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Heat capacity measurements and modeling of polystyrene glass transition in a wide range of cooling rates

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ABSTRACT

Polymers are known to be good glass formers, allowing one to study glass transition effects as well as to verify the applicability of various theoretical models. In this work experimental and theoretical investigations of glass transition of atactic polystyrene (PS) in a broad range of cooling rates ($5\cdot10^{-6}$–2 K/s) are presented. The capability of commonly employed theoretical techniques for C_p modeling to describe the obtained data is considered. It is shown that the extended Tool–Narayanaswamy–Moynihan (TNM) model with Vogel–Fulcher–Tammann–Hesse (VFTH) or Adam–Gibbs (AG) expressions for relaxation time with the common single set of parameters do not fit the experimental data well. Moreover, the values of parameters required to produce an adequate fit of the whole set of heating curves are quite different from their estimates obtained from independent additional experiments. An additional expression for relaxation time is proposed within the Gutzow–Schmelzer (GS) approach for describing the kinetics of glass transition leading to results of similar precision. The obtained results reconfirm the general conclusion that the considered models of glass transition require parameter readjusting for different cooling or heating rates in order to adequately describe the experimental data.

1. Introduction

Glass transition can be considered as a process of transformation of a material from a (metastable) equilibrium glass-forming melt into a frozen-in, amorphous non-equilibrium state, the glass. The glass transition can be caused by variations of temperature, pressure or other appropriate thermodynamic control parameters.

The formulation of a comprehensive theory of the glassy state and of the glass transition remains one of the challenges for modern physics (for reviews on this field, see, for example, [1–5]). This is one of the reasons of the continuing interest in analysis of these problems. In addition, also from a practical viewpoint, experimental study and theoretical description of glass transition are very important topics, due to the wide distribution of modern technological applications of glasses as well as their frequent occurrences in everyday life. The kinetics of change of different properties of glass-forming melts during the glass transition and the dependence of the properties of respective substance in vitreous state on different rates of change of control parameters can give an insight into the mechanisms of the vitrification process.

One of the common experimental techniques employed for these purposes is differential scanning calorimetry (DSC). Recent developments of this experimental method allow one to highly extend the ranges of rates of temperature changes, giving us thus the possibility to obtain qualitatively new results in understanding of the behavior of glass-forming systems. New opportunities are also opened with the extended use of temperature-modulated differential scanning calorimetry [6] and accompanied by simultaneous studies of the dynamic glass transition of the same substances [7,8].

A particularly interesting field of research in this respect is the investigation of glass transition of polymers [9–15]. Many polymers being studied are applied in modern technologies and new fields of application are emerging. By this reason, such systems as polystyrene, polyvinyl chloride, polyvinyl acetate, and others have been studied both experimentally and theoretically for more than 30 years. The works by Hodge [10–12,16,17], Cowie [18,19], and others [13,20–33] are to be mentioned in this respect. These analyses are attempted to be expanded in the present investigation increasing considerably the cooling rates in transformation of the respective systems into the vitreous state.

As one particular study in this respect, the present work is devoted to experimental investigations of the glass transition of polystyrene in a wide range of cooling rates and the theoretical analysis of the obtained results. Compared to the above cited previous experiments the range of cooling rates used is extended significantly. The behavior of polystyrene at cooling rates in the range from 2 K/s down to $5\cdot10^{-6}$ K/s has been studied. The obtained results supply us with the opportunity to analyze the variation of polystyrene glass transition properties, such as glass transition temperature T_g, width of the glass transition range and others when the temperature change rate is varied within six decades. The description of these results is shown to present a real challenge for

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theoretical modeling when one is attempting to describe the whole set of heat capacity curves with a single set of parameters.

The current activities in the theoretical description of glass transition phenomena represent a large field with different approaches, both microscopic and macroscopic, being applied [1,34–40]. In the present work we focus upon the widely used macroscopic theories for description of the kinetics of glass transition. The foundation of these approaches is the work by F. Simon and others treating glass transition as a freezing-in process [41]. In describing this process theoretically, different methods for modeling the system relaxation have been developed and applied for the evaluation of glass-former properties during the glass transition at different conditions. Among the basic work in this field one can mention the classical works by Tool [42], Adam and Gibbs [43], Narayanaswamy [44], and some others [10,45–48]. An approach developed by Gutzow and Schmelzer [1,36,49,50] is based on thermodynamics of irreversible processes and can be applied in general form to all types of glass-formers. We employ in the present analysis some set of different approaches sketched above to model the DSC data on polystyrene and discuss their advantages and shortcomings with respect to their accuracy in the description of experimental results.

The article is structured as follows: in the experimental part (Section 2) we describe the procedure of the measurements performed and the data treatment method. We present the obtained heat capacity curves in the glass transition interval of polystyrene. In the theoretical modeling section (Section 3), the results of application of different approaches for fitting the experimental data are presented, analyzed and compared with each other. We show that along with the commonly employed Tool–Narayanaswamy–Moynihan (TNM) and Adam–Gibbs (AG) approaches, the kinetic model developed by Gutzow and Schmelzer shows comparable results and can thus, after appropriate development, be used in similar cases. A brief discussion and comparison of the obtained results is given in Section 4. Conclusions complete the paper.

