Corresponding states relationship for electrical resistivity of glassy polymers

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Using the glass transition as a corresponding state for polymers, a relationship has been found between reduced electrical resistivity and reduced temperature for a large number of polymers in the glassy state. As a consequence of this relationship and the Arrhenius temperature dependence of the unreduced data, the activation energy for electrical conduction is shown to be directly proportional to the glass transition temperature and linearly related to the activation energy for the glass transition. A molecular model is proposed to explain these results in terms of the number of polymer segments involved in electrical conduction (~10) and the activation energy per segment (~4 kcal/mol).

INTRODUCTION

The principle of corresponding states[1] was first applied to the pressure-volume-temperature (p-V-T) properties of a fluid by van der Waals. He defined reduced variables as those variables obtained by dividing p, V and T by their values at the critical point. His major assumption was that the critical point is a corresponding state for fluids. Therefore, all fluids have the same reduced volume when compared at the same reduced temperature and pressure. Similar reasoning has been applied to transport phenomena in fluids. For example, fluids have the same reduced viscosity at the same reduced temperature.

While most of the work in the field of corresponding states has been empirical, some theoretical studies have also been done[2,3]. Corresponding states relationships have been demonstrated for various types of chain substances and solids[4,5] and applied to solid polymers[6] by recognizing that the glass transition is a corresponding state for these solids[7]. Therefore, polymers should have the same reduced properties when compared at the same reduced temperature. That such behaviour exists has been demonstrated for a number of polymer properties including bulk modulus[8], viscosity[9], ratio of the heat capacities at constant pressure and constant volume[10] and shear strength[11].

These relationships have been employed to estimate the magnitude of the properties of one polymer from the measured properties of other polymers where no data exist and no satisfactory theory is available. Even for simple fluids, this procedure is no more accurate than ±10% and, in the more complicated case of polymers, one may expect even more scatter; still these relations are of practical utility and represent a first step in the theoretical understanding of polymer properties.

Presented in this paper is experimental evidence that the law of corresponding states applies to the electrical volume resistivity of polymers in the glassy state. As a consequence of this reduced relationship and the Arrhenius temperature dependence of the unreduced data, the activation energy for electrical conduction is shown to be directly proportional to the glass transition temperature and thereby linearly related to the activation energy for the glass transition. A simple molecular model is proposed to explain these results in terms of the number of polymer segments involved in each process and the activation energy per segment.

CORRESPONDING STATE RELATION

Typical plots of electrical resistivity as a function of temperature for various polymers are shown in *Figure 1*[12,13]. All of the measurements shown in *Figure 1* were made in the glassy state, i.e. below the glass transition temperature. Here, and throughout this paper, only the glassy state will be considered. It is generally accepted[12,14–16] that the mechanism of electrical conductivity in glassy polymers involves an ionic process with an Arrhenius temperature dependence

$$\rho(T) = \rho_0 \exp(E_c/RT) \qquad (1)$$

where $\rho(T)$ is the resistivity in ohm-cm at temperature T, ρ_0 is a constant, E_c is the activation energy in kcal/mole, R is the gas constant and T is the absolute temperature. Thus, a plot of $\log\rho$ vs. $1/T$ should be a straight line of slope $E_c/(2.303R)$. As can be seen in *Figure 1*, the magnitude and temperature dependence of the resistivity differs from polymer to polymer. These plots for the glassy state have a change in slope at the glass transition. This change in slope was used[12,14–16] to determine the glass transition temperatures used in this work. It has previously been established[12] that glass transition temperatures determined in this manner are in good agreement with values determined in other ways.

The principle of corresponding states, when applied to the electrical resistivity of these polymers, states that polymers at the same reduced temperature should have the same reduced resistivity. Using the glass transition as a corresponding state, the reduced temperature, τ, is given by T/T_g and the reduced resistivity by $\rho(T)/\rho(T_g)$. Replotting all the data from the four polymers in *Figure 1* and data from two additional amorphous glassy polymers as log of reduced resistivity vs. reciprocal reduced temperature, we obtain the result shown in *Figure 2*. The different magnitudes and slopes

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of the data of *Figure 1* now lie on the same master curve. The results on *Figure 2* lend support to the assumption that the glass transition is a corresponding state for electrical resistivity of polymers in the glassy state. Data for other polymers also fall on the master curve on *Figure 2* but are not plotted to maintain clarity.

