

Notes to the Editor

amounts of OH, COOH, and NH₂ groups per 100 g of copolymer. The final inflection of the potentiometric curves of the fractions 3, 4 and 5 only, coincided with the complete neutralization of NH₂ groups. As stated earlier, this may be related to the composition of the copolymers.

The most interesting feature of the titration curves is the presence of a 'smallest interval' between any two consecutive breaks/inflections, and the remaining breaks or inflections in the titration curves occur in simple multiples of this smallest interval. The smallest interval has been found to be different for the copolymer and the various fractions. Of course, this interval is identical for a particular fraction, irrespective of whether it is titrated with an acid or a base. The fact that some of the functional groups in the copolymer chain have been neutralized in a stepwise manner, indicates that they have hyperacid/hyperbasic character. This enhanced acidity/basicity could be attri-

buted to intramolecular hydrogen bonding between neighbouring functional groups. Indeed, infra-red spectra of the copolymer and all the fractions indicated sharp absorptions in the range 3450–3600, and 3070–3350 cm⁻¹, showing the probable presence of O–H···O and N–H···N intramolecular hydrogen bonding. Of course, the presence of such hydrogen bonding has already been reported in phenolic oligomers from infra-red⁵, conformational⁶ and titrimetric studies⁷. The more distinct stepwise neutralization of the functional groups in conductometric titration curves compared to potentiometric curves may be due to the formation and different degree of dissociation of acid–anion or base–cation complexes which might be present in a medium of low dielectric constant. As expected, these effects had little influence on the potentiometric curves. Moreover, the formation of homoconjugate complexes in a medium of low dielectric constant may

also have pronounced influence on the nature of the conductometric titration curves⁸.

Thus non-aqueous titrations may provide a rapid and convenient method for determining the relative amounts of different repeating units present in copolymers with acidic and basic functional groups.

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Molecular interpretation of correlation between polymer glass transition T_g and an e.s.r. parameter T_{50G}

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INTRODUCTION

It has been shown that the glass transition temperature, T_g , of polymers can be measured by means of nitroxide spin probes incorporated in the polymer matrix^{1–4}. In particular, the so-called T_g , T_{50G} correlation, first reported by Rabold¹ and semiquantitatively characterized by Kumler and Boyer⁴ using 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (BzONO) radicals, is a valuable tool for T_g determination because T_{50G} can be measured straightforwardly. T_{50G} is the temperature at which the separation of the outermost peaks of the electron spin resonance (e.s.r.) spectrum of probes in polymer matrix is 50 G (gauss). The bulky nitroxide radicals which experience the

dynamic state of their microenvironment are supposed to be located in amorphous regions of polymers. Thus it seems probable that the T_g , T_{50G} correlation will be a potential method for determining T_g for non-homogeneous polymer systems, e.g. polymer blends, filled and reinforced polymers. Therefore, the molecular origin of the T_g , T_{50G} correlation should be exactly determined. Here we have studied this relationship for some amorphous carbon backbone polymers which can be regarded as one phase systems. The experimental results are explained quantitatively on the basis of thermally activated motions of polymer segments.

EXPERIMENTAL

Materials

E.s.r. measurements were carried out with the following high molecular

weight polymers: polyisobutylene (PIB) Oppanol B 200 obtained from BASF; poly(ethyl acrylate) (PEA) and poly(methyl acrylate) (PMA) from Röhm; poly(vinyl acetate) (PVAc) from Hoechst and suspension polymerized poly(vinyl chloride) (PVC) from BASF.

Methods

The spin probe radical BzONO was prepared according to the method of Rozantsev⁵. Solid BzONO at a concentration of 100 ppm was added to a solution of polymer in an appropriate solvent. A solid sample was obtained by evaporation of the solvent. The resultant sample was dried in a vacuum oven at 313–323K overnight. E.s.r. spectra were recorded over a suitable temperature range using an AEG 12 X spectrometer equipped with a temperature accessory. The measurement conditions were controlled to avoid overmodulation and saturation effects⁶. The parameter T_{50G} , related to the tumbling frequency of the paramagnetic probe with an effective frequency of

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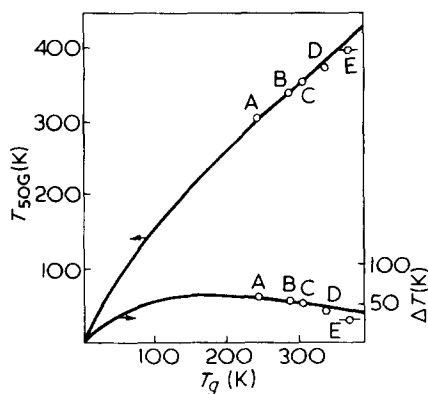


