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

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The tumbling of five nitroxide spin probes (molecular weights between 172–486 g/mol) in a standard unfractionated polyisobutylene [$\bar{M}_v$ = (1.26 ± 0.18) × 10^6 g/mol] has been studied by means of the electron spin resonance (e.s.r.) technique. The temperature at which the separation of the outermost peaks of the e.s.r. spectrum is 50 G (T_{50G}) attained a limiting value T^l_{50G} = 330K at probe M_w = 332 g/mol. This temperature coincided with the temperature of the loss maximum of the merged glass transition (T_g) and segmental relaxations at the corresponding frequency (3 × 10^7 Hz). A literature survey indicated that an analogous situation exists in the case of poly(vinylidene fluoride) and polyamide-6,10 while T^l_{50G} values of poly(2,6-dimethyl phenylene oxide) and polycarbonate are correlated only to segmental relaxations of polymer chains. It is concluded that the equation:

$$T_{50G} = T_g[1 + (\exp T_g/T_c)^{-1}]$$

describes generally the temperature shift between glass transitions at low and high frequencies and can be applied to determine experimentally low frequency T_g values from T^l_{50G} values if T_g and $T < T_g$ relaxations (if any are present) are already merged at this temperature.

INTRODUCTION

In recent reports the usefulness of the so-called T_g, T_{50G} correlation in the determination of glass transition temperatures (T_g) of polymers has been clearly demonstrated[1–5]. T_{50G} is the temperature at which the separation of the outermost peaks ($2A'_{ZZ}$) of the electron spin resonance (e.s.r.) spectrum of stable free nitroxide radicals in polymer matrix is 50 G (gauss)[6].

The T_g, T_{50G} correlation was derived for the 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (BzONO) radical[1–5]. The molecular interpretation of the correlation is that these probe radicals respond at T_{50G} to the motion of polymer chains at the T_g relaxation. Previous experimental results suggest that nitroxides of varying size and functionality may respond differently to the same morphological transition[1,4,7,8]. On the other hand, it has been reported that the rotational correlation times (τ_R) of large, flexible probes rapidly approach limiting values as a function of their molecular weight[7]. These limiting values represent fairly well the frequencies of combined T_g and segmental $T < T_g$ (γ) relaxations in the high frequency region[8]. This observed radical–polymer interrelationship is explained quantitatively assuming that increasing molecular weight (M_w) of flexible radicals leads to increased possibilities of intermolecular interactions between radicals and polymer chains. Evidently the radical motions couple with the rotations of polymer segments and as a consequence the motional state of large radicals approaches that of polymer chains[8].

Because T_{50G} is a dynamic parameter (the corresponding rotation frequency of radicals is $\sim 10^7$–10^8 Hz [1–3,5]), it should also approach a limiting value as a function of probe M_w. According to the proposed coupling mechanism[8] it can be assumed that the rotational frequencies corresponding to this limiting value should represent relaxation frequencies of polymer chains.

We have tested the validity of the above hypothesis by studying the tumbling of five different spin probes in polyisobutylene (PIB). A brief literature survey of T_{50G} values is also given.

EXPERIMENTAL

A standard unfractionated high molecular weight sample $\bar{M}_v$ = (1.26 ± 0.18) × 10^6 g/mol of PIB from BASF was dissolved in chloroform and precipitated with methanol.

The probe radicals I–V were prepared by methods given earlier[5,9]:

Probe	M_w(g/mol)
I	172
II	183
III	276
IV	332
V	486

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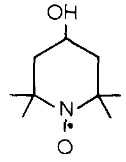
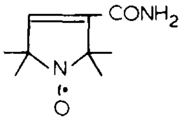


(I)



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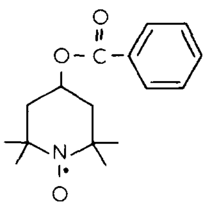

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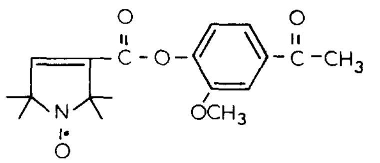

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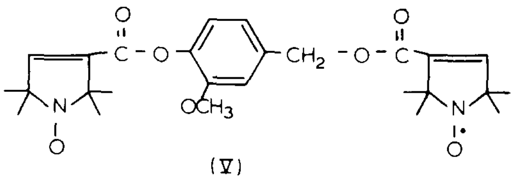

(V)

Solid solutions of probe radicals in PIB were prepared by dissolving appropriate amounts of probes in chloroform solutions of PIB and by evaporating the solvent. The samples were dried overnight in a vacuum oven at 320K. The 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 effects[10].

