

Synthesis of high-molecular-weight polyamine by radical polymerization of *N,N*-diallyl-*N*-methylamine

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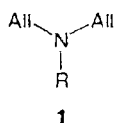
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The first synthesis of high-molecular-weight poly(*N,N*-diallyl-*N*-methylamine) by thermal (at 30 and 50 °C) and photoinduced (at 21 °C) radical polymerization of *N,N*-diallyl-*N*-methylamine (DAMA) in aqueous solution in the presence of an equimolar amount of trifluoroacetic acid (TFA) and by polymerization of the newly synthesized equimolar DAMA · TFA salt is reported. Data of ¹H NMR spectroscopy indicate that the molecules of the monomer under chosen conditions are in the protonated form. This leads to a decrease in the contribution of the reaction of degradative chain transfer to the monomer and its transformation into effective chain transfer to the monomer. A bimolecular chain termination mechanism was established and the possibility of controlling the polymerization rate and the molecular weight of the polymer was demonstrated.

Key words: *N,N*-diallyl-*N*-methylamine, trifluoroacetic acid, protonation, radical polymerization, degradative chain transfer to monomer, poly(*N,N*-diallyl-*N*-methylamine).

The present study is devoted to the solution of one of the problems of polymer chemistry, namely the involvement of prospective monomers of the *N,N*-diallylamine series (**1**) in radical polymerization to give polymers of relatively high molecular weights (MW).

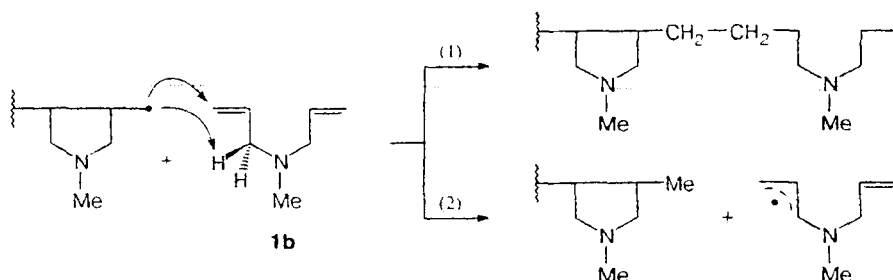
The mentioned process of polymerization is difficult to perform because the reaction of degradative chain transfer to the monomer occurs with the abstraction of the α -hydrogen atom of the allyl group of the monomer by radicals and with the formation of a weakly reactive, stable allyl radical. This results in the termination of the kinetic chain, and hence, only oligomers with low MW can be produced in this process^{1–8} (see also Refs. 7, 8) (Scheme 1).



R = H (a), Me (b), Bu^t (c)

It is known, that the polymerization rate for allyl and diallyl monomers as well as the MW values of oligomers obtained substantially increase in complex-forming and acidic media, the reaction rates and MWs of products increasing with increase in the proton-donor properties (or complexing ability) of the acidic solvent and in the monomer basicity.^{2–7} This effect is explained by the enhancement of the α -C–H bond strength in the allyl group upon monomer protonation (or complex formation) and by the increase in the reactivity of the allyl radical in such a media, *i.e.*, by partial transformation of degradative chain transfer into the effective one.^{2–7} Nevertheless, even in acidic medium, polyamine with sufficiently high MW could be obtained from the most basic allylamine monomer only by radiation-induced polymerization.⁴ At the same time, the quaternary forms of monomers **1** (salts of derivatives

Scheme 1



Note: reaction (1) – chain propagation, reaction (2) – degradative chain transfer to monomer.

