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Crystal melting processes of propylene carbonate and 1,3-propanediol investigated by the reed-vibration mechanical spectroscopy for liquids*

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The melting of crystals is one of the most common and general phase transition phenomena. However, the mechanism of crystal melting is not well understood, and more experimental measurements and explorations are still needed. The mechanical spectra of propylene carbonate and 1,3-propanediol during the crystal melting processes are measured by the reed vibration mechanical spectroscopy for liquids (RMS-L) for the first time. The experimental results show that as the temperature increases, the real part of the complex Young modulus first decreases slowly, and then quickly drops to zero; meanwhile, its imaginary part increases slowly at first, then goes up and drops quickly to zero, showing a peak of internal friction. Preliminary analyses indicate that both the real and imaginary parts can present some characteristics of the melting process, such as the transition from the disconnected liquid regions to the connected liquid regions, that from the connected crystal regions to the disconnected crystal regions, and so on. In addition, the results show that the melting rate per unit volume of crystalline phase versus temperature satisfies the Arrhenius relation at the initial stage of melting, and deviates from this relation as the temperature increases to a certain value. Therefore, the RMS-L will provide an effective supplement for the further study of melting.

Keywords: crystal melting, mechanical spectroscopy, complex Young modulus, percolation

PACS: 64.70.dj, 62.90.+k, 62.40.+I, 64.70.–p **DOI:** 10.1088/1674-1056/ab327d

1. Introduction

The melting of crystals is one of the most common and general phase transition phenomena, which has been studied for more than 100 years and new research is continuing.[1–11] It has been observed that not only the melting of bulk crystals occurs at the melting point,[6,9–11] but also the pre-melting at crystal surfaces,[2,10,12] grain boundaries,[3,7,8,13] dislocations, etc.[6,7,10] takes place below the melting point. Various theories describing the melting process[6,9,10,14] have been established from different aspects. For example, Lindemann[6,9,11] proposed that melting is caused by vibrational instability in the crystal lattice when the root-mean-square displacement of the atoms reaches a critical fraction of distance between them, i.e., Lindemann criterion; Pluis *et al.*[15] used the semi-empirical Landau model describing the surface induced melting; Mishin *et al.*[5] employed phase field model to express the grain boundary pre-melting behavior in alloys; Burakovsky *et al.*[16] presented the crystal melting as a dislocation-mediated phase transition, and so on.[7,17–22] It could be seen that the understandings of crystal melting among the above theories are inconsistent with each other, and many aspects of melting are to be understood and the intrinsic mechanism of melting in solids is still a mystery.[6,9,10] Therefore, more experimental explorations of crystal melting are still needed.[6,23]

The method of reed-vibration mechanical spectroscopy for liquids (RMS-L) has high sensitivity and can detect the information of complex Young modulus in real time and effectively give the change characteristics of crystallization,[24] crack-healing,[25,26] glass transition,[27] and so on.[28] Because the melting is an inverse process of crystallization, it is feasible to apply the RMS-L method to study the melting of crystals. In this paper, the melting of propylene carbonate (PC) and 1,3-propanediol (PD) crystals is studied by RMS-L method for the first time.

2. Experimental section

The main experimental equipment is the PJ-II RMS-L, the patent of which is owned by Nanjing University. And it can give the complex Young modulus $Y^* = Y' + \mathrm{i}Y''$ of sample versus temperature T or time t, where Y' is the real part which is generally called as the Young modulus, Y'' is the imaginary part which is related to systemic friction behavior, and i is the imaginary unit. The measurement principle of RMS-L and experimental procedure are detailed in Ref. [24]. In the ex-

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periment, the substrate used is the single crystal silicon with a size of 40 mm×4 mm×0.4 mm, the fundamental resonant frequency is about 2000 Hz, and the frequency variation of the system is about 20 Hz with the addition of samples. The sample chamber is kept in the vacuum environment (about 10^{-3} torr).

The samples are PC and PD, which are typical glass materials, and are difficult to crystallize during cooling from liquids and crystallize only when undergoing certain low temperature conditions. Therefore, the crystals of both PC and PD are prepared on cooling first and then heating. The melting processes of the crystals are investigated in heating with the rate $\dot{T}$ of about 1 K/min.

Because the main interest in this paper is the relative changes of Y^* during the melting of crystals, the reduced complex Young modulus

$$y^* = \frac{Y^*}{Y'|_{T_r}} = y' + \mathrm{i}y'' \tag{1}$$

is used in this paper, where $Y'|_{T_r}$ is Y' of the sample at the chosen reference temperature T_r, and $y' \equiv Y'/Y'|_{T_r}$ and $y'' \equiv Y''/Y'|_{T_r}$ are the real and imaginary parts of y^*, respectively.

