity of the solutions. At the same time, the structural viscosity regions form an envelope, which is uniform for almost all solutions, including solutions containing copolymers obtained by radiolysis.

As a starting point for the study of terpolymer solutions, the dependences of components of the complex elastic modulus on the strain amplitude were determined in the dynamic mode at a constant frequency of 1 Hz (Fig. 2).

All the solutions studied are characterized by an extended region of linear viscoelasticity, which follows from the fact that the complex elastic modulus remains constant when the deformation amplitude is varied. The least viscous solution of sample K1 is an exception from the general rule. This may be due to the fact that the sensitivity of the device is insufficient for measuring such small torques proportional to the shear stress.

The frequency dependences of the elastic G' and loss G'' moduli measured in the linear region of viscoelasticity at the strain of 1% are given in Fig. 3.

The behavior of the storage modulus is similar for the solutions of all studied samples and is typical of polymer systems. In the low-frequency range, the slope of the frequency dependence of the elastic modulus ranges from 1.8 for K1 to 1.5 for B1, which is somewhat lower than the theoretical value of the tangent, which should be equal to two in the low-frequency limit. Over a wide frequency interval, the behavior of the loss modulus is also uniform for poly-

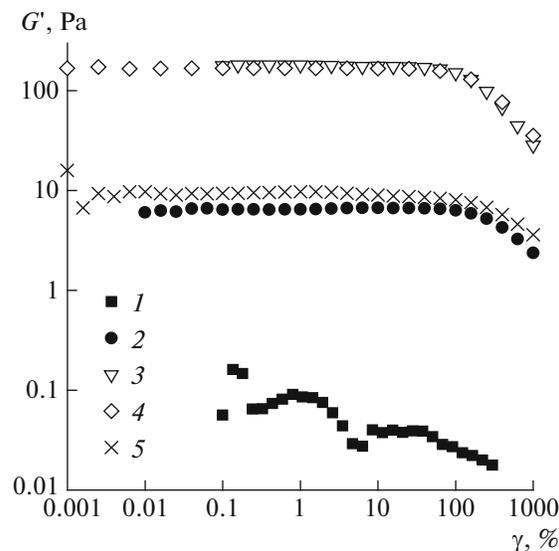


Fig. 2. Dependence of the shear storage modulus G' on the strain amplitude for solutions of the following copolymer samples: K1 7.6% (1), K2 11.2% (2), B2 14.4% (3), B1 17.6% (4), and CS 15% (5). (In Fig. 2–9, samples obtained by the RAFT process are represented by light dots; samples obtained by the traditional radical polymerization method, by dark dots; and the reference polymer, by crosses).

mer solutions obtained by classical radical polymerization and by the RAFT method. Moreover, the slope in the low-frequency region is equal to unity, which corresponds to the theory of linear viscoelasticity. Similar behavior is exhibited by the commercial CS terpolymer.

The conclusion on the qualitative similarity of the behavior of all the studied polymer solutions can also be drawn from the analysis of the temperature dependences of viscosities of equal concentration solutions at 20–80°C (Fig. 4). Noteworthy is the single envelope of the dependences in the non-Newtonian flow region, which reflects the expansion of the constant viscosity region and the gradual transition to a non-Newtonian flow with increasing temperature. This again proves that the rheological behavior is similar for the solutions of all samples. On the basis of the data, the activation energy of the viscous flow was calculated by the Arrhenius equation. The activation energy for the solutions of all samples was within the range of 32–35 kJ/mol.

As can be seen from the results presented above, there is no significant difference in the rheological behavior of the concentrated solutions of terpolymers obtained by different methods. However, the effects caused by the MW of the polymer and the concentration of the solution cannot be distinguished. It can only be assumed that a higher molecular weight sample dissolved in DMSO in large quantities should have a higher viscosity and higher viscoelastic characteristics.