2. Experimental

For the experiments, polystyrene (PS) was chosen as the object of investigation, because of its pronounced thermal stability. Even at very slow cooling, where for several days the sample stays above the glass transition temperature, no degradation of the polymer was observed. The atactic polystyrene, PS168N with $M_w = 270{,}000$ g/mol and $M_n = 95{,}000$ g/mol used in this work, was taken from BASF. The bulk sample was put into a standard PerkinElmer aluminum pan. It had a mass of about 3.8 mg.

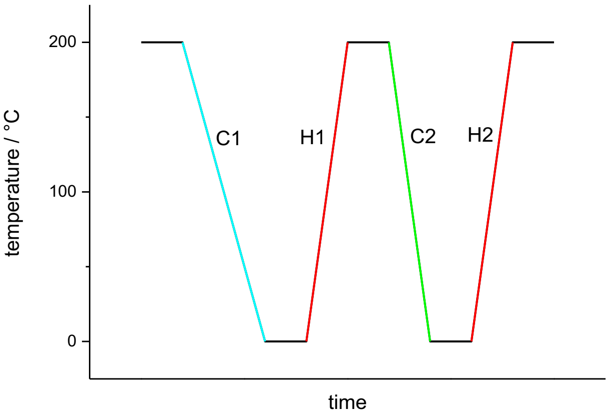

Fig. 1. Profile of temperature change during a single DSC measurement on polystyrene.

The experimental data were acquired with a PerkinElmer Pyris1 DSC. The temperature profile used for each of the measurements is presented in Fig. 1. One measurement cycle went as follows: A starting temperature of about 200 °C was chosen corresponding to the sample molten state. Then the system was cooled with a certain cooling rate (C1, light blue curve in Fig. 1). This cooling rate, C1, was altered in every next run and covered a range between $5 \cdot 10^{-6}$ K/s and 2 K/s. All of the following steps of measurements were the same for each run. The sample was reheated always with the same heating rate of 0.5 K/s back up to the initial temperature of 200 °C (H1). In heating, the system passes the glass transition region, again. The response of the system in heating is shown to reflect the peculiarities of the cooling applied. The respective experimental heat capacity curves vary with the chosen cooling rate applied in the first cooling run, C1.

The next step is cooling (C2) with 0.5 K/s followed by reheating with 0.5 K/s (H2), again. These two steps (denoted as C2 and H2 on Fig. 1) are performed after every run with some given cooling rate C1, giving a reference curve at which the excess heat capacity is being calculated. The reference curve has to be measured and calculated after every run (for different C1 rates). This is necessary because for very low cooling rates in step C1 the measurement takes several days and even weeks, and it is unlikely that the previously measured reference curves correspond to exactly the same experimental conditions.

The excess heat capacity curves were calculated employing the Pyris software. For the reference curve (H2) the sample mass was set to zero to choose it as baseline curve inside the software. This experimental procedure has advantages regarding stability of the measurement because of missing sample changes between measurements with sample and reference, respectively. Furthermore, determination of the excess heat capacity removes the influences of the different slopes of glassy and liquid heat capacities outside the glass transition range. This way operator dependent subjective influences as common for the C_p^{red} determination, see below, are excluded when $C_p^{\mathrm{norm}}$is employed for the comparison of model and experimental data. One example, for the cooling rate C1 equal to $q = 5 \cdot 10^{-3}$ K/s, is shown in Fig. 2. After that the excess heat capacity curves were normalized by the step height of the glass transition of PS. The procedure can be expressed by the relation:

$$C_p^{\mathrm{excess}}(T) = C_p^{H1}(T) - C_p^{H2}(T). \quad (1)$$

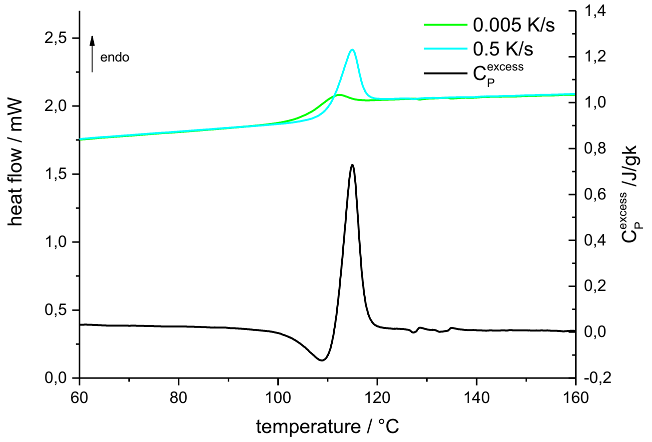

Fig. 2. Example of the treatment of a single experimental data set with described procedure and Eq. (1). The upper two curves correspond to the heat flow from the sample during heating at 0.5 K/s after cooling at 0.5 K/s and 0.005 K/s. The lower curve represents the obtained via Eq. (1) excess heat capacity for heating after cooling at 0.005 K/s.