

POLYMERIZATION

# The Influence of the Activating Agent on the Controlled Synthesis of Polyacrylonitrile Using Systems Based on Copper(I) Bromide and Tris(2-pyridylmethyl)amine

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**Abstract**—The polymerization of acrylonitrile in the presence of catalytic systems based on copper(I) bromide, tris(2-pyridylmethyl)amine, and different reducing/activating agents is studied. It is found that the polymerization is controlled and that the activating agent is regenerated by a single-electron transfer. Moreover, the polymerization leads to the formation of polymers with high molecular weight and relatively narrow molecular-weight distribution. It is found that glucose and ascorbic acid are the most efficient among the studied activating agents in terms of the polymerization rate and the control over the molecular-weight characteristics of synthesized polymers.

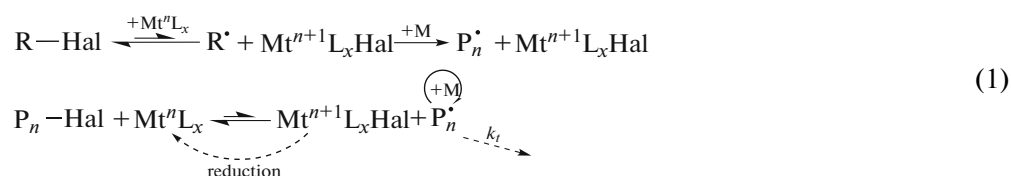
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Carbon fibers are widely used as a basis for high-strength structural materials that are required in many fields of the high-tech industry (e.g., aerospace industry, arms industry, construction, and medicine) and in the production of sports equipment and various household products [1–6]. A great interest in carbon fiber results from its unique features, primarily its high modulus of elasticity and particular thermophysical, electrochemical, and sorption properties [7, 8]. Presently, the main precursor for the production of carbon fiber is acrylonitrile-based copolymers that contain more than 95% acrylonitrile [9, 10]. To obtain a high-quality material with a high modulus of elasticity, it is preferable to use polymers with a molecular weight (MW) of  $\sim 10^5$  and a relatively narrow molecular-weight distribution ( $M_w/M_n < 2$ ) as the precursor [11–13]. The use of a precursor with a lower MW results in the formation of a carbon fiber with low strength, whereas an increase in the MW to  $(5–10) \times 10^5$  makes the polymer less soluble in a spinning solution. The advantage of using copolymers with narrow molecu-

lar-weight distribution is that they do not contain an insoluble high-molecular-weight fraction. This feature contributes to a high compositional homogeneity and better solubility of the polymer and leads to the production of a fiber with fewer defects [13].

At present, controlled radical polymerization is one of the most effective methods to produce polymers with a narrow molecular-weight distribution and a predetermined MW [14–17]. This methodology, which combines the simplicity of classical radical polymerization with the possibilities provided by “living” anionic polymerization, has recently become a powerful tool for synthetic polymer chemistry. Atom transfer radical polymerization (ATRP) stands out among different ways to implement controlled radical polymerization [18–20].

The catalytic process of ATRP is based on the reversible transfer of a halogen atom between a growing polymeric chain and a transition metal complex. The reversible transfer is accompanied by the alternation of the chain between its active and inactive (“dormant”) states:



As the result, polymer chains grow simultaneously in a step by step manner over the entire polymerization process, yielding samples with a narrow molecular-weight distribution and a predetermined MW. Atom transfer polymerization that proceeds in accordance with scheme (1) is always accompanied by side reactions of irreversible chain termination. Consequently, metal complexes containing the metal in its highest oxidation state accumulate in the system. Its accumulation shifts the equilibrium even further toward the dormant chains, causing the polymerization to stop long before a high degree of monomer conversion is achieved, and necessitates the use of relatively large quantities of a metal-containing catalyst. This problem can be eliminated by supplying the system with an additional activator that regenerates the active form of the catalyst. In fact, this approach known as activators regenerated by electron transfer (ARGET) [21–23] gave a second birth to the ATRP method by increasing the rate of the process and decreasing the concentration of the applied metal complex without sacrificing a high degree of control over the process.

The appeal of the ARGET ATRP methodology for the production of homo- and copolymers of acrylonitrile, which are then converted into carbon fiber, lies in the possibility to continue the process until a high degree of conversion is reached and in the possibility of obtaining a product with high MW. Moreover, ARGET ATRP requires lower concentrations of a metal-containing catalyst and thereby makes it possible to significantly reduce the costs of cleaning the resulting precursor from the unreacted metal-containing compound and the activator.