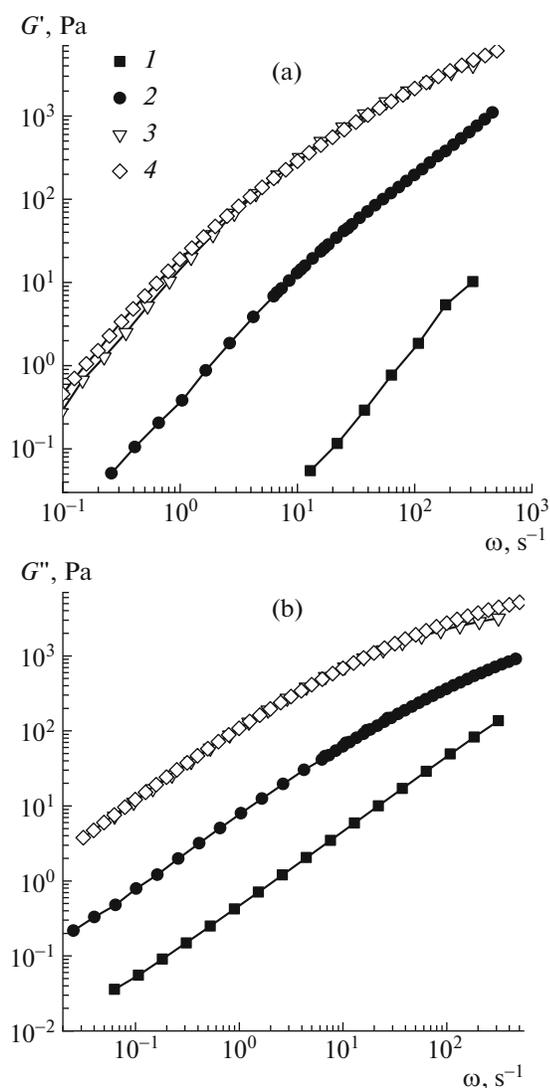


Fig. 3. Frequency dependence of the shear storage G' (a) and loss G'' (b) moduli for solutions of the following samples: K1 7.6% (1), K2 11.2% (2), B2 14.4% (3), and B1 17.6% (4).

Since the method of synthesis and the reagents used were not the same, it is necessary to understand what differences in the structure of macromolecules could be caused by the variations in the synthesis procedure. Apparently, one could expect, firstly, different branching of the chains and, secondly, a different distribution of comonomers along the chain in different macromolecules, i.e., composite inhomogeneity. Experience has shown that such “structural details” are not evident in concentrated solutions and that the main factors determining the rheological properties are the MW and the polymer concentration in the solution. However, the chain microstructure and the features of the interaction between the macromolecules and the solvent can be revealed by analyzing the behavior of dilute solutions.

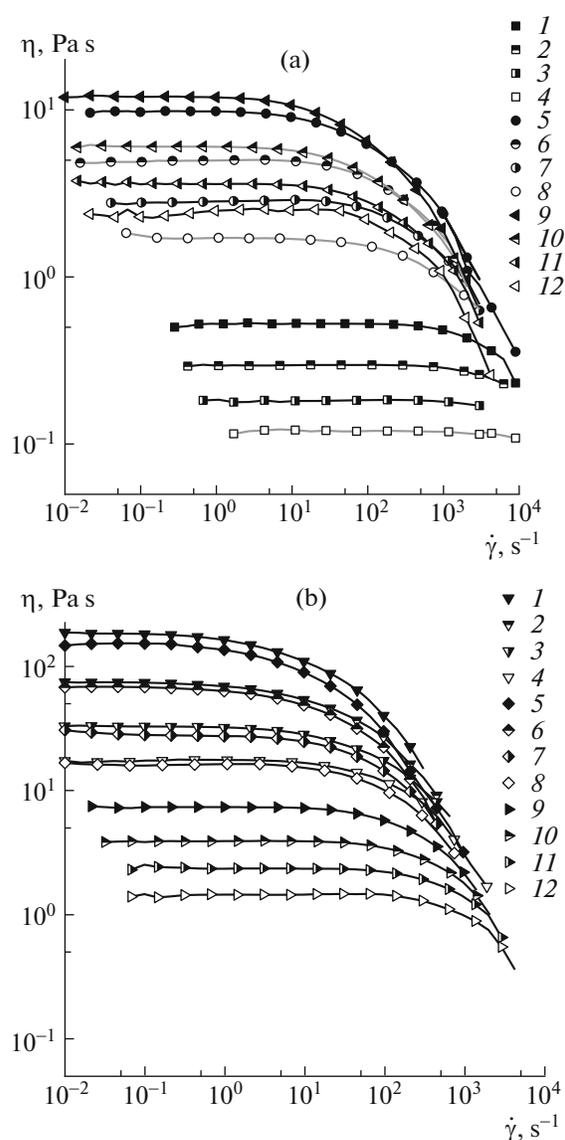


Fig. 4. Flow curves for 10% PAN solutions in DMSO for samples K1–K3 obtained by classical radical polymerization (a) and for samples B1–B3 obtained by RAFT polymerization (b). The temperatures were as follows: 20 (1, 5, 9), 40 (2, 6, 10), 60 (3, 7, 11), and 80°C (4, 8, 12).

