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Experimental confirmation of oscillating properties of the complex conductivity: Dielectric study of polymerization/vitrification reaction

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Abstract

Clear evidence of the existence of fractional kinetics containing the *complex power-law* exponents were obtained by conductivity measurements of polymerization reaction of polyvinylpyrrolidone (PVP) performed inside a dielectric cell. We established the relationship between the Fourier image $R(j\omega)$ of the complex memory function $K(t)$ and the time-dependent mean square displacement $\langle r^2(t) \rangle$. This relationship helps to understand the origin of the different power-law exponents appearing in the real part of complex conductivity $\text{Re}[\sigma(\omega)]$ and find a physical/geometrical meaning of the power-law exponents that can form the complex-conjugated values. The complex-conjugated values of the power-law exponents leading to oscillating behavior of conductivity follows from the fractional kinetics suggested by one of the authors (R.R.N.). The relationships $[R(j\omega) \iff \text{Re}[\sigma(\omega)] \iff \langle r^2(t) \rangle]$ are becoming very efficient in classification of different types of collective motions belonging to light and heavy carriers involved in the relaxation/transfer process. The conductivity data obtained for $\text{Re}[\sigma(\omega)]$ during the whole polymerization process of the PVP at different temperatures (80, 90, 100 °C) are very well described by the fitting function that follows from the suggested theory. Original fitting procedure based on the application of the eigen-coordinates (ECs) method helps to provide a reliable fitting procedure in two stages and use the well-developed and statistically stable linear least square method (LLSM) for obtaining the correct values of the fitting parameters that describe the behavior of $\text{Re}[\sigma(\omega, T_r)]$ in the available frequency range for the current time of the chemical reaction T_r measured during the whole process of polymerization. The suggested theory gives a unique possibility to classify the basic types of motions that take place during the whole polymerization process. © 2007 Published by Elsevier B.V.

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1. Introduction

Despite substantial progress in experimental measurements in dielectric spectroscopy [1] the modern state of the theory of dielectric relaxation remains *unsatisfactory*. At the present time (as before) a number of empirical relationships are used in order to fit the broadband dielectric

spectra for a wide class of heterogeneous materials. The most popular empirical expression which is used to describe the generalized broadened asymmetric relaxation loss peak is the Havriliak–Negami (HN) expression [2].

Traditionally, the measured permittivity–frequency data are interpreted and analyzed quantitatively using the HN expression or its linear combinations. However, in this description the fitting power-law exponents remain *empirical* and the desired relationship with structural or microscopic motion parameters of the material considered is *unknown*.

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