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Effect of chemical structure of amorphous polymers on heat capacity difference at glass transition temperature[1]

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Abstract

The heat capacity of 21 kinds of glassy polymers, mainly synthesized in our laboratory, was measured by differential scanning calorimetry. Glass transition temperature (T_g) and the heat capacity difference between the molten state and the glassy state (ΔC_p) at T_g were evaluated. A linear relationship was obtained between ΔC_p and T_g for almost all glassy polymers including engineering plastics, in a temperature range from 230 to 520 K, except for those having large side chains and/or inter-molecular hydrogen bondings. It was suggested that configurational entropic factors must be taken into consideration for analyzing glass transition.

Keywords: Amorphous polymer; Glass transition temperature; Heat capacity

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1. Introduction

It is known that glassy polymers are in a non-equilibrium thermodynamic state and have various enthalpy levels, especially when molten polymers are frozen to the glassy state in different conditions [1]. Recently, it was reported that the rate of enthalpy relaxation of a new type of glassy polymer, having rigid phenyl groups in the main chain, is higher than that of ordinary glassy polymers [2,3]. This indicates that the glass transition behavior of the polymers is difficult to explain only by iso-free volume theory.

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Wunderlich summarized all of the reported values of glass transition temperature (T_g) values and heat capacity data in 1960 and suggested that heat capacity difference at T_g (ΔC_p) is the same for all polymers regardless of chemical structure [4]. He went on to explain that the fundamental units of molecular chains contain the same amount of free volume of polymers at T_g. Ichihara recalculated the relationship between T_g and ΔC_p using almost the same reported data as Wunderlich utilized and from his results concluded that ΔC_p decreased with increasing T_g [5].

The above inconsistency leads to us various difficulties, such as the molecular design of engineering plastics and also estimation of functionality of polymers. It is also necessary to know the T_g–ΔC_p relationship when the solidification of polymers is investigated. In the above studies [4,5], the original data of T_g and C_p were extracted from the reported values which were measured by many researchers using various apparatus.

During the last 20 years, we have investigated the glass transition phenomena of various types of polymers using thermo-analytical methods and accumulated T_g and C_p values of amorphous polymers and related model compounds which were mostly prepared in our laboratory. In this study, we summarize T_g and the heat capacity data around the glass transition for a variety of glassy polymers using the same measurement procedure.

2. Experimental

2.1. Sample

Table 1 shows the sample used in this study. The preparation method and references are given in Table 1.

2.2. Measurements

Heat capacity measurements were carried out using a Perkin Elmer differential scanning calorimeter DSC II. The sample was heated to a temperature 30 K higher than T_g, quenched to a temperature 50 K lower than T_g and then measured at 10 K min^{-1}. Sample weight was 5–6 mg. T_g was defined according to the previous report [16].

The measurement procedure of the heat capacity of polymers was reported previously [17,18]. T_g and ΔC_p defined in this study are shown in the schematic DSC curve (Fig. 1).

3. Results

The thermal and mechanical pre-history of the samples were erased by heating to a temperature 30 K higher than T_g. In the DSC curves, an endothermic peak due to enthalpy relaxation of the glassy state was not observed for all samples. T_g and ΔC_p of all samples shown in Table 1 are correlated in Fig. 2. It is clearly seen that ΔC_p values are on a line for almost all samples including engineering plastics.

Fig. 3 shows the relationship between ln ΔC_p and T_g of oligomers of methyl methacrylate (No. 14 in Table 1); this is a part of Fig. 2 enlarged at a temperature ranging

Table 1

Samples used in this experiment

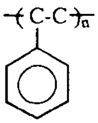
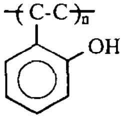
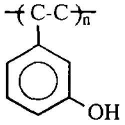
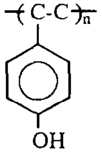
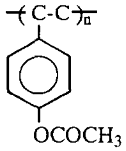
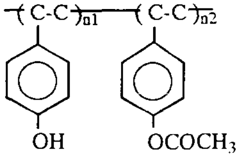
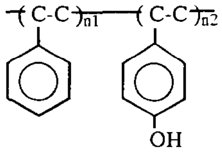
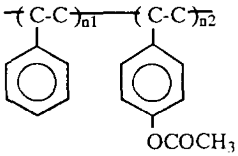
No.	Name	Chemical Structure	Ref.
1.	Styrenes (PSt)		[6]
2.	Poly(2-hydroxy styrene) (P*o*HS)		[6]
3.	Poly(3-hydroxy styrene) (P*m*HS)		[7]
4.	Poly(4-hydroxy styrene) (P*p*HS)		[7]
5.	Poly(4-acetoxy styrene) (P*p*AS)		[8]
6.	P*p*HS-P*p*AS Co-polymers		[8]
7.	PSt-P*p*HS Co-polymers		[9,10]
8.	PSt-P*p*AS Co-polymers		[9]