RESULTS AND DISCUSSION

In *Figure 1* are given, as an example, the e.s.r. spectra of radical III in PIB at 233K ($T < T_{50G}$), 321K ($T \sim T_{50G}$) and at 381K ($T > T_{50G}$).

The separations of the outermost peaks ($2A'_{zz}$ in G) of the three-line e.s.r. spectra of probes I–V in PIB are given as a function of temperature in *Figure 2*. Sigmoidal curves are obtained as has been generally reported earlier[3,6,10]. The curves all show a fairly sharp break whose midpoint is at ~50 G. T_{50G} values which can be measured from *Figure 2* are given as a function of M_w of probes in *Figure 3*. Additionally we have collected in *Figure 3* available literature T_{50G} data of different spin probes in some polymers.

It can be seen that T_{50G} values of different probes in PIB, poly(vinylidene fluoride) (PVF$_2$), poly(2,6-dimethylphenylene oxide) (PDMPO), poly(4,4'-isopropylidene-1,1'-diphenylene carbonate) (PC) and poly(4,4'-isopropylidene-2,2',6,6'-tetrachloro-1,1'-diphenyl carbonate) (PCCl$_4$) rapidly approach limiting values as a function of M_w. The T_{50G} values of the probe radicals in polystyrene (PS) have evidently not yet attained the limiting value in the studied M_w region although the trend to a limiting value can be clearly seen.

These results can be understood if it is assumed that label and probe radicals 'see' the dynamic state of their immediate environment. *Figure 3* indicates that at high M_w values the dynamic state of the radical is no more a function of M_w but it is principally determined by the dynamic state of polymer matrix.

The dynamic state of nitroxides is usually characterized by means of two theories; (a) rapid rotations[14,15] and (b) slow rotations[16]. The rapid rotation theories are valid in the rotational region where the e.s.r. spectra are symmetrical and the hyperfine components do not overlap[17,18] ($4 \times 10^{-9} \gtrsim \tau_R > 10^{-11}$ sec; the rotational correlation time τ_R is defined in terms of statistical fluctuations of angular variables[14,15]). The theories of slow rotations can be used to estimate τ_R

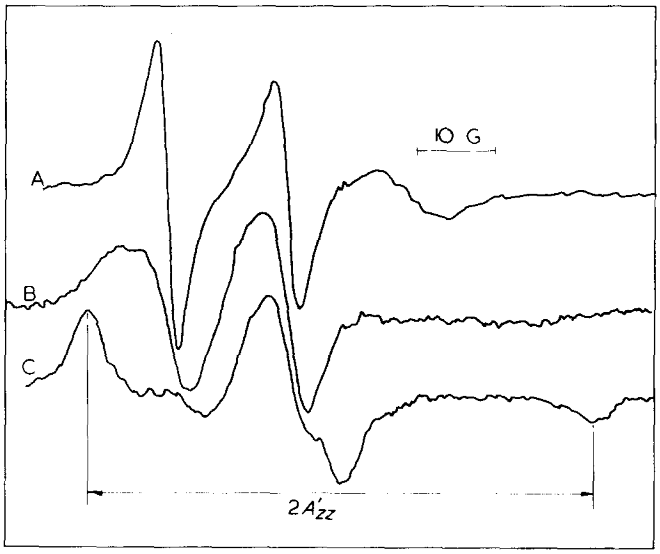

Figure 1 The e.s.r. spectra of radical III in polyisobutylene with temperature as variable. A, 381K; B, 321K; C, 233K