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of **1**) polymerize relatively easily by chemical initiation with the formation of rather high molecular weight cationic polyelectrolytes.^{8,9}

As was shown earlier,¹ the competitiveness of chain transfer and propagation reactions is controlled by the difference between their activation energies. Based on these results, we used quantum-mechanical calculations to study the possible mechanisms for the effect of protonation and quaternization of **1** on the competitiveness of two reactions — chain propagation and chain transfer to monomer.¹⁰ We demonstrated that at ambient temperatures the radical polymerization of the stable protonated forms of **1**, e.g., *N,N*-diallyl-*N*-methylammonium (**2**), also may give a product of fairly high MW.¹⁰ The protonation of **1b**, as well as its quaternization leads to increase in the activation energy for α -hydrogen abstraction due to the enhancement in the α -C—H bond strength,¹⁰ which is in accordance with the results of Refs. 2—7. The advantage of the use of the quaternary form of the amine consists in the additional increase in the activation energy for chain transfer because of solvation effects (the decreasing of the free energy of solvation of bulky structures). It is no less important that in this case the existence of the stable ionogenic forms of monomer and chain propagation radicals is also provided.¹⁰

Thus, to create the stable protonated forms of **1** (with the practically total absence of non-protonated forms) in polymerization medium is the key point for solving the discussed problem. The aim of the present work was to search for the system where monomer **1b** almost completely exists as the stable protonated form **2** and to study the possibility of obtaining products of high MWs by radical polymerization of this system.

Results and Discussion

Monomer system

The analysis of the data available in the reviews^{11,12} (see also references therein) on the acid-base equilibrium existing in complexes of amines of various natures with known acids shows that the formation of ionic proton-transfer complexes (highly dissociated or as ion pairs, depending on the solvent) is the most probable in equimolar mixtures of amine—trifluoroacetic acid (TFA). However, allylamine complexes (in particular, **1**) with various acids including TFA were not studied. It was established for equimolar complexes of pyridines with TFA in aprotic non-polar solvent that in the case of pyridines with $pK_a \geq 7.4$ the equilibrium is shifted toward the exclusive formation of proton-transfer ion pairs.¹³ Taking into account that compounds **1** are even stronger acceptors of a proton (values of $pK_a > 9$), TFA was chosen as protonizing agent.

To confirm the fact of protonation, the ¹H NMR spectra of solutions of equimolar **1b**—TFA mixture and

compound **1b** in Me₂O-d₆ were investigated at various concentrations. The degree of amine protonation was judged by the position of the peaks arising from methyl protons of monomer **1b**, which are typically shifted downfield upon protonation in TFA media (see, for example, data¹⁴ for the tertiary amines R₃NMe).

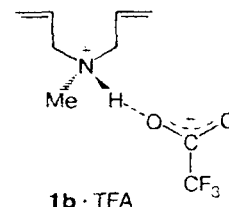
It was established that a significant downfield shift of Me proton resonance is observed for the solution of a **1b**—TFA mixture in comparison with the solution of neutral amine containing no TFA ($\Delta\delta = 0.59$ to 0.61; the concentration of **1b** amine in the mixture changed from 4.08 to 1.13 mol L⁻¹; its concentration in the solution of neutral amine was 1.13 mol L⁻¹).

The mobile protons of the α -CH₂ group were even more sensitive to protonation of the nitrogen atom. For them a downfield shift by 0.77 ppm was observed irrespective of the concentration of solution. The resonances of other allyl protons, especially of protons of CH₂ end groups, are also shifted downfield in the presence of TFA, but to a lesser extent. Change in the position of the α -CH₂ proton resonance is especially indicative if one takes into account that α -C—H bonds are slightly shortened and strengthened upon protonation, as was mentioned above.¹⁰

Since prolonged time is required for reaching complete acid-base equilibrium in the sufficiently viscous solutions of **1b**—TFA mixture, the problem of incomplete protonation arises (i.e., the dimer forms of TFA and non-protonated amine molecules may exist in the more concentrated mixtures, which is typical for the systems containing carboxylic acids and, in particular, TFA^{11–13}). Therefore the equimolecular salt of *N,N*-diallyl-*N*-methylammonium trifluoroacetate (**1b**·TFA) was synthesized by the specially developed procedure. Its composition was confirmed by elemental analysis. At ambient temperature, the synthesized **1b**·TFA salt is a transparent viscous oily liquid.

The analysis of ¹H NMR spectra obtained for solutions of this salt in Me₂CO-d₆ at concentrations analogous to those of solutions of a **1b**—TFA mixture has shown that the downfield shifts of methyl proton resonances ($\Delta\delta = 0.59$ to 0.62) are equal to the shifts of corresponding signals in the spectra of a **1b**—TFA mixture, while the shifts of proton resonances derived from the α -CH₂ group ($\Delta\delta = 0.77$ to 0.82) are even somewhat higher than for the mixture.

