Novel Copper-Based Catalytic Systems for Atom Transfer Radical Polymerization of Acrylonitrile

Ivan D. Grishin * , **Elizaveta I. Zueva, Yulia S. Pronina and Dmitry F. Grishin**

Department of Chemistry, Lobachevsky State University of Nizhny Novgorod, 23 Gagarin Prosp., 603950 Nizhny Novgorod, Russia
* Correspondence: grishin_i@ichem.unn.ru

Abstract: Atom Transfer Radical Polymerization (ATRP) is an effective catalytic process leading to well-defined polymers with desired properties. This process based on reversible deactivation of propagating chains has a lower rate in comparison with conventional radical polymerization, especially in the case of obtaining polymers with high molecular weights. Thus, the increase of the rate of this process with preserving control over molecular weight distribution is a challenging task. In this work, novel catalytic systems for Activators Generated by Electron Transfer (AGET) ATRP of acrylonitrile based on copper (II) bromide complexes were proposed. It was found that Rochelle salt (potassium sodium tartrate tetrahydrate) may be used as a reducing agent for regeneration of copper-based catalysts to increase the rate of the process. The provided UV-vis spectroscopy experiments have confirmed the reducing ability of tartaric anion. It was found that the use tandem catalytic system based on two copper complexes with different ligands also increases the polymerization rate. The performed experiments allowed us to develop a catalytic system for rapidly obtaining polyacrylonitrile polymers with desired molecular weights exceeding 100 kDa.

Keywords: acrylonitrile; reversible-deactivation radical polymerization; atom transfer radical polymerization; copper (II) bromide; tris[(2-pyridyl)methyl]amine; N,N,N′,N″,N″-pentamethyldiethylenetriamine; rochelle salt; cyclic voltammetry

1. Introduction

Atom Transfer Radical Polymerization (ATRP) is one of the state-of-the-art ways of synthesis of well-defined polymers and different macromolecular structures [1–5]. It is a catalytic process based on reversible halogen transfer between propagating chain and a complex of a transitional metal (Scheme 1). This transfer is accompanied by oxidation of the metal complex and formation of a dormant chain. Due to the reversible nature of the process, dormant chains can be reactivated (k_a) and additional monomer units may be added to the growing chain. Realization of this mechanism results in increase of polymer molecular weight with conversion and provides opportunity to obtain block-copolymers and more complex objects [6].

The contribution of the side reaction of bimolecular radical termination (k_t) is reduced by decreasing the concentration of active species, but it cannot be fully avoided. The termination results in formation of "dead" chains and leads to the accumulation of the catalyst in higher oxidation state, making reinitiating the process impossible in spite of the presence of high amount of dormant chains and leading to the retardation of the process. This problem is solved by addition of a reducing agent capable to regenerate the catalyst. This method known as Activators Generated by Electron Transfer (AGET) ATRP [7,8] allows increasing the rate of polymerization even at low catalysts loadings. In spite of the recent achievements in ATRP, the rate of polymerization is still lower than of a conventional one. Because of the simultaneous growth of all chains with increase of conversion, this problem is especially prevalent when the synthesis of the samples with high molecular weight is required.
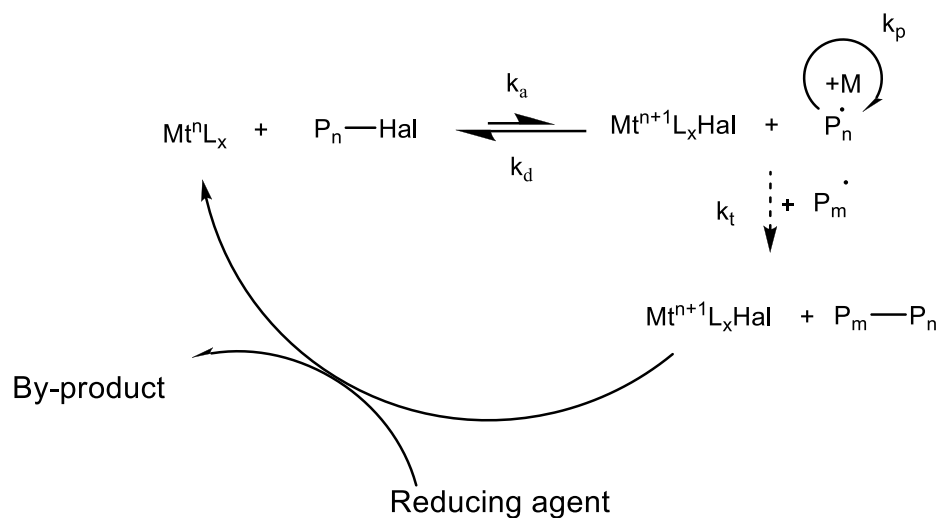
Scheme 1. The mechanism of AGRET ATRP. Mt^nL_x—metal complex in oxidation state n; $Mt^{n+1}L_xHal$—metal complex in oxidation state (n+1); P_n-Hal—dormant, halogen-capped polymer chain; P_m, P_m—active macroradicals; M—monomer unit; k_a, k_d, k_p, k_t—rate constant for activation, deactivation, propagation, and termination reactions, respectively.

