

MACROMOLECULAR COMPOUNDS  
AND POLYMERIC MATERIALS

# Radical Polymerization of Acrylonitrile under the Action of Catalytic Systems Based on Zero-Valent Copper

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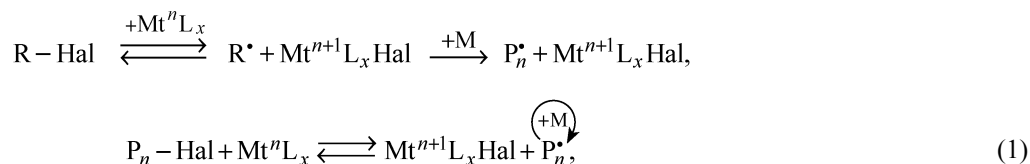
**Abstract**—Specific features of the (co)polymerization of acrylonitrile in the presence of a catalytic system based on zero-valent copper and 2,2-bipyridyl in various solvents was studied. It is shown that these systems can be successfully used in the presence of halogen-containing initiators to obtain homo- and copolymers of acrylonitrile with dimethyl itaconate and methyl acrylate in the controlled mode. It was found that introduction of comonomers (methyl acrylate and dimethyl itaconate) in low concentrations has no effect on parameters of the acrylonitrile polymerization process, but strongly affects some properties and characteristics of samples being synthesized.

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Homo- and copolymers of acrylonitrile (AN) find wide use in various modern industries [1]. The ability of polymers of this kind to form fibers with properties close to those of natural materials predetermines their application not only in textile industry, but also in manufacture of various components for building industry and technology. The recent interest in polymers based on acrylonitrile is due to the possibility of processing of polyacrylic fibers into carbon fibers and to their potential application in development of organic conducting materials [2]. Certain requirements are imposed on the molecular weight characteristics of polymers used as raw materials for processing into high-tech articles.

In particular, to facilitate the processing and obtain particularly mechanically strong fibers, it is necessary to use acrylonitrile (co)polymers with a certain molecular weight and comparatively low polydispersity [3].

The controlled radical polymerization is one of the most effective ways to obtain polymers with required molecular-weight characteristics [4–8]. Of particular interest among the known methods for controlled synthesis of macromolecular compounds is the atom-transfer radical polymerization (ATRP) [9–12]. The process under consideration is catalytic and originates from the known reaction of addition of alkyl halides at the double bond of alkenes, discovered by Kharasch [13]:



where M is a monomer; Mt, metal; and R<sup>•</sup>, growing polymeric radical.

The recent development of ARTP methods is primarily associated with the elaboration of systems making it

possible to perform the polymerization process at a low catalyst concentration with more readily available and easy-to-use catalysts. In particular, it has been found that a controlled synthesis of polymers is possible with metallic

copper and zero-valent iron used in combination with various organic ligands to perform the ARTP [14–18].

For example, Chinese researchers have demonstrated the possibility of performing the polymerization of acrylonitrile in a solution of dimethylsulfoxide (DMSO) or dimethylformamide (DMF) with systems based on zero-valent copper and various organic compounds actually serving as ligands [14, 15]. The authors of the above-mentioned studies could synthesize polymers with a sufficiently high conversion. However, the molecular weight (MW) of the resulting polyacrylonitrile (PAN) was very low, on the order of several thousand, which dramatically diminishes the practical value of these studies.

The goal of our study was to determine the optimal conditions of the controlled polymerization of acrylonitrile in the presence of zero-valent copper in order to obtain (co)polymers with large final values of their molecular weight on the basis of AN.

## EXPERIMENTAL

DMF and DMSO were dried over sodium hydroxide, distilled under reduced pressure, and after that were again dried over a calcined 4A zeolite and again distilled. The resulting compounds were stored in dark vessels over 4A molecular sieves. Acrylonitrile (Sigma) was distilled in the atmosphere of argon over calcium hydride. Methyl acrylate was purified to remove the inhibitor with an aqueous solution of an alkali, dried first over calcium chloride and then over calcium hydride, and distilled under reduced pressure. The physicochemical constants of all the compounds used were in agreement with published data.