It is known that the fact of protonation of the base in the presence of an acid in an aprotic solvent guarantees that in the aqueous solution the given base will be completely protonated.^{11,12} Therefore we believe that in acidic aqueous solutions amine **1b** would exist exclusively in the protonated form **2**.



Synthesis and some properties of polymers

We carried out the radical polymerization of **1b**-TFA mixture and **1b**·TFA salt initiated by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ at 30 and 50 °C, as well as photoinitiated at 21 °C in aqueous solutions at several initial concentrations of monomer. After heating or photolyzing, the products were isolated both as the polysalt (**3**) and as the polybase (**4**); the ^1H and ^{13}C NMR spectra of various samples and their viscosity and molecular mass characteristics were studied.

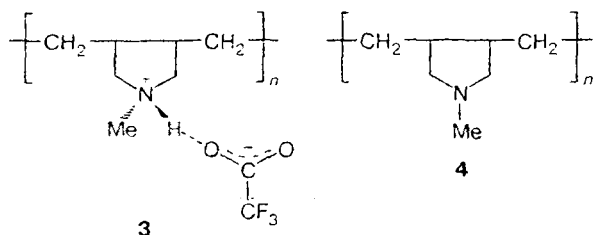
The polymer **3** and polybase **4** are yellowish crystalline solids. The solubility of monomers and synthesized polymers is characterized as follows (s = soluble, i = insoluble):

Solvent	Sample			
	1b	1b ·TFA	3	4
H ₂ O	i*	s	s	i
Et ₂ O	s	s	i	i
Me ₂ CO	s	s	s	i
CHCl ₃	s	s	i	s
MeOH	s	s	s	s
Hexane	s	i	i	i
Benzene	s	i	i	i

* <8%.

It is known, that the polymerization of alkylated monomers of series **1** gives cycloliner polymers with five-membered pyrrolidine rings in the chain.^{8,9,15–17} The structures of the synthesized polymers were established on the basis of the elemental analysis data and by comparison of the ^1H and ^{13}C NMR spectra (Fig. 1) with the literature data.^{8,15,16} The analysis for fluorine has shown that the formed polysalt **3** contains one molecule of TFA per unit of monomer. The results suggest the structures of poly(*N,N*-diallyl-*N*-methylammonium trifluoroacetate) (**3**) and poly(*N,N*-diallyl-*N*-methylamine) (**4**) shown in Scheme 2.

Scheme 2



The ^{13}C NMR spectrum of the isolated polyamine **4** is identical to the spectrum of the analogous polymer (of degree of polymerization of 20).¹⁶ Comparison of the relative intensities of the pairs of signals assigned to the C(3) and C(4) atoms of the *cis*- and *trans*-substituted pyrrolidine rings of polyamine **4** (see Fig. 1, a) indicates a *cis* : *trans* ratio of approximately 5 : 1, which is in accordance with the data.¹⁶