Copper compounds play a special role among metal-containing catalysts that make it possible to carry out the controlled synthesis of polyacrylonitrile and a number of acrylonitrile-based copolymers. K. Matyjaszewski et al. carried out the pioneering studies in this field [24, 25]; these studies were based on the use of copper halides in combination with 2,2'-bipyridyl. In spite of the fact that the authors obtained narrowly dispersed polyacrylonitrile ( $M_w/M_n \sim 1.2$ ), the polymerization was characterized by a relatively low degree of conversion (less than 40% in 23 h) and low MW of the resulting polymer. In their later studies, K. Matyjaszewski et al. successfully applied the ARGET ATRP to perform the controlled synthesis of polyacrylonitrile using the systems based on  $\text{CuCl}_2$  in combination with tris(2-pyridylmethyl)amine (TPMA) and various reducing agents [26]. The use of these systems made it possible to perform the polymerization of acrylonitrile at temperatures of 40–65°C and at the copper catalyst concentration of 75 or 25 ppm. This feature makes these systems attractive in terms of reducing the costs of purification of the product from

the catalyst. The reviews [19, 27] summarize data on the polymerization of acrylonitrile under the effect of metal-containing compounds and other agents of controlled polymerization in more detail.

The aim of this study was to find the optimal conditions for the controlled polymerization of acrylonitrile in order to produce samples with high molecular weight and narrow molecular-weight distribution. We selected the catalytic system based on copper(I) bromide in combination with TPMA, which is used as a complexing ligand [26, 28, 29]. Copper(0), glucose, ascorbic acid, tin(II) 2-ethylhexanoate, and isopropylamine were used as agents reducing the catalyst. This study analyzes the influence that the process conditions and the ratio between the concentrations of the components in the polymerization system have on the process rate and the yield and characteristics of the produced polymer.

## EXPERIMENTAL

Acrylonitrile (Sigma) was purified by distillation over calcium hydride under argon immediately before use. DMSO was dried over sodium hydroxide, distilled under reduced pressure, redried over the calcined 4-Å zeolite, and then again distilled. The physicochemical constants agreed with the published data. Copper (I) bromide, ethyl 2-bromoisobutyrate (EBIB, 98%), glucose, and tin(II) ethylhexanoate (Aldrich) were used without preliminary purification. The TPMA ligand was obtained according to the known procedure [30]. The metallic copper was in the form of a wire 1 mm in diameter. Pieces of copper wire (5 mm long) preactivated with hydrochloric acid were placed in prepared glass ampoules during the experiment.

Calculated amounts of TPMA, copper(I) bromide, glucose, or ascorbic acid (as activators) were placed in a Schlenk flask equipped with a magnetic stirrer. The flask was degassed three times and filled with argon. The calculated amounts of DMSO, acrylonitrile, tin ethylhexanoate, or isopropylamine (as activators) and ethyl 2-bromoisobutyrate were then added. The resulting mixture was dispensed into prepared ampoules. When copper(0) was used as a reducing agent, a copper wire 1 mm in diameter and 5 mm in length was activated with hydrochloric acid and placed in the ampoules before the prepared polymerization mixture was added. The ampoules were degassed three times, sealed, and placed in a thermostat for a predetermined time. The polymerization was stopped by freezing the ampoule in liquid nitrogen. The polymerization product was dissolved in DMF and precipitated in distilled water. The polymer obtained by filtration was dried to constant weight at 70°C under reduced pressure.

The molecular-weight characteristics of polyacrylonitrile (PAN) were studied by gel-permeation chromatography on a Knauer system equipped with a linear column with the exclusion limit of  $2 \times 10^6$  MW (Phenomenex, Nucleogel GPCM-10, USA) at 40°C. The detector was an RI Detector K-2301 differential refractometer and the eluent was DMF containing 10 mmol LiBr. The instrument was calibrated using narrow-dispersion PMMA-based standards. The molecular weight of PAN was calculated from a universal calibration curve and the Mark–Kuhn–Houwink equation using the coefficients for PAN and PMMA known from the literature [31]. The calculation formula was as follows:

$$\log M_{\text{PAN}} = \frac{1 + \alpha_{\text{PMMA}}}{1 + \alpha_{\text{PAN}}} \log M_{\text{PMMA}} + \frac{1}{1 + \alpha_{\text{PAN}}} \log \frac{K_{\text{PMMA}}}{K_{\text{PAN}}}$$

Chromatographic data were interpreted by ChomGate software.