A typical copper-based AGET ATRP system consists of Cu(II) salt, a nitrogen-based ligand that forms a metal complex in situ, and a reducing agent. Each of the components of the catalytic system has an impact on the polymerization rate and the molecular weight distribution (MWD) of polymer samples, thus the tuning of the process is a rather complex task. The proper choice of reducing agent is crucial for ATRP as it or the by-products of its oxidation may interact with monomers of propagating species. Among the widely used reducing agents for copper-mediated AGET ATRP, such organic compounds as glucose [9] or ascorbic acid should be mentioned [10]. The recent works of Matyjaszewski indicate that sodium pyruvate may be also used as a reducing agent for photoinduced polymerization [11,12]. Taking into account that pyruvic acid may be easily obtained from tartaric acid on heating [13], we decided to test it as a reducing agent for AGET ATRP. According to the ability of acids to react with nitrogen-containing ligands, a potassium sodium tartrate tetrahydrate (Rochelle salt, RS) was used instead of acid.

Copper-based complexes with nitrogen-based ligands are known as the most popular catalysts of ATRP due to their high activity and availability. The proper choice of the ligand allows for obtaining a catalyst with the desired activity suitable for the polymerization of the chosen monomer [14,15]. It was shown that the structure of the ligand and its donating ability influence its redox potential, which correlates with activity [16]. The decrease of the potential of Cu(I) | Cu(II) couple leads to an increase in equilibrium constant $K_{ATRP} = k_a / k_d$, which is considered a measure of a degree of control over a process [17].

Our recent studies have shown that the simultaneous use of two copper complexes with different redox potentials allows for increasing the rate of copper-mediated ATRP of acrylonitirle [18]. In such systems, the more reducing complex acts as an activator rapidly generating active species, while the more oxidizing one transfers them to the dormant state.

Thus, the use of tandem catalysis and application of novel reducing agents may be considered as two parallel ways of improving AGET ATRP systems from the point of view of the acceleration of the process and obtaining polymers with high molecular weights. In this work, both of the approaches were tested separately and simultaneously to increase the rate of AGET ATRP of acrylonitrile. Polyacryloniirle (PAN) is widely used for fiber production. The molecular weight of the polymer and its dispersity are key parameters that have a high great influence on the fiber strength and processability [19]. Thus, obtaining PAN samples with high molecular weight and low dispersity is a challenging task that can be solved by novel approaches for the ATRP method.

2. Results

2.1. Rochelle Salt as a Reducing Agent for AGET ATRP of Acrylonitrile

To investigate the possibility of the use of RS as the reducing agent, the polymerization of acrylonitrile in the presence of a $CuBr_2$-based catalytic system was provided. The polymerization was conducted in dimethylsulfoxide (DMSO) media, tris[(2-pyridyl)methylamine] (TPMA) was used as a ligand to form a catalytically active system. Ethyl-2-bromoisobutyrate, ethylene-bis(2-bromoisobutyrate) (2FBiB), diethyl-2-bromo-2-methylmalonate, and carbon tetrachloride (CCl_4) were used as halogen-containing initiators.

The kinetic plots for AN polymerization in the presence of 2FBiB and CCl_4 as initiators and different [RS]/[Cu(II)] ratios are shown in Figure 1. It should be mentioned that the provided dependences of the logarithm of initial to current monomer concentrations ratio on time are linear, indicating the constant number of propagating chains during the process. The process has the first order relative to the monomer typical for ATRP processes. The decrease of [RS] to [Cu(II)] ratio has no significant influence on the polymerization rate (lines 1 and 2). At the same time, the use of carbon tetrachloride as initiator results in a decrease of polymerization rate (lines 2 and 3; 4 and 5). This fact may be explained by the higher energy of C-Cl bond in comparison with C-Br one. According to the obtained results, RS seems to be a more effective reducing agent than glucose as the lower quantity of RS allows for conducting the process at a higher rate (lines 5 and 6). The decrease of initiator to monomer ratio expectedly resulted in the decrease of polymerization rate, making the synthesis of the samples with high molecular weight challenging (see lines 2 and 4; 3 and 5).
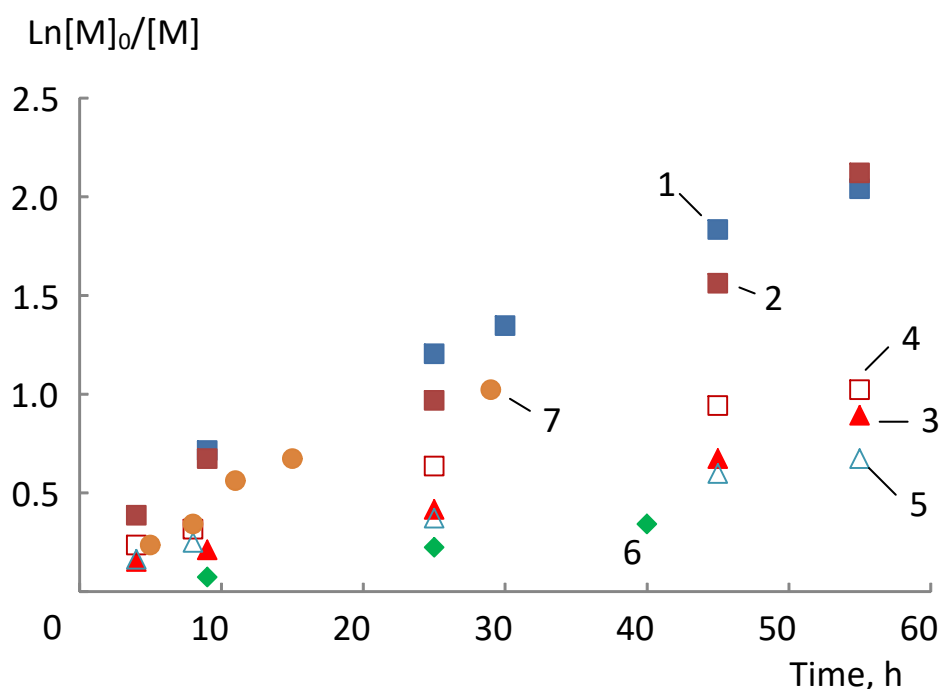

