

INVESTIGATION OF THE TRANSITIONS OF OLIGO-POLYSULFONES BY DSC*

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ABSTRACT

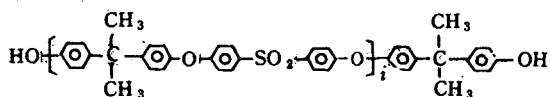
The transitions of bisphenol A and phenolphthalein oligopolysulfones were investigated by DSC. It is found that both the oligomers have three transitions within the temperature range (230–550K) studied. Considering the strong dependence of the appearance of the two transitions, lower and higher than T_g , on the specimens' thermal history, i.e., temperature and time of heat-treatment, and their particular molecular structure, it is proposed that these two transitions are morphological in origin and are due to the disordering of relatively short range order of very small regions, and to the disordering of relatively well-ordered intra- or /and intermolecular segments, respectively. Equations for linear relationship between T_g and $1/\bar{M}_n$ for both the oligomers are given in the paper.

Extensive study has been given to the syntheses and structure-properties relationship of segmented copolymers, as these polymers possess a variety of unique properties suitable for special uses. Naturally, the dependence of segmented copolymers' morphological structure and properties on the nature of their oligomers has aroused the interests in the study of oligomers.

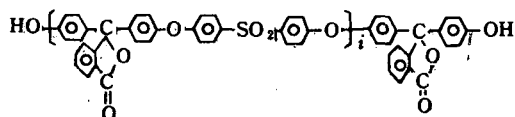
This paper presents our preliminary investigation on the transitions of two types of oligo-polysulfones, bisphenol A polysulfone and phenolphthalein polysulfone, by differential scanning calorimetry (DSC).

EXPERIMENTAL

Hydroxy-terminated bisphenol A polysulfones, $H_1(i)$ (where i represents the number of repeating units),



and phenolphthalein polysulfone, $H_4(i)$ (where i is the same as in $H_1(i)$)



* Presented before the Polymer Symposium, Polymer Division, CCS, Beijing, August, 1985.

A part of DONG Lisong's M.S. Thesis, Changchun Institute of Applied Chemistry, 1984.

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Received September 21, 1986

were prepared by nucleophilic condensation reaction through controlling the molar ratio of the repeating monomers. Vapor pressure osmometry (VPO) and potential titration were used for determination of the number average molecular weights ($\bar{M}_n$) of the oligomers^[1]. Results obtained by these two methods are in good agreement, and also in agreement with the designed values.

The calorimeter used in the study is Perkin-Elmer DSC-2C; temperature range and rate of heating used were 230—550K and 20K/min. respectively. Sample weights were all around 15 mg.

RESULTS AND DISCUSSION

Studies on the transitions of polysulfones by various techniques have been reported, most of which gave three transitions^[2,3]. The low temperature transition (163—197K) was assigned to the motion of phenylene units coupled with oscillation motion of nearby polar units^[3]. The transition occurring near 333K was related to the specimen's thermal history, i.e., relaxation process occurring in defect regions frozen in by rapid quenching from the melt, and to the onset of motions proceeding the long-range segmental motions occurring at T_g ^[4-7]. The one at 450K is its T_g .

