polymer reports

Pressure dependence of transitions

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(*Received* 15 *July* 1981; *revised* 21 *June* 1982)

Empirical observations indicate that secondary transitions, T_{sec}, in polymers exhibit smaller pressure dependence than do glass transitions, T_g. To explain these results, we have formulated a molecular model, known as the isosegmental model, which relates the pressure dependence of polymer transitions to the number of polymer segments involved in the transition. The model predicts a linear relation between the pressure dependence of T_{sec} and T_g and the number of polymer segments involved. This prediction is supported by experimental results.

Keywords Transition; glass; secondary; pressure; dependence; segments

INTRODUCTION

The purpose of this report is to present an empirical relationship between the pressure dependence of transitions and the number of polymer segments involved. Specifically, both glass and secondary transitions are considered. A number of investigators have made qualitative observations about the pressure dependence of transitions. Heydemann and Houck[1] noted that the small pressure dependence of secondary transitions is characteristic of processes consisting of the motion of small side groups rather than motion of the main polymer chain. Parry and Tabor[2] attributed the small pressure dependence of secondary transitions to the small amount of free volume available in the glassy state. In an earlier paper[3], we pointed out that the smaller activation volume for a secondary transition compared with a glass transition explained the reduced pressure dependence. Boyer[4] found that the pressure dependence of a liquid state transition was greater than that of the glass transition. He stated that this was consistent with the greater amount of free volume in the liquid state. Since the number of segments involved in a transition should be related to the volume required for the transition, it is reasonable to expect that the pressure dependence of a transition is related to the number of segments involved in the transition.

In the sections to follow, we will estimate the number of segments involved in both glass and secondary transitions, find a relationship between these numbers and pressure dependence, and, in the last section, reach some conclusions about polymer transitions.

TRANSITION SEGMENT NUMBER

The estimation of the number of polymer segments involved in either a glass or secondary transition is made using the model developed in our earlier paper[3]. In this model, the energy required to move a polymer segment from one position to another is a constant, ε, for any given polymer, and the total activation energy, E, required for a transition is the product of ε times the number of segments involved, N,

$$E = N\varepsilon \qquad (1)$$

As detailed earlier[3], values of N were found from electrical resistivity measurements by adapting a method used by Eby[5] for dynamic mechanical measurements. Since the number of segments in this case refers to the electrical conduction process, N_c is used to designate the number. Likewise, the activation energy for electrical conduction is designated by E_c. (When E_c and N_c are used in equation (1) to calculate ε, however, no subscript is needed on ε because ε is assumed to be the same regardless of the molecular process.)

Using the N_c values calculated in the above manner and experimental E_c values, one can calculate ε from equation (1). The values are listed in *Table 1*. As can be seen, ε varies from 2 to 5 kcal mol^{-1}.

Knowing ε for a series of polymers, the number of segments involved in a transition can be calculated from equation (1) for any transition for which the activation energy is known. In *Table 2* we have collected activation energies, for both glass and secondary transitions, for

0032-3861/82/121835-03$3.00

Table 1 Input data for calculation of ϵ

Polymer	E_c (kcal mol^{-1})	N_c	ϵ (kcal mol^{-1})
Glass transitions			
Poly(methylmethacrylate)	33.4^a	7^b	4.7
Polystyrene	30^c	9^b	3.3
Poly(vinylchloride)	32.5^d	15^b	2.2
Polypropylene	34.6^e	19	1.8
Poly(vinylbutyral)	29.5^f	9	3.2
Poly(vinylacetate)	25^f	8.5	2.9
Secondary transitions			
Phenolic polymer	69^g	18	3.8
Polyepoxide	38^h	23	1.7

[a] Ref. 12; [b] Ref. 3; [c] Ref. 13; [d] Ref. 14; [e] Ref. 15; [f] Ref. 16; [g] Ref. 17; [h] Ref. 18

Table 2 Transition properties

Polymer	E (kcal mol^{-1})	N	dT/dP (°C/kbar)
Glass transitions			
Poly(methylmethacrylate)	100^a	21^b	24^e
Polystyrene	100^a	30^b	29^e
Poly(vinylchloride)	70^a	32^b	15^e
Polypropylene	28^a	15.5	20^f
Poly(vinylbutyral)	66^b	21	25^g
Poly(vinylacetate)	44^a	15	23^h
Poly(tetrafluoroethylene)	–	22^d	19^i
Polyethylene	–	22^d	22^j
Secondary transitions			
Phenolic polymer	32^c	8	10^c
Polyepoxide	19^m	10	7.2^k
Poly(chlorotrifluoroethylene)	–	2^d	7.8^l

[a] Ref. 19; [b] Ref. 3; [c] Ref. 23; [d] Ref. 5; [e] Ref. 20; [f] Ref. 11; [g] Ref. 21; [h] Ref. 7; [i] Ref. 22; [j] Ref. 1; [k] Ref. 24; [l] Ref. 25; [m] Ref. 21

various polymers. Using ε values from *Table 1*, transition segment numbers were calculated and are also listed in *Table 2*. For three polymers for which the electrical resistivity data was not available, N values in *Table 2* were taken from Eby. As can be seen, N values for the glass transition range from 15 to 32 while N values for secondary transitions range from 2 to 10.