Table 1 (*continued*)

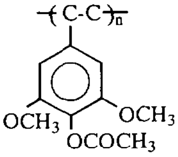
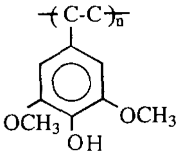
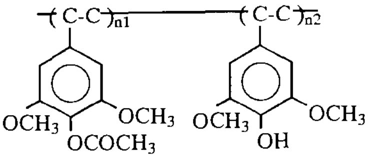
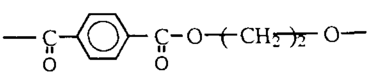
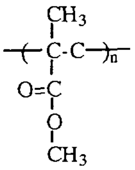
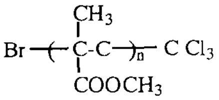
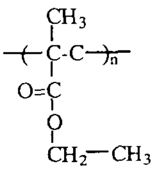
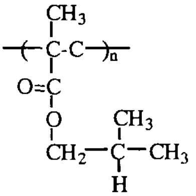
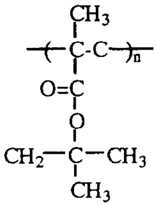
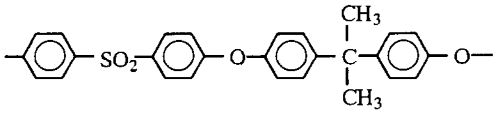
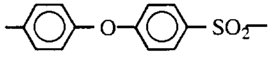
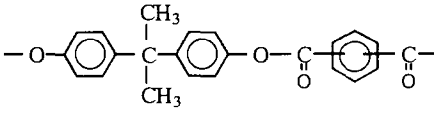
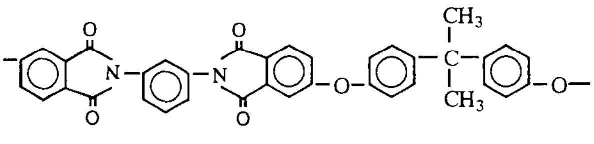
No.	Name	Chemical Structure	Ref.
9.	Poly(4-acetoxy-3,5-dimethoxy styrene) (PAD MS)		[11]
10.	Poly(4-hydroxy-3,5-dimethoxy styrene) (PHD MS)		[11]
11.	PADMS-PHDMS Copolymers		[11]
12.	Poly(ethylene terephthalate) (PET)		[12]
13.	Poly(methyl methacrylate) (PMMA)	 $-(\overset{CH_3}{\underset{O=C-O-CH_3}{C}}-C)_n-$	[13]
14.	PMMA Oligomers	 $Br-(\overset{CH_3}{\underset{COOCH_3}{C}}-C)_n-CCl_3$ n=1,2,3,5,18	[14]
15.	Poly(ethyl methacrylate) (PEMA)	 $-(\overset{CH_3}{\underset{O=C-O-CH_2-CH_3}{C}}-C)_n-$	[13]

Table 1 (*continued*)

No.	Name	Chemical Structure	Ref.
16.	Poly(isobutyl methacrylate) (P*i*BMA)		[13]
17.	Poly(tert-butyl methacrylate) (P*t*BMA)		[13]
18.	Polysulfone (PSF)		[12]
19.	Poly(ether sulfone) (PESF)		[12]
20.	U-Polymer		[15]
21.	Poly(ether imide)		[12]

from around 250 to 350 K. Brackets in the figure indicate the *n*-mer (repeating unit of monomer chain). It is clearly seen that ΔC_p values of the *n*-mers larger than 18-mer merge in the line of polymers.