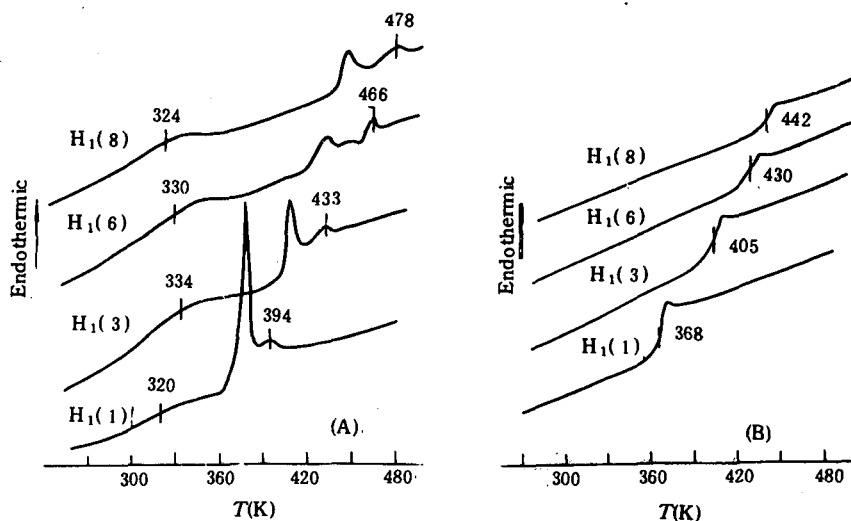


Fig. 1 DSC thermograms of $H_1(i)$ samples

A) first heating, B) second heating

It is found that in this work within the temperature range studied, the thermal behavior of the oligomers followed a general pattern. Figure 1 compares the DSC curves of the samples of $H_1(i)$ series as a function of $\bar{M}_n$ (Fig. 1A) obtained by the first and second heating processes (Fig. 1A and B). As shown in Fig. 1A, regardless of their $\bar{M}_n$, there appear three endothermic transitions for all the samples. The first one (around 330K) is common to all of them. However, the positions and intensities of the other two transitions at higher temperatures are dependent on their $\bar{M}_n$. It is noted that the first (around 330K) and the last endotherms disappeared from the DSC curves of the second heating processes, while the second one, more normal as a glass transition, remained there (Fig. 1B).

The endotherm near 330K is in agreement with that found by Fried and Kalkanoglu^[4]. However, the thermal history of the samples of this work and that of Fried and Kalkanoglu were

quite different. Samples of this work were actually annealed, as they, after purification, were dried under vacuum at 350K until constant in weight, then cooled to room temperature (RT) and kept at RT for a certain length of time before use, while Fried and Kalkanoglu's samples were quenched from melt to 0°C . We tried quenching our samples as Fried and Kalkanoglu did, but no endotherm appeared at 330K on the DSC curves. Seymour and Cooper have assigned the transition first to hydrogen bonding dissociation, which was proved not the case by the IR data of their own later work, in which they proposed that this transition was morphological in origin, representing the disordering of segments with relatively short-range order^[8,9]. Since the transitions around 330K of our samples disappeared on the DSC curves of the second heating process, we agree with Seymour and Cooper that this transition is in relation to the disordering of some sort of short-range order within very small regions, which is well supported by our results obtained by TBA^[10].

In general, it is considered that polysulfones are amorphous. Blackadder and Ghovamkai discovered that under certain conditions polysulfone solution did exist birefringence effect^[11]. The results of a study with polarized microscopy by Zhou et al.^[12] has shown that polysulfones had depolarizing effect, and small angle light scattering gave structural characteristics of crystalline polymer. Hence they concluded that polysulfones are in mesomorphic state.

The high rigidity of the backbone chains of samples of $H_1(i)$, which is composed of benzene rings, and sulfur and oxygen with strong electro-negativity, may make the chains arranged in certain degree of order under favorable conditions. However, it is easily seen that the formation of order would be rather difficult; it needs time and temperature. So we consider that the endotherm appeared after T_g for samples of $H_1(i)$ might be in relation to the disordering of relatively well-ordered intra- and intermolecular segment aggregations.

