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Application of iniferters for obtaining composition homogenous copolymers

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Summary

An original way of reducing composition heterogeneity has been proposed for copolymers obtained at high conversions. The main idea underlying this method consists in application as initiators of special compounds (iniferters) leading to alteration of the mechanism of polymer chain growth.

Introduction

It is generally known that, when obtaining copolymers via radical mechanism one applies traditional initiators (peroxides, azo-compounds and etc.), in many cases at high conversions heterophase turbid products with inferior service properties (1) are formed. This phenomenon is due to considerable composition inhomogeneity of copolymers caused by the drift of monomer mixture composition in the course of the process of batch copolymerization of monomers with rather different relative reactivities r_1, r_2.

We put forward an original way to obtain at high conversions composition homogeneous copolymers for any values of r_1 and r_2. The main idea of the method consists in the application of nontraditional radical initiators, so called Iniferters. Such initiators have been widely used to synthesize homopolymers (2)-(4), alternating (5) and block-copolymers (6)-(8). The data on the synthesis of statistical copolymers (9), obtained under the action of iniferters are considered in the present communication.

As examples we have selected two thoroughly investigated systems: Styrene + Methyl acrylate (St+MA) (10) and Styrene + Acrylonitrile (St+AN) (11). It is known (10),(11) that, when AIBN is used as initiator for bulk copolymerization within a certain region of monomer feed composition, turbid heterophase copolymers are obtained at high conversions.

Results and Discussion

We performed bulk photo- and thermoinitiated copolymerization of St+MA applying as iniferters respectively benzyl dithiocarbamate ($T=25^{\circ}$) and N,N,N',N'- tetraethylthiuram disulphide ($T=80^{\circ}$). The latter has been also used when carrying out thermoinitiated copolymerization for the system (ST+AN) in the range of 80°-130°. During these experiments the

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value of weight conversion of monomers in three mentioned systems reached 98%, 84% and 94% respectively. Copolymerization products obtained by the above procedure retain full optical transparency over the whole range of examined conversions. In contrast, copolymers St+MA and St+AN, synthesized under the same conditions but in the presence of AIBN, were turbid.
The reason for improved composition homogeneity of copolymers obtained in the presence of iniferters arises from a nontraditional mechanism of polymer chain growth (12), (13). It is of stepped character, so that each macromolecule in the course of the process increases its length. As a result, the composition of this macromolecule apparently changes along the chain showing a tendency to impoverishment in the more active component as is the case for graded copolymers. Since the period of dissociation of the used Iniferters is far shorter than the copolymerization time, considering products obtained at high conversions, it is reasonable to suppose that all polymer chains commence their growth practically simultaneously. In this case the conversional composition inhomogeneity of the copolymers will obviously be considerable less than that of copolymers obtained in the presence of traditional initiators.

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