An immediate consequence of this corresponding state relation is that E_c is directly proportional to T_g. This occurs in the following manner. From equation (1)

$$\log(\rho(T)/\rho_0) = E_c/(2.303RT) \tag{2}$$

Then when $T = T_g$

$$\log(\rho(T_g)/\rho_0) = E_c/(2.303\,RT_g) \tag{3}$$

subtracting (3) from (2) yields

$$\log(\rho(T)/\rho(T_g)) = [E_c/(2.303\,RT_g)]\,(T_g/T - 1) \tag{4}$$

Therefore, a plot of log $(\rho(T)/\rho(T_g))$ vs. T_g/T for a given polymer obeying the law of corresponding states should be a straight line of slope $E_c/(2.303\,RT_g)$. All polymers that obey the law of corresponding states should fall on the same straight line and, hence, have the same value of E_c/RT_g. This is demonstrated for six polymers in *Figure 2*.

Conversely, if a series of polymers all have the same value of E_c/RT_g, then they obey the law of corresponding states. Compiled results for 23 polymers are listed in *Table 1*. With-

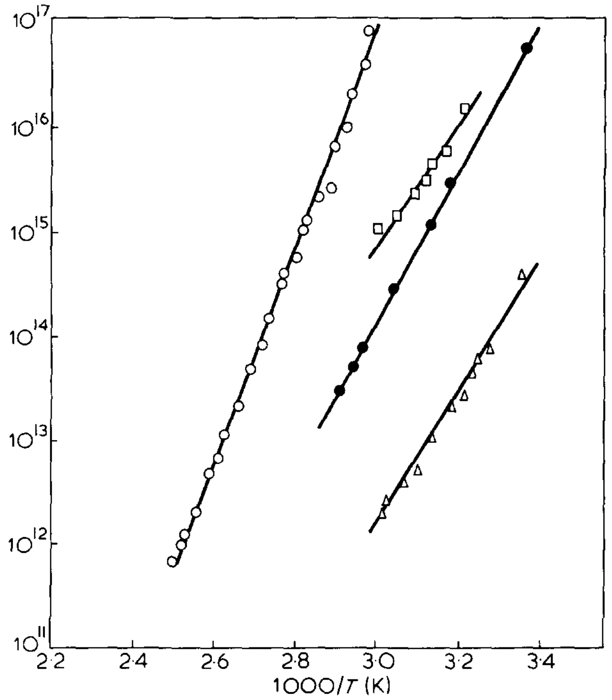

Figure 1 Temperature dependence of the electircal resistivity of polymers. ○, polyester; △, polydiallyl phthalate; ●, polystyrene; □, polyepoxide + D

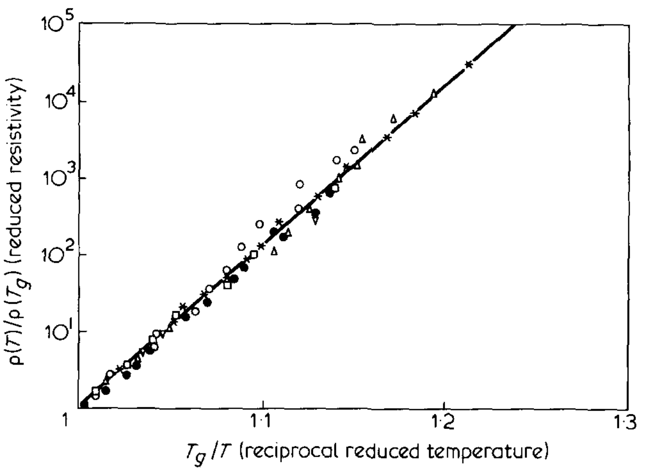

Figure 2 Master curve of reduced temperature vs. reduced resistivity. ○, polyester; △, polyepoxide + DDSA + 1%D; △, polystyrene; *, polyepoxide + DETA; ●, polydiallyl phthalate; □, polyepoxide + DEAPA

Table 1 Activation energies, glass transition and calculated values for polymers

Polymer	E_c (kcal/mole)	T_g, (°K)	E_c/RT_g	Reference for E_c and T_c	E_a (kcal/mole) (Reference 20)
Polyester	25	328	38	30	
Polyvinyl chloride	32.5	347	47	30	70
Polyepoxide and DEAPA	38	383	50	12	
Polyepoxide and D	30	339	45	12	
Polyepoxide and MPDA	38	431	44	12	
Polyester (30% styrene)	46	398	58	12	
Polyepoxide	27.4	385	36	16	
Polyethylmethacrylate	28	338	42	33	50
Poly n-butylmethacrylate	21	293	36	33	29
Polyvinyl acetate	25	304	41	34	44
Polyethylene terephthalate	38	342	56	35	87
Polyurethane	36	364	50	15	
Polyvinyl fluoride	23	253	46	36	40
Polymethylmethacrylate	33	374	44	29	100
Polystyrene	30	355	43	17	100
Polyacrylonitrile	35	378	47	37	
Polyvinyl butyl	29.5	337	44	34	
Polyvinyl formal	42.8	360	60	34	
Polyester (19% styrene)	43	338	64	38	
Polyester (23.6% styrene)	38.5	343	56	38	
Polyester (30% styrene)	36	337	54	38	
Polyester (40% styrene)	31	339	46	38	
Polydiallyl phthalate	29	335	43	13	