The following equation is usually used to describe the concentration dependence of the reduced viscosity, η_{sp}/c : $\eta_{sp}/c = [\eta] + K_H[\eta]^2c$. Here, η_{sp} is the specific viscosity, $[\eta]$ is the intrinsic viscosity, and K_H is the Huggins constant describing the intensity of interaction between macromolecules and the solvent.

Another equation for the concentration dependence of the viscosity of dilute solutions is the Martin equation: $\ln(\eta_{sp}/c[\eta]) = K_M c[\eta]$. This equation uses the same variables as the Huggins equation. The K_M coefficient is called the Martin constant. It has the same meaning as the Huggins constant. Figure 5 shows the concentration dependence of the reduced

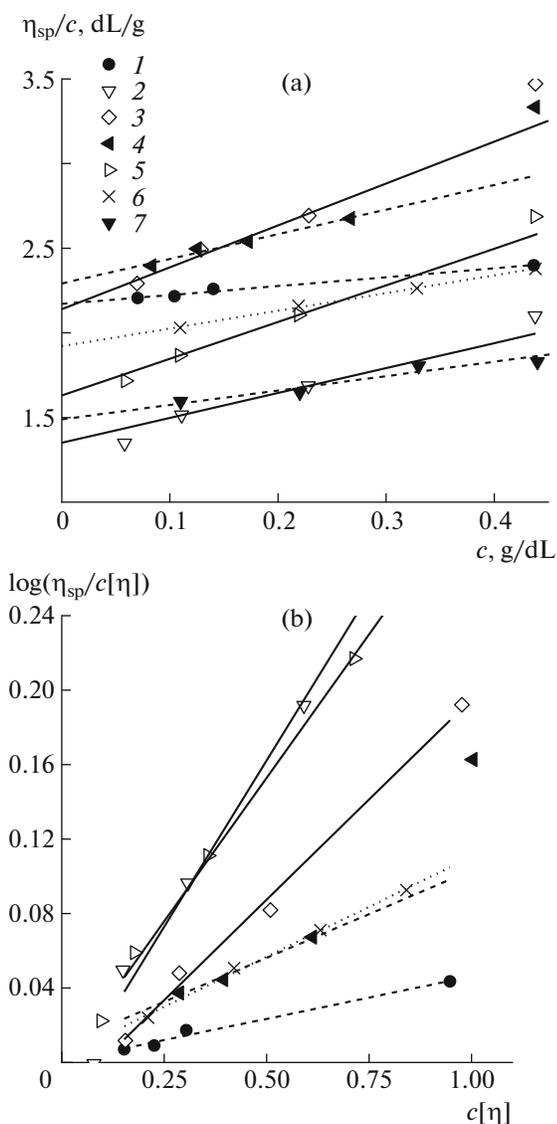


Fig. 5. Results of viscometric measurements obtained for dilute PAN solutions of samples K1 (7), K2 (1), K3 (4), B1 (2), B2 (3), B3 (5), and CS (6) and constructed in the coordinates of the Huggins equation (a) and those obtained for dilute PAN solutions of samples K2 (1), K3 (4), B1 (2), B2 (3), B3 (5), and CS (6) and constructed in the coordinates of the Martin equation (b).

viscosity in the coordinates of these two equations. When determining the intrinsic viscosity $[\eta]$ and the angular coefficient k , the linear regression parameters for the concentration dependence of the reduced viscosity were calculated by the least squares method.

