Molecular interpretation of low-temperature heat capacity of aliphatic oligo-urethane

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ABSTRACT

The low-temperature heat capacity of semi-crystalline aliphatic oligo-urethane obtained from the reaction between butane-1,4-diol and hexamethylene 1,6-diisocyanate was measured using a Quantum Design PPMS (Physical Property Measurement System) in the temperature range of (2.04–292.38) K. The experimental heat capacity data below the glass transition temperature of 280.2 K (7.05 °C) were interpreted in terms of molecular motion and were linked to the vibrational spectrum of oligo-urethane structure. The presented approach applies the classical Einstein, Debye and Tarasov treatments using the ATHAS Scheme. The low-temperature solid heat capacity was estimated by separately approximating the group and skeletal heat capacities from their vibrational spectra. The group vibrational heat capacity was calculated based on the chemical structure and molecular vibrational motions (N_{gr} = 90) derived from infrared and Raman spectroscopy. The skeletal vibrational heat capacity contribution was estimated by a general Tarasov equation with thirty skeletal modes (N_{sk} = 30). The solution of this equation gave the values of characteristic Debye temperatures as: Θ_1 = 493.6 K, Θ_2 = 133.9 K, and Θ_3 = 51.6 K. The result indicates the existence of planer (Θ_2) interactions in the oligo-urethane molecules, in addition to linear (Θ_1) and special (Θ_3) interactions, which are attributed to a possible branched structure mixed with the linear form of the oligomer. The total vibrational heat capacity, being the sum of the group and skeletal heat capacities, was extended to higher temperatures and analysed further.

The liquid heat capacity of semi-crystalline aliphatic oligo-urethane was approximated from experimental data by a linear regression and was compared with the estimated linear contributions of polymers that have the same constituent groups and were expressed as C_p(liquid) = 0.406T + 428.5 in J·K^{-1}·mol^{-1}. The solid and liquid heat capacities of oligo-urethane were applied as equilibrium baselines for advanced thermal analysis of the experimental, apparent heat capacity data.

Using estimated parameters of transitions and solid and liquid heat capacities at equilibrium, the integral thermodynamic functions of enthalpy, entropy and free enthalpy as functions of temperature were calculated.

1. Introduction

Linear oligo-urethanes obtained from aliphatic diisocyanates and diols of low molecular weight with different chemical structures easily crystallize and have good properties for fibre formation. Most linear urethanes are semi-crystalline oligomers or polymers that have a high degree of crystallinity and a high melting temperature [1].

At present, one of the main methods for producing linear oligo-urethanes and polyurethanes is the reaction of diols containing m

—CH$_2$— groups with diisocyanates having n —CH$_2$— groups. On this basis, linear oligo-urethanes (labelled as m,n-OU) are produced [1].

To determine properly the phase content and other thermal properties of OU more quantitatively, the equilibrium solid and liquid heat capacities should be used. The calculation of the solid vibrational heat capacity of molecules is well established in literature [2]. The heat capacity of solid macromolecules using an approximation of the vibrational spectrum is described by the Advanced Thermal Analysis System (ATHAS) [3,4]. This approach is based on the classical Einstein [5], Debye [6] and Tarasov treatments [7]. The general scheme for estimating the vibrational heat capacity C_p (vibrational) of the solid state C_p (solid) of oligomers is presented below and is based on experimental low-temperature data and vibrational spectra of the given oligomer.

Herein, it was assumed that below the glass transition temperature only the contribution to the experimental heat capacity derived from vibrational motion is significant. The experimental low-temperature heat capacity has traditionally been measured by adiabatic calorimetry but has been measured more recently using a relaxation technique on a Physical Property Measurement System (PPMS) in the temperature region of 2 K–300 K [8].

In this approach, the vibrational heat capacity at low temperatures is arbitrarily separated into two independent contributions: one, the low-frequency part, coming from the skeleton; the other, the high-frequency portion, from the group – structure vibrations. The former is approximated by the Tarasov function that describes heat capacities with three characteristic temperatures Θ_1, Θ_2, and Θ_3 [7]. The latter is derived from the known group vibrations inverted to heat capacities using the Einstein function for single frequencies and box-distributions for broader frequency regions [9].

In the initial calculations of the vibrational heat capacity in the solid state, the low-temperature experimental heat capacities at constant pressure $C_p(\exp)$ are converted into heat capacities at constant volume $C_v(\exp)$ using the following equation [4,10,11]:

$$C_p(\exp) - C_v(\exp) = \frac{TV\alpha^2}{\beta} \tag{1}$$

where V is the molar volume, α is the expansibility (also the thermal expansion coefficient), and β represents the compressibility; all parameters are functions of temperature, T [9,10,12]. If the expansibility and compressibility values are not available, then the constant volume heat capacity can be approximated from the expression [9,10,13,14]:

$$C_p(\exp) - C_v(\exp) = 3RA_0 \frac{C_p^2(\exp)}{C_v(\exp)} \frac{T}{T_m^o} \tag{2}$$

where A_o is equal to the constant 0.0039 K·mol·J^{-1}, T is the temperature in Kelvin, T_m° is the equilibrium melting temperature, and R is the gas constant.