Figure 1. The kinetic plots for AN polymerization in DMSO at 60 °C. [AN] = 4 M. 1—[AN]:[2FBiB]:[CuBr$_2$]:[TPMA]:[RS] = 912:1:0.24:2.4:1.2; 2—[AN]:[2FBiB]:[CuBr$_2$]:[TPMA]:[RS] = 912:1:0.24:2.4:0.48; 3—[AN]:[CCl$_4$]:[CuBr$_2$]:[TPMA]:[RS] = 912:1:0.24:2.4:0.48; 4—[AN]:[2FBiB]:[CuBr$_2$]:[TPMA]:[RS] = 4000:1:0.24:2.4:0.48; 5—[AN]:[CCl$_4$]:[CuBr$_2$]:[TPMA]:[RS] = 4000:1:0.24:2.4:0.48; 6—[AN]:[CCl$_4$]:[CuBr$_2$]:[TPMA]:[glucose] = 4000:1:0.24:2.4:1.2; 7—[AN]:[2FBiB]:[CuBr$_2$]:[PMDTA]:[RS] = 4000:1:0.24:2.4:0.48.

The dependences of molecular weights and dispersity (Đ = M_w/M_n) of the samples on conversion are provided in Figure 2. The polymerizations at $[I]_0:[M]_0$ = 1:900 ratio proceed with the linear increase of molecular weights of the samples with conversion. A good agreement with theoretically calculated values typical for ATRP processes is observed. The

highest deviation between the obtained and theoretically calculated values is observed for the process provided at [Cu(II)]:[RS] = 1:5 ratio. This system also leads to the samples with the highest dispersity. The decrease of the RS concentration down to [Cu(II)]:[RS] = 1:2 results in the decrease of the dispersity of the samples and leads to better accordance of the molecular weights with theoretically calculated values. The samples obtained in the presence of CCl_4 as an initiator are characterized by the lowest dispersities in agreement with the lower rate of the process.
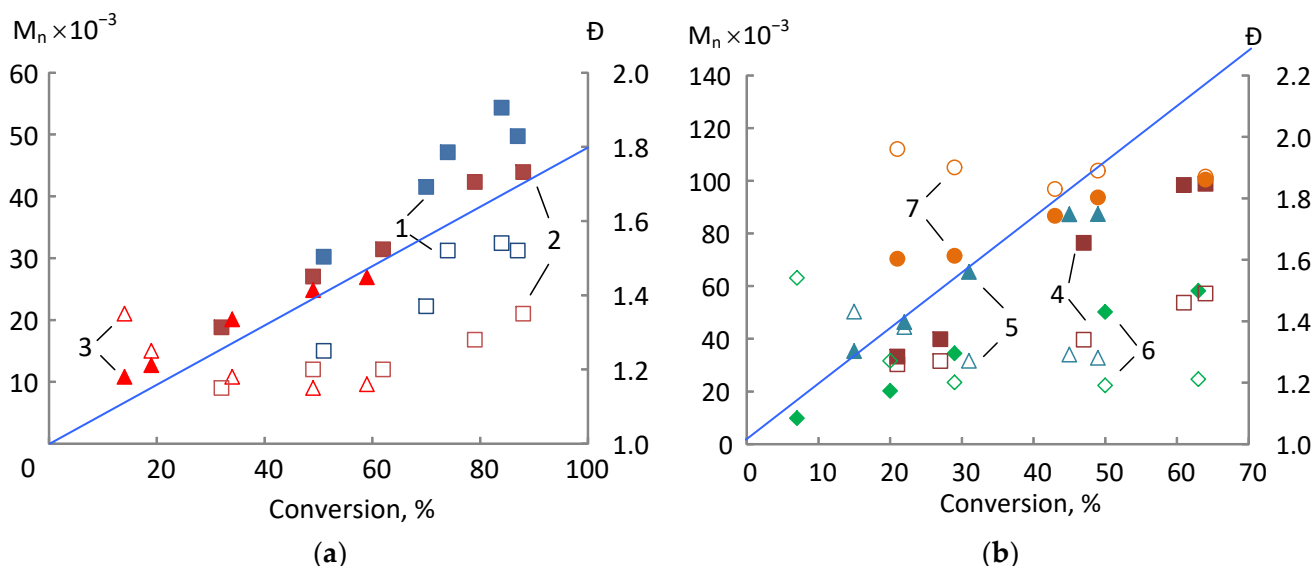

