Synthesis of high-molecular-weight polyamine by radical polymerization of \(N,N\)-diallyl-\(N\)-methylamine


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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 \(^1\)H 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 \(\alpha\)-hydrogen atom of the allyl group of the \(R = H, Me, Bu\) 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 (Scheme 1).

It is known, that the polymerization rate for allyl and diallylamines 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 \(\alpha\)-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...
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 \(\alpha\)-hydrogen abstraction due to the enhancement in the \(\alpha\)-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 ionicogenic 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 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 \(^1\)H NMR spectra of solutions of equimolar 1b—TFA mixture and compound 1b in \(Me_2SO-d_6\) 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, data\(^14\) for the tertiary amines \(R_2NMe\)).

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 \(\alpha\)-CH\(_2\) 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 CH\(_2\) end groups, are also shifted downfield in the presence of TFA, but to a lesser extent. Change in the position of the \(\alpha\)-CH\(_2\) proton resonance is especially indicative if one takes into account that \(\alpha\)-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 \(^1\)H NMR spectra obtained for solutions of this salt in \(Me_2CO-d_6\) 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 \(\alpha\)-CH\(_2\) 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.