DEPA = crosslinked with 5.7% of diethylaminopropylamine
D = crosslinked with 13% of Tris (dimethylaminomethyl) phenol tri(2-ethyl hexate)
MPDA = crosslinked with 12.6% of *m*-phenylenediamine

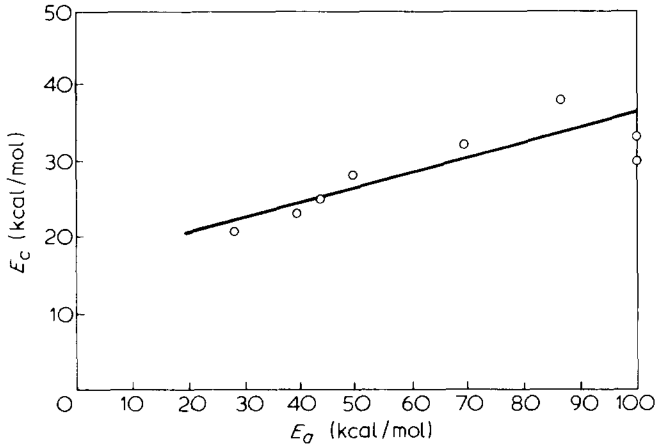

Figure 3 Activation energy for electrical conduction E_c vs activation energy for glass transition E_a

out any evaluation of these data, one finds an average value of $E_c/RT_g = 47$ with individual values differing as much as 36%, with more of them higher than lower than average. On closer examination, most of the high values result from measurements made on the styrene crosslinked polyester series. Eliminating these five, we see that there is a roughly normal distribution of values with only two exceptions that appear anomalous: poly(ethylene terephthalate) and poly(vinyl formal), both of which are high. Without attempting to decide whether these polymers are anomalous because of errors in the experimental measurements or because of some other physical mechanism, we eliminated these polymers from further consideration. The remaining sixteen polymers are of widely differing chemical structure and morphology but have an average value of $E_c/RT_g = 43$, with a normal distribution around this value and with all values within 15% of the average. This is as good as can be expected from measurements by different investigators on different polymers. The deviations from the average are typical of that observed in other corresponding states relations and empirical rules for polymers[10,18–20].

This is the first time it has been shown that a relationship exists between the activation energy for electrical conduction and the glass transition. While the relationship between E_c and RT_g is a consequence of the law of corresponding states, it had been suggested on other grounds in an earlier paper[17].

Similar relationships have been noted by other workers. Turnbull and Cohen[18] found for non-polymeric glass forming liquids that E_v/RT_g has an average value of 44, where E_v is the heat of vaporization. Breitling and Magill[19] found a corresponding states relationship between log reduced viscosity, log (η/η_s) and reduced reciprocal temperature T_g/T. Based upon this relationship, these workers set up a molecular model which led to the conclusion that E_η/RT_g was approximately a constant (E_η is the activation energy for viscous flow). From their data, E_η/RT_g has an average value of 49.

Finally, it has been shown by Boyer[20] that the activation energy for a glass transition, E_a, is related to the transition temperature, T_g. Therefore, since we have shown that E_c is related to T_g and Boyer has shown that E_a is related to T_g, it follows that E_c is related to E_a. That such a relation exists is shown by the data on *Figure 3*. *Table 1* also includes the data from which *Figure 3* is prepared.

MOLECULAR MODEL

While the glass transition is a relaxation process and electrical conduction is an ionic diffusion (transport) process, both involve the cooperative motion of segments of polymer chains. We will assume that at the molecular level the mechanisms of relaxation and diffusion are similar. Eby[21] has previously speculated that this is the case.

The molecular model we propose to explain the results presented in this paper is based on the assumption that both relaxation and diffusion processes in glassy amorphous polymers involve the cooperative rearrangement of polymer segments from one configuration to another. The activation energy required to move a single polymer segment from one position to another is assumed to be a constant, ϵ, for any given polymer, and the total activation energy required for either relaxation or diffusion is the product of ϵ times the number of polymer segments involved, N, or

$$E = N\epsilon \tag{5}$$

It will be assumed that E and N depend on the particular process but ϵ is the same for both diffusion and relaxation. Subscripts c and a will be used on E and N to refer to electrical conduction and the glass transition, respectively.