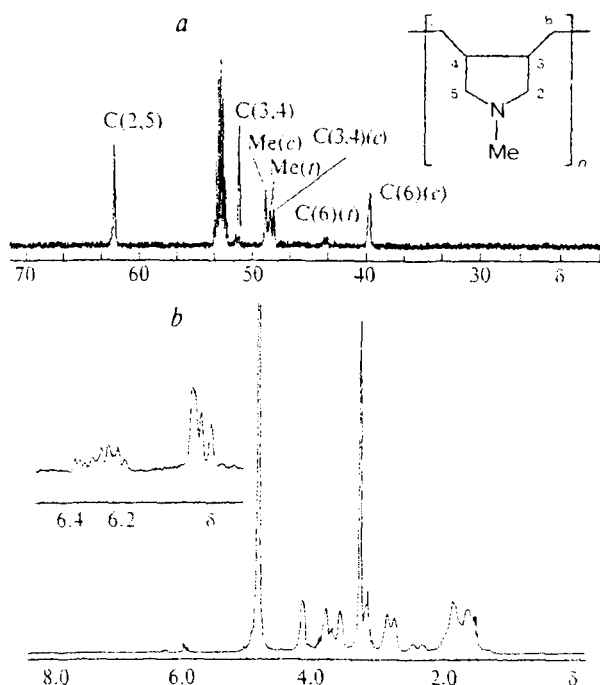


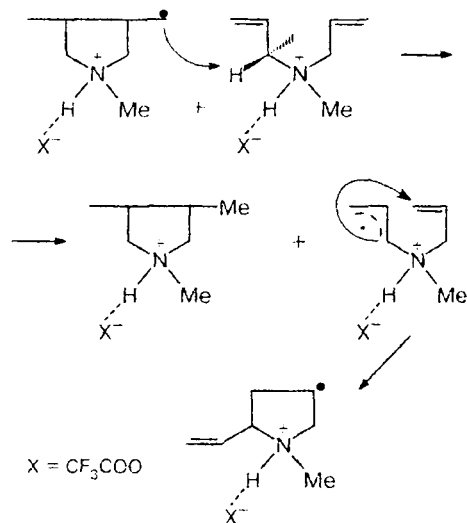
Fig. 1. NMR spectra: a, ^{13}C NMR spectrum of polyamine **4** in CD_3OD , $[\eta] = 0.47 \cdot 10^2 \text{ mL g}^{-1}$, see Table 1; b, ^1H NMR spectrum of polysalt **3** in D_2O (c – *cis*, t – *trans*), polymer sample was prepared from mixture (**1b**-TFA) at 30 °C, $[\text{M}] = 2 \text{ mol L}^{-1}$, $[\text{I}] = 5 \cdot 10^{-3} \text{ mol L}^{-1}$.

The ^1H NMR spectrum of the synthesized polymeric salt **3** (see Fig. 1, b) contains low-intensity proton resonances of vinyl end groups (5.9–6.4 region). These signals were first observed¹⁵ in the ^1H NMR spectrum of quaternary polysalt poly(*N,N*-diallyl-*N,N*-dimethylammonium chloride) (**5**). This suggests that in the observed process the reactive radicals of chain propagation are generated during the chain transfer to the monomer, and, thus, the acts of chain transfer to the monomer become effective by analogy with the mechanism suggested in Refs.^{8,15} (Scheme 3).

According to the kinetic data^{3,4,7} obtained for the polymerization of allyl monomers in acidic or complex-forming media, the allyl radical of chain transfer also becomes rather reactive under these conditions. As a result, the chain transfer to the monomer substantially transforms into the effective one (it was shown,⁵ that the polymerization of AlNH_2 in H_3PO_4 medium is characterized by a value of the probability of initiation by the allyl radical of chain transfer of 0.86).

The reasons for activation of allyl radicals of chain transfer, *i.e.*, why these radicals get the ability to take part in the reaction of addition to a double bond (transformation into the propagation radicals) under protonation, complexing, or quaternization conditions, are not absolutely clear yet in the case of polymerization of both allyl and diallyl monomers. The authors^{3,4,7} explain it

Scheme 3



by the increase in the stability of the allyl radical caused by reduction of its mobility because of the formation of a grid of hydrogen bonds network with the solvent molecules. We believe that the ability of protonated or quaternary allyl radical to take part in the addition to a double bond (for diallyl radicals it is an intramolecular cyclization, see Scheme 3) can be caused by the localization of unpaired electron density onto the α -C atom. This localization might arise in forms containing the positively charged N atom due to the low electronegativity of the α -CH-NR₃⁺ group. As was established,¹⁸ the similar localization of electron density onto the end-group X (perturbation of delocalization) is characteristic for simple allyl radicals of the CH₂=CH-X' type containing group X less electronegative than the CH₂ group (see also references in the work¹⁸). This question is of interest and should be considered separately.