## RESULTS AND DISCUSSION

### *Characteristics of Acrylonitrile Polymerization with Use of Copper(0) as a Reducing Agent*

One of the ways to regenerate the catalyst in controlled radical polymerization that proceeds by the atom transfer mechanism is the use of condensed metals as reducing agents. The processes in which copper(0) is used as an activator in combination with halogen-containing copper compounds used as catalysts are generally considered a separate group of ATRP processes. The polymerization proceeds in this system under the conditions of dynamic equilibrium between the compounds of copper(I), copper(II), and free metal. This equilibrium is described in the literature using the schemes of SARA ATRP [32, 33] and SET LRP [34, 35], which differ in the estimation of the contribution of disproportionation and coproportionation reactions. Regardless of the exact scheme, the essential merit of this method is the availability of zero-valent metals used as reducing agents and the ease of removing the unreacted activator.

In this paper, we studied the possibility of using copper(0) as a catalyst-regenerating agent for the process that proceeds in DMSO at different temperatures. Previous studies showed that DMSO is the optimal solvent for the polymerization of acrylonitrile (AN) under the action of systems based on copper(I) bromide [36]. Polymerization of acrylonitrile was carried out at temperatures of 40–80°C at different initial concentrations of the monomer and different ratios between the amount of the monomer and the initiator.

The experimental results are given in Table 1. They indicate that the selected system can be used to produce polyacrylonitrile with the  $M_w$  value of  $(50\text{--}60) \times$

$10^3$  and the polydispersity coefficient of 1.4–1.5. Interestingly, the temperature increase from 40 to 80°C does not lead to an increase in the polymer yield. On the contrary, the conversion of the monomer over a given time decreases in several cases. Moreover, the polydispersity of the obtained samples increases as the temperature of synthesis rises to 80°C. This temperature effect on the course of the process can be explained by an increase in the contribution of secondary processes of chain termination and transfer with increasing temperature. The increase in temperature promotes the formation of a larger number of active sites at the initial time. This, in turn, intensifies the bimolecular termination and the accumulation of “dead” polymer and decreases the number of “live” chains that can continue the process. By reducing the monomer concentration in the polymerization system from 5 to 4 mol/L, the degree of control over the process can be slightly improved and the samples with a narrower molecular-weight distribution can be obtained.

The advantage of controlled radical polymerization methods is the ability to control the molecular-weight characteristics of the resulting polymers by changing the ratio between the amounts of the monomer and the initiator. It follows from the data in Table 1 that the decrease in the amount of the initiator leads to the production of polymers with a higher molecular weight, which is of practical importance for the production of polymers suitable for processing into high-strength carbon fiber. However, we should note that the obtained samples have relatively high polydispersity coefficients. It is possible that they result from the heterogeneity of the applied system.

### *The Use of Glucose as a Reducing Agent in the Controlled Synthesis of Polyacrylonitrile*

A number of studies have shown that glucose can be used as a reducing agent that reduces a copper catalyst to a lower oxidation state [26]. Good solubility of glucose in polar media such as DMSO makes it possible to perform the polymerization under homogeneous conditions. The essential advantages of glucose are its availability (including its low cost) and nontoxicity. These factors make the use of glucose as a reducing agent attractive from an environmental and economic point of view. Experiments have shown that a system based on copper(I) bromide, TPMA, and glucose can be used in the controlled polymerization of acrylonitrile, leading to the synthesis of samples with the required molecular-weight characteristics (Table 2).

It follows from the analysis of the data in Tables 1 and 2 that the use of glucose makes it possible to obtain samples with high values of number-average molecular weights and relatively narrow molecular-weight distribution. The polydispersity coefficient in some cases does not exceed 1.3. It should be noted that

**Table 1.** Results of the experiments on the polymerization of AN in the presence of Cu(0) ([EBIB] : [CuBr] : [TPMA] = 1.0 : 0.2 : 2.2)

[AN] : [EBIB]	[AN], mol/L	Time, h	$T$ , °C	Conversion, %	$M_n \times 10^{-3}$	$M_w/M_n$	$M_{theor} \times 10^{-3}$
900 : 1	4	75	40	61	53.3	1.38	29.2
			60	72	56.0	1.37	34.4
			80	58	51.4	1.48	27.7
	5	80	40	85	52.9	1.75	40.5
			60	73	53.9	1.39	34.7
			80	63	31.5	2.36	29.9
1200 : 1	5	80	40	65	66.7	1.50	41.3
			60	63	61.2	1.48	39.8
			80	64	64.0	1.57	40.8

**Table 2.** Results of the experiments on the polymerization of AN in the presence of glucose as a reducing agent ([AN] : [CuBr] : [glucose] : [TPMA] = 900 : 0.2 : 2.0 : 2.2)