Figure 2. The dependences of M_n (filled markers) and Đ (empty markers) on conversion for AN polymerization. Strait line—theoretically calculated values. (**a**) [AN]:[initiator]=912:1; (**b**) [AN]:[initiator] = 4000:1. 1—[AN]:[2FBiB]:[CuBr$_2$]:[TPMA]:[RS] = 912:1:0.24:2.4:1.2; 2—[AN]:[2FBiB]:[CuBr$_2$]:[TPMA]:[RS] = 912:1:0.24:2.4:0.48; 3—[AN]:[CCl$_4$]:[CuBr$_2$]:[TPMA]:[RS] = 912:1:0.24:2.4:0.48; 4—[AN]:[2FBiB]:[CuBr$_2$]:[TPMA]:[RS] = 4000:1:0.24:2.4:0.48; 5—[AN]:[CCl$_4$]:[CuBr$_2$]:[TPMA]:[RS] = 4000:1:0.24:2.4:0.48; 6—[AN]:[CCl$_4$]:[CuBr$_2$]:[TPMA]:[glucose] = 4000:1:0.24:2.4:1.2; 7—[AN]:[2FBiB]:[CuBr$_2$]:[PMDTA]:[RS] = 4000:1:0.24:2.4:0.48.

The increase of monomer amount allows for increasing the molecular weight of the polymers up to 80 kDa. A linear increase of molecular weight with conversion is observed for polymerizations initiated by 2FBiB, thus by CCl_4. The later initiator allows for obtaining samples with lower dispersity. The use of RS as a reducing agent allows for achieving a close correlation of the molecular weights with the theoretically calculated values. At the same time, in the case of glucose, the molecular weights of the samples are lower, but the molecular weight distribution (MWD) is narrower.

Thus, we may conclude that RS can be successfully applied as a reducing agent for AGET ATRP of AN catalyzed by Cu(II)/TPMA system.

It is well-known that the nitrogen-based ligand is a keystone of the catalytic system in the copper-catalyzed ATRP [3]. To evaluate the possibility of the use of RS as a reducing agent for other catalytic systems, we have explored the polymerization in the presence of CuBr$_2$/ N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDTA) system [20]. The results are summarized in Table 1.

The obtained results show that the proposed systems allow for obtaining polyacrylonitrile with good yields. The highest yields are observed in the case of the use of bromine-containing initiators. In spite of the obtained samples having broader MWD, the molecular weights are in good agreement with theoretically calculated values, indicating the controlled nature of the process. The lower dispersities were also obtained in the presence of a chlorine-based initiator as in the case of the CuBr$_2$/TPMA system.

Table 1. The results of polymerization of acrylonitrile in the presence of CuBr$_2$/PMDTA and different initiators. Time—20 h.

Initiator	Conversion, %	M$_n \times 10^{-3}$	Đ	M$_n$, Theor
2FBiB	80	54.5	1.89	38.7
Ethyl-2-bromoisobutyrate	67	45.4	1.59	32.4
Diethyl-2-bromo-2-methylmalonate	81	39.5	1.57	39.1
CCl$_4$	65	28.8	1.43	31.4

The detailed investigation of the process was performed at [I]:[M] = 1:4000 ratio using 2FBiB as initiator. The kinetic plot of the process (Figure 1, curve 7) has some curvature indicating the decrease in the number of propagating chains during the process. The molecular weights of the samples (Figure 2b, line 7) increase with conversion, but a deviation from the calculated values is observed. At the same time, the dispersities of the samples are higher than those obtained in the case of catalytic systems based on CuBr$_2$/TPMA. These facts indicate that the process is not fully controlled and some parallel processes occur.

Thus, we may conclude that RS may be used as a reducing agent in copper-catalyzed AGET ATRP.