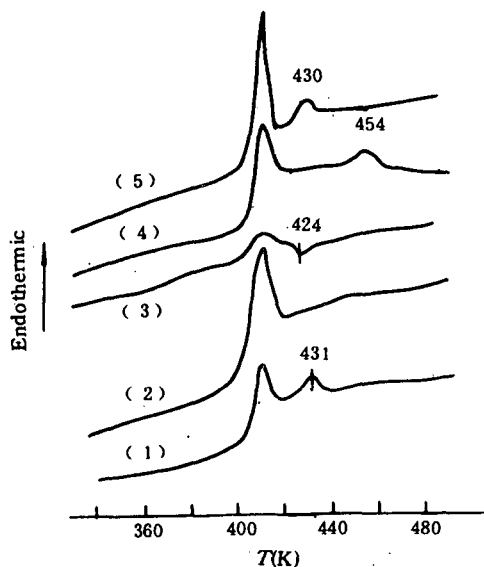


Fig. 2 DSC thermograms of $H_1(3)$ with different heat-treatment

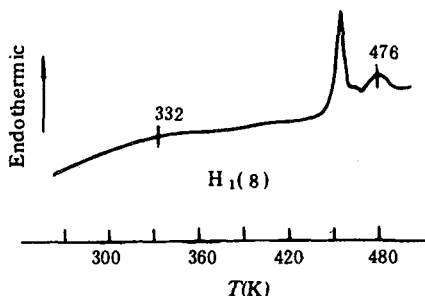
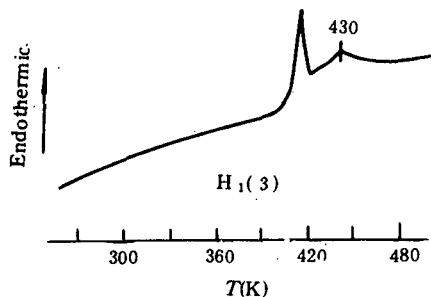
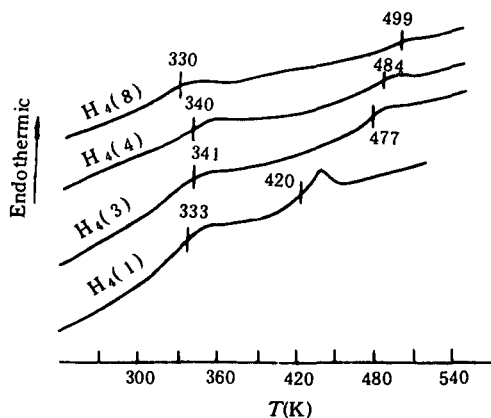


Fig. 3 DSC thermogram of $H_1(8)$ (85 h. at 470K)

In order to illustrate the existence of and to find out the conditions necessary for the formation of such order, different heat-treatments were given to sample $H_1(3)$, which were then studied with DSC. The results are given in Fig. 2. Curve (1) is for the specimen heat-treated at

420K under vacuum for one week and then cooled gradually to RT . The curve is almost the same as that of the control on first heating (Fig. 1A). This means that such heat-treatment is not enough to change the original structure. Curve (2) is for the specimen heated under vacuum to its viscous-flow state and then gradually cooled to RT . This curve only shows a typical glass transition, no other enthalpy changes. This might suggest that due to the rigidity of the molecular chains, there is not enough time for the molecules to get into order during the process of vetrification. Curve (3) is for a specimen, which was dissolved, precipitated, and then dried at 350K under vacuum for 48 hours. There is still no endotherm showing up after T_g . This again means that such treatment is not enough for the sample to get some ordered structure. However, it should be pointed out that there exists an exothermic peak after T_g . It is reasonable to consider that during this treatment the ordered structure was completely destroyed, hence when heated to higher temperature range (410—430K) the molecules obtained enough energy to start getting into order, thus releasing heat. But such order is not well enough, so that it was gradually destroyed as the temperature was continuously increased, making the base line deviate slightly instead of the appearance of an endotherm. Curve (4) represents a specimen cooled down from its viscous state to 420K and then annealed at 420K for one week. This curve not only shows up a T_g , but also an endotherm following T_g , the temperature of which is even higher than the corresponding peak of the control $H_1(3)$. This, we consider, is due to the formation of order and also higher in degree of order, since higher temperature (420K) and longer time (1 week) gave the molecules more energy and time to get into order. Curve (5) is for the same sample of curve (3) but with one more week of heat-treatment at 420K, which is in good agreement with curve (1). Moreover, the DSC thermogram of another sample $H_1(8)$ heat-treated at 470K for 85 hours is given in Fig 3 which shows more pronounced peaks than those on the curve of control $H_1(8)$ in Fig. 1A. It is evident that annealing at higher temperature is favorable to the ordering of molecular segments. In order to elucidate what made the formation of order in the original samples which were not given any heat-treatment besides drying. Hence some $H_1(3)$ was taken and heated to its viscous-flow state, and then kept at RT for two months after gradually cooling down. The DSC thermogram of this sample is shown in Fig 4. It may be seen that this curve is in good agreement with that of the control (Fig. 1A, curve $H_1(3)$). This suggests that even at RT , if enough time is given, the rigid molecules of $H_1(i)$ oligomers would gradually get into order.