Figure 1 Calculated and measured ΔT and T_{50G} values as a function of the dynamic (10^2 Hz) glass transition temperature. Experimental values: A, PIB; B, PEA; C, PMA; D, PVAc; E, PVC; (—), calculated according to equations (5) and (6)

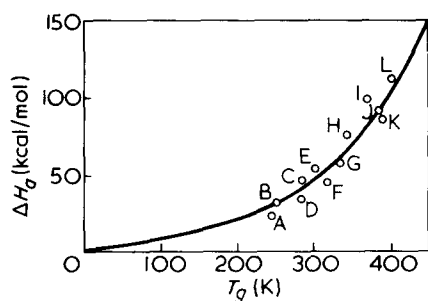


Figure 2 Apparent activation energy for the T_g relaxation of amorphous carbon backbone polymers as a function of the dynamic (10^2 Hz) glass transition temperature. Experimental values based on McCrum's⁷ and manufacturers' data. A, Polyisobutylene; B, poly(*n*-propyl acrylate); C, poly(ethyl acrylate); D, poly(isobutyl methacrylate); E, poly(methyl acrylate); F, poly(*n*-butyl methacrylate); G, poly(vinyl acetate); H, poly(methyl methacrylate) isotactic; I, poly(vinyl chloride); J, poly(ethyl methacrylate); K, polystyrene; L, poly(methyl methacrylate) random; (—), calculated according to equation (7)

about 10^7 Hz (ref 4) was graphically determined when the outermost peaks of the three line e.s.r. spectra were plotted vs. temperature.

ANALYSIS OF T_g , T_{50G} CORRELATION

If f is the frequency at which a mechanical or dielectric loss peak in a polymer has a maximum at temperature T , the examination of relaxation maps, e.g. those compiled by McCrum *et al.*⁷, indicates that two types of $\log f$ vs.

$1/T$ correlation are possible. We observe either simple linear Arrhenius behaviour or a non-linear Williams-Landel-Ferry behaviour for which a sharp curvature of the relaxation curve is seen at low frequencies⁴. Difficulties arise from this in the calculation of the apparent activation energy (ΔH_a) for the T_g relaxation process as Kumler and Boyer have discussed earlier⁴. They elected to use the Arrhenius behaviour in the frequency range from 1 to 10^7 Hz because it is simpler and secondary relaxations frequently follow it exactly over an even broader frequency range than does the T_g .

For a further minimization of the error, which in the case of some polymers (e.g. PIB and PVAc) arises from the assumption of the simple Arrhenius behaviour, we have restricted our analysis to the frequency range from 10^2 to 10^7 Hz. Accordingly, the ΔH_a for T_g relaxation can be calculated using the Arrhenius equation:

$$f = f_0 \exp(-\Delta H_a/RT) \quad (1)$$

Making use of the Arrhenius equation (1) for T_g and T_{50G} and assuming identical values for the pre-exponential factor, f_0 , the frequency shift is obtained:

$$\ln \frac{f T_{50G}}{f T_g} = -\frac{\Delta H_a}{R} \left(\frac{1}{T_{50G}} - \frac{1}{T_g} \right) \quad (2)$$

which is correlated to the temperature shift:

$$\Delta T = T_{50G} - T_g \quad (3)$$

By inserting equation (3) into equation (2) we obtain, after some rearrangement for equation (2):

$$\Delta T = \frac{T_g^2}{\{\Delta H_a [R \ln(f T_{50G}/f T_g)]\} - T_g} \quad (4)$$

CALCULATED AND EXPERIMENTAL RESULTS

In Figure 1 the experimental ΔT and T_{50G} values are given as a function of the dynamic (10^2 Hz) glass transition temperatures T_g which were obtained from the manufacturer or from the literature⁷. On the basis of these data we propose the following expression for the T_g , ΔT dependence:

$$\Delta T = \frac{T_g}{\exp(T_g/T_c)} \quad (5)$$

where T_c is a correlation temperature. For the T_g , T_{50G} relationship it follows from equations (3) and (5):

$$T_{50G} = T_g \left[1 + \frac{1}{\exp(T_g/T_c)} \right] \quad (6)$$

For $T_g \gg T_c$ the T_g dependence of T_{50G} is linear with slope = 1. For the one parameter representation of ΔT and T_{50G} as a function of T_g a value of $T_c = 173$ K is obtained by best fit method. The corresponding calculation curves are also given in Figure 1. Within experimental error, there is a satisfying agreement between experimental and calculated results. If the proposed relationship (5) is valid, the experimental values for the apparent activation energy ΔH_a as a function of T_g must obey the following equation (7), which results directly from the equations (4) and (5):