2.2. Tandem Catalysis by Two Copper Complexes

It was recently shown that the efficiency of AGET ATRP may be significantly increased in the case of simultaneous introduction in the polymerization media of two copper complexes with different ligands [18]. In according with this observation, we have studied the polymerization of AN in the presence of a catalytic system containing both CuBr$_2$/TPMA and CuBr$_2$/PMDTA complexes with different initiators and reducing agents. The results are summarized in Figure 3.
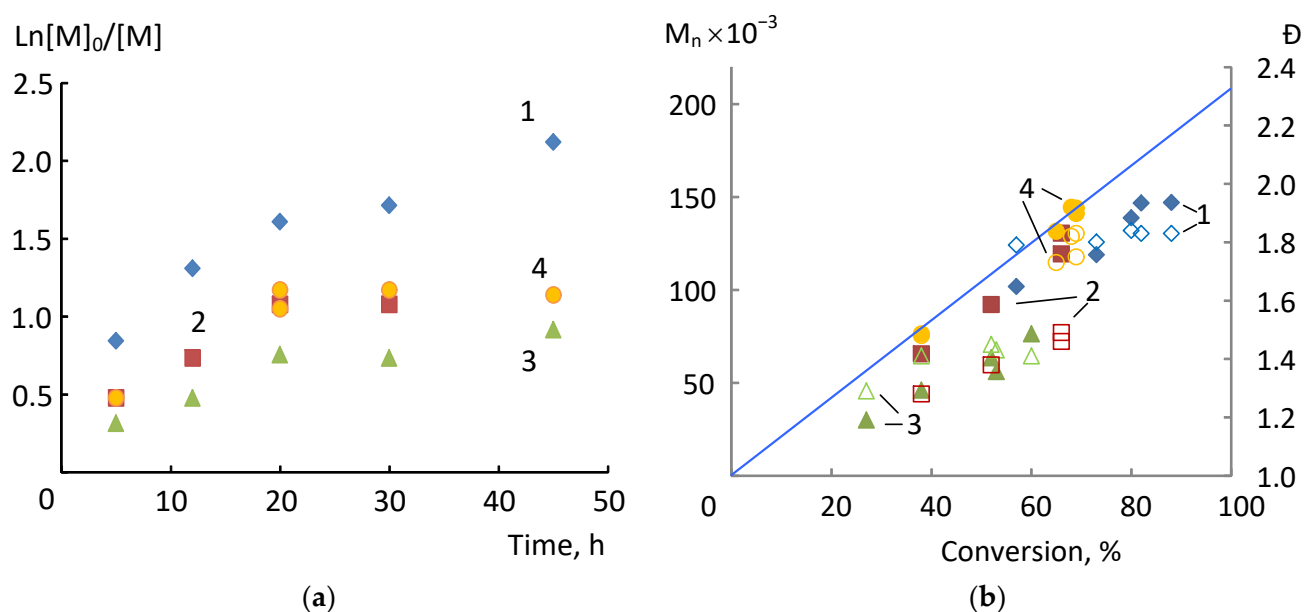

Figure 3. Tandem catalysis of AN polymerization in DMSO at 60 °C. [AN] = 4M. (**a**) The kinetic plot; (**b**) the dependences of M$_n$ and Đ on conversion. 1—[AN]:[2FBiB]:[CuBr$_2$]:[PMDTA]:[TPMA]:[RS] = 4000:1:0.24:1.2:1.2:1.2; 2—[AN]:[2FBiB]:[CuBr$_2$]:[PMDTA]:[TPMA]:[glucose] = 4000:1:0.24:1.2:1.2:1.2; 3—[AN]:[CCl$_4$]:[CuBr$_2$]:[PMDTA]:[TPMA]:[RS] = 4000:1:0.24:1.2:1.2:0.48; 4—[AN]:[2FBiB]:[CuBr$_2$]:[PMDTA]:[TPMA]:[RS] = 4000:1:0.24:1.2:1.2:0.48.

The simultaneous use of two complexes leads to the increase of polymerization rate and monomer conversions for the set times at the earlier stage of the process. At the same

time, the kinetic plots provided in Figure 3 are not linear, indicating a decrease in the number of active species during the process. The highest rate of the process was observed in the case of the use of RS as a reducing agent at $[Cu(II)]_0$:[RS] = 1:5 ratio (Figure 3a, line 1). In this case, 57% conversion was observed after 5 h of the process. The molecular weights of the samples gradually increased with conversion, but the molecular weight distribution was high and Đ exceeded 1.7 (Figure 3b, line 1). The decrease in RS concentration down to $[Cu(II)]_0$:[RS] = 1:2 (Figure 1, line 4) allowed to improve the control over the process at earlier stages but resulted in the decrease in the monomer conversion for the set time.

The use of CCl_4 as an initiator (Figure 3a, line 3) led to a decrease in the polymerization rate as in the case of $CuBr_2$/TPMA systems discussed above. Note that the molecular weights of the samples were slightly lower than theoretically calculated, but Đ did not exceed 1.5.

Polymerization of AN in the presence of glucose (Figure 3, line 2) as a reducing agent taken in $[Cu(II)]_0$:[glucose] = 1:5 ratio also resulted in the formation of samples with rather low Đ. The use of this system allowed for obtaining samples with M_n exceeding 100 kDa in 20 h. The rate of polymerization is comparable with the same for $[Cu(II)]_0$:[RS] = 1:2.

Thus, we may conclude that the use of $CuBr_2$/(TPMA + PMDTA) complex polymerization system with RS or glucose as reducing agents allows for obtaining polyacrylonitrile samples with high molecular weights.