The values of intrinsic viscosity $[\eta]$ in MeOH were determined (at 25 °C) for the various samples of polyamine **4** obtained under both thermal and photoinitiation (Table 1). The viscosity measurements carried out for one of the samples in MeOH and in a methanolic solution of LiCl have shown that in pure MeOH the electroviscous effect is observed. This effect is typical for very diluted solutions of polyelectrolytes (Fig. 2). Therefore the values of viscosity of the polyamine samples were determined by standard extrapolation to the axis of ordinates.

As shown in Table 1, the $[\eta]$ values obtained are sufficiently high and vary with changing process temperature, initiation method, type of monomer (salt or mixture), and initial concentration of monomer and initiator. The value of the average MW (M_w) for the polymer sample prepared from **1b**-TFA mixture at 30 °C was 32000, as measured by sedimentation ultracentrifugation. This fact indicates that we succeeded in the synthesis of polyamine of an average degree of

Table 1. Intrinsic viscosity ($[\eta]$) (in MeOH) for the various samples of polyamine **4** prepared in aqueous solutions under thermo- (Δ) and photoinitiation ($h\nu$) in the presence of (NH₄)₂S₂O₈

Monomeric system	Initiation		T^a /°C	τ^b /h	$[\eta] \cdot 10^{-2}$ /mL g ⁻¹	
	Type	$[I] \cdot 10^{-3}^c$				
Type	$[M]^d$					
1b -TFA	2	Δ	5	30	50	0.51 ^f
1b -TFA	2	Δ	5	50	50	0.47
1b -TFA	2	Δ	10	30	50	0.45
1b -TFA	2	Δ	20	30	50	0.39
1b -TFA	2	$h\nu^g$	5	21	2.67	0.71
1b ·TFA	2	Δ	5	30	50	0.80
1b ·TFA	3	Δ	5	30	50	1.07

^a Polymerization temperature.

^b Polymerization period.

^c The values of viscosity averaged for several samples of each polyamine obtained under various polymerization conditions are given.

^d $[M]$ /mol L⁻¹ — concentration of monomer.

^e $[I]$ /mol L⁻¹ — concentration of (NH₄)₂S₂O₈ initiator.

^f $M_w \approx 32000$ (sedimentation ultracentrifugation).

^g A DRS-250 lamp, quartz reactor.

polymerization of ~300 under the conditions of thermal initiation. This value is more than one order of magnitude higher than the values obtained earlier with polymerization of hydrochloride **1b**·HCl under conditions of thermal initiation by various initiators, where the average degree of polymerization of polyamine was about 20 at 30 °C¹⁶ and not higher than 5 at 65 °C.¹⁷ It is also known,¹⁹ that the attempts to overcome the mentioned difficulties and to synthesize polymers of actually high MWs from the monomers of series **I** did not lead to considerable success. The maximum value of $[\eta]$ (in 1M NaCl solution, 30 °C) found for the samples of polymeric salt prepared from **1b**·HCl was 29 mL g⁻¹.

In a series of works³⁻⁷ polymerization of allyl monomers and monomers **I** in various acidic media under conditions of thermal initiation did not lead to the formation of polymers or oligomers. Only upon photoinitiation (20 °C) of the most basic monomer

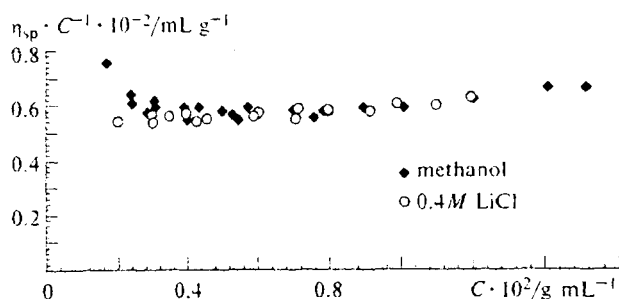


Fig. 2. Dependence of the specific viscosity η_{sp} of polyamine **4** (per the concentration of **4**) on the concentration of polymer **4** (C), 25 °C, solvents — MeOH and 0.4 M LiCl in MeOH.

from the considered series — $\text{Al}(\text{NH}_2)_3$ — was the polyamine with MW of ca. 10000 obtained in the presence of 3-fold excess of H_3PO_4 . This MW value corresponds to an average degree of polymerization equal to 175 (under the conditions of radiative initiation, MW of the polymer reached ca. 140000).⁴

In the present work the use of photoinitiation along with reduction in the process temperature to 21 °C has allowed us to obtain polyamine **4** with a degree of polymerization much higher than 300, as can be seen from comparison of the viscosities of the polymer samples synthesized at 21 and 30 °C (Table 1).

