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Glass-forming ability of butanediol isomers

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Abstract In this study, the thermal behavior of butanediol isomers is investigated for temperatures ranging from 103 to 303 K using differential scanning calorimetry, complemented, when necessary, by polarized light thermal microscopy. The butanediol isomers display quite different thermal behaviors: for 1,2- and 1,3-isomers, glass transition is the only thermal event observed; for 1,4-butanediol, crystallization occurs on cooling even at a high scanning rate and no glass formation was detected; and for the 2,3-isomer, glass or crystal formation is dependent on the experimental conditions employed. The glass-forming ability of the isomers is correlated with data available on their molecular symmetry.

Keywords Butanediols · Thermal behavior · Glass-forming ability · Differential scanning calorimetry (DSC)

Introduction

Butanediols make up an interesting class of compounds from the structural point of view. They are constituted by both polar and nonpolar groups and, as isomers, the relative position of the OH groups is different, giving rise to a great diversity of inter- and intramolecular interactions, namely hydrogen bonds. Having a flexible backbone, these molecules can also adopt many conformations characterized by different OH groups' orientations. All of these structural features are expected to determine their structure in the different states of matter and, consequently, their thermal behavior.

Besides the importance that results from butanediol molecular features, these are compounds widely used in industry, for instance, as intermediates in the production of polyurethanes [1]. Aqueous solutions of butanediols are also employed in cryopreservation processes [2–8], and several studies exist on the thermal behavior of those diol–water mixtures [6–8] in the pursuit of the best glass-forming ability on cooling and higher stability of the amorphous state.

In this study, the thermal behavior of (±)-1,2-butanediol (1,2-BD), (±)-1,3-butanediol (1,3-BD), (*R*)-1,3-butanediol (*R*-1,3-BD), (*S*,*S*)-2,3-butanediol (2,3-BD), and 1,4-butanediol (1,4-BD) is studied from 103 to 303 K, by differential scanning calorimetry (DSC), complemented, when necessary, by polarized light thermal microscopy (PLTM). As far as we know, no systematic study on the thermal behavior of pure butanediols is available. This is expected to be an important contribution to the characterization of their condensed state structure.

Experimental

Butanediols used in this study were purchased from Aldrich Company and were the best quality available, corresponding to a mass fraction better than 0.99 for all substances, except (*R*)-1,3-butanediol for which $\times > 0.98$. This compound was purified by sublimation using a cold finger technique. Purity was checked by gas–liquid chromatography using a polar

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column [DB-wax poly(ethyleneglycol)] and a nonpolar one (OV-1 poly(dimethylsiloxane)). Values in the range $0.991 \leq \times \leq 0.998$ were found for the mass fraction. The samples were kept in a desiccator over P_2O_5 and manipulated in a dry nitrogen box.

Measurements were carried out in the temperature range between T = 103 and 303 K using a Perkin-Elmer Pyris 1 power compensation calorimeter. A liquid nitrogen Cryofill cooling unit was used, and helium at a 20 mL/min flux was employed as the purge gas. Perkin-Elmer 40-μL aluminum pans suitable for volatile substances were used, being the reference an empty pan. Cooling/heating cycles were performed in the temperature range of interest, at 1, 10, and 25 K/min scanning rates. For 1,4-butanediol, cooling experiments at higher scanning rate were also carried out.

Temperature calibration was performed using benzophenone, $T_{\mathrm{fus}} = 321.20$ K [9] cyclohexane, $T_{\mathrm{fus}} = (279.81 \pm 0.04)$ K, $T_{\mathrm{trs}} = (186.22 \pm 0.02)$ K [10] and cyclopentane, $T_{\mathrm{trs}} = (138.06 \pm 0.05)$ K; $T_{\mathrm{fus}} = (179.72 \pm 0.05)$ K [10]. Cyclohexane $\Delta_{\mathrm{trs}}H = (6713 \pm 74)\ \mathrm{J{\cdot}mol^{-1}}$ was used for enthalpy calibration [10].

The 1,4-butanediol isomer was also studied by PLTM between 233 and 303 K at a 10 K/min scanning rate. PLTM experiments were carried out using a Linkam system DSC600 with a Leica DMRB microscope, and a Sony CCD-IRIS/RGB video camera. The images were obtained by combined use of polarized light and wave compensators, using a 200× magnification. Image analysis was performed with a Linkam system software with Real Time Video Measurement System.