Fig. 4 shows the relationship between ΔC_p and the composition of polystyrene-poly(4-hydroxy styrene) copolymers (No. 7 in Table 1) and polystyrene-poly(4 acetoxy styrene) copolymers (No. 6 in Table 1).

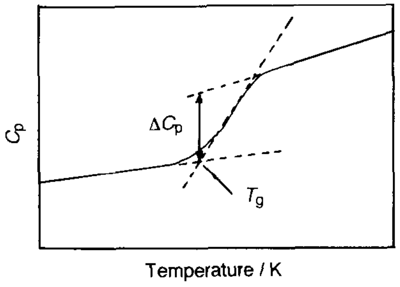


Fig. 1. Schematic DSC curves showing T_g and ΔC_p.

Fig. 5 shows the relationship between ln ΔC_p and T_g of the same copolymers shown in Fig. 4. The corresponding line in Fig. 2 is shown as a broken line.

4. Discussion

Molecular relaxation at around T_g has been investigated using thermal analysis. Volume, dielectric and mechanical relaxations correspond to enthalpy relaxation evaluated by DSC. Changes of expansion coefficient ($\Delta\alpha$) and ΔC_p at T_g are important thermodynamic quantities, when volume relaxation or enthalpy relaxation is investigated at around T_g. The above values, $\Delta\alpha$, ΔC_p at T_g have been studied in order to explain the physical properties of glass transition phenomena. At the same time, the effect of molecular structure on $\Delta\alpha$ and ΔC_p values were investigated.

Wunderlich suggested that the fundamental units of substance to fit the hole theory

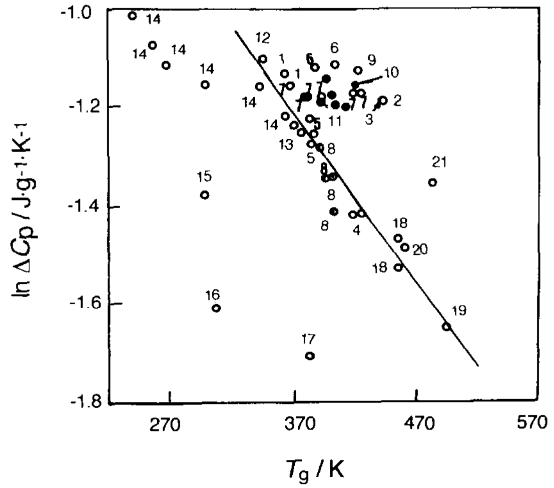


Fig. 2. Relationship between ln ΔC_p and T_g of the samples listed in Table 1.

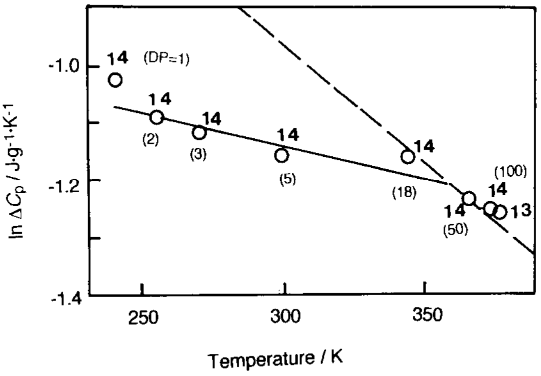


Fig. 3. Relationship between ln ΔC_p and T_g of methyl methacrylate oligomers (No. 14; ref. Table 1 (*n*), *n*-mer).

existed as "beads". He considered that $\Delta C_p = 11.3$ J K^{-1} (mol of beads) at T_g for organic substances including polymers [4]. Temperature range of T_g was ca. 100–350 K. The main difficulty of the above concept is how to decide the size of beads for each polymer and how to avoid arbitrary factors. In contrast, the size of the beads was determined in order to obtain the constant ΔC_p value. Another empirical equation, $\Delta C_p T_g$ = constant, was suggested by several authors [19,20].