The results of calculating the values of the intrinsic viscosity and the Huggins and Martin constants are given in Table 2. It is evident that polymers B1–B3 obtained by RAFT polymerization have higher values of the Martin and Huggins constants at similar intrinsic viscosity values. According to [28], the Huggins coefficient decreases with improvement of the quality

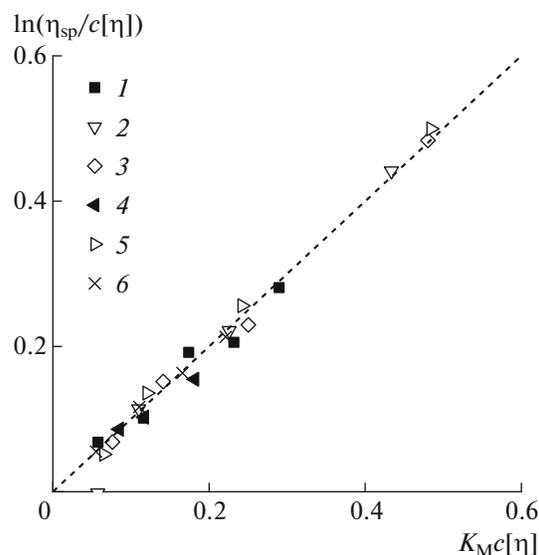


Fig. 6. Generalized concentration dependence of the reduced viscosity in the region of dilute solutions of the following samples: K1 (1), K3 (2), B1–B3 (3–5), and CS (6).

of the solvent. This indicates that DMSO is a better solvent for PAN copolymers synthesized by the classical method than for copolymers synthesized using RAFT polymerization. Despite the fact that the CS copolymer was obtained in an aqueous solution of sodium thiocyanate, the properties of its dilute solutions are similar to those of the former.

Thus, the study of dilute solutions demonstrated the effect of the synthesis method on the nature of the interaction between PAN macromolecules and the solvent. This effect may be caused by a difference either in chain branching or in compositional heterogeneity. By taking into account these differences expressed in terms of the Huggins or Martin constants and constructing a generalized concentration dependence of the viscosity on the dimensionless parameter $K_M c[\eta]$ (Fig. 6), it is possible to obtain, using the coordinates of the Martin equation, a single common dependence of the reduced viscosity on the reduced concentration in the region of dilute solutions.

An attempt to extend this approach to concentrated solutions was unsuccessful (Fig. 7), although there are papers (see, for example, [29]) where, over a wide range of compositions, common concentration dependences of the viscosity were obtained for solutions of a single polymer in different solvents using the coordinates of the Martin equation. In our case, when studying a broad concentration region, there are deviations from this approach. Moreover, although solutions of copolymers obtained by the RAFT method fit in a single dependence with a certain degree of error, solutions of copolymers synthesized by classical radical copolymerization not only clearly differ from the above-mentioned case but also differ among them-

Table 2. Values of the intrinsic viscosity, the Huggins and Martin constants, and the crossover point

Sample	$[\eta]$, dL/g	K_H	K_M	c_c , wt %
K1	1.49	0.38	0.35	4.0
K2	2.17	0.11	0.11	3.0
K3	2.29	0.28	0.26	3.0
B1	1.35	0.81	0.73	5.3
B2	2.14	0.54	0.51	3.7
B3	1.63	0.82	0.68	3.0
CS	1.92	0.28	0.26	3.0