Results

All the butanediol isomers abridged in this study are liquids at 303 K, the starting temperature in our experiments. Therefore, the thermal study always began by cooling runs. In the analysis of results that follows, the compounds were gathered together accordingly to the resemblance of their thermal behavior.

1,2- and 1,3-butanediols

For the (±)-1,2-butanediol, (±)-1,3-butanediol, and (*R*)-1,3-butanediol isomers, a similar thermal behavior has been observed: glass transition occurs on cooling, and in the subsequent heating runs, devitrification is the only event registered. This behavior has been obtained for all the scanning rates employed. Typical cooling and heating DSC curves are exemplified in Fig. 1 for the 1,2-isomer, and in Table 1, the glass transition temperatures, measured in the heating runs at 10 K/min, are presented. For 1,3-butanediol, a value of $T_g = 173$ K, determined by quasi-elastic light scattering experiments, is reported by Drake et al. [11], which is close to the value obtained in this study.

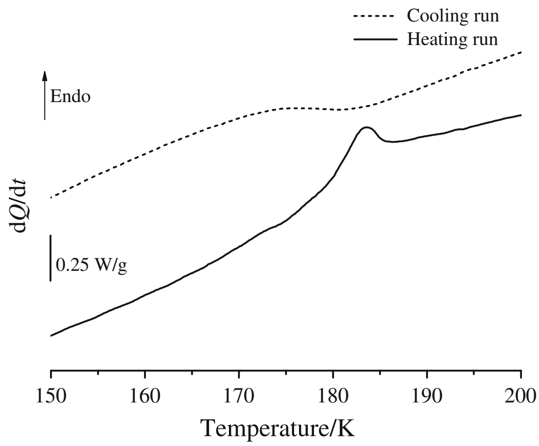

Fig. 1 Typical cooling and heating runs for (±)-1,2-butanediol at a scanning rate of 10 K/min

The nucleation process that gives rise to crystallization depends on various factors [12] and is critically dependent on temperature. On the one hand, an appropriate degree of supercooling is needed. On the other hand, at low temperature, a sharp viscosity increase occurs resulting in restricted molecular motion which may prevent the formation of ordered crystal structures. Tamman [13] has suggested that the maximum crystallization rate from melts is achieved at

$$T = T_{\mathrm{fus}} - \left|\Delta_{\mathrm{crys}}H/C_{\mathrm{p}}\right| \tag{1}$$

$\Delta_{\mathrm{crys}}H$ is the crystallization enthalpy and C_{p} is the melt heat capacity. Also, the following relationship between T_{fus} and T_{g} has been reported for many substances [14–17]

$$T_{\mathrm{fus}} = 3/2\,T_{\mathrm{g}} \tag{2}$$

In order to try to crystallize the 1,2- and 1,3-butanediols, annealing experiments were then performed at different temperatures (T = 210 K and T = 233 K) for periods of time up to 2 h. The annealing temperature values were chosen using Eq. 1 together with Eq. 2 as a guideline. $\Delta_{\mathrm{crys}}H$ was estimated as the value obtained for $-\Delta_{\mathrm{fus}}H$ for the 2,3-isomer (see Table 1), and for C_{p}, at the calculated melting temperature, the result from a group contribution method [18] was used ($C_{\mathrm{p}} \sim 195\ \mathrm{J\ mol^{-1}\ K^{-1}}$). However, no crystallization took place in any of the experiments performed.

(*S*,*S*)-2,3-butanediol

The thermal behavior observed for (*S*,*S*)-2,3-isomer depends on the experimental conditions employed: at the higher scanning rates, glass transition is the only observed transformation upon cooling; while at the lower cooling rates,

Table 1 Thermodynamic parameters for butanediol isomer phase transitions, studied between 103 and 303 K, at a 10 K/min heating rate

