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ENTHALPY RELAXATION OF POLYETHERS HAVING PHENYLENE GROUPS IN THE MAIN CHAIN

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SUMMARY

Two aromatic polyethers and a polysulfide having phosphine oxide group in the main chain were synthesized and the thermal properties of the polyethers and polysulfide were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). The samples were thermally stable and starting temperatures of decomposition were found at around 750 to 800K. The x-ray diffractograms showed a halo pattern for all samples. The heat capacities of the samples annealed at various temperatures and for various times were measured by DSC. The excess enthalpy of annealed samples was evaluated and the relaxation time was calculated. It was found that the 2, 2-diphenylpropane group accelerated the relaxation rate due to internal rotation of the molecular chain. At the same time, the polysulfide structure was found to contribute to the high relaxation rate.

INTRODUCTION

Recently, attention has been paid to the polymers having phenylene groups in the main chain, owing to their functional properties, such as thermal stability, high elastic modules, etc. In order to investigate the thermal properties of the "engineering plastics", thermogravimetry (TG) and differential scanning calorimetry (DSC) are extensively used [refs. 1-4].

We have synthesized aromatic polyethers and polyesters from bisphenols which were derived from phenols having a core structure of lignin [refs. 5, 6]. It was found that the decomposition temperature and glass transition temperature markedly increased due to the introduction of phenyl groups into the main chain. We have also reported the thermal relaxation behaviour of several kinds of engineering thermoplastics obtained

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commercially [refs. 7, 8]. Using heat capacity data measured by DSC, the excess enthalpy of glassy samples and the rate of relaxation were investigated. The results strongly indicated that the polymers having phenylene groups in their main chain showed a high relaxation rate.

In this study, we synthesized polyethers having phosphorus and sulfur with phenylene groups in the main chain and also investigated the effect of chemical structure on the rate of enthalpy relaxation.

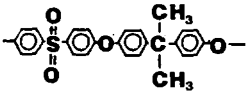
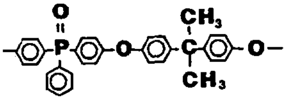
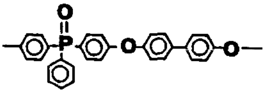
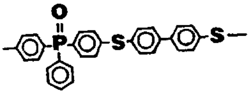
METHODS

Sample Preparation

The chemical structure of the samples used in this study is shown in Table 1. All samples, except for polysulfone (PSF), were synthesized in our laboratory.

Table 1

Chemical structure of the samples used in this study.

Abbreviation	Name	Chemical structure	Synthetic procedure
PSF	Poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene-oxy-1,4-phenylene iso-propylidine-1,4-phenylene)		
I	Poly(oxy-1,4-phenylene phenylphoshonyl-1,4-phenyleneoxy-1,4-pnenlene-isopropylidene-1,4-phenylene)		ref.9
II	Poly(oxy-1,4-phenylene phenylphoshonyl-1,4-phenyleneoxy-4,4'-biphenylene)		ref. 9
III	Poly(thio-1,4-phenylene phenylphoshonyl-1,4-phenylenethio-4,4'-biphenylene)		ref. 10

Measurement

A Shimadzu thermogravimeter TG-30 was used for the measurement of thermal degradation. Sample weight was ca. 3 mg, heating rate 10K/min, N_2 flow rate 20ml/min. Temperature ranged from 300 to 1000K. A Perkin Elmer differential scanning calorimeter DSC II and a Seiko thermal analysis system SSC 5000 were used. Sample weight was 3 mg, heating rate 10K/min. Samples were sealed in aluminium vessels. The sample was heated to a temperature higher than T_g+50K, quenched to 300K and heated at 10K/min. The quenched samples were annealed at various temperatures and times in the DSC holder.

Heat capacity (C_p) [ref. 11] and glass transition temperature (T_g) were measured as reported previously [ref.12].

RESULTS AND DISCUSSION

Fig. 1 shows TG curves of samples listed in Table 1. The decomposition temperatures are defined as shown in in Fig. 1. The values of decomposition temperatures obtained from TG curves are shown in Table 2. The samples started to decompose at around 750 to 800K and finished decomposing at around 850 to 950. Among four samples, sample I showed the highest thermal stability. This fact was attributed to the fact that the dissociation energy of C-O bond (422KJ/mol) is higher than that of C-S bond (369KJ/mol) [ref. 11].

TABLE 2

Decomposition and glass transition temperatures of the samples.