Dimethyl itaconate was produced by the standard procedure of esterification of dibasic carboxylic acids [19]. In particular, a round-bottomed flask was charged with 10 g of itaconic acid and 15.8 mL of methanol and 31 mL of benzene were added. After that, 1.76 mL of concentrated sulfuric acid was added. The reaction mixture was heated to boiling for 5 h. The organic layer was separated and the water layer was twice washed with diethyl ether. The combined organic layer was dried with calcium chloride. After that the solvent was evaporated on a rotary evaporator. The remaining product was distilled under reduced pressure. A 6.2-g portion of dimethyl itaconate was obtained in the form of colorless crystals with mp 37–39°C.

When a polymerization experiment was performed, a piece of copper wire (diameter 1 mm, length 5 mm) preliminarily activated with concentrated hydrochloric acid was placed in each glass ampule. A Schlenk flask equipped with a magnetic rabble was charged with calculated amounts of 2,2'-bipyridyl, copper(I) bromide, and dimethyl itaconate. The flask was evacuated and filled with argon. After that, calculated amounts of solvents (DMSO or DMF) degassed or distilled in argon, acrylonitrile, methyl acrylate, and ethyl-2-bromoisobutyrate were added. The resulting mixture was poured into the prepared ampules, and the ampules were evacuated, sealed, and placed in a thermostat for a prescribed time. After the process was complete, the reaction mixture was diluted with DMF and poured into a 0.1% sodium sulfate solution. The precipitated polymer was separated by filtration and dried at 70°C under reduced pressure to constant weight.

The molecular-weight characteristics of PAN were determined by gel-permeation chromatography on an installation (Knauer) with a linear column and separation limit of  $2 \times 10^6$  Da (Phenomenex, Nucleogel GPCM-10 United States) at a temperature of 40°C. A RI Detektor K-2301 differential refractometer served as detector. DMF containing 10 mM LiBr was used as eluent. The instrument was calibrated against narrow-dispersion PMMA-based reference samples. The MW of PAN was calculated by using the universal calibration lot and coefficients of the Mark–Kuhn–Houwink equation for PAN and PMMA, known from the literature [20], by the formula

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

The chromatographic data were interpreted with the ChomGate software.

Calorimetric measurements were made on a Setaram DSC-131 apparatus in a flow of argon (20 mL min<sup>-1</sup>) at a sample heating rate of 5 deg min<sup>-1</sup>.

## RESULTS AND DISCUSSION

**Specific features of acrylonitrile polymerization in the presence of copper.** One of specific features of the polymerization of acrylonitrile, compared with other acrylic monomers, is the insolubility of the resulting PAN in its own monomer [21]. At the same time, a

**Table 1.** Effect of polymerization conditions on the molecular-mass characteristics of PAN samples BiB/Cu/Bipy/AN = 1/0.5/1.5/300, [AN] = 4.3 M

Solvent	$T, ^\circ\text{C}$	$\tau, \text{h}$	Conversion, %	$M_n$	Polydispersity coefficients
DMF	25	46	65	14700	1.58
DMF	40	46	62	9900	1.53
DMSO	25	50	68	17200	1.55
DMSO	40	17	85	20100	1.43
DMSO <sup>a</sup>	40	50	57	30700	1.51
DMSO <sup>b</sup>	40	50	23	2600	1.48

<sup>a</sup> EBiB/Cu/Bipy/AN = 1/1.5/3/900.

<sup>b</sup> CCl<sub>4</sub> as initiator, CCl<sub>4</sub>/Cu/Bipy/AN = 1/0.5/1.5/150. [AN] = 3.0 M.