According to the assumption that heat capacity at constant volume $C_v(\exp)$ contains only vibrational contributions below the glass transition temperature, it is separated into the group $C_v(\text{gr})$ and skeletal $C_v(\text{sk})$ vibration heat capacities [10]:

$$C_v(\exp) = C_v(\text{gr}) + C_v(\text{sk}) \tag{3}$$

where $C_v(\text{gr})$ is described as a sum of normal modes having a single frequency Einstein mode, $C_v(\text{Einstein})$, which can be written as [4,9,12,15]:

$$\frac{C_v(\text{Einstein})}{N_E R} = \sum_i E\left(\frac{\Theta_{Ei}}{T}\right) = \sum_i \frac{(\Theta_{Ei}/T)^2 \exp(\Theta_E/T)}{[\exp(\Theta_{Ei}/T) - 1]^2} \tag{4}$$

In Eq (4), N_E is number of the Einstein vibrations, $\Theta_{Ei} = h\nu/k$, represents the Einstein frequencies in Kelvin, and h and k are the Planck and Boltzmann constants, respectively (note that 1.0 Hz = 4.799 × 10^{-11} K, and 1.0 cm^{-1} = 1.4388 K) and a box-like distribution, $C_v(\text{box})$, calculated by the following equation [2,4,9,10]:

$$\frac{C_v(\text{box})}{N_{\text{box}} R} = B\left(\frac{\Theta_U}{T}, \frac{\Theta}{T}\right) = \frac{\Theta_U}{\Theta_U - \Theta_L}\left[D_1\left(\frac{\Theta_U}{T}\right) - \left(\frac{\Theta_L}{\Theta_U}\right)D_1\left(\frac{\Theta_U}{T}\right)\right] \tag{5}$$

where N_{box} is the number of vibrational modes for the frequency distribution, R is the gas constant, B can be called the box function, T is the temperature in Kelvin, D_1 is a one-dimensional Debye function, and Θ_U, Θ_L are the upper and lower frequencies, respectively.

The vibrational spectrum of a solid oligomer of 4,6 OU consists of $3N$ vibrational degrees of freedom where N represents the total number of atoms in the repeating unit. These vibrations are separated into group (N_{gr}) and skeletal (N_{sk}) vibrations and are expressed by the sum: $3N = N_{\text{gr}} + N_{sk}$. The types and numbers of group vibrations are generated based on infrared and Raman spectroscopy using normal modes established in the literature [3,10,16]. The skeletal vibrations are described as the remaining part of the total numbers of vibrators and are used for fitting the experimental heat capacity data to a Tarasov function [4]. In consequence, after subtracting the group vibrations from $C_v(\exp)$, the skeletal, experimental heat capacity, $C_v(\text{sk})$, is fitted in the low temperature region to the general Tarasov equation, $T(\Theta_i/T)$ [4,7]:

$$\begin{aligned}\frac{C_v(\text{sk})}{NR} &= T\left(\frac{\Theta_1}{T}, \frac{\Theta_2}{T}, \frac{\Theta_3}{T}\right) \\ &= D_1\left(\frac{\Theta_1}{T}\right) - \left(\frac{\Theta_2}{\Theta_1}\right)\left[D_1\left(\frac{\Theta_2}{T}\right) - D_2\left(\frac{\Theta_2}{T}\right)\right] \\ &\quad - \left(\frac{\Theta_3^2}{\Theta_1\Theta_2}\right)\left[D_2\left(\frac{\Theta_3}{T}\right) - D_3\left(\frac{\Theta_3}{T}\right)\right]\end{aligned} \tag{6}$$

The results from this fitting give three characteristic Debye temperatures: Θ_1, Θ_2 and Θ_3. These parameters represent the maximum frequencies corresponding to skeletal distributions in Kelvin ($\Theta = h\nu/k$) [4,10,14]. The functions D_1, D_2, D_3 in Eq. (6) correspond to the one-, two-, and three-dimensional Debye functions, given as [4,9,10]:

$$\frac{C_v}{NR} = D_i\left(\frac{\Theta i}{T}\right) = i\left(\frac{T}{\Theta_1}\right)^i \int_0^{\Theta_{i/T}} \frac{\left(\frac{\Theta}{T}\right)^{i+1}\exp\left(\frac{\Theta}{T}\right)}{\left[\exp\left(\frac{\Theta}{T}\right) - 1\right]^2} d\left(\frac{\Theta}{T}\right), \tag{7}$$

in which i = 1, 2 and 3, N is the number of the vibrators and, R is the gas constant.

The best fit of the experimental, skeletal heat capacity was obtained by minimizing the chi-square function χ^2 (a weighted sum of squares) according to the following expression [9,10]:

$$\chi^2 = \sum_i \left[\frac{C_v^{\exp}(\text{sk})(T_i) - C_v^{\text{calc}}(\text{sk})(T_i, \Theta_3, \Theta_2, \Theta_1)}{\sigma_i}\right]^2 \tag{8}$$

where σ_i is the standard deviation of the experimental values taken at the temperatures of T_i, and $C_v^{\exp}(\text{sk})$ and $C_v^{\text{calc}}(\text{sk})$ are the experimental and calculated skeletal heat capacities, respectively.

The total heat capacity at constant volume $C_v(\text{total})$ can be calculated as the sum of the skeletal heat capacities (obtained using three characteristic temperatures Θ_1, Θ_2, and Θ_3) and the group heat capacities. Next, the $C_v(\text{total})$ is converted to a calculated heat capacity at constant pressure, $C_p(\text{vibrational})$, using Eq. (2). All computations were performed in the Mathematica 3.0™ programming language [4,17].

In this paper, the aliphatic oligo-urethane was obtained by oligomerization of hexamethylene 1,6-diisocyanate and butane-1,4-diol (4,6-OU) [18–20].

Thermal properties such as phase transition parameters and heat capacity were measured. The low temperature experimental heat capacity of 4,6-OU obtained with a PPMS was interpreted in terms of molecular vibrational motions. Solid, vibrational heat capacities together with liquid heat capacities and phase transitions parameters in the equilibrium state were used to establish the integral thermodynamic functions such as enthalpy (H), entropy (S), and free enthalpy (Gibbs function) (G) over the entire temperature range of (0–1000) K.