



Perspective Article

Polymerization kinetics of adamantane-based dicyanate ester and thermal properties of resulting polymer

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A B S T R A C T

The kinetics of liquid-state polymerization of adamantane-based dicyanate ester has been studied for the first time by means of conventional and temperature-modulated DSC. It has been detected that the later stages of polymerization undergo a transition from kinetic- to diffusion-controlled regime. Detailed analysis of the polymerization kinetics in the reaction-controlled regime has revealed that the process rate can be well described in the frameworks of the presently proposed autocatalytic quasi-one-step model. The proposed model eliminates arbitrarily guessing the value for the initial conversion that provides a reasonable alternative to the broadly used truncated Sestak-Berggren model. The adamantane-based dicyanate ester polymerization product demonstrates markedly higher thermal stability and glass transition temperature compared to those of dicyanate esters with flexible hydrocarbon bridging units. The obtained experimental results confirm our hypothesis about the influence of the rigidity of cyanate ester molecule on its reactivity and thermal properties of the corresponding polymer product.

1. Introduction

High-performance thermosets based on cyanate resins play an important role in the electronic, military, and aerospace industries because the resulting materials possess unique mechanical, thermal, and dielectric properties [1–4]. Their irreplaceable practical utility promotes fundamental studies of intrinsic relationships between the structure of cyanate esters and their reactivity, as well as properties of the final polymeric materials. Such studies are essential for directed design of thermosets with desired properties [3,5–7]. The thermal stability and glass transition temperature are the most important thermal properties that determine possible areas and conditions of the application of thermosets.

The influence of the polymer structure on the thermal properties of polymers is generally well studied. It is known that introduction of rigid fragments into the main polymer chain increases both thermal stability and glass transition temperature (T_g) of the corresponding polymers [8]. The presence of polar side groups or groups capable of forming hydrogen bonds tends to decrease the segmental mobility of polymer chains and thus results in higher glass transition temperatures of the corresponding polymers [9–12]. The effect of aforementioned groups on thermal stability of polymers is more complex and depends on particular nature of

the group and may either increase or diminish thermal stability [13,14]. The introduction of adamantane groups into polymer structure is of special interest because of their rigidity and high thermodynamic stability. Being introduced into the main chain or as side group, adamantane increases thermal stability of the polymeric material [15,16].

Finding general relationships between the structure of a monomer and its reactivity is a difficult task because of numerous possible mechanisms of polymerization process (cationic, anionic, radical, coordination, etc). For example, electron-withdrawing groups accelerate anionic-polymerization of vinyl monomers, but inhibit its cationic polymerization [17,18]. Also, the process may switch from a kinetic- to diffusion-controlled regime during the polymerization progress that further complicates the task. However, since this switch is usually observed near the glass transition temperature of the reaction mixture one can expect that the structural factors decreasing the segmental mobility (i.e., those increasing T_g) should promote an earlier transition of the reaction kinetics to diffusion-controlled regime during polymerization. This idea is illustrated schematically in Fig. 1, where two monomers of similar reactivity (similar α -T curves), but with markedly different T_g 's (both for monomers and polymers) have significantly different points of intersection of the corresponding α -T and T_g - α curves. It is seen that polymerization of a monomer that gives rise to a polymer

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