3. Results and discussion

Figure 1 shows y' and y'' of PC and PD crystals versus T in the melting range, and the values of T_r are 212.5 K for PC and 224.5 K for PD. The experimental results show that with the increase of T, y' decreases slowly first, and then quickly drops to zero near the crystal melting point T_m;[29,30] at the same time, y'' increases slowly at first, then goes up and drops quickly to zero below T_m, i.e., a peak of internal friction appears. The temperatures T_s of y' and y'' reaching zero as shown in Fig. 1 are 220.9 K for PC and 241.8 K for PD, respectively.

The y' is composed of the bulk modulus and shear modulus. The bulk modulus of crystal and liquid has little change before and after the phase transition, so the changes of y' mainly come from the shear modulus. In the experiment with the pressure of 10^{-3} torr, the melting of crystal is the first-order phase transition. According to Landau theory of the first-order phase transition, the shear modulus will show a step-type variation at the phase transition point; specifically, the shear modulus of crystal phase is almost independent of T, and the one of liquid phase will nearly equal zero comparing to that of crystal phase when the measurement frequency is about 2000 Hz. In the initial stage of melting, because the volume fraction v of liquid phase is smaller, it could be expected that y' decreases as v increases, that is,

$$v \approx 1 - y'. \tag{2}$$

If the liquid phases are randomly distributed in space during melting, according to the percolation theory,[31–33] it could be known that a few liquid regions connected in the whole sample will form when $v \approx 0.3$, while the connected regions of crystal will disappear when $v \approx 0.7$. Therefore, with the change of v, the samples will undergo three states during melting: the crystal regions are connected (the liquid regions are disconnected), both the liquid and crystal regions are connected, and the liquid regions are connected (the crystal regions are disconnected); the corresponding ranges of v are approximately $v < 0.3$, $0.3 \leqslant v \leqslant 0.7$, and $v > 0.7$ in turn (in the experiments, melting generally starts from the defects of crystal, so the corresponding v values of the three states may deviate from the above). When $v > 0.7$, due to the disconnection of crystal regions in the whole sample and the fact that the y' of the sample will be close to that of liquid, $v \approx 0.7$ at T_s in Fig. 1.

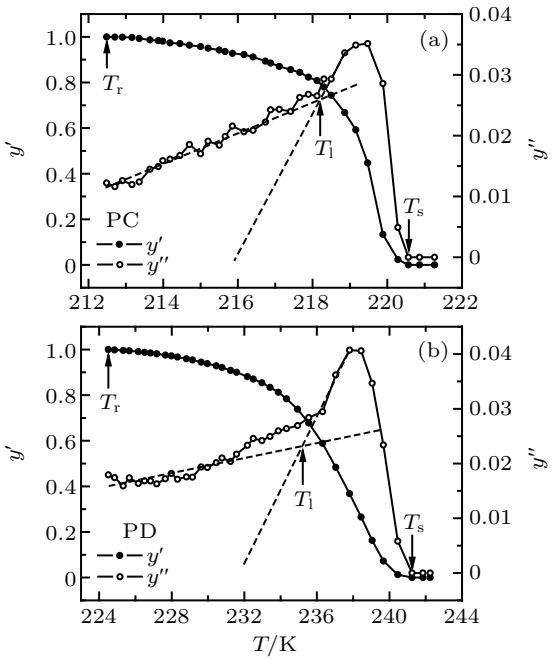


Fig. 1. On heating, y' and y'' versus T of (a) PC and (b) PD in the melting range.

The y'' reflects the energy loss of the sample. The change of y'' in Fig. 1 can be explained as follows.

(I) For $T \geqslant T_s$, the sample is in the state of the liquid regions connected and the external force directly drives the liquid. However, the shear modulus of the liquid is small for the frequency is about 2000 Hz, difficult to drive the movement of the sold–liquid interfaces (i.e., the interfaces between the crystal and the liquid regions), so the value of y'' is very small and close to that of the liquid, which also states that at T_s, $v \approx 0.7$.

(II) At the initial stage of melting (about $v < 0.3$), the sample is in the state of the connected crystal regions (the liquid regions are disconnected), the external force directly acts on the crystal and drives the viscous motion of the sold–liquid

interfaces and the thermal activation motion of defects in the crystal phase,[34,35] showing a large y''. With the increase of v, the area of the sold–liquid interfaces increases gradually, causing y'' to go up. When $v \approx 0.3$, the sample transforms from the state of the connected crystal regions (the liquid regions are disconnected) to that of the connected liquid and crystal regions, and the tendency of increasing y'' should present a turn. The corresponding temperatures T_l are 218.2 K for PC and 235.2 K for PD as shown in Fig. 1. In fact, $y' \approx 0.7$ at T_l, so it can be obtained that $v \approx 0.3$ according to Eq. (2).

