

The 1,3-dipolar cycloaddition to nitrones and their photorearrangement as activation methods of alkoxyamine homolysis

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Radical controlled polymerization in the presence of nitroxide radicals (NMP) is one of the promising methods for obtaining polymers with a narrow molecular weight distribution of a given structure and composition. The initiators for this type of polymerization are alkoxyamines, organic compounds with the general formula R1R2NOR3, which are reversibly decomposed by a homolysis reaction into a stable nitroxide radical, and an alkyl macroradical growing in the presence of a monomer. Thus, due to the peculiarities of the mechanism of radical controlled polymerization, the initiator is not consumed over time, but gradually turns into the polymer R1R2NO(M)nR3. This causes a linear increase in the molecular weight of the polymer with the conversion of the monomer, and the resulting polymer chains are close in length. However, this is possible only under optimal conditions, in particular, at some optimal temperature. The optimal polymerization temperature follows from the equilibrium «alkoxyamine-radicals» and the activation energy of the homolysis reaction. The lower the activation energy of homolysis, the lower the temperature at which a favorable equilibrium «alkoxyamine-radicals» is achieved. However, the synthesis of a too labile initiator is extremely difficult. Thus, an ideal alkoxyamine initiator should be labile during polymerization and, at the same time, stable enough for its synthesis. As a solution to this problem, in this work, we propose two methods for the activation of non-labile alkoxyamines based on 2,2,5,5-tetramethyl-3-imidazoline-3-oxide-1-oxyl: 1,3-dipolar cycloaddition, and photochemical rearrangement.

Within the framework of this work, the kinetics of 1,3-dipolar cycloaddition to 13 different monomers was studied and the Arrhenius parameters were determined. The influence of the structure of the used monomer on the rate of 1,3-dipolar cycloaddition as well as on homolysis activation barrier was determined. The photochemical rearrangement was studied by NMR spectroscopy, and the quantum yield and composition of the products were determined. For both methods of activation, their effect on the activation barrier of homolysis of the studied alkoxyamines was determined, and a conclusion was made about their applicability in the context of radical controlled polymerization.

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