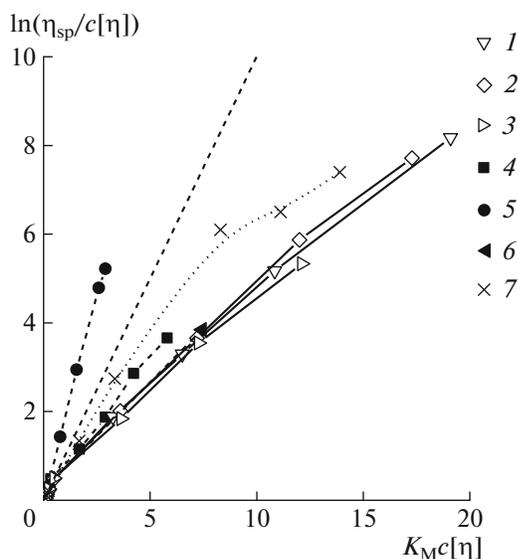
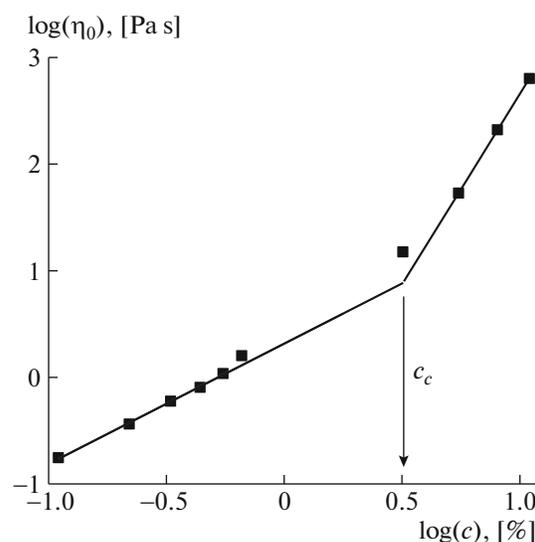
selves. In general, this means that the microstructure of the chain differs not only in the two series of copolymers but also within the “classical” series. In the region of dilute solutions, this factor can be taken into account by using parameters that characterize the interaction of macromolecules with the solvent. However, when studying the region of concentrated solutions, where a mesh network exists, it is necessary to introduce one more parameter that reflects the moment of formation and the density of such a network. The crossover concentration c_c and the c/c_c ratio, respectively, can be used as such parameters. This was first proposed in [30].

The c_c value is usually determined by the concentration dependence of the viscosity, as shown in Fig. 8 for solutions of the K1 sample. At low concentrations of the polymer, an increase in the viscosity is proportional to the concentration. In this region, the flow of the solution occurs via independent displacement of macromolecular coils that do not interact with one

another. Upon reaching the critical concentration c_c , the coils begin to intertwine, forming a fluctuation mesh network. This results in a sharp increase in the growth rate of the viscosity. The concentration dependences of all samples, and the respective c_c values are grouped in Table 2. Figure 9 shows a generalized dependence of the viscosity on the molecular parameters of copolymers. This dependence accounts for the concentration corresponding to the mesh network formation and for the network density. It is evident that taking this parameter into account makes it possible to obtain a dependence that is invariant with respect to molecular characteristics within the entire concentration range.

CONCLUSIONS

The systematic analysis of the rheological properties of PAN copolymer solutions in DMSO made it possible to draw the following conclusions. Both in the steady-state flow mode and in the mode of low-amplitude oscillations, concentrated solutions of PAN copolymers obtained by different synthetic procedures have similar rheological properties. For dilute solutions, a difference has been identified in the nature of interactions between macromolecules of copolymers synthesized by different methods and the solvent. This effect manifests itself in substantially higher values of the Huggins and Martin constants for copolymers formed by the RAFT process. By taking these constants into account, it became possible to obtain generalized dependences of the intrinsic viscosity on the molecular parameters. By introducing the c/c_c ratio to the generalized argument, a generalized viscosity

**Fig. 7.** Generalized dependence of the reduced viscosity on the concentration of the following samples: B1–B3 (1–3), K1–K3 (4–6), and CS (7).**Fig. 8.** Dependence of the reduced viscosity on the concentration of solutions of sample K1.

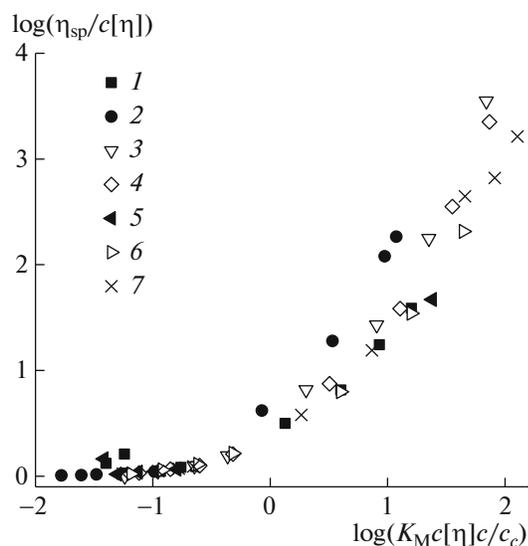


Fig. 9. Generalized dependence of the reduced viscosity on the concentrations of K1–K3 (1–3), B1–B3 (4–6), and CS (7).

dependence on the molecular characteristics of copolymers has been obtained for the entire composition range.

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