Sample	T_{di}'	T_{di}	T_{dm} in N2	T_{de}	T_{de}'	T_{gi}'	T_{gi}	T_{gm} /K
PSF	746	781	798	817	920	450	457	460
I	778	808	816	833	856	448	453	457
II	808	839	863	873	943	483	491	498
III	758	798	823	838	893	497	503	508

X-ray diffractograms of these samples showed an amorphous halo pattern, indicating that no first-order phase transition exists in the samples.

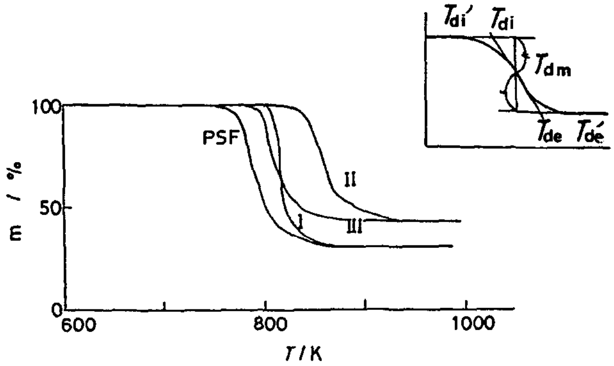
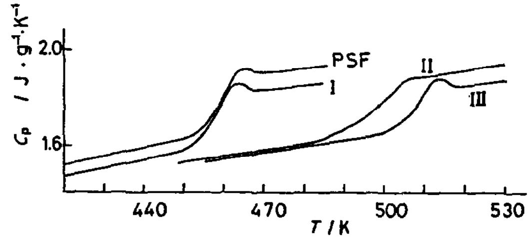


Fig. 1 TG curves of the samples.
abbreviations are the same as shown in Table 1.



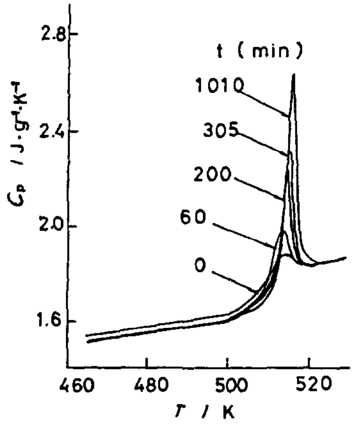


Fig. 2 C_p curves of the samples. Abbreviations are the same as shown in Table 1.

Fig. 3 C_p curves of sample III. T_a=482K, the annealing times are shown in the figure.

Fig. 2 shows C_p curves of the samples. A jump in the C_p at T_g is clearly observed. T_g values are shown in Table 1 together with decomposition temperatures.

Fig. 3 shows representative DSC curves of the quenched and annealed sample III. The endothermic peak shown in Fig. 3 increased with increasing annealing time. The enthalpy of equilibrium state at a temperature below T_g was estimated by assuming that the C_p at the liquid state could be interpolated to T_g-50K. Based on the above assumption, the excess enthalpy (ΔH_o) of the samples can be defined as follows;

$$\Delta H_o = \int_{T_a}^{T_g} C_{pl}\ (T_i)dT - \int_{T_a}^{T_g} C_{pg}\ (T_i)dT \tag{1}$$

where C_{pl} is the C_p at the liquid state and Cpg is that of the glassy sample immediately after quenching from the liquid state.

$$T_a = T_g - a \tag{2}$$

In this experiment a=15K was used. Instead of equation (1), equation (3) can be used [ref. 13].

$$\Delta H_o = \Delta C_p \times a \tag{3}$$

where $\Delta C_p = C_{pl} - C_{pg}$ at T_g. The enthalpy difference between the annealed glass and the quenched glass can be obtained from the experimental data as follows;

$$\Delta H_a = \int_{T_g-a}^{T_g+a} C_{pa}(T_i)dT - \int_{T_g-a}^{T_g+a} C_{pq}(T_i)dT \tag{4}$$

where C_{pa} is heat-capacity of the annealed glass and C_{pq} is that of quenched glass. The total excess enthalpy of an annealed sample, ΔH_t, can be obtained as follows;

$$\Delta H_t = \Delta H_o - \Delta H_a \tag{5}$$

when the annealing time increases, ΔH_a increases and ΔH_o decreases, i.e. the state of the sample approaches the equilibrium state. The rate of this change, the relaxation time, τ, can be also calculated from

$$\Delta H_t = -\Delta Hq \exp\ (-t/\tau) \tag{6}$$

where ΔHq is the enthalpy of quenched glass and t is annealing time. The value of ΔHq is almost the same as ΔH_o.