[AN] : [EBIB]	[AN], mol/L	$T$ , °C	Time, h	Conversion, %	$M_n \times 10^{-3}$	$M_w/M_n$	$M_{theor} \times 10^{-3}$	
900 : 1	3.0	40	6	9.3	10.6	1.26	4.4	
			36	22.8	22.4	1.25	10.9	
			75	48.5	33.1	1.28	23.2	
	3.0	60	6	14.0	10.8	1.28	6.7	
			36	40.0	35.7	1.30	19.1	
			75	71.6	50.3	1.51	34.2	
	3.0	80	6	33.3	28.4	1.31	15.9	
			36	52.0	41.6	1.71	24.8	
			75	58.0	43.2	1.72	27.8	
	4.0	40	36	30.6	21.8	1.18	14.6	
			60	36	66.0	44.5	1.33	31.5
			80	36	64.7	57.7	1.75	30.9
5.0	40	36	28.2	15.8	1.38	13.5		
		60	36	61.7	49.8	1.35	29.5	
		80	36	62.6	53.0	1.67	29.9	
1200 : 1	5.0	40	75	42.8	45.4	1.27	27.3	
		60	75	79.6	77.2	1.49	50.7	
		80	75	62.0	72.3	1.42	39.4	
	4.0	40	75	35.0	35.3	1.25	22.2	
		60	75	93.0	83.2	1.42	59.1	
		80	75	44.0	46.1	1.68	28.0	
1900 : 1	4.0	60	100	95.0	68.4	1.40	95.8	
		80	100	98.0	105.8	1.62	98.8	

this result is very good for the controlled radical polymerization of acrylonitrile. The number-average molecular weights of the samples obtained using this system reach  $80 \times 10^3$  at the given ratio between the concentrations of the monomer and the initiator. It is noteworthy that the polydispersity coefficient of the

samples does not exceed 1.5 even at such a high molecular weight.

Table 2 shows the data that reflect the temperature effect on the polymerization process. The increase in temperature from 40 to 60°C leads to an increase in the monomer conversion over a given time. Interestingly,

the conversion rate does not increase with the further increase in the reaction temperature to 80°C. In fact, in some cases, the polymer yield decreases. The polymer samples obtained at 80°C are characterized by higher values of the polydispersity coefficients. This fact indicates that the process performed at higher temperatures is less controlled, as in the above-described case of the systems based on using copper(0) as an activator. At the same time, the molecular weights of the synthesized polymers increase with an increase in the conversion and differ slightly from the respective theoretically calculated values.

The results on the polymerization of acrylonitrile in the presence of glucose as a reducing agent (Table 2) are in good agreement with the results reported by K. Matyjaszewski [26] in the study on the synthesis of PAN using a catalytic system based on copper(II) chloride, TPMA, and bromopropionitrile as an initiator. In this case, an increase in the polymerization temperature leads to an increase in the process rate and simultaneously broadens the molecular-weight distribution of the polymers.

We obtained the most narrowly dispersed samples of PAN when the process was performed at 40°C. However, it takes considerable time to achieve high conversion ratios and high MW values when the polymerization is performed at this temperature. This fact significantly limits the practical application of this method for the production of PAN and PAN-based precursor under industrial conditions. In this respect, it is more rational to perform the polymerization at 60°C. Although the samples synthesized at 60°C have a somewhat broader molecular-weight distribution, the polymerization proceeds with a higher yield of the desired product and makes it possible to obtain a polymer with a higher molecular weight.

The process rate increases with an increase in the concentration of acrylonitrile in the initial polymerization mixture. This effect is expressed in an increase in the degree of monomer conversion over a given time. In this case, the product with a higher molecular weight is formed in accordance with the mechanism of fragment-by-fragment chain growth. This effect is most pronounced at the temperature of 60°C, which turned out to be the most preferable for the production of PAN with predetermined characteristics in terms of combining an acceptable polymerization rate and achieving a high degree of control over the process. As can be seen from the presented data, an increase in the concentration of acrylonitrile in the polymerization mixture from 3.0 to 4.0 mol/L leads to a 1.5-fold increase in the polymer yield in 36 h. Thus, the analysis of the experimental data in Table 2 shows that, in terms of producing a polymer with predetermined molecular-weight characteristics and in terms of

reaching high degrees of monomer conversion, it is preferable to carry out the synthesis of PAN at the acrylonitrile concentration of 4.0 mol/L in the reaction mixture.