An increase in the concentration of initiator results in characteristic²⁰ (for radical polymerization) reduction in the viscosity of polymers obtained at the same temperature.

The aforesaid variation of viscosity values for polymer **4** with changes of polymerization conditions relates to the polymerization of **1b**–TFA mixture. Even higher viscosity values were found for samples of polyamines synthesized by the polymerization of **1b**·TFA salt (Table 1). This effect was expected, since during the polymerization of **1b**–TFA mixture with the concentration greater than 1 mol L⁻¹ an acid-base equilibrium might be established incompletely, as was mentioned above. With the use of **1b**·TFA salt the opportunity has also appeared to carry out the reaction at higher concentrations of monomer (> 2 mol L⁻¹), which has resulted in substantial increase in polymer viscosity under comparable conditions. The analysis of the submitted data enables us to believe that the photoinitiated polymerization of **1b**·TFA salt at concentrations of initiator as low as possible is the most promising from the viewpoint of obtaining polymers of the highest MWs.

Study of some kinetic characteristics

To study the polymerization kinetics the GLC method was used. For this purpose the method of quantitative estimation (by GLC) of consumption of monomer during cationic stepwise polymerization developed earlier²¹ was modified and adapted to the described process under discussion. The advantage of this method is that GLC (unlike dilatometry) allows one to study (with sufficiently high accuracy and reproducibility of results) kinetics of the radical polymerization at relatively low rates of monomer consumption. This method can be applied both at low monomer conversions (that are necessary for studies of stationary kinetics) and at high degrees of monomer conversion.

The initial rates (ν) of radical polymerization of **1b**·TFA salt (at 5–6% conversion of the monomer) were measured at concentration of the monomer $[\text{M}] = 2 \text{ mol L}^{-1}$ and concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ initiator $[\text{I}] = 5 \cdot 10^{-3} \text{ mol L}^{-1}$ (the results obtained are given in comparison with the data⁸ on the initial rate of poly-

merization of *N,N*-diallyl-*N,N*-dimethylammonium trifluoroacetate (**6**):

Monomer	$T/^\circ\text{C}$	$\nu \cdot 10^6$ /mol (L·s) ⁻¹
1b ·TFA	30	4.4±0.4
1b ·TFA	50	11±1
6	60	66

Change in the reaction temperature causes the appropriate change in the polymerization rate. One can see that the polymerization rate of **1b**·TFA salt found at 50 °C is comparable to that⁸ of quaternary salt **6** at 60 °C. This fact strongly suggests the relatively high reactivity of **1b**·TFA salt.

Fig. 3 shows the dependence of the initial polymerization rate on the initial concentration of initiator. The kinetic reaction order with respect to the initiator (0.51) obtained from the data of Fig. 3 evidences the bimolecular mechanism of chain termination. A rather important conclusion follows from this, namely that in the given system acts of degradative chain transfer to monomer, which are characteristic of allyl monomers, can not be found, *i.e.*, the chain transfer to monomer becomes the effective one. The obtained result also indicates that in the considered process the monomer molecules and propagation and chain transfer radicals are protonated (for detailed discussion see above). In this connection note that in the early works^{3,4,7} on polymerization of allyl monomers in acidic media, in particular on the polymerization of the $\text{Al}(\text{NH}_2)_3\text{--H}_3\text{PO}_4$ system, the kinetic order of 1 with respect to the initiation was observed. We believe that in the mentioned systems only part of the monomer molecules and part of the radicals were in the stable protonated forms. This assumption is also proved indirectly by the impossibility of obtaining the corresponding polymers and even oligomers as a result of polymerization of these monomers under thermal initiation conditions.