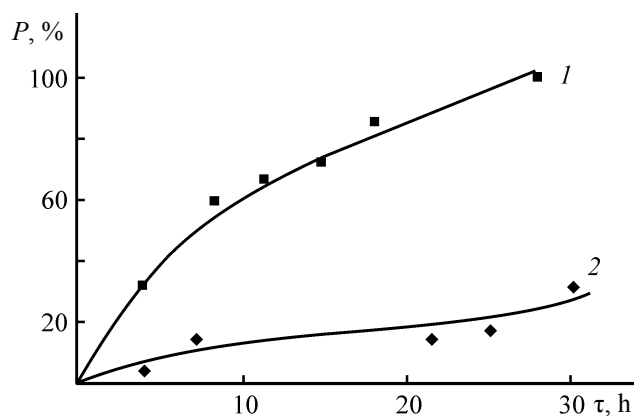
necessary condition for the occurrence of a controlled radical polymerization is the homogeneity of the polymerization system [7, 8]. Thus, the controlled synthesis of polyacrylonitrile is only possible in the presence of a solvent in the system. Therefore, to determine the optimal polymerization conditions of acrylonitrile, we studied the process of PAN synthesis with a catalytic system based on a powder of zero-valent copper and 2,2'-bipyridyl (Bipy) as a complex-forming agent in various solvents and, in particular, DMF and DMSO. As the polymerization initiator served ethyl-2-bromoisobutyrate (EBiB) whose interaction with metals may yield carbon-centered radicals [18].

It follows from the data in Table 1 that the suggested catalytic formulation based on zero-valent copper, bipyridyl, and ethyl-2-bromoisobutyrate can initiate polymerization of AN at temperatures of 25°C and higher. In this case, DMSO as a solvent is preferable to DMF as regards both reaching a higher conversion and controlling the molecular-weight distribution of the samples. Raising the temperature to 40°C results in that the yield of the polymer in a prescribed time increases and the polydispersity coefficients of the resulting samples become smaller, which makes these conditions more effective as regards the directed synthesis of PAN. With the concentration of the initiator lowered relative to that of the monomer, it is possible to obtain a polymer with a larger value of the molecular weight, but this leads to a decrease in the process rate and makes the yield of the polymer lower.

As can be seen from these results, use of carbon tetrachloride as initiator instead of ethyl-2-bromoisobutyrate

results in that the yield of the target product becomes lower and a polymer is formed with very small molecular weight, which points to the poor efficiency of the given system for obtaining a macromolecular PAN.

The polymerization of acrylonitrile, initiated by EBiB at 40°C, makes it possible to obtain polymers in a rather high yield and comparatively low polydispersity ( $M_w/M_n < 1/5$ ). Therefore, we studied specific kinetic features of the polymerization of AN in the presence of Cu(0) just at this temperature. Figure 1 shows how the conversion of AN depends on the polymerization duration. The process in which the polymer is synthesized occurs uniformly without auto-acceleration. The polymerization in DMSO occurs at a substantially higher rate, compared with DMF. It follows from the

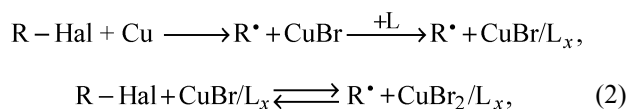


**Fig. 1.** Conversion  $P$  of the monomer vs. time  $\tau$  in AN polymerization in (1) DMSO and (2) DMFA.  $T = 40^\circ\text{C}$ , [EBiB]/[Cu]/[Bipy]/[AN] = 1/0.5/1.5/300. [AN] = 3.0 M.

**Table 2.** AN polymerization with an excess of zero-valent copper in the form of a wire  $T = 40^\circ\text{C}$ , DMSO as solvent,  $[\text{PAN}] = 3.0 \text{ M}$ 