Isomer	T_g/K	T_{fus}/K	$\Delta_{fus}H$/(kJ mol^{-1})
(±)-1,2-butanediol	178.9 ± 0.4 (*n* = 5)	–	–
(±)-1,3-butanediol	175.6 ± 0.5 (*n* = 5)	–	–
(*R*)-1,3-butanediol	175.4 ± 0.5 (*n* = 5)	–	–
(*S*,*S*)-2,3-butanediol	195.1 ± 0.4 (*n* = 6)	291.3 ± 0.2 (*n* = 6)	11.6 ± 0.2 (*n* = 6)
1,4-butanediol	–	292.6 ± 0.2 (*n* = 6)	18.1 ± 0.8 (*n* = 6)
		289 ± 1 (*n* = 4)	17 ± 1 (*n* = 4)

n-number of samples analyzed

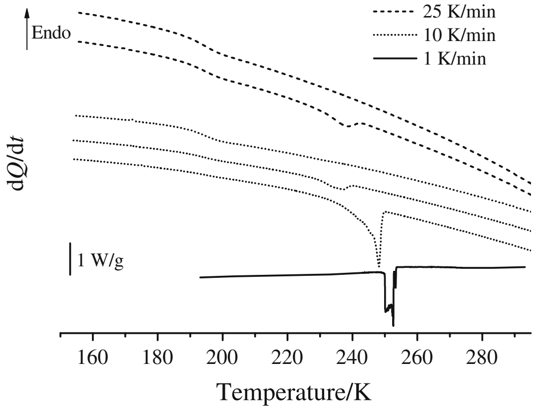

Fig. 2 Typical cooling runs for (*S*,*S*)-2,3-butanediol

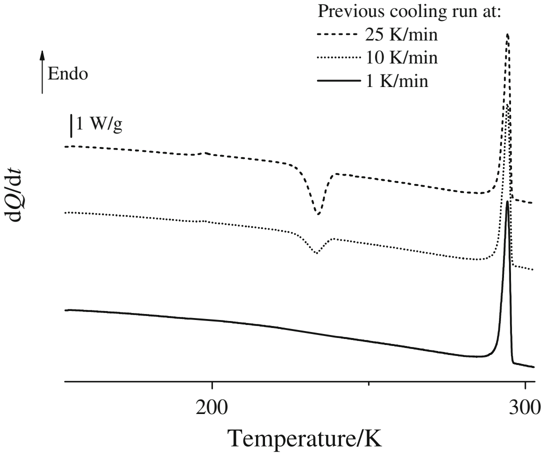

Fig. 3 (*S*,*S*)-2,3-butanediol typical heating curves, obtained at 10 K/min. The curves presented were preceded by cooling runs at different scanning rates

partial or complete crystallization takes place. Devitrification, cold crystallization, and fusion are the transitions undergone upon heating, depending on the preceding cooling run. The melting process gives rise to a simple curve.

Figures 2 and 3 exemplify these findings in the cooling and heating runs, respectively. Glass transition temperature and the thermodynamic parameters for fusion are presented in Table 1.

1,4-butanediol

The 1,4-isomer exhibits quite a different behavior. Indeed, no glass formation could be detected even at the maximum cooling rate achieved by the equipment (nominal 500 K/min), and fusion is the only transition observed in the heating scans. Figures 4 and 5 are examples of DSC curves obtained. The melting temperature and enthalpy are presented in Table 1. Using a cooling rate of 10 K/min, two different patterns were observed in the crystallization process: in the first, the solidification takes place at a temperature between 273 and 283 K; while in the second one, it occurs in the range 243–263 K (see Fig. 4). The heating curves following each of the crystallization paths are displayed in Fig. 5. The melting process following the second crystallization pattern, lower scan in Fig. 5, gives rise to a composite curve, with a low onset temperature (T_{fus} = 289 K), suggesting the presence of more than one solid phase. The analysis of these experimental DSC curves was performed using a peak-fit program, Origin, 2002 [19]. The best goodness-of-fit was achieved by using two double asymmetric sigmoidal curves [20]. The result obtained is illustrated in Fig. 6, and suggests the presence of two distinct solid forms, one melting at T_{fus} ~289 K and the other one at T_{fus} ~292 K.

The PLTM study carried out on 1,4-butanediol confirms the formation of two distinct forms. Typical PLTM results are summarized in Fig. 7. In the experiments performed, crystallization took place between 253 and 263 K, and the solid phase obtained goes through well visible modifications in the heating run. The fusion process is clearly apparent at 290 K.

