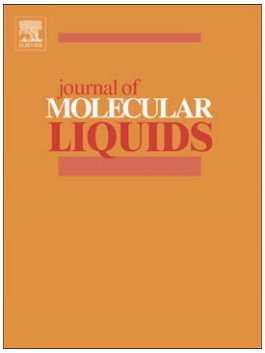

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On the possibility of modeling of polymers glass transition in a wide range of cooling and heating rates

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The presented work continues the investigation of the problems connected with modeling of the kinetics of polymers glass transition in a wide range of temperature change rates. In our previous work [1], an attempt to model a big set of heat capacity curves of polystyrene glass transition has been made, and the inability of the common methods to do this within a single set of parameters has been demonstrated. To go a step further, in this work we proceed with the common and several novel methods of modeling. To normalize the models with each other, a fit of the 10 K/min cooling/heating DSC curves of polystyrene is made, and the literature model parameters readjusted. Further, the modeling of the reduced heat capacity curves at the cooling and heating rates in a wide range of q=10^{-6}-10^{6} K/s with a logarithmic step is performed. The comparison of $T_g(q)$ behavior with lately measured data for polystyrene is made. It is shown, that the methods need some modifications to qualitatively describe details of the glass transition kinetics in a wide range of q. Some of the possibilities to advance the models are discussed.

1. Introduction

The glass transition, or freezing-in, of various liquids is presently considered to be a very interesting phenomenon [2]. The non-stopping efforts of the scientists to provide a consecutive and complete description of this kinetic effect, as well as the structure of the glass, are not yet successful. The amount of different theoretical methods and approaches in this field can be compared only with the diversity of the types of the systems, where transitions bearing similar features have been discovered [3,4]. To the classical molecular liquids one can add polymers, colloids, granular materials, spin and Coulomb glasses, and even certain systems in computer science. There are no big doubts in the similarity of the features of the occurring transitions, thus from theoretical point of view it is both important to provide the general models of these effects, and also to develop separate theoretical approaches to account for specific features in each case.

Polymers of different kinds present an important system for various applications, and also an interesting object of research. The transition of different (mainly atactic) polymers from liquid to the glassy state has been intensively investigated both experimentally and theoretically for almost a decade. Different phenomenological and microscopic theoretical models were proposed [5]. Yet, presently, there exist no method for consistent description of the effect for all the possible thermal histories applied to the sample. The modern calorimetric techniques allow one to probe a wide range of cooling and heating rates, starting from as slow as 10^{-6} K/s and going up to high values of 10^{6} K/s. Lately [1] an attempt to describe the glass transition of polystyrene measured via temperature dependencies of the heat capacity, $C_p(T)$, by such theoretical methods as Tool-Narayanaswamy-Moynihan (TNM), Adam-Gibbs (AG), or Gutzow-Schmelzer (GS) has been made. As the result, it was shown, that if a single set of model parameters is used, an