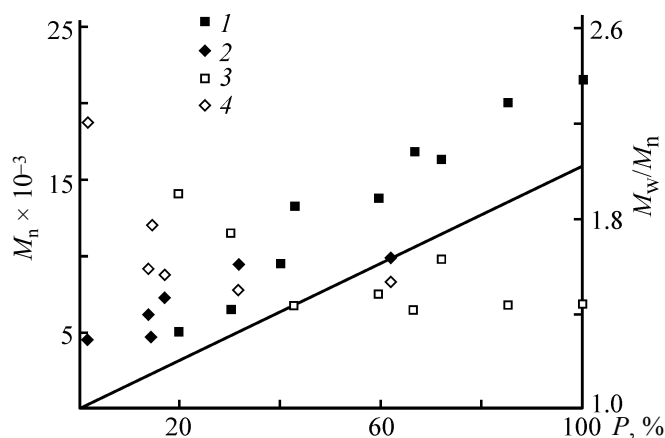
Initiator	$\tau$ , h	Conversion, %	$M_n$	$M_w/M_n$	[Initiator]/[Bipy]/[AN]
EbiB	47	86	15900	1.91	1/3/600
$\text{CCl}_4$	46	98	9300	1.87	1/1.5/300
$\text{CCl}_4$	46	72	17000	1.83	1/4.5/900
$\text{CCl}_4$	45	40	26300	1.68	1/9/1800

dependence of the molecular weight and polydispersity coefficients of the samples on the conversion (Fig. 2) that the MW of the polymer linearly grows with increasing conversion of the monomer. It is known [1, 4, 5] that this behavior is characteristic just of radical polymerization processes occurring in the “living” chain mode. The rise in MW with increasing conversion is observed for samples obtained in both DMF and DMSO. The molecular weight of the samples is somewhat smaller than that calculated theoretically on the assumption that one initiator molecules generates a single polymer chain. Presumably, this occurs because the initiator is consumed for the formation of copper bromide in the reaction with the zero-valent metal in the initiation stage:



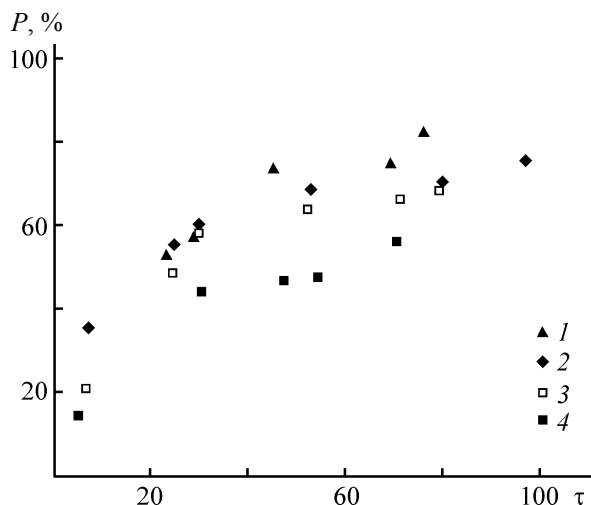
where L is a ligand.

The polydispersity coefficients of the samples are about 1.5 and decrease with increasing monomer conversion.



**Fig. 2.** (1, 2) Molecular weight  $M_n$  and (3, 4) polydispersity coefficients of polymers vs. the conversion  $P$  in AN polymerization in (1, 3) DMSO and (2, 4) DMF. The straight line represents the theoretical value of  $M_n$ ; the same for Fig. 4.

According to the concept of the controlled radical polymerization by the mechanism with a supplemental activator and reducing agent atom transfer radical polymerization (SARA ATRP) [22–25], zero-valent copper serves in the systems under consideration as a primary activator and reducing agent converting the catalyst from the highest (+2) to the lower (+1) oxidation state. The regeneration of the catalyst must occur permanently and at a low rate during the whole polymerization duration to maintain constant the number of active centers and provide a uniform course of the process. To provide a permanent regeneration of the catalyst at a low rate, it is advisable to use a metal (copper in our case) in a condensed state, e.g., as a wire. The smaller surface area hinders formation of an excess number of reaction centers at the initial instant of time. Using the metal in a condensed state is also more convenient as regards practical applications because of facilitating the removal of the catalyst upon completion of the process. The results of experiments on AN polymerization with copper in the condensed state are listed in Table 2.