Discussion

As shown above, the butanediol isomers display quite a different thermal behavior. For 1,2- and 1,3-butanediol, no crystal formation occurred neither on the cooling nor on the heating runs. The 1,4-isomer crystallizes readily on cooling even at a high scanning rate. The 2,3-isomer crystallizes on

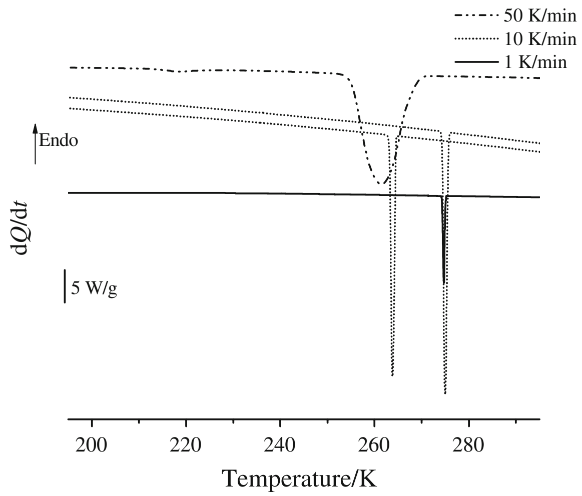

Fig. 4 Typical cooling runs for 1,4-butanediol

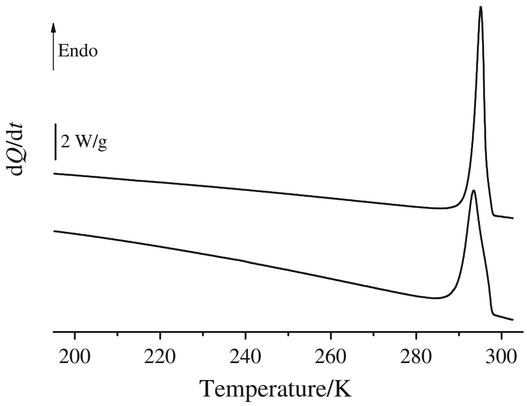

Fig. 5 1,4-butanediol typical heating curves, scanning rate 10 K/min

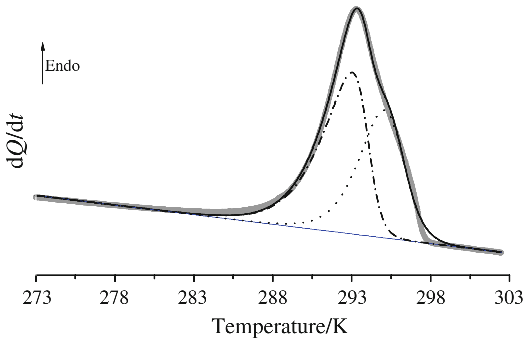

Fig. 6 Component curves obtained by a peak-fitting analysis (correlation factor = 0.9986) of a 1,4-butanediol fusion curve (m = 2.05 mg, heating rate = 10 K/min)

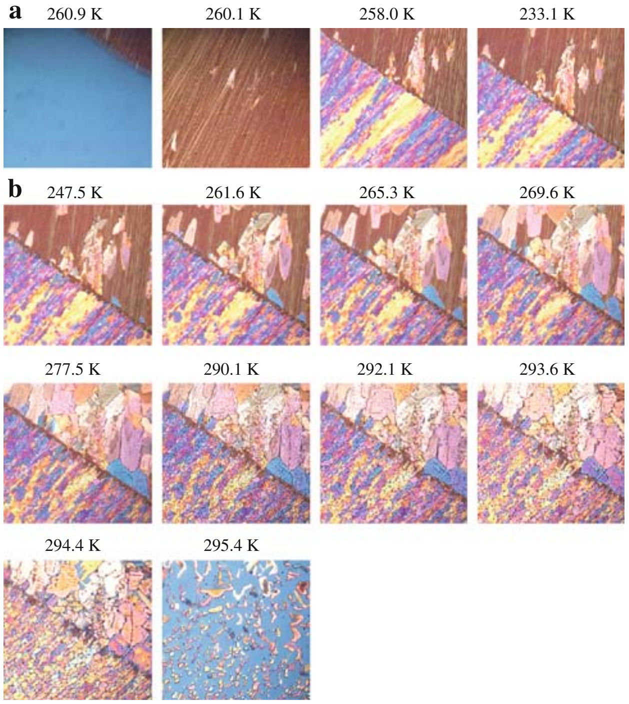

Fig. 7 **a** PLTM images of the crystallization of 1,4-butanediol, cooling run, **b** PLTM images for the heating process following (**a**)

the cooling or on the heating runs depending on the scanning rate employed. The glass-forming ability of butanediols increases in the order 1,4-BD < 2,3-BD < 1,3-BD ~ *R*-1,3-BD ~ 1,2-BD. Although no systematic study on the thermal behavior of butanediols could be found on the literature, some work exists on the lower diol family members, namely, ethyleneglycol and the propanediols, all of them showing quite different thermal behaviors. For example, ethyleneglycol [21–24] and 1,3-propanediol [21, 25] crystallize readily on cooling, while for (±)-1,2-propanediol [23, 26, 27] and 2-methyl-1,3-propanediol [25], crystallization was not found to occur.