It follows from the provided data that the values of number-average molecular weights for the obtained samples of PAN exceed in all cases the theoretically calculated values and that the values of  $M_w/M_n$  are relatively low. This fact can be associated with deactivation of growing macroradicals that occurs at the initial step of the process because of a bimolecular termination and leads to a reduction in the total number of active radicals in the system. Macromolecules that enter the subsequent stages of successive “dormancy” and growth reach the maximum possible “size” and form the high-molecular-weight fraction of PAN samples. In practice, such a discrepancy between  $M_n$  and  $M_{\text{theor}}$  and the absence of a strict pattern in the variation of one parameter with the variation of the other makes it hard to synthesize macromolecules with strictly predetermined MW. However, this drawback is not critical for the synthesis of the precursor for the production of carbon fiber because, in this case, the need to achieve the highest possible MW of the samples prevails over the need to achieve a given pre-defined MW. The analysis of the data from Table 2 enables us to assume that the  $M_n$  value for polyacrylonitrile produced using this system will be 1.5–2.0 times higher than the theoretically calculated value.

To obtain polymers with an even higher MW, it is necessary to carry out the process using a smaller content of the initiator. The experiments showed that the synthesis of PAN performed at the [monomer] : [initiator] ratio of 1200 : 1 provides polymer samples with a molecular weight of  $80 \times 10^3$  and higher. A decrease in the amount of the initiator leads to a decrease in the degree of monomer conversion over a given time, which is consistent with a decrease in the number of reaction centers. The advantage of this system is the fact that the polymerization of acrylonitrile under these conditions can proceed up to high conversions, which is especially important in terms of practical use. For instance, the synthesis of PAN performed at the initial acrylonitrile concentration of 4 mol/L in DMSO at 60°C can result in a monomer-to-polymer conversion of up to 90–95%. The resulting polymer has the following parameters:  $M_n$  of the samples is approximately  $83 \times 10^3$  and the polydispersity coefficient is 1.42. It is interesting that an increase in the monomer concentration decreases the process rate at high conversions and reduces the maximum conversion to 80%. By performing the process at the monomer-to-initiator concentration ratio of 1900 : 1, we managed to obtain a polymer with  $M_n > 105 \times 10^3$  and a polydispersity coefficient of ~1.6.

**Table 3.** Results of the experiments on the polymerization of AN in the presence of Sn(EH)<sub>2</sub> as a reducing agent ([AN] : [EBIB] : [CuBr] : [Sn(EH)<sub>2</sub>] : [TPMA] = 900 : 1 : 0.2 : 2.0 : 2.2)

[AN], mol/L	Time, h	T, °C	Conversion, %	$M_n \times 10^{-3}$	$M_w/M_n$	$M_{\text{theor}} \times 10^{-3}$
3.0	36	40	13.3	13.1	1.27	13.9
		60	44.6	33.4	1.39	19.9
4.0	37	40	28.0	28.8	1.49	13.4
		60	47.6	52.1	1.70	22.7
		80	34.7	38.0	1.95	16.6
5.0	36	40	32.5	43.6	1.28	15.5
		60	50.3	57.2	1.54	24
		80	35.2	53.7	1.49	16.8

In general, the data indicate that the system based on copper(I) bromide, TPMA, and glucose can be used to obtain polymers of acrylonitrile that are potentially applicable as a basis for the production of high-strength carbon fiber.

#### *Polymerization of Acrylonitrile in the Presence of Tin(II) 2-Ethylhexanoate as a Reducing Agent*

Compounds of divalent tin, particularly tin(II) 2-ethylhexanoate (Sn(EH)<sub>2</sub>) [37, 38], can act as reducing agents for an effective ATRP process. This fact is confirmed by the results of the polymerization of acrylonitrile in DMSO in the presence of Sn(EH)<sub>2</sub> at the initial monomer concentration of 3.0–5.0 mol/L and different temperature. The main molecular-weight characteristics of the PAN samples obtained under these conditions are given in Table 3.

It is evident from the provided data that the proposed system can also be used to obtain PAN samples in a controlled manner. The experimental results show that an increase in the process temperature leads to an increase in the process rate, which is expressed in an increase in the acrylonitrile conversion over a given time and which is especially pronounced at low concentrations of the monomer (3.0 mol/L). The increase in the conversion with the temperature is accompanied by an increase in the values of the number-average MW and of the polydispersity coefficient. This fact indicates that the process becomes less controlled. Similar trends are observed upon an increase in the monomer concentration in the initial polymerization medium. For instance, when the polymerization is performed at 40°C, the change in the monomer concentration from 3.0 to 4.0 mol/L contributes to an increase in the monomer conversion (13.3% and 28% in 36–37 h) and in the  $M_w/M_n$  value (from 1.26 to 1.49). Thus, the aforementioned change in the composition of the reaction mixture makes the system more efficient in terms of achieving a high yield of the desired product but leads to an increase in the polydispersity coefficient.