2.3. UV-VIS Study of Cu(II) Reduction by Roshelle Salt

Experimental confirmation of the ability of RS to reduce Cu(II) species was provided by the use of UV-Vis spectrometry. The recorded UV-Vis spectra in DMSO are shown in Figure 4.
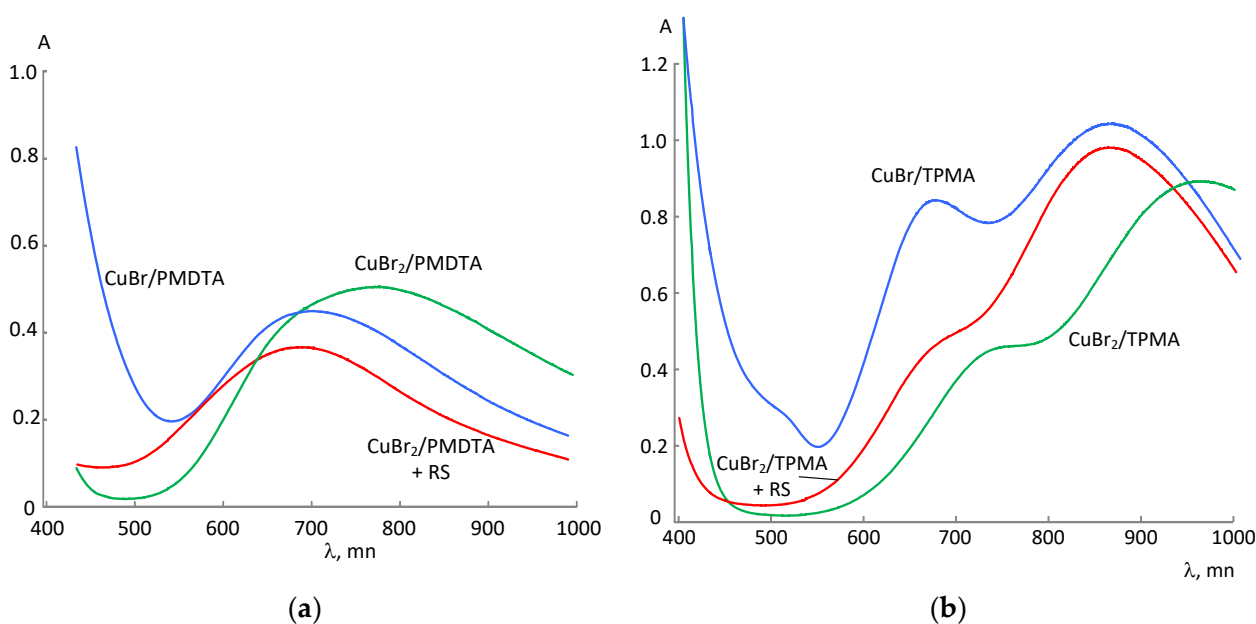

(**a**)   (**b**)

Figure 4. The UV-VIS spectra of DMSO solutions of copper complexes in DMSO. [Cu] = 0.005 M, [ligand] = 0.0075 M, [RS] = 0.05 M. T = 25 °C: (**a**) Complexes with PMDTA; (**b**) Complexes with TPMA.

Cu(I) and Cu(II) complexes have different spectra in the range of 500–1000 nm. Independent of the nature of the ligand, the maximal absorbance for Cu (II) complexes is observed at higher wavelengths in comparison with Cu(I) species. The addition of RS to the solution of $CuBr_2$/PMDTA or $CuBr_2$/TPMA results in the shift of the absorbance maximum to the shortwave area. In both cases, the λ_{max} for the spectra of Cu(II) solution containing RS is the same for the corresponding Cu(I) complex. The performed experiments indicate that RS is capable to reduce Cu(II) species even at room temperatures. The high reducing ability of RS allows for using it in lower concentrations than glucose.