Vaporization enthalpies are related to the intermolecular forces in the liquid state, although a contribution due to conformational changes is also included. We could expect a correlation between vaporization enthalpy values and the glass-forming ability. For the compounds abridged in this study, the vaporization enthalpies at $T = 298$ K increase in the following order: 2,3-BD < 1,3-BD ~ *R*-1,3-BD ~ 1,2-BD < 1,4-BD [28]. On the contrary, the strength of the hydrogen bonds in the pure liquid, as measured by the shift in the OH stretching vibration relatively to that of free OH, is similar for the vicinal diols and higher for 1,3-BD and 1,4-BD [29]. These results do not point a reasonable rationalization for the different thermal behaviors observed for the isomers.

Tanaka [30, 31] supports that the glass-forming ability of a liquid depends on the development of short-range ordered structures with symmetry that is incompatible with that of the crystal. The existence of such local ordered structures will increase the interfacial tension between the supercooled liquid and the crystal and decrease the free-energy difference between them [30], factors that contribute to the decrease of nucleation rate [12, 32]. On the grounds of these assumption, it is expected that the butanediol isomers having higher symmetry will have a lower number of favorable orientations for intermolecular interactions in the liquid, thus, reducing the possibility of generating clusters with a symmetry different from that of the crystal and, consequently, having a lower glass-forming ability. The conformational space of the butanediol isomers has also been studied in our research group. Concerning (*R*)-1,2-BD [33] and (*R*)-1,3-BD [34], all possible local minima (81 for each compound) have C_1 symmetry. For (*S*,*S*)-2,3-BD [35] 14 true minima were found, 8 of them belonging to the C_1 symmetry point group and 6 to the C_2 group. The existence of an intramolecular hydrogen bond is only possible in some C_1 symmetry conformers, and it is expected that their contribution to the conformational distribution in the liquid phase will be less significant than in the gas phase. Regarding the 1,4-BD [36], 65 structures correspond to true minima, with symmetry C_1 (48 conformers), C_i (4 conformers), C_2 (12 conformers), and C_{2h} (the all-*trans*-conformer). The three most stable conformers in the gas phase (C_1 symmetry, 41% of the total population) have a folded backbone conformation, giving rise to an intramolecular hydrogen bond interaction and, as for the 2,3-isomer, their contribution in the liquid is anticipated to be diminished and that of the all-*trans*-conformer to be increased. In fact, the comparison of infrared spectra of butanediols solutions in carbon tetrachloride with those of the pure liquids gives evidence that intramolecular hydrogen bonds are absent, or have a residual contribution in the pure liquid state [29].

Taking into account the theoretical data available for the butanediol isomers, we will expect the 1,4- and the 2,3-isomers to be more easily crystallized and 1,2- and 1,3-butanediol to be better glass formers. From our experimental results on the thermal behavior of butanediol isomers, this is actually observed for the studied compounds.

Conclusions

Butanediol isomers were studied by DSC between $T = 103$ and 303 K, and quite different thermal behaviors were observed.

For the (±)-1,2- and (±)-1,3-and (*R*)-1,3-butanediols, no crystal formation was detected in any of the studied conditions. At a scanning rate of 10 K/min, the former presents a glass transition at 178.9 K and for the 1,3-BD and the (*R*)-1,3-enantiomer, the glass transition occurs at $\sim$175.6 K. For the 1,4-isomer, no glass phase could be produced. Two crystalline phases were identified for this compound with melting temperatures equal to 289 and 292.6 K. For (*S*,*S*)-2,3-butanediol, total or partial vitrification occurs, depending on the cooling rate. Devitrification, $T_g = 195.1$ K, cold crystallization and fusion, or just the last transition, were observed on the heating runs, depending on the experimental conditions employed. A simple melting curve was obtained with $T_{fus} = 291.3$ K.

A relationship between the glass-forming ability and the molecular symmetry of the butanediol isomers can be established.

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