Real time dielectric monitoring of glass transition in *n*-vinyl pyrrolidone polymerization

F. Salehli [a],[*], I. Bayrak [a], R. Nigmatullin [b], A. Arbuzov [b]

[a] *Department of Physics, Istanbul Technical University, Maslak 34469, Istanbul, Turkey*
[b] *Department of Theoretical Physics, Kazan State University, Kremlevskaya street 18, 420008 Kazan, Tatarstan, Russian Federation*

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Abstract

Real time dielectric spectroscopy was used for monitoring the dynamics during liquid glass transition in radical bulk polymerization of *n*-vinyl pyrrolidone. Two different relaxation mechanisms were identified. Initially segmental α-relaxation was dominant. Subsequently, contribution from slower motions became more significant and $\varepsilon'(t_r, \omega)$ underwent maxima in all frequency bands up to 10 MHz. Peak amplitude increased and the occurring time was delayed with decreasing frequency. The slow region dynamics were similar to the dynamics of Chamberlin's domain-like model of glass transition. The glassy phase is formed by a segmental relaxation and a relaxation due to glassy regions. The characteristic relaxation times of slow and segmental motions were well described by a modified Vogel–Fulcher–Tammann relation. The high frequency behavior, associated with the segmental motions, is well described by Havriliak–Negami and Kohlrausch–Williams–Watts formulas, which did not provide satisfactory fittings for the dynamics of slow regions. Both real and imaginary parts of the dielectric data were fully described by a complex dielectric relaxation function, the parameters of which are found by the eigen-coordinates (EC) method.
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1. Introduction

Dielectric spectroscopy (DS) of a polymerization medium measures the total response of changes of mobilities of various dipole species and ions, which contribute to real and imaginary parts of the dielectric constant on different time scales of dielectric spectra. Studies by Shephard and Senturia [1], Kranbuehl et al. [2,3], Johari [4–6], Rolla [7] Williams [8–10], Mijovic [11–13] and Friedrich [14] were mostly devoted to epoxy systems and their modifications. These works established the dipolar aspects of molecular dynamics, α- and β-relaxation kinetics, and the contribution of different relaxation processes to the dielectric function.

When bulk polymerization is conducted at a temperature (T_r) below the glass transition temperature (T_g) of bulk polymer, the final product is glass. The degree of conversion depends on T_r [10].

Spatial heterogeneity in glass transition was discussed by Sillescu [15]. The 'independently relaxing domains' model was used by Chamberlin [16] for theoretical description of dielectric properties of supercooled salol and glycerol at glass transition [17,18]. The model gives an excellent agreement of evolution of average domain size with slowing of relaxation rates as temperature decreases. The molecular motions within the glassy regions are strongly cooperative. The boundaries of glassy regions expand with approach to the glass transition and as pointed out by Colby, the relation between the relaxation times of clusters and their sizes are described by the dynamic scaling theory [19].

* Corresponding author. Tel.: +90 212 285 3258; fax: +90 212 285 6386.
 E-mail address: salehli@itu.edu.tr (F. Salehli).