2.4. Electrochemical Studies of Copper-Based Catalytic Systems

To understand the performance of the proposed complex catalytic system based on two complexes and tartrate as a reducing agent, cyclic voltammetry (CVA) experiments were performed. The experiments were conducted in DMSO to provide the proper weight to the solvent coordination ability. The recorded CVA curves and the values of measured redox potentials are provided in Figure 5. The $CuBr_2$ complexes with PMDTA and TPMA undergo a reversible reduction in DMSO media, similarly as was observed by Tang and Matyjaszewski in acetonitrile [21]. The difference between cathodic and anodic peaks is 80 mV, $i_a/i_p = 1$. According to the provided data, the reduction of $CuBr_2/TPMA$ complex occurs at lower potentials in accordance with previous observations. At the same time, the absolute values of potentials in DMSO are lower than those measured in acetonitrile. According to [21], the $E_{1/2}$ values for $CuBr_2/PMDTA$ and $CuBr_2/TPMA$ in acetonitrile are -80 and -240 mV versus SCE, respectively. Taking into account that the oxidation potential of ferrocene $E_{1/2}(Fc \mid Fc^+) = 430$ mV versus SCE [22], the corresponding potentials referred to ferrocene in acetonitrile should be -510 and -670 mV, respectively. Another point that should be mentioned is that the change of solvent results in a decrease in the difference between oxidation potentials of the complexes from 160 to 65 mV.
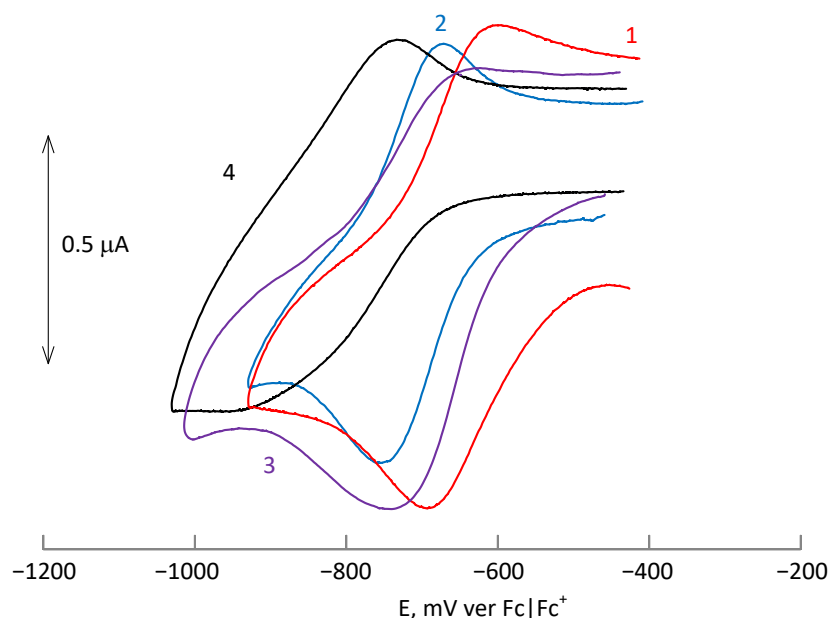

Figure 5. The CVA curves recorded in DMSO media at 25 °C. Supporting electrolyte—n-Bu_4PF_6 (0.2 M). $[CuBr_2] = 0.0045$ M. [ligand] = 0.005 M. [RS] = 0.009 M. 1—$CuBr_2/PMDTA$, $Ep_a = -610$ mV. $Ep_c = -690$ mV, $E_{1/2} = -650$ mV; 2—$CuBr_2/TPMA$, $Ep_a = -675$ mV, $Ep_c = -755$ mV, $E_{1/2} = -715$ mV; 3—$CuBr_2/TPMA:CuBr_2/PMDTA = 1:1$, $Ep_a = -640$ mV, $Ep_c = -740$ mV, $E_{1/2} = -690$ mV; 4—$CuBr_2$ + RS + (TPMA:PMDTA = 1:1), $Ep_a = -730$ mV, $Ep_c = -930$ mV.

The position of cathodic and anodic peaks on the CVA curve recorded for the equimolar mixture of complexes is approximately in the middle between the peaks of the pure complexes. At the same time, the increase in the distance between Ep_a and Ep_c up to 100 mV is observed, similar to the earlier studied system based on TPMA and Me_6TREN [18]. The separation of anodic and cathodic peaks confirms the proposition that the more reducing $CuBr/TPMA$ complex probably acts as an activator, while more oxidizing $CuBr_2/PMDTA$ complex acts as a deactivator.

It should be noted that the addition of RS neither to any of the discussed $CuBr_2$/ligand complexes nor to its mixture has no influence on the CVA curve. At the same time, the change in the order of the addition of the components led to unexpected results. The CVA curve recorded to the solution obtained by the addition of the equimolar mixture of PMDTA and TPMA to the solution of $CuBr_2$ and RS in DMSO is clearly shifted to the area of low

potentials relative to the previously discussed for $CuBr_2$/TPMA, $CuBr_2$/PMDTA, and their mixture. The cathodic peak is smoothed, while the anodic one is observed at -730 mV versus ferrocene. This fact testifies to the formation of novel more complex species in the presence of RS.

3. Discussion

In this paper, two ways of increasing the rate of AN AGET ATRP were proposed. The first one is the use of RS as a reducing agent. Due to its ability to reduce Cu(II) species at room temperature, it can be used in a lower amount than glucose. It is noteworthy that the use of RS as a reducing agent allows for achieving a perfect correlation between experimental and theoretically calculated molecular weights.

The reducing ability of tartaric acid towards transition metal cations had been observed by Fenton in 1894 [23] and was further confirmed by numerous studies. It was found that tartaric acid may be oxidized by strong oxidizing agents like Cr(VI) [24] or V(V) [25], so by the more mild ones, such as Mn(II) [26] or Ce(IV) [27]. It can be also oxidized in an electrochemical cell [28]. In the latter case, two subsequent one-electron peaks are observed. The proposed schemes of oxidation of tartaric acid include different intermediate products such as oxalic or formic acid, indicating the complex nature of the process. At the same time, the electrochemical exploration of the catalytic system indicates that in the presence of RS, some novel copper complexes with high reducing ability may be formed. Formation of such species during polymerization should result in the activation of dormant chains and increasing the rate of the process. The discussed species may be considered either as an intermediate in the process of Cu(II) reduction or act as a real catalyst of ATRP. The detailed study of the mechanism of oxidation of RS by Cu(II) species is undoubtedly interesting and will be studied by us later. Independent of the mechanism of the process, we may conclude that RS along with sodium pyruvate [11] may be used in AGET ATRP. Moreover, we may propose that the salts of the related hydroxy acids or oxyacids may be also used as reducing agents.