TRANSITION PRESSURE DEPENDENCE

The pressure dependence of the transitions for all of these polymers is listed in *Table 2*. For the glass transition, dT/dP ranges from 15° to 29°C/kbar while for the secondary transitions, dT/dP ranges from 7° to 10°C/kbar.

Noting that a large pressure dependence is found when a large number of segments is involved and small pressure dependence when a small number is involved, we prepared a plot of N vs. dT/dP with the result shown in *Figure 1*. With the exception of poly(vinylchloride), a linear relation between dT/dP and N with a correlation coefficient of 0.9 is observed. Considering that the number of segments is estimated using data from several different workers on different batches of polymers, the agreement is reasonable. It is not clear why poly(vinylchloride) shows poorer agreement, but we note that dT/dP for poly(vinylchloride) is intermediate between the values for glass transitions and for secondary transitions. O'Reilly and Mosher[6] have recently shown that the apparent effect of pressure on poly(vinylchloride) in the rubbery state is to vitrify the high energy conformations. This freezing of motions may account for the low value of dT/dP.

A qualitative explanation of the above relationship can be based on our earlier model[3]. In this model, we assumed that, at one atmosphere pressure, a certain number of segments were involved in a transition. We now assume that the same number of segments are involved at elevated pressure. This assumption can be contrasted with other assumptions that have been made in the literature as follows. A simple way to specify a transition phase line in temperature–pressure space is to require that the polymer volume at the transition be a constant. The slope of the phase line would then be $(\partial T/\partial P)_v$ in this, isovoluminous, theory. Recognizing that the volume of a polymer is a sum of free volume and van der Waals volume, an improvement to this theory is to require that the free volume at the transition be a constant. In this, iso-free volume, theory, the slope would be $(\partial T/\partial P)_{v_f}$. It has been pointed out[7,8,9] however that this theory neglects the change in van der Waals volume with pressure and temperature. In the model presented here, the number of segments at the transitions is a constant so that the slope is given by $(\partial T/\partial P)_N$ in this, isosegmental, model. Both glass and secondary transitions follow the same model. Note that the model allows for a decrease in the volume of the polymer at the transition as the pressure increases.

In general, the physical properties of polymers depend not only on T and P, but also on an internal ordering parameter, z, which is primarily determined by the time scale of the vitrification process. However, it is found experimentally[10,11] that dT/dP is only slightly dependent on z if at all. In the approximate isosegmental model presented here, the internal ordering parameter will be neglected and it will be assumed that at any given temperature and pressure there will be sufficient free volume for a certain number, n, of segments to move.

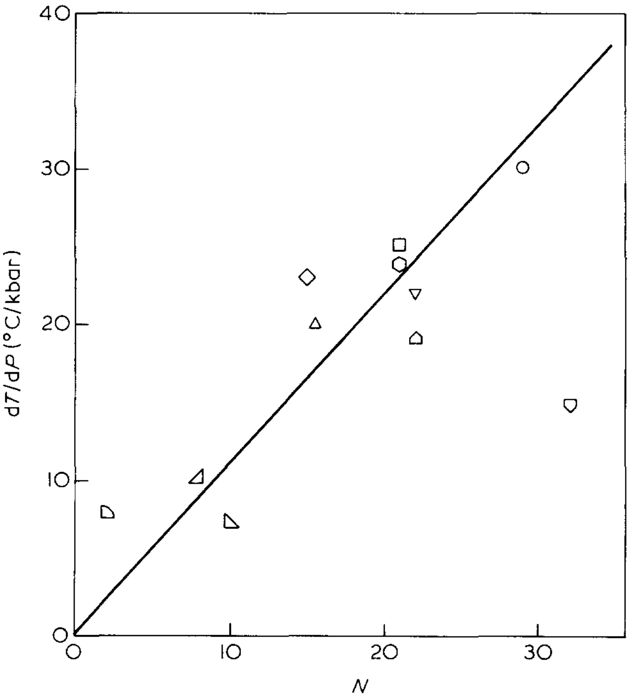

Figure 1 Pressure dependence of transition temperature vs. number of segments. Glass transitions: ○, poly(methylmethacrylate); ○, polystyrene; ▽, poly(vinylchloride); △, polypropylene; □, poly(vinylbutyral); ◇, poly(vinylacetate); ⌂, poly(tetrafluoroethylene); △, polyethylene. Secondary transitions: ◿, phenolic polymer; ◺, polyepoxide; ▷, poly(chlorotrifluoroethylene)