As shown in Fig. 2, the linear relationship between ln ΔC_p and T_g was obtained for almost all polymers in a temperature range from 230 to 530 K. If we consider that the relationship between ln ΔC_p and T_g is satisfied by almost all polymers in the broad

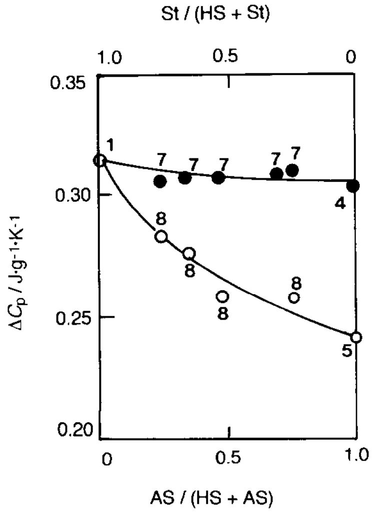


Fig. 4. Relationship between ΔC_p and composition of copolymers of PSt-PpHS (No. 7 in Table 1) and PSt-PpAS (No. 6 in Table 1).

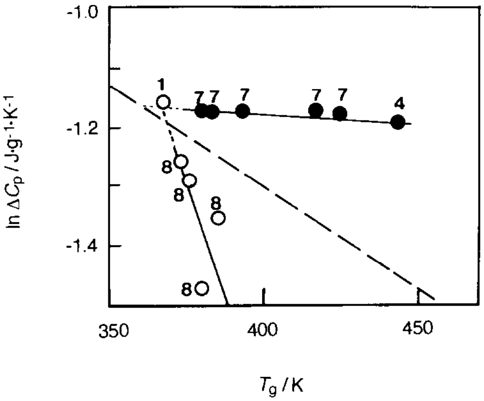


Fig. 5. Relationship between ln ΔC_p and T_g of PSt-PpHS (No. 7 in Table 1) and PST-PpAS (No. 6 in Table 1).

temperature range, and T_g is described according to Hirai-Eyring theory [21] as $\Delta C_p(-\varepsilon_h/RT)$, where ε_h is the hole creation energy and R is the gas constant, it seems to be natural to accept that ΔC_p decreases with increasing T_g.

We have reported that ΔC_p is not a constant value but dependent on T_g values [22,23]. However, it is necessary to discuss the influence of molecular structures on the deviation of ΔC_p values from the general straight line. As shown in Fig. 2, when the samples have oligomeric molecular weights, ΔC_p values were separated from the straight line. MMA oligomers showed low ΔC_p values as shown in Fig. 3. As described in our previous report [24], if the molecular weight decreases, molecular motion of the end groups begins to affect the main chain motion, i.e. rotation of the end groups cannot be ignored and enhances the whole chain movement. In that situation, the C_p of the glassy state is high and a small ΔC_p value resulted at T_g.

Similarly, the samples with a long side chain or bulky side chain, such as PEMA (No. 15, in Fig. 2), PiBMA (No. 16), PtBMA (No. 17), are not on the straight line as shown in Fig. 2. The side chain motion started at a temperature lower than T_g; this leads to the high C_p of the glassy state being enough to decrease the ΔC_p value. The number of side chain groups also affects deviation. However this is not as marked as PEMA having long alkyl side chains.

As reported in our previous report, intermolecular hydrogen bonding increases T_g and the increment linearly correlates to the number of hydrogen bondings [8]. T_g of PHS-PAS copolymers increases from 385 to 460 K with increasing OH content [9], ΔC_p maintains an almost constant value. This can clearly be seen in Figs. 4 and 5. ΔC_p of PHS is almost the same as PSt, regardless of T_g variation. This suggested that inter-molecular force disturbs the initiation of free molecular motion, however, once hydrogen bonding starts to break, ε_h seems to be similar to the samples with no hydrogen bonding.

As Ichihara pointed out [5], if configurational contribution to the glass transition phenomena is taken into consideration based on the iso-configurational entropy theory, the role of inter-molecular force is important. In this case, the series of PHS-PSt, and PAS-

PSt copolymers are good model compounds since the inter-molecular and intra-molecular contributions to the glass transition can be clearly observed.

From heat capacity data obtained in our laboratory, it is concluded as follows: (1) a linear relation between ΔC_p and T_g is established in a temperature from 200 to 530 K for various types of polymers; (2) when the samples have a large side chain and local mode relaxation is enhanced in the glassy state, ΔC_p determined at T_g apparently decreases due to high C_p values at the glassy state. In this case, the ΔC_p deviates from the general line; (3) inter-molecular force contributes mainly to T_g increase and this causes apparent increase of ΔC_p for the samples having inter-molecular bondings.

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