

Polymerization Kinetics Photoinduced by Derivatives of Para-Nitroaniline in the Presence of N,N-Dipropylaniline

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Abstract

We investigated a possibility of the para-nitroaniline applying as a photopolymerization initiator. To carry out photo polymerization a system consisting of para-nitroaniline and N,N-Dipropylaniline was irradiated with UV light with a wavelength at 365 nm. When adding monomer in this system there was observed polymer formation. It is important to note that these results were not detected using either the nitro compound or the amine monomer as well as to the system without the monomer. The paper shows the kinetics of polymerization at low conversion with different ratios of amine and nitro compounds.

Keywords: photo polymerization initiator, para-nitroaniline, N,N-Dipropylaniline.

Introduction

Recently, isomers of nitro compounds - nitroso oxides received great interest. These compounds are potential oxidants, sources of singlet oxygen, easily abstract hydrogen atoms, can serve as the sources of atomic oxygen. Nitrobenzene derivatives in the presence of tertiary amines behave as efficient photo initiators of the methacrylic and acrylic monomers. It is possible because the nitro compound under the influence of ultraviolet light can easily pass into the triplet state and then it can react with the compound active hydrogen. This process is possible even at the room temperature[1-3]. The result of this interaction is formation the

radicals, which possibly can initiate photo polymerization. The possibility of the polymerization initiation of vinyl monomer system containing the amine and nitro compound was studied in our work. For that purpose we have used mixtures of para-nitroaniline and N,N-Dipropylaniline in various ratios as initiator, and Triethylene glycol dimethacrylate as the monomer. Polymerization was performed in bulk. We also have investigated the kinetics at low conversion stages.

Experimental

Triethylene glycol dimethacrylate was purified by washing with 10% NaOH solution and then distilled under vacuum[4]. N, N-Dipropylaniline was passed through the chromatographic column and vacuum-distilled before use. Para-nitroaniline was purified by recrystallization from EtOH.

Polymerization was performed in a thin layer in the presence of atmospheric oxygen and a temperature of 25°C. Irradiation was carried out with the use of ultra-high pressure mercury lamp DRC-120. The cutoff filters were used to isolate the 365 nm line. Concentrations of para-nitroaniline in the initiator system were measured by the spectrophotometer SF-2000 at various durations of the process to obtain kinetics of the initiation

The study of photoinitiation was performed at different ratios of reactants concentrations in the initiator system. The concentration of para-nitroaniline in the system was a constant and equals to 0.05 mol/l. We investigated the cases when molar ratios of N, N-Dipropylaniline relative to para-nitroaniline were 1:1, 2:1, 4:1, 8:1, 1:2.

Results and discussion

The initiator system was tested without N,N-dipropylaniline and in this case the polymerization was not observed. The concentration of para-nitroaniline also was not changed. The polymerization was not observed in the similar experiment with the initiator system without para-nitroaniline. These facts allow us to suppose that only the initiator system including both para-nitroaniline and N,N-dipropylaniline can initiate the polymerization.

In the experiment with the molar ratio of N, N-Dipropylaniline relative to para-nitroaniline 1:2 observed that the concentration of para-nitroaniline was changing very slow and the polymerization was not detected .

A significant change in the concentration of para-nitroaniline and the polymerization were observed in the experiments with molar ratios of N, N-Dipropylaniline relative to para-nitroaniline equal to 1:1, 2:1, 4:1, 8:1. Fig. 1 presents the kinetic curves of changes in the concentration para-nitroaniline in time for various molar ratios of the initiator system components.

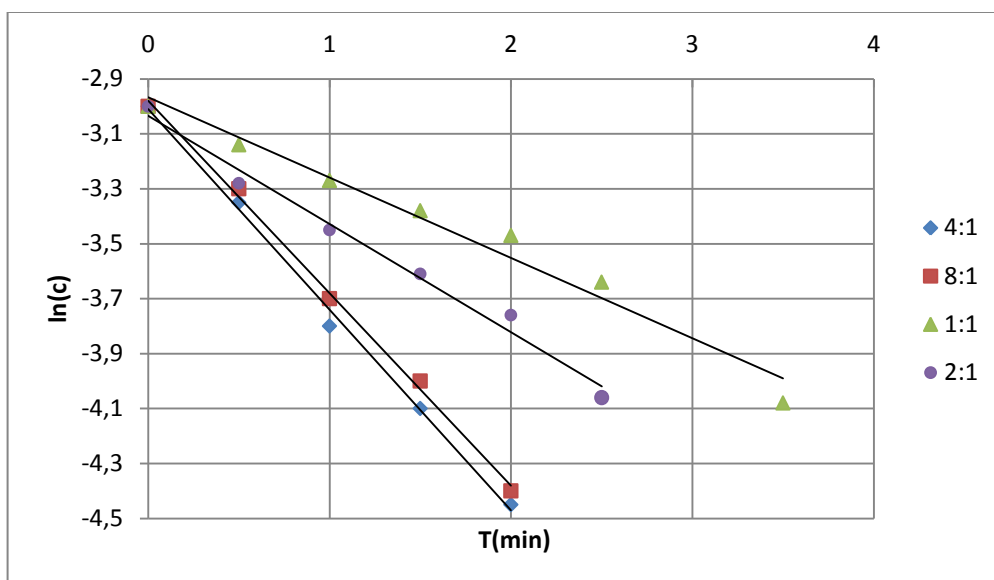


Fig. 1: Concentration change of para-nitroaniline at various molar ratios of the initiator system components

With increasing of molar fraction of N,N-Dipropylaniline the system increases rate of the photoinitiation. Such trends are observed for reactant ratio of 1:1, 1:2, 1:4. It is obvious that the maximum rate of initiation of para-nitroaniline and N, N-Dipropylaniline observed at the ratio of reactants equal to 1:4. The effective rate constant calculated for the last case is 0.73^{-1} sec. In the experiment with molar ratios of N,N-Dipropylaniline relative to para-nitroaniline equal to 8:1 the conversion rate of para-nitroaniline was lesser than expected. We supposed that N,N-Dipropylaniline reacts with oxygen of air and this process competes with initiation process that

causes a decrease in the initiation efficiency. This supposition will be checked in our later papers.

References

1. **The kinetics of photoreduction of isomeric nitroanilines** *Zelentsov S.V., Simdyanov I.V., Kuznetsov M.V.* High Energy Chemistry. 2005. 39. № 5. C. 309-312.
2. **Photopolymerization in the system oligomer-aromatic nitro compound-aniline derivative** *Zelentsov S.V., Gusev S.V., Zelentsova N.V., Kuznetsov M.V.* High Energy Chemistry. 2004. 38. № 2. P. 115-119
3. **An ESR and UV spectroscopic study on the photoreduction of para-nitroaniline** *Zelentsov S.V., Zelentsova N.V., Kuznetsov M.V., Simdyanov I.V.* High Energy Chemistry. 2004. 38. № 1. P. 25-30.
4. **Polymerisation kinetics photoinduced by derivatives of 4-nitroaniline in the presence of N,N-dimethylaniline studied by Real-Time IR spectroscopy.** *M Rodríguez, I García-Moreno, O García, R Sastre,* Polymer, Volume 41, Issue 21, October 2000, Pages 7871-7875.