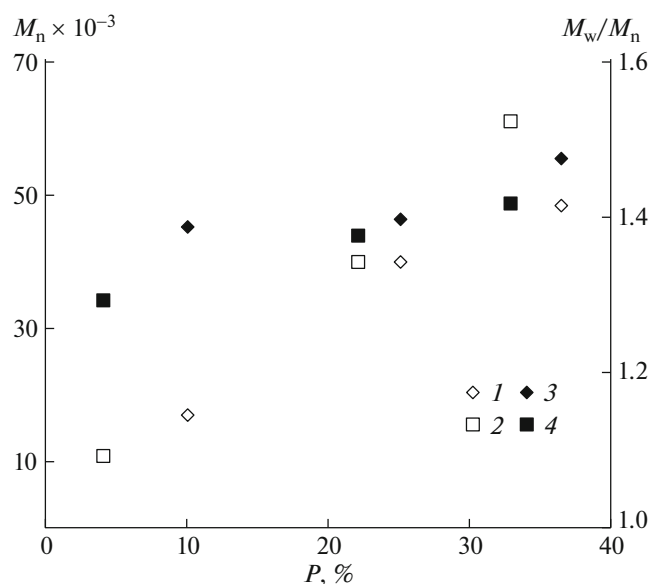
On the basis of the results obtained, we can conclude that, for the preparation of PAN precursor whose characteristics will make it possible to use it in the synthesis of high-quality carbon fiber, it is best to perform the process at low initial concentrations of the monomer (3.0–4.0 mol/L) and relatively low temperatures (up to 60°C).

The system based on copper bromide and Sn(EH)<sub>2</sub> was used to obtain polyacrylonitrile with high molecular weight. Figures 1 and 2 show how the molecular-weight characteristics of the samples that were obtained at 40 and 60°C, respectively, depend on the monomer conversion. It can be seen that an increase in the molecular weight of the samples during the polymerization increases with the conversion, which indicates that the polymer synthesis is controlled. Similar dependences are also observed when using a system based on copper(II) chloride in combination with TPMA [26]. It should be noted that an increase in temperature leads to a broadening of the molecular-weight distribution. This effect is most pronounced at the monomer concentration of 4.0 and 5.0 mol/L.

Thus, the use of tin(II) ethylhexanoate as a reducing agent makes it possible to carry out an efficient synthesis of high-molecular-weight and narrowly dispersed polyacrylonitrile in DMSO at relatively low temperatures (up to 60°C) and low monomer concentrations (up to 4.0 mol/L) in the initial polymerization mixture. It should be noted that the use of Sn(EH)<sub>2</sub> as a reducing agent results in the production of samples with a slightly broader molecular-weight distribution than in the samples obtained in the presence of glucose as a reducing agent.

#### *Isopropylamine as a Catalyst-Reducing Agent in ATRP Process*

It has been shown in several studies devoted to the development of effective systems for controlled radical polymerization that different amines can act as reducing agents that activate the catalyst and thereby activate the reaction in accordance with the ARGET



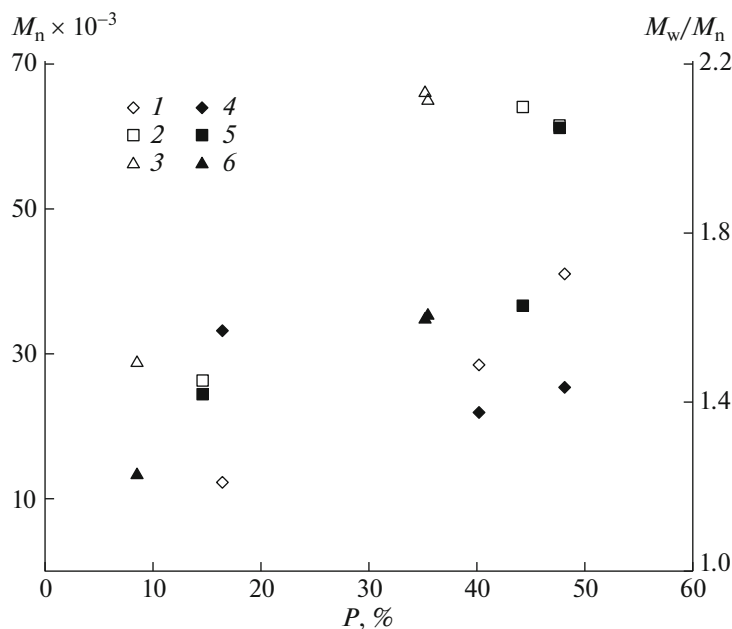
**Fig. 1.** Dependence of the number-average molecular weight (1, 2) and the polydispersity coefficient (3, 4) for the samples of PAN on the monomer conversion.  $T = 40^\circ\text{C}$ ,  $[\text{AN}] = 4.0$  (1, 3) and  $5.0$  mol/L (2, 4), and  $[\text{AN}] : [\text{EBIB}] : [\text{CuBr}] : [\text{Sn}(\text{EH})_2] : [\text{TPMA}] = 1200 : 1.0 : 0.2 : 2.0 : 2.2$ .