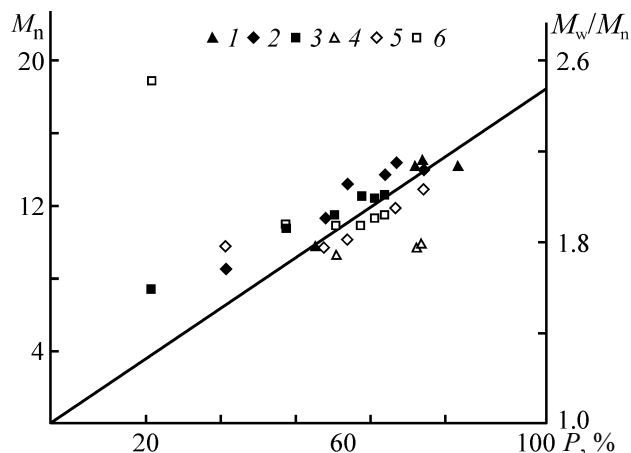


**Fig. 3.** Conversion  $P$  vs. time  $\tau$  in copolymerization of (1) AN–MA, (2) AN–DMI, and (3) AN–DMI–MA.  $T = 40^\circ\text{C}$ , DMSO as solvent,  $[\text{AN}] = 3.0 \text{ M}$ ,  $[\text{AN}]/[\text{DMI}] = 80/1$ ,  $[\text{AN}]/[\text{MA}] = 40/1$ ; the same for Fig. 4.  $[\text{EbiBr}]/[\text{Bipy}]/[\text{AN}]$ : (1–3) 1/3/600 and (4) 1/4.5/900.

As follows from the above data, performing the process under the specified conditions makes it possible to synthesize polymers to high monomer conversions and obtain PAN with high MW. Use of zero-valent copper in the form of a wire enables use of carbon tetrachloride as initiator. The results we obtained indicate that lowering the concentration of carbon tetrachloride leads to an increase in the molecular weight of the resulting polymer. At the same time, the conversion of the monomer becomes lower, in agreement with the decrease in the number of polymerization reaction centers.

**Copolymerization of acrylonitrile with methyl acrylate and dimethyl itaconate with Cu(0).** As already noted, an important application area of acrylonitrile-based polymers is their thermal processing into carbon fibers. To obtain carbon fibers with required characteristics and properties, it is preferable to use copolymers based on acrylonitrile [1–3]. Introduction of comonomers into the polymerization systems accelerates cyclization processes and levels out the exothermic effect, which makes it possible to obtain fibers with better physicomechanical properties. To monomers of this kind, accelerating the cyclization processes, belong methyl acrylate (MA) and itaconic acid [26–29]. Direct application of itaconic acid as a comonomer when using the chosen catalytic system seems to be impossible because of the occurrence of side reactions associated with the interaction of copper with the carboxy group. Therefore, we suggested using instead of itaconic acid its derivative, dimethyl itaconate (DMI), which is chemically inert toward copper.

In particular, the catalytic system based on zero-valent copper and Bipy was used to obtain double AN–MA copolymers and triple AN–MA–DMI copolymers. Figure 3 shows time dependences of the conversion of the polymerization mixture. It can be seen from the data presented above that introduction of comonomers into the reaction mixture hardly affects the process rate. The polymerization occurs to a conversion of about 60%



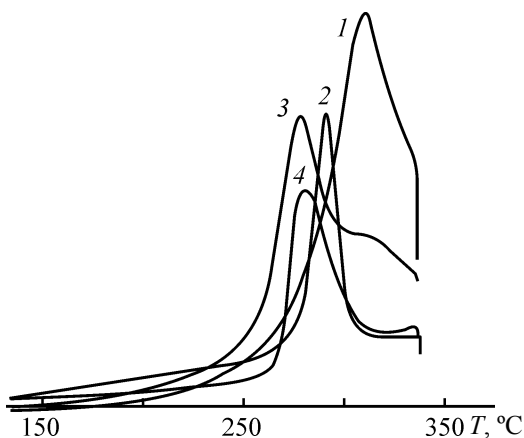
**Fig. 4.** (1–3) Molecular mass  $M_n$  and (4–6) polydispersity coefficients of the synthesized samples vs. the conversion  $P$  in copolymerization of (1, 4) AN–MA, (2, 5) AN–DMI, and (3, 6) AN–DMI–MA.

in 50 h; as the polymerization process is made longer, the conversion does increase further. The graphical dependences in Fig. 4 demonstrate that the molecular weight of the copolymer linearly grows with increasing conversion in agreement with the theoretically calculated values. The molecular-weight distribution of the samples obtained is somewhat wider than that in the case of the previously synthesized AN homopolymers with a similar molecular weight. The widest molecular-weight distribution is observed for DMI-containing copolymers.