The second way of accelerating of copper-catalyzed AGET ATRP is tandem catalysis based on the simultaneous use of two complexes. Similar to the earlier studied Cu(I)/TPMA + Cu(I)/Me_6TREN system [18], the proposed Cu(II)/TPMA + Cu(II)/PMDTA one shows faster polymerization relative to the systems containing only one of the mentioned complexes. The acceleration of polymerization is due to the activation of the process by the more reducing complex with Cu(I)/TPMA and its deactivation by more oxidizing Cu(II)/PMDTA.

The combination of the mentioned approaches allowed for obtaining PAN with M_n exceeding 100 kDa in 5 h using only 0.06 ppm of copper catalyst relative to monomer. In spite of the Đ of the obtained samples being rather broad, the linear increase of M_n with conversion in good agreement with theoretically calculated values confirms the AGET ATRP mechanism of the process.

4. Materials and Methods

4.1. General Considerations

Acrylonitrile (AN, Aldrich, The Netherlands) was purified by distillation over calcium hydride under argon immediately before use. Dimethyl sulfoxide (DMSO, Component Reactive, Moscow, Russia) and dimethyl formamide (DMF, Component Reactive, Moscow, Russia) were dried over sodium hydroxide, distilled under reduced pressure, redried over the calcined 4-A zeolite, and then again distilled. Copper (II) bromide (Aldrich, Germany), lithium bromide (Aldrich, Germany), pentamethylethylenediamine (PMDTA) (Aldrich, USA), potassium sodium tartrate tetrahydrate (Khimreactive, Moscow, Russia) were used without further purification. Tris(2-pyridylmethyl)amine (TPMA) was obtained according to the known procedure from 2-picolylamine (Aldrich, Germany) and 2-(chloromethyl)pyridine hydrochloride (Aldrich, China) [29]. Ethyle-bis(2-bromoisobutyrate) (2FBib) was obtained by previously published procedure [30].

4.2. Polymerization Procedure

A typical polymerization procedure is listed below. The experiments with different ratios between components were conducted in the same manner. The determined amounts of copper (II) bromide (2.8 mg, 0.012 mmol), a TPMA ligand (33 mg, 0.12 mmol), 2FBiB as an initiator (17.6 mg, 0.05 mmol), RS (16.9 mg, 0.06 mmol) 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 argon-flushed DMSO (15 mL, 211 mmol), and acrylonitrile (3 mL, 46 mmol) were then added. The resulting mixture was dispensed into prepared ampoules. The ampoules were degassed by three freeze–pump–thaw cycles, sealed, and placed in a thermostat at 60 °C for a predetermined time. The polymerization was stopped by freezing the ampoule in liquid nitrogen. The polymerization product was dissolved in dimethyl formamide and precipitated in distilled water. The polymer obtained by filtration was dried to constant weight at 70 °C under reduced pressure. The monomer conversion was determined gravimetrically.

4.3. Polymer Characterization

The molecular weight characteristics of (co)polymers were determined by gel-permeation chromatography on a Knauer system equipped with a linear column with the exclusion limit of 2×10^6 (Phenomenex, Nucleogel GPCM-10, Torrance, CA, 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-dispersed PMMA-based standards (Polymer Standards Service) ranging from 2400 to 970,000 g/mol. 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:

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

4.4. UV-VIS Spectrometry

The UV-VIS spectra were recorded at 25 °C in DMSO solution in a 10 mm quartz cuvette using Shimadzu UV-mini spectrometer. The typical procedure is listed below. 5 mg of $CuBr_2$, 9.6 mg of TPMA and 62 mg of RS were placed in a glass vial, followed by 5 mL of DMSO. After dissolution, the solution was transferred in a quartz cuvette and a spectrum was recorded.

4.5. Cyclic Voltammetry

Electrochemical measurements were conducted in DMSO at 25 °C with 0.2 M n-Bu_4PF_6 as the supporting electrolyte. These measurements were carried out under argon atmosphere in a conventional three-electrode cell with a Pt disk (0.8 mm in diameter) as the working electrode, a Pt wire as the counter electrode and Ag/0.01 M $AgNO_3$ plus 0.2 M n-Bu_4NPF_6 in acetonitrile as the reference electrode [22]. Electrochemical measurements were performed with an IPC Pro-M potentiostate with the digital recording of the results.

Author Contributions: CVA study, manuscript concept, supervision, and manuscript writing, I.D.G.; polymerization experiments, UV-VIS study E.I.Z.; polymerization experiments, MWD determination, Y.S.P.; supervision, D.F.G. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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