ATRP mechanism [39–42]. The mechanism of the activating action of an amine is based on the reduction of copper to a monovalent state. In this process, the amine undergoes one-electron oxidation with the for-

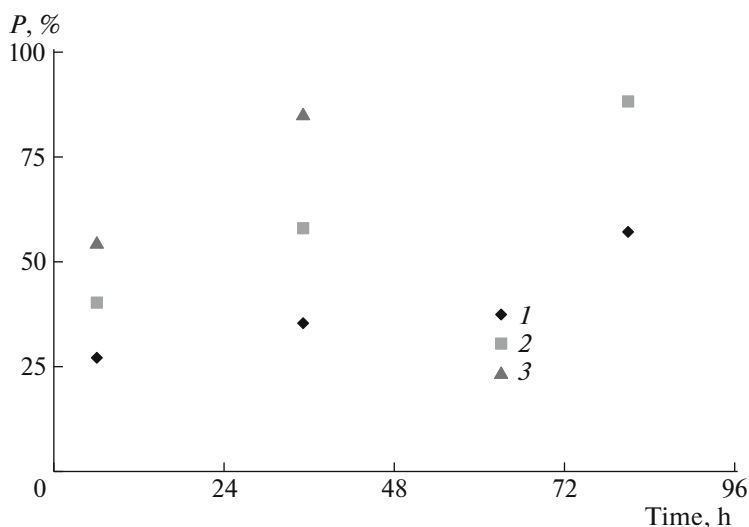
mation of unstable radical cations; they, in turn, undergo a disproportionation [39, 43, 44].

We studied the possibility of synthesizing a high-molecular-weight and narrowly dispersed polyacrylonitrile using isopropylamine  $i\text{-PrNH}_2$  as an agent that reduces a catalyst during polymerization. In this case, we chose carbon tetrachloride as the initiator of polymerization: this compound is often used in ATRP processes as a source of carbon-centered radicals [16–19]. Figure 3 shows the dependence between the monomer conversion and the duration of polymerization, whereas Fig. 4 shows the molecular-weight characteristics of the resulting polymer samples. As evident from Fig. 3, a sequential temperature increase from  $40$  to  $80^\circ\text{C}$  substantially accelerates the process and makes it possible to reach  $85\text{--}90\%$  conversion in  $80$  h, which is a good result in terms of the depth of acrylonitrile conversion.

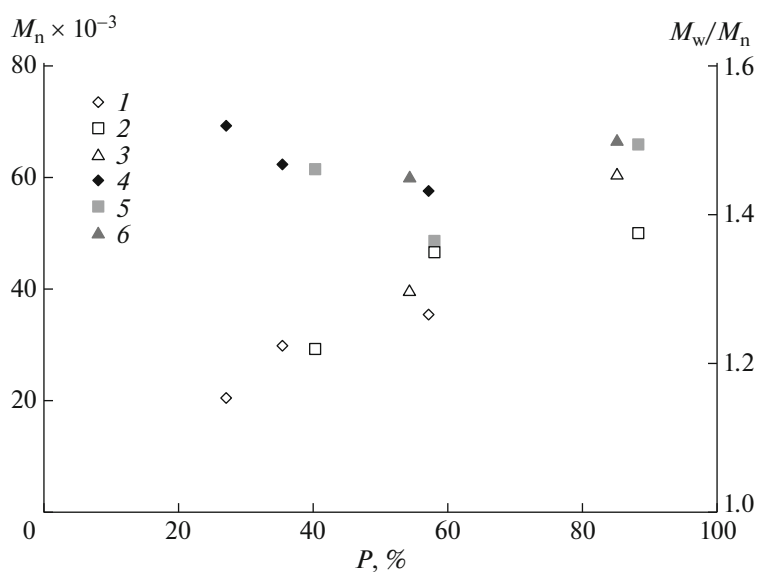
The resulting polymer is characterized by relatively high values of number-average MW (Fig. 4). The MW values of the polymer increase with the conversion, which is typical of controlled processes. The polydispersity coefficients are approximately  $1.5$ . These values are somewhat higher than the respective parameters of the samples obtained in the presence of glucose. As in the above-described cases of conducting the process with other reducing agents, an increase in the temperature of the experiment makes the process less controlled but helps to obtain products of higher molecular weight.