The polymers obtained under these conditions have molecular weights that are comparatively small for their successful application as a precursor of carbon fibers. To make larger the molecular weight of the final product, copolymerization of the above monomers was performed in the presence of a smaller amount of the initiator. To make faster the reaction onset, copper(I) bromide occasionally used to polymerize (meth)acrylic monomers by the ATRP mechanism was introduced into the system. The experimental results presented in Table 3 indicate that a decrease in the amount of the initiator

**Table 3.** Results of experiments on triple AN–DMI–MA copolymerization with different amounts of the initiator  $T = 40^\circ\text{C}$ , DMSO as solvent,  $[\text{AN}] = 3.0 \text{ M}$

$[\text{EbiBr}]/[\text{Bipy}]/[\text{CuBr}]/[\text{AN}]$	$\tau$ , h	Conversion, %	$M_n$	Polydispersity coefficient
1/4.5/0.5/900	21	27	9800	1.51
1/14/1.4/2700	80	26.4	25800	1.61



**Fig. 5.** DSC curves recorded in an inert atmosphere for (1) AN homopolymer and (2) AN-MA, (3) AN-DMI, and (4) AN-DMI-MA copolymers. Heating rate 5 deg min<sup>-1</sup>. (T) Temperature.

decelerates the process slower and reduces the monomer conversion in a prescribed time, but makes it possible to obtain a polymer with a larger molecular weight. It is remarkable that copolymers with a narrower molecular-weight distribution are formed under these conditions.

**DSC analysis of the copolymers obtained.** Heating the acrylonitrile-based copolymers to above 200°C in an inert atmosphere results in that polyconjugated structures are formed [3]. This process is exothermic and the energy released in the process may lead to overheating of a sample and its disintegration. An important problem to be tackled with for obtaining a high-quality carbon fiber is to level out the temperature effect and make lower the process temperature. We carried out a thermodynamic study of the samples of a homopolymer of acrylonitrile and its copolymers. Figure 5 shows the curves recorded by the DSC method, and Table 4 lists the results of thermodynamic measurements.

It can be seen from these data that introduction of comonomers into the process of AN polymerization hardly

**Table 4.** Results of a DSC study of AN (co)polymer samples

Sample	$M_n$	$T_{\text{peak}}, ^\circ\text{C}$	$T_{\text{peak}}, ^\circ\text{C}$
PAN	26500	104	310
PAN-MA	14300	107	291
PAN-DMI	19800	106	278
PAN-MA-DMI	26600	103	280

affects the glass transition temperature of the polymeric product being formed but affects the nature of the exothermic effect and the temperature of its maximum intensity. The highest temperature of the peak exothermic effect is observed for the homopolymer of acrylonitrile. The DSC curve for the homopolymer shows a clearly pronounced signal corresponding to the thermal transformation. Introduction of MA as a comonomer somewhat shifts the maximum of the exothermic effect to lower temperatures. In this case, the peak has a sharp shape, as also that of the starting polymer. The lowest temperatures of the maximum exothermic effect are observed for the DMI-containing copolymers. The presence of this component leads not only to a lower cyclization temperature, but also to a broader peak of the temperature transition. The heat release becomes more uniform, which must improve the quality of the resulting fiber.

## CONCLUSIONS

The study demonstrated that systems based on zero-valent copper can be successfully used to obtain homo- and copolymers of acrylonitrile in a controlled mode. It was found that introduction of comonomers (methyl acrylate and dimethyl itaconate) in low concentrations has no effect on the parameters of acrylonitrile polymerization, but strongly affects the properties of the samples being synthesized.

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