Fig. 4 DSC thermogram of $H_1(3)$ (2 months at RT)Fig. 5 DSC thermograms of $H_4(i)$ samples

The above results illustrate that annealing at higher temperature with longer time or even being kept at RT with considerable length of time will lead to the formation of segmental order, the degree of which increased with the increase in annealing temperature and time.

Figure 5 shows the DSC thermograms of the samples of $H_4(i)$ series, which are somewhat different from that of $H_1(i)$ series, showing up only two endotherms, one at 330—340K and the T_g , but not any higher than T_g . It is considered that the origin of the endotherms at 330—340K is the same as that around 330K for $H_1(i)$ samples. Since the molecules of this $H_4(i)$ series consisted of benzene rings and large side groups of five-member ring lactone, and also the possibility of forming hydrogen bonding between the lactone side groups and hydroxy groups, the molecular movement would be even more difficult than that of $H_1(i)$ under the same conditions. According to such consideration, some $H_4(3)$ was taken and annealed at 470K under vacuum for 85 hours and then gradually cooled down to RT . The DSC thermograms of this specimen is shown in Fig 6. It is clearly seen that an endotherm exists beyond its T_g , at 529K, which is about 100 degrees higher than that of $H_1(3)$ with corresponding molecular weight. It is quite reasonable that more energy will be needed to overcome the hinderance given by the big side groups for the molecules to move into order.

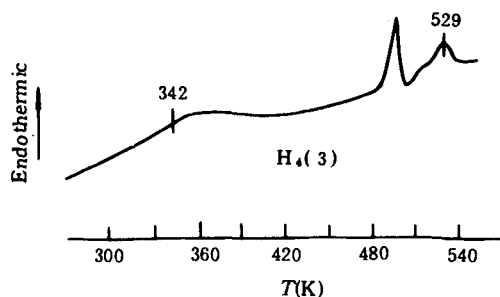


Fig. 6 DSC thermograms of $H_4(3)$

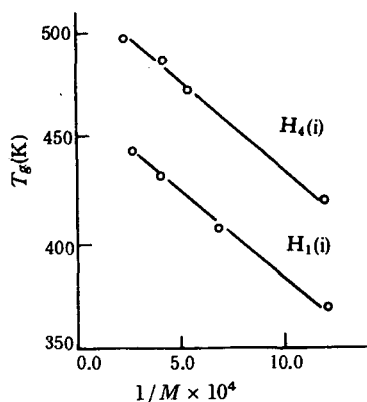


Fig. 7 T_g vs. $1/\bar{M}$ curves

The dependence of T_g on molecular weight for these two series of oligo-polysulfones is shown by the plots of T_g vs. $1/\bar{M}$ in Fig 7. Good linear relationship was obtained for both series. The equations obtained by treatment of the data with least square method are as follows:

$$\text{Series } H_1(i): \quad T_g = 462 - 8.07 \times 10^4 / \bar{M}$$

$$\text{Series } H_4(i): \quad T_g = 519 - 8.33 \times 10^4 / \bar{M}$$

The results of the study well illustrate that the two transition peaks other than T_g observed for samples of these two series oligo-polysulfones may both be ascribed to morphological effects. The appearance of them depends strongly on their thermal history, i.e., temperature and time. However, molecular structure and molecular weight also play an important role on the position, i.e., temperature, and intensity of the third peak. All these might be useful to the design and selection of processing conditions for these types of polysulfone segmented copolymers.

Keywords:

Oligo-polysulfone; DSC; transitions; morphology

Acknowledgement The authors wish to express their sincere thanks to the DSC Group of our Institute for kindly providing us the use of the DSC.

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