**Fig. 2.** Dependence of the number-average molecular weight (1–3) and the polydispersity coefficient (4–6) for the samples of PAN on the monomer conversion.  $T = 60^\circ\text{C}$ ;  $[\text{AN}] : [\text{EBIB}] : [\text{CuBr}] : [\text{Sn}(\text{EH})_2] : [\text{TPMA}] = 1200 : 1.0 : 0.2 : 2.0 : 2.2$ ; and  $[\text{AN}] = 3.0$  (1, 4),  $4.0$  (2, 5), and  $5.0$  mol/L (3, 6).



**Fig. 3.** Dependence of the monomer conversion on the duration of polymerization at 40 (1), 60 (2), and 80°C (3). The solvent is DMSO, [AN] = 3.0 M, and [AN] : [CCl<sub>4</sub>] : [CuBr] : [*i*-PrNH<sub>2</sub>] : [TPMA] = 900 : 1.0 : 0.2 : 2.0 : 2.2.



**Fig. 4.** Dependence of the number-average molecular weight (1–3) and the polydispersity coefficient (4–6) for the samples of PAN on the monomer conversion. [AN] = 3.0 M; [AN] : [CCl<sub>4</sub>] : [CuBr] : [*i*-PrNH<sub>2</sub>] : [TPMA] = 900 : 1.0 : 0.2 : 2.0 : 2.2.  $T = 40$  (1, 4), 60 (2, 5), and 80°C (3, 6).

#### *The Polymerization of Acrylonitrile with Ascorbic Acid as a Reducing Agent*

The use of ascorbic acid additives as a catalyst-reducing agent makes it possible to perform controlled polymerization of acrylonitrile that yields polymers with the polydispersity coefficient of no higher than 1.5. The results presented in Table 4 indicate that the use of ascorbic acid as a reducing agent enables the acrylonitrile polymerization to reach high monomer conversion even at 40–60°C. The increase in tempera-

ture significantly accelerates the process. This effect is expressed in an increase in the monomer conversion over a given time and it is especially pronounced at the early stages of the process. It should be noted that an increase in the temperature of the experiment does not lead to a significant broadening of the molecular-weight distribution in contrast with the processes performed in the presence of Sn(EH)<sub>2</sub>. The use of ascorbic acid as an activator makes it possible to obtain



**Table 4.** Results of the experiments on the polymerization of AN in the presence of ascorbic acid (AA) as a reducing agent ([AN] : [CCl<sub>4</sub>] : [CuBr] : [AA] : [TPMA] = 900 : 1 : 0.2 : 2.0 : 2.2 and [AN] = 4.0 mol/L)

<i>T</i> , °C	Time, h	Conversion, %	$M_n \times 10^{-3}$	$M_w/M_n$	$M_{theor} \times 10^{-3}$
40	6	25.5	14.3	1.39	12.2
	36	56.8	31.9	1.30	27.1
	75	73.9	36.7	1.36	35.3
60	6	43.0	24.0	1.35	20.5
	36	76.0	41.5	1.37	36.3
	75	87.3	47.7	1.38	41.7
80	6	58.3	31.1	1.42	27.8
	36	99.0	63.5	1.51	52.8

samples of polyacrylonitrile with molecular weights that agree well with theoretical values.

From the analysis of the presented data, it can be concluded that the proposed catalytic system based on copper(I) bromide in combination with TPMA, which acts as a complexing ligand, and ascorbic acid, which acts as a reducing agent, is very efficient. The use of this composition makes it possible to obtain a high yield of narrowly dispersed polyacrylonitrile with a predetermined molecular weight.

## CONCLUSIONS

The results of the conducted experiments show that different types of reducing agents can be used in the polymerization of acrylonitrile by the ARGET ATRP mechanism in the presence of copper bromide as a catalyst. The most promising reducing agents in terms of high efficiency are glucose and ascorbic acid, which are also notable for their low toxicity, availability, and ease of use. In future, the studied systems may be of interest for the preparation of acrylonitrile-based copolymers with predetermined molecular-weight characteristics.

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