The C_p data shown in Figs. 2 and 3 were applied for the calculation of ΔH_a and ΔH_t using equations (4) and (5). Fig. 4 shows relationship between ΔH_t and t of sample III. Using equation (6), τ value can be calculated. Fig. 5 shows the relationship between and ΔH_t.

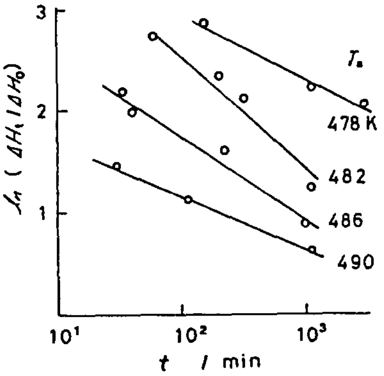


Fig. 4 Relationship between ΔH_t and t of sample III.

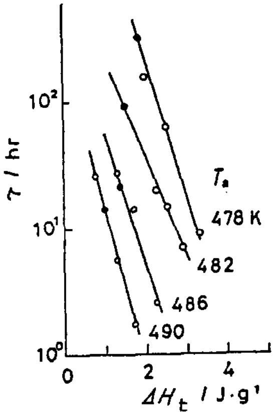


Fig. 5 Relationship between τ and ΔH_t of sample III.

Fig. 5, the relaxation time at $\Delta H_t/\Delta H_0 = 0.5$ ($\tau_{1/2}$ value) can be evaluated for each annealing temperature. Fig. 6 shows the relationship between $\tau_{1/2}$ and $(T_g - T_a)$ for all samples studied. In order to compare the values of the samples used in this study and those of ordinal polymers, $\tau_{1/2}$ values of polystyrene are shown in Fig. 6 (broken line). The $\tau_{1/2}$ values of the samples I, II, III and PSF were shorter than those of ordinal polymers such as polystyrene.

From various factors affecting the T_g increase, the contribution of the phenyl group or the diphenylene group in the main chain is the most important. This was supported by the fact that high T_g values were observed for the samples used in this study. the 2,2'-diphenylpropane unit reduces the T_g values. This reduction is observed in the cases of T_g values of samples II and III which are higher than those of PSF and sample I.

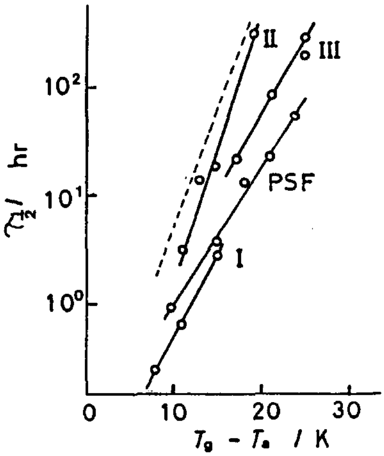


Fig. 6 Relationship between relaxation time ($\tau_{1/2}$) and (T_g-T_a). Abbreviations are the same as shown in Table 1. -----;Pst

As shown in Fig. 6, the $\tau_{1/2}$ value decreased in the order of polyethers II, polysulfide III, PSF and polyether I at a constant T_g-T_a. Previous studies strongly suggested that internal rotation of the main chain was related to the enthalpy relaxation of the amorphous chain, since it is difficult to assume the molecular rearrangement of long range order at a temperature below T_g. The diffference of $\tau_{1/2}$ values between sample I and II suggested that the molecular relaxation was accelerated in the presence of 2,2'-diphenylpropane group in the main chain. Internal rotation of the molecular chain is considered to occur easily in the presence of the bulky side group, such as methyl group.

The $\tau_{1/2}$ of the sample I was slightly shorter than that of PSF as shown in Fig. 6. It is considered that free volume of sample I increases due to the phenylphosphine oxide group which has more bulky structure than that of the sulfone group.

The difference in relaxation times between sample I and sample III could be explained by the difference between the resonance of phenylsulfide and that of diphenylether. For instance the electrondonnating resonacne effect of oxygen is stronger than that of sulfur, and on this account double-bond character of diphenylether is stronger than that of diphenylsulfide. This suggests that the internal rotation occurs more readily in polysulfide than that in polyether.

The above results suggest that the 2,2-diphenylpropane group accerelated the relaxation rate due to the internal rotation of the molecular chain. At the same time, the polysulfide structure also contributes to high relaxation rate.

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