When $n=N$, a particular transition will occur. Assuming that

$$n=n(T,P) \tag{2}$$

it follows that

$$\mathrm{d}n=\left(\frac{\partial n}{\partial P}\right)_T \mathrm{d}P+\left(\frac{\partial n}{\partial T}\right)_P \mathrm{d}T \tag{3}$$

Along the phase line, $n=N=$constant so that

$$\left(\frac{\partial T}{\partial P}\right)_N=-\left(\frac{\partial n}{\partial P}\right)_T \Big/ \left(\frac{\partial n}{\partial T}\right)_P \tag{4}$$

The right hand side of equation (4) is some unknown function of n evaluated at $n=N$. Assuming that, to lowest order, this function is proportional to N, equation (4) becomes

$$\left(\frac{\partial T}{\partial P}\right)_N=\omega N \tag{5}$$

where ω is a proportionality constant. Equation (5) is an expression of the relationship in *Figure 1*, where it is seen that the numerical value of the slope is $\omega \approx 1$°C/kbar segment.

Integrating equation (5) yields

$$T_x-T_x^{\circ}=\omega NP \tag{6}$$

where T_x is the transition temperature, either glass or secondary, at any pressure and T_x° is the transition temperature at zero pressure. Thus the isosegmental model leads to the conclusion that phase lines should be plotted using reduced variables $T_x-T_x^{\circ}$ and NP. Taking all of the input data used to evaluate the slopes in *Table 2*, we obtain the reduced variable plot shown in *Figure 2*. Considering the variability of different literature values for the same polymer, the spread in the data is to be expected.

CONCLUSIONS

Based on observations of phase lines for both glass and secondary transitions and our earlier model for the number of polymer segments involved in a transition, we have reached the following tentative conclusions:

(1) the pressure dependence of transitions is proportional to the number of segments;

(2) polymer transition phase lines are isosegmental states;

(3) polymer transitions follow the equation $T_x-T_x^{\circ}=\omega NP$ where ω is the same for all polymers.

It should be noted that the above conclusions apply equally well to glass and secondary transitions. In the model presented here, glass and secondary transitions differ only in the number of segments involved.

In the isosegmental model, any transition can be characterized by the number of segments that cooperate to produce the transition. The transition occurs whenever there is enough volume for the segments to move, but this transition volume is not a constant as the pressure increases. In this way, pressure dependence measurements can now be used to help determine the molecular motion responsible for a particular transition.

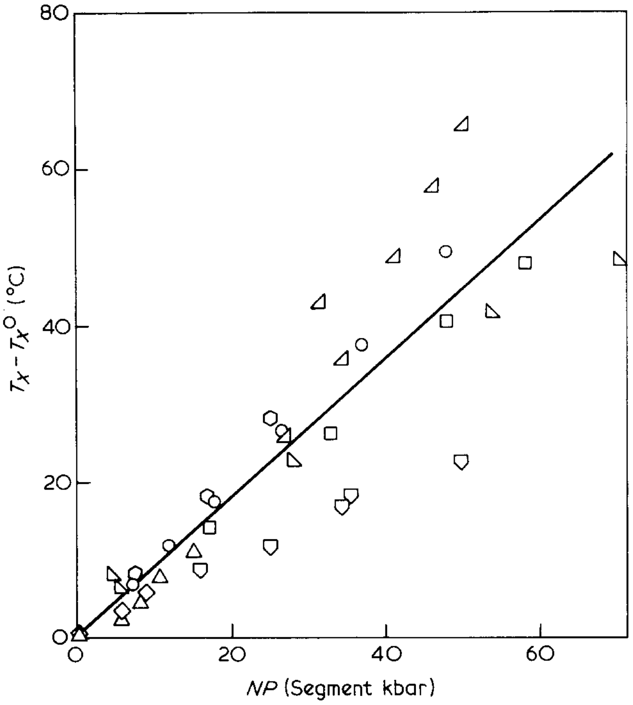

Figure 2 Reduced transiton temperature vs. reduced pressure. Glass transitions: O, poly(methylmethacrylate); ○, polystyrene; ▽, poly(vinylchloride); △, polypropylene; □, poly(vinylbutyral); ◇, poly(vinylacetate). Secondary transitions: ⊿, phenolic polymer; ◺, polyepoxide

ACKNOWLEDGEMENT

This work was sponsored by the Center's Independent Research Program.

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