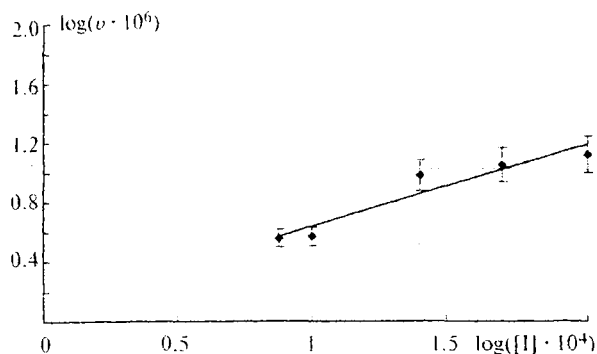


Fig. 3. Dependence of the initial rate (ν) of polymerization of monomer **1b**·TFA salt on the concentration $[\text{I}]$ of the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ initiator (logarithmic scale); $[\text{M}] = 2 \text{ mol L}^{-1}$, $T = 50 \text{ }^\circ\text{C}$.

Thus, a high molecular weight polyamine has been synthesized for the first time by radical polymerization of a monomer of the diallylamine series in the presence of a common radical initiator under relatively mild conditions. The bimolecular mechanism of the chain termination reaction has been established; the opportunity of control of the reaction rate and molecular weight of the polymer has been shown.

The results of this work confirm the efficiency of the suggested approach for the preparation of high molecular weight polymers from allyl monomers by polymerization in the media where the monomer is protonated.^{3–7,10} They also justify, as we believe, the choice of the monomeric system made in the present work. The advantage of our system consists in that the interaction of TFA with an amine with $pK_a > 7$ at a molar ratio TFA : amine of 1 : 1 leads in water and even in less polar, aprotic solvents to the formation of a stable ionic pair (highly dissociated or associated, depending on the type of the solvent).^{11,13} It is possible to state that in none of the polymerization media considered earlier^{3–7,17,18} was the acid-base equilibrium achieved so that the monomer would be mainly in the protonated form (the amount of non-protonated monomer molecules and propagation radicals would be insignificantly small).

In our opinion, further systematic studies will allow us to estimate quantitatively a number of elementary kinetic constants of the polymerization process. At the same time, it is already clear that the results obtained basically make it possible to synthesize new cationic polyelectrolytes of sufficiently high molecular weight from monomers of series **1**, as well as to modify them subsequently.

Experimental

¹H and ¹³C NMR spectra were recorded on a Bruker MSL-300 spectrometer (300 MHz) in Me₂CO-d₆, CD₃OD and D₂O. The chemical shifts in the ¹H NMR spectra are reported relative to residual protons of the solvent.

GLC-analysis was carried out on a Tzvet-3 chromatograph using a digital integrator ID-26, a flame ionization detector, and a 1 m x 3 mm glass column filled with 5% SE-30 on Chromaton N-AW (particle size of 0.20–0.25 mm). Nitrogen was used as a carrier gas; the gas flow rate was 20 mL min⁻¹. The column was heated from 70 to 150 °C at 12 °C/min. The injector temperature was 200 °C. The content of monomer in polymerization media was determined using β-picoline+EtOH as the internal standard; the time of the analysis did not exceed 3 min. To take a sample of the polymerization mixture, the process was terminated by addition of 94 mg (2.35 mmol) NaOH to 2 g of polymerization mixture; then 266 mg (5.79 mmol) of homogenizer (EtOH) and 172 mg (2.15 mmol) of internal standard (β-picoline) were added. The molar ratio of **1b**·TFA : NaOH : EtOH : β-picoline was equal to 1.00 : 1.52 : 3.74 : 1.39.

The determination of \bar{M}_w values was carried out on an MOM 3180 ultracentrifuge at 20 °C and 40000 rpm using methanol as a solvent.

Reagents of chemically pure grade produced domestically except for (NH₄)₂S₂O₈ (Germany, "pure for analysis" grade) and TFA (Germany, Riedel-de Haën AG, purity of 99%) were used for the experiments.