Since from *Table 1* for both polystyrene and poly(methyl methacrylate) $E_a/E_c \sim 3$, it follows from equation (5) that we would predict that $N_a/N_c \sim 3$, i.e. the glass transition in these polymers involves the cooperative motion of about three times as many segments as does electrical conduction. On the other hand, for poly(vinyl chloride) $E_a/E_c \sim 2$ so that for this polymer twice as many segments should be involved in the glass transition as in electrical conduction.

Eby[21] has shown how to estimate the average number of polymer segments involved in the glass transition (N_a). We will use this same method to estimate the average number of polymer segments involved to allow an ionic current carrier to diffuse in a polymer (N_c).

The number of segments involved in any given process is estimated[21] to be the activation volume, ΔV^*, divided by the average volume occupied by a mole of main-chain atoms and pendant groups, $\bar{V}$

$$N = \Delta V^*/\bar{V} \tag{6}$$

where the activation volume is given by

$$\Delta V^* = (\beta/\alpha)\Delta S^* \tag{7}$$

Here β is the compressibility, α is the thermal expansion coefficient, and ΔS^* is the activation entropy. In the case of electrical conduction, ΔS^* is given[22] by

$$\Delta S^* = R \ln(\rho_0 h/kT) \tag{8}$$

where h is Planck's constant, k is Boltzmann's constant, and ρ_0 is defined in equation (1). Using literature values for compressibility[10,23,23a,24] and thermal expansion coefficient[10,24a,25] at room temperature and calculated[26] values of $\bar{V}$, N_c was calculated for polystyrene (PS), poly(methyl methacrylate)(PMMA), and poly(vinyl chloride)(PVC) with the result that $N_c = 9$ for PS, $N_c = 7$ for PMMA, and $N_c = 15$ for PVC.

It has been estimated[20,27] that, for many polymers, $N_a \sim 15$ to 30. For PS and PMMA then, $N_a/N_c \sim 3$, as predicted above from the ratio of the activation energies. For PVC, $N_a/N_c \sim 2$, also as predicted.

It should be noted that secondary transitions have much lower activation energies than glass transitions[20]. According to equation (5), this implies that fewer segments are involved. Thus, the total activation volume for a secondary transition should be less than for the glass transition which explains the observed[28] reduced pressure dependence of secondary transitions compared with the glass transition. Furthermore, based on the model presented here, the activation energy for a secondary transition should be related to the secondary transition temperature, and such a relation has been observed[20,32].

Using our model, the activation energy per segment can be estimated from equation (5). In units of kcal/mole, $\epsilon(\mathrm{PS}) = 3.3$, $\epsilon(\mathrm{PMMA}) = 4.7$, and $\epsilon(\mathrm{PVC}) = 2.2$. In an independent calculation, Adam and Gibbs[27] found[31] values in reasonable agreement with ours: $\epsilon(\mathrm{PS}) = 4.3$, $\epsilon(\mathrm{PMMA}) = 4.0$, and $\epsilon(\mathrm{PVC}) = 3.0$.

Having ϵ values determined from electrical conduction measurements, we can calculate the number of segments involved in the glass transition, using literature values of E_a[20]. We find $N_a(\mathrm{PS}) = 30$, $N_a(\mathrm{PMMA}) = 21$, and $N_a(\mathrm{PVC}) = 32$, in excellent agreement with the estimates of $N_a \sim 15$ to 30 in the literature[20,27].

In a similar manner we can calculate the number of segments involved in the secondary transition, N_{sec}, using literature values of the activation energy for this transition[20]. We find $N_{sec}(\mathrm{PMMA}) = 4$ and $N_{sec}(\mathrm{PVC}) = 9$.

CONCLUSIONS

1. There is a corresponding states relationship between reduced electrical resistivity and reduced temperature for a large number of glassy polymers.
2. For many polymers, a relationship exists between the activation energy for electrical conduction and the glass transition temperature with an average value of $E_c/RT_g = 43$.
3. A relationship also exists between the activation energy for electrical conduction and the activation energy for the glass transition.
4. The molecular mechanism for relaxation processes is similar to that for diffusion processes.
5. The total activation energy for either a relaxation or a diffusion process is the product of the energy to move one segment times the number of segments involved (i.e. $E = N_\epsilon$) in a cooperative motion.

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