(III) When both the liquid and crystal regions in the sample are connected (about $0.3 \leqslant v \leqslant 0.7$), with the proceeding of the melting, the area of the sold–liquid interfaces goes up first, causing the increase of y'', and then reduces, resulting in the decrease of y'', i.e., y'' presents a peak (Fig. 1). It could be imagined that y'' has the greatest value when the area of the sold–liquid interfaces is the largest. Since the area of the sold–liquid interfaces between the liquid and crystal regions would reach the largest value for $v \approx 0.5$, the authors speculate that the maximum of y'' in Fig. 1 corresponds to the value of $v \approx 0.5$.

In order to further analyze the dynamics characters of crystal melting, the change rate R of y' is defined as

$$R \equiv -\frac{\mathrm{d}y'}{\mathrm{d}t} = -\dot{T}\frac{\mathrm{d}y'}{\mathrm{d}T}. \tag{3}$$

The results of R are shown in the insets of Fig. 2, and the change of R is very similar to that of y''. Moreover, the temperatures corresponding to the maximum values of R and y'' are almost the same, which indicates that the change of y' and y'' may come from the same mechanism.

In addition, the melting rate per unit volume of crystalline phase is

$$r \equiv -\frac{1}{1-v}\frac{\mathrm{d}(1-v)}{\mathrm{d}t}. \tag{4}$$

In the initial stage of melting, based on Eq. (2), r can be expressed as

$$r \approx -\frac{1}{y'}\frac{\mathrm{d}y'}{\mathrm{d}t} = -\frac{\dot{T}}{y'}\frac{\mathrm{d}y'}{\mathrm{d}T}. \tag{5}$$

The r value versus T of PC and PD is shown in Fig. 2. It is easy to see that in the low temperature range, the relation between $\ln r$ and T^{-1} is linear, i.e., r versus T satisfies the Arrhenius relation. However, when the temperature increases to a certain temperature (T_d, 217.9 K for PC and 233.4 K for PD) as shown in Fig. 2, $\ln r$ obviously deviates from the linear behavior. The value of T_d is very close to that of T_l, which further shows that the changes of y' and y'' may come from the same mechanism, i.e., the change from the connected crystal regions (the liquid regions are disconnected) to the connected liquid and crystal regions.

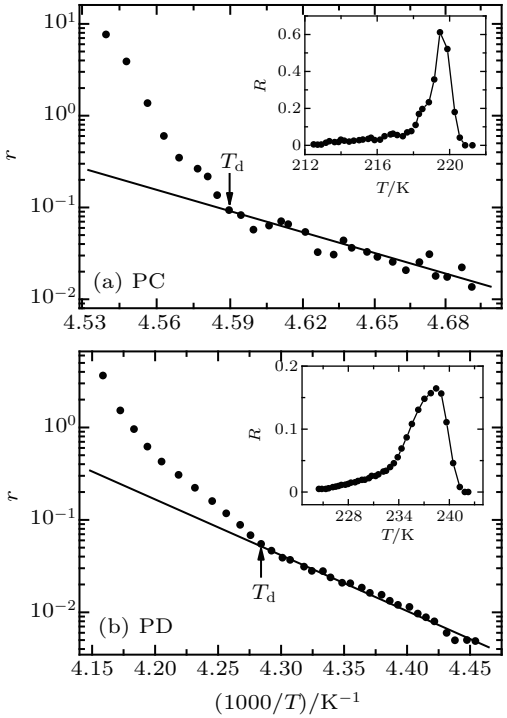


Fig. 2. The r of (a) PC and (b) PD versus T^{-1}. The insets show R versus T in the melting range.

4. Conclusion

In this paper, the melting processes of PC and PD crystals are measured by RMS-L for the first time. The experimental results show that with the increase of T, y' decreases slowly first, and then quickly drops to zero near T_m; meanwhile, y'' increases slowly at first, then goes up and drops quickly to zero below T_m, i.e., a peak of internal friction appears. Preliminary analysis shows that the experimental results of both y' and y'' can present some characteristics of the melting process, such as the temperatures of $v \approx 0.3$, 0.5, and 0.7. The results also show that r versus T satisfies the Arrhenius relation at the initial stage of melting and deviates from this relation when the temperature goes up to a certain value. The researches here will provide an effective supplement for the deep study and understanding of melting.

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