***N,N*-Diallyl-*N*-methylamine (1b)**. This compound was obtained according to the known procedure.²² A 25% aqueous solution of MeNH₂ (1 mol) was placed in a three-necked flask, equipped with a stirrer, a reflux condenser, and a dropping funnel, and AlCl₃ (2 mol) and 50% aqueous solution of NaOH (2 mol) were successively added at 0–5 °C with no overheating allowed. Then the reaction mixture was heated to 70 °C and kept at this temperature for 5 h. The organic layer was separated, dried over NaOH for 40 h, and distilled on a column to give 69.93 g (63%) of chromatographically pure **1b**: b.p. 108–110 °C; n_D¹⁹ 1.4308; ¹H NMR (1.13 mol L⁻¹; Me₂CO-d₆), δ: 2.16 (s, 3 H, CH₃N); 2.98 (d, 4 H, 2 α-CH₂); *J* = 5.89 Hz; 5.13 (m, 4 H, 2 γ-CH₂); 5.78 (m, 2 H, 2 β-CH).

***N,N*-Allyl-*N*-methylammonium trifluoroacetate (1b·TFA)**. To a solution of 28.9 g (0.26 mol) TFA in 200 mL of anhydrous hexane 28.9 g (0.26 mol) of **1b** at 5–0 °C was added dropwise over 2 h with vigorous stirring in an argon flow. A salt **1b**·TFA precipitated as a slightly yellowish oil was washed twice with hexane. Residues of the solvent were removed on a rotary evaporator. The product was purified by precipitation upon adding hexane to the solution in MeOH. The yield was 49.73 g (85%). Found (%): C, 47.75; H, 6.08; N, 6.79; F, 26.03. C₉H₁₄NO₂F₃. Calculated (%): C, 48.00; H, 6.22; N, 6.22; F, 25.33. ¹H NMR (1.13 mol L⁻¹; Me₂CO-d₆), δ: 2.78 (s, 3H, CH₃N); 3.80 (d, 4 H, 2 α-CH₂); 5.53 (m, 4 H, 2 γ-CH₂); *J* = 6.96 Hz; 6.03 (m, 2 H, 2 β-CH).

Poly(*N,N*-diallyl-*N*-methylamine) (4). Method A (preparation from **1b**–TFA mixture). To 56.03 g (3.11 mol) of H₂O 22.71 g (0.2 mol) of TFA, 22.11 g (0.2 mol) of **1b**, and 113.5 mg (0.498 mol) of (NH₄)₂S₂O₈ were added.

Method B (preparation from **1b**·TFA salt). To 45.00 g (0.2 mol) of **1b**·TFA 56.03 g (3.11 mol) of H₂O and 113.5 mg (0.498 mol) of (NH₄)₂S₂O₈ were added.

A solution was charged into an ampoule, degassed in vacuo (10⁻³ Torr) by 4–5 repeated freeze (liquid N₂) – thaw cycles, and sealed and the ampoule was kept at the desired temperature (the reaction temperature and time are specified in Table 1). When the photoinitiation was carried out, the degassed solution was placed in a quartz reactor in an argon flow and irradiated with the full light of a DRS-250 lamp (irradiation time is specified in Table 1). The polymer thus obtained was precipitated with 40% aqueous solution of NaOH pre-cooled to 0 °C, washed carefully with distilled H₂O until neutral reaction, and then reprecipitated with water from the solution in MeOH. The yield was 2.34 g (5.2 %). Found (%): C, 73.53; H, 13.75; N, 12.08. C₇H₁₃N. Calculated (%): C, 75.68; H, 11.71; N, 12.61.

Poly(*N,N*-diallyl-*N*-methylammonium trifluoroacetate) (3). The preparation of initial solutions and polymerization reaction was carried out by the procedures described above for the synthesis of compound **4**. An excess of H₂O was evaporated from the polymerization mixture using a rotary evaporator. The polymer was precipitated by pouring a reaction mixture into 500 mL of anhydrous Et₂O and purified by reprecipitation with Et₂O from the solution in MeOH. The yield was 3.78 g (8.4%). Found (%): C, 47.00; H, 6.07; N, 6.12; F, 25.03. C₉H₁₄NO₂F₃. Calculated (%): C, 48.00; H, 6.22; N, 6.22; F, 25.33.

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