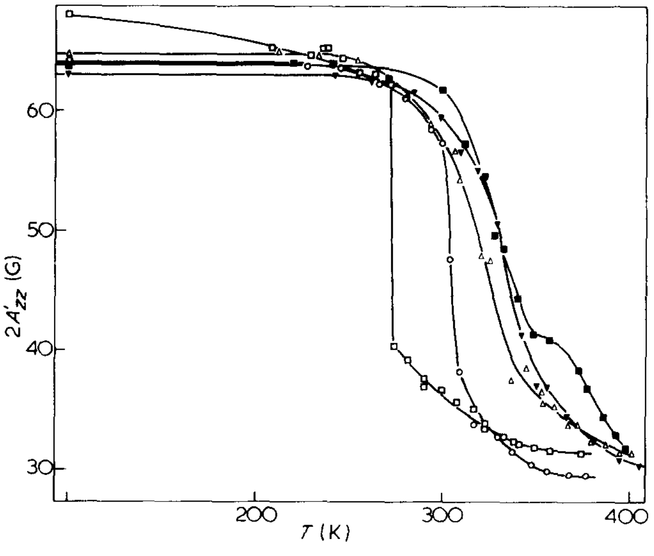

Figure 2 Plots of extrema separation ($2A'_{zz}$) vs. temperature in the e.s.r. spectra of radicals: □, I; ○, II; △, III; ▼, IV; ■, V. Solvent, polyisobutylene

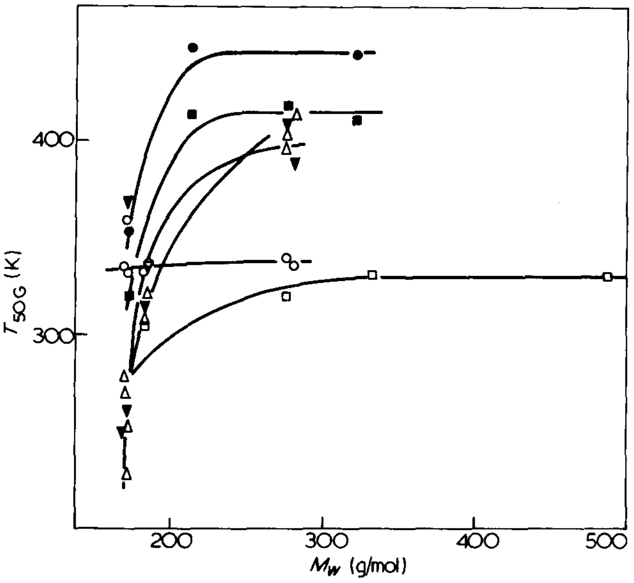

Figure 3 T_{50G} vs. probe molecular weight: □, PIB (from *Figure 2*); ○, PVF_2[4]; △, PS[4,13]; ▼, PDMPO[12,4]; ■, PC[3,11]; ●, $PCCl_4$[11]

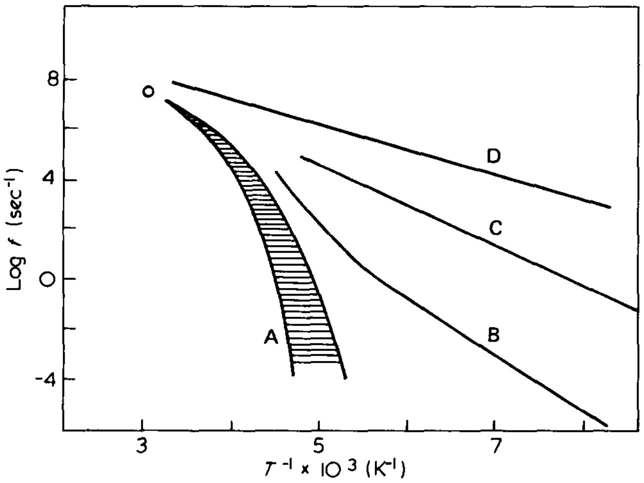

Figure 4 Schematic relaxation map of PIB showing A, $T_g(\beta)$, B, γ(segmental), C, γ (segmental) and D, δ($-CH_3$ group rotation) relaxations[19–21]; ○, T^l_{50G} of *Figure 3*

values from the asymmetrical e.s.r. spectra when the outer lines do not converge to the motionally narrowed spectrum ($10^{-7} > \tau_R > 10^{-8}$ sec)[16]. When $2A'_{ZZ}$ is 50G the outer lines clearly converge to the motionally narrowed spectrum although the hyperfine components still overlap considerably as can be seen from *Figure 1* for $T = 321$K. Therefore the values of τ_R corresponding to T_{50G} evidently lie between 4×10^{-9} and 10^{-8} sec. When these τ_R values are converted into the corresponding effective frequencies $f = (2\pi \tau_R)^{-1}$ a practical mean frequency $f = 2.8 \pm 1.2 \times 10^7$ sec^{-1} corresponding to T_{50G} is obtained. Using this frequency value, we have compared the limiting T_{50G} values (T^l_{50G}) of *Figure 3* with the temperature–frequency relationships of schematic relaxation diagrams of PIB, PVF_2, PDMPO and PC. The results are given in *Figures 4–7*.