$$\Delta H_a = R \ln \frac{f T_{50G}}{f T_g} T_g [1 + \exp(T_g/T_c)] \quad (7)$$

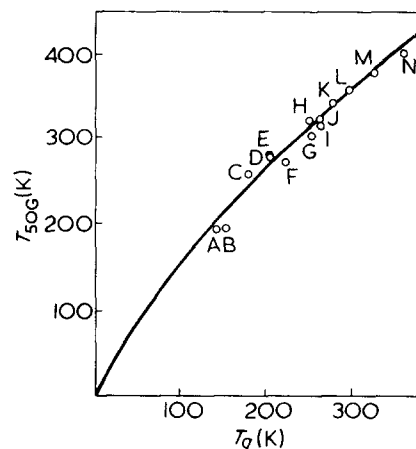


Figure 3 E.s.r. parameter T_{50G} as a function of T_g of amorphous and semicrystalline carbon backbone and heterogeneous backbone polymers. Experimental values: A, poly(methyl ethyl siloxane)⁴ (T_g 1 Hz)⁴; B, poly(dimethyl siloxane)⁴ (T_g 10² Hz)⁹; C, polybutadiene¹⁰ (T_g 1 Hz)⁴; D, polyethylene⁴ (T_g 10² Hz)¹¹; E, polyethylene¹ (T_g 10² Hz)¹¹; F, polyoxyethylene⁴ (T_g 10² Hz)¹²; G, polyisobutylene (T_g 10² Hz)¹³; H, polyoxymethylene⁴ (T_g 1 Hz)⁴; I, polypropylene¹ (T_g 10² Hz)¹⁴; J, poly(vinyl fluoride)⁴ (T_g 10² Hz)¹⁵; K, poly(ethyl acrylate) (T_g 10² Hz)¹³; L, poly(methyl acrylate) (T_g 10² Hz)⁷; M, poly(vinyl acetate) (T_g 10² Hz)⁷; N, poly(vinyl chloride) (T_g 10² Hz)⁷

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The apparent activation energy increases strongly as a function of T_g in accordance with the statement of Boyer⁸.

Figure 2 shows the ΔH_a values for some linear amorphous carbon backbone polymers of widely varying activation energies and glass temperatures⁷. It can be seen that the curve calculated according to equation (7) gives a good fit to the experimental data. This good agreement verifies the validity of the proposed equation (5). We therefore propose that for linear amorphous carbon backbone polymers the dynamic T_g value and, from this, the apparent activation energy ΔH_a can be determined once T_{50G} is known.

Kumler and Boyer⁴ developed a semi-quantitative equation to relate T_{50G} to selected data of T_g at 1 Hz as follows:

$$T_{50G} = T_g / \left(1 - \frac{0.03 T_g}{\Delta H_a} \right) \quad (8)$$

It can be shown, that the relationship (8) of Kumler and Boyer⁴ describes the same behaviour and is of the same form as equation (6). To show this, the expression for ΔH_a (equation 7) is inserted into equation (8). After some rearrangements the following expression is obtained:

$$T_{50G} = T_g \left[\frac{1 + \exp(T_g/T_c)}{1 + \exp(T_g/T_c) - \alpha} \right] \quad (9)$$

where

$$\alpha = 0.03/R \ln \frac{f_{T_{50G}}}{f_{T_g}}$$

For the case $\alpha = 1$, equations (8) and (6) are identical. With the frequency shift of $\sim 10^7$ Hz given by Kumler and

Boyer⁴ α has indeed the value of ~ 1 and it is related to the physical quantity:

$$R \ln \frac{f_{T_{50G}}}{f_{T_g}}$$

CONCLUSIONS

It was shown that the experimental T_g , T_{50G} correlation of amorphous linear carbon backbone polymers can be explained quantitatively by means of T_g -relaxation data.

It is also interesting to examine if semicrystalline polymers and polymers with heterogeneous chain structure obey equation (6). We have therefore collected the literature T_g , T_{50G} data of these polymers in addition to our own results in Figure 3. The T_g values are dynamic ones (10^2 Hz) with some exceptions which are given in the caption of Figure 3.

It is seen that virtually all studied polymers obey equation (6) because a good correlation within the experimental error is found. From this it may be concluded that the apparent activation energy for the T_g relaxation of polymers with different chain structures and crystallinity may also be expressed by means of equation (7).

However, one important limitation of equation (6) must be taken into account: the relative size of a polymer segment (characterized by means of the activation volume ΔV^\ddagger by Boyer¹⁶) must be smaller than the size of the probe radical. When ΔV^\ddagger is greater than the volume of the probe radical and the frequency of $T < T_g$ relaxations (β , γ , δ) attains the order of 10^7 Hz, already below T_g , the rotations of BzONO radicals evidently are determined by these local segmental relaxations. This may be the reason for

some reported $T_{50G} - T_g < 0$ values^{4,17,18}.

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