Additionally we extrapolated from low temperature literature data of spin-labelled polyamide (PA) 6,10 ($\bar{M}_v$ = 4000 g/mol) a T^l_{50G} value 410K (label radical: 3-chloroformyl-2,2,5,5-tetramethylpyrroline-1-oxyl)[29]. This is justified because (i) the low temperature τ_R data of spin labelled PA 6,10 are in good agreement with the frequencies of segmental $T < T_g$ (γ) relaxation of PA 6,10[29], and (ii) the spin labels are bonded covalently to the host polymer molecules and therefore labels can be regarded as 'macroprobes' whose M_w is equal to the average M_w of the polymer. When it is assumed that the behaviour shown in *Figure 3* is general it can be concluded that in the case of PA 6,10 the T_{50G} value of label radicals is equal to T^l_{50G}. The schematic Arrhenius plot of PA 6,10 with the above T^l_{50G} value is given in *Figure 8*.

Figures 4–8 show that:

(1) the T^l_{50G} values of PIB, PVF_2 and PA 6,10 at the corresponding effective frequency $f \sim 3 \times 10^7$ Hz lie upon the relaxation line which is composed of the merged T_g and segmental relaxations;

(2) the T^l_{50G} values of PDMPO and PC clearly do not represent T_g relaxations but are determined by segmental relaxations alone.

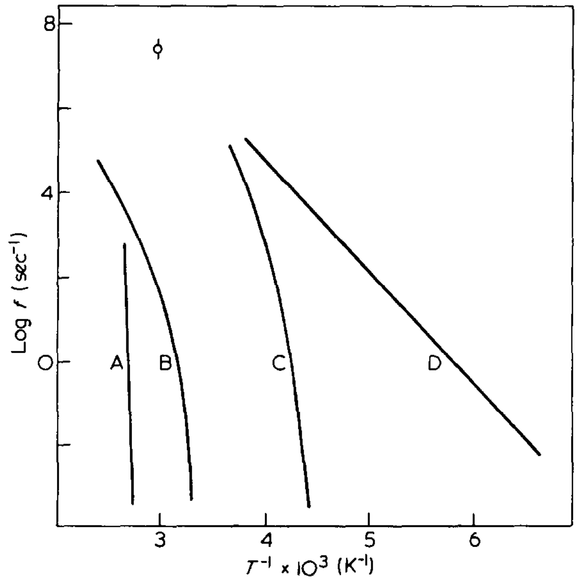

Figure 5 Schematic relaxation map of PVF_2 showing A, $T\alpha_c$ (crystalline phase), B, T_g (*U*) (loop and tie molecule T_g relaxation), C, T_g (*L*) (β, the conventional T_g) and D, γ (segmental) relaxations[22]; ○, T^l_{50G} of *Figure 3*

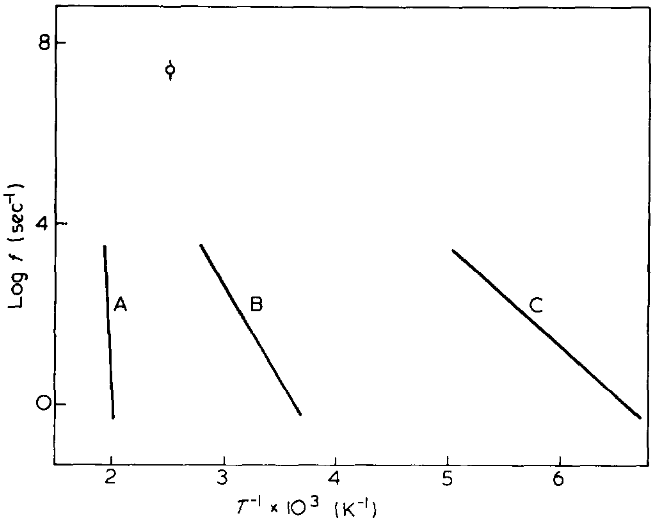

Figure 6 Schematic relaxation map of PDMPO showing A, $T_g(\alpha)$, B, β(segmental) and C, γ(segmental) relaxations[23–28]; ○, T^l_{50G} of *Figure 3*

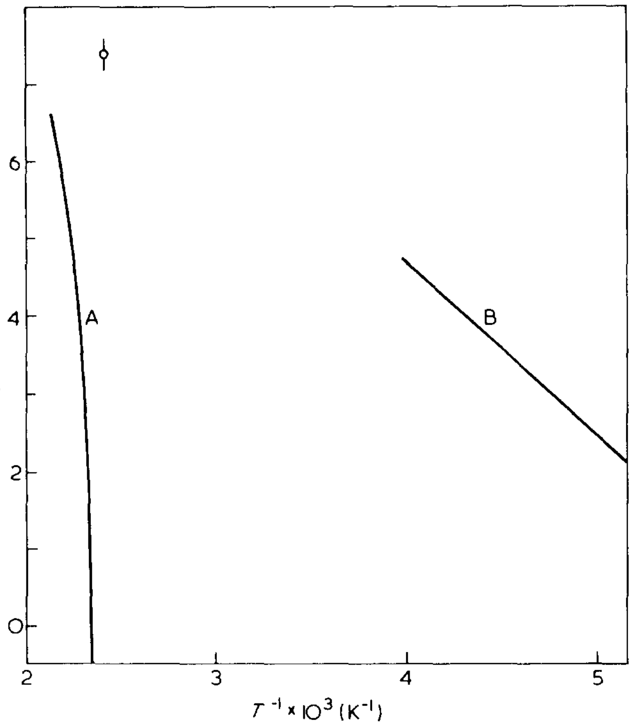

Figure 7 Schematic relaxation map of PC showing A, T_g (β) and B, γ(segmental) relaxations[19]; ○, T'_{50G} of *Figure 3*

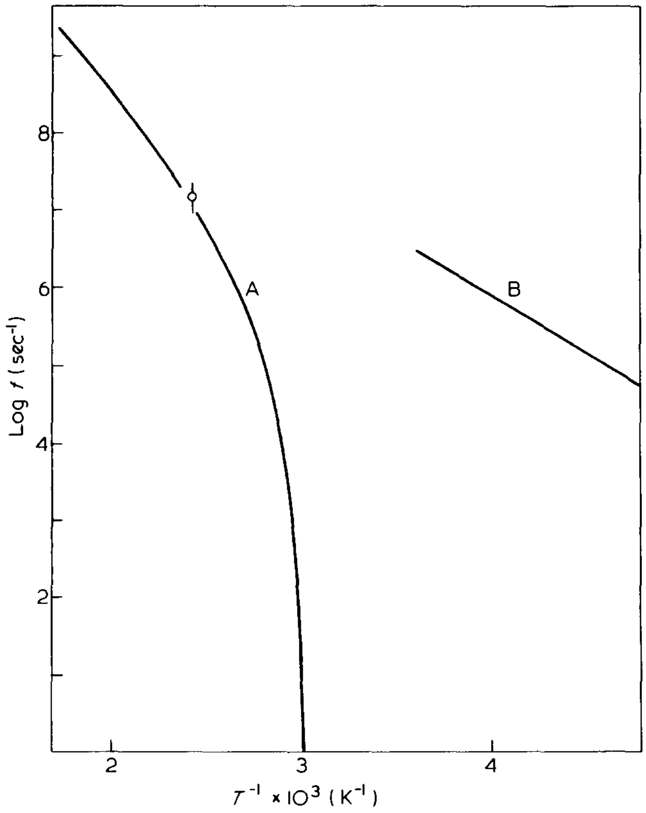

Figure 8 Schematic relaxation map of PA 6,10 showing A, T_g (β) and B, γ(segmental) relaxations[19,30]; ○, T'_{50G} extrapolated by means of low temperature literature data for τ_R[29]

These results show the important role of molecular relaxations in radical–polymer relationships[8,29,31,32].

It is generally accepted that when several short segments undergoing segmental relaxations coordinate their motions, the combined motion gives rise to the glass transition since larger segments of the polymer chain are now mobile[33]. Because the activation energy of the glass transition is considerably larger than that of segmental relaxations the processes merge at high temperatures T'. It can be concluded that whenever $T'_{50G} \geqslant T'$ a monotonic correlation exists between T_g and T'_{50G}.

It can be seen from *Figures 4–8* that in the case of PIB, PVF$_2$ and PA 6,10 $T'_{50G} \geqslant T$. Therefore it is interesting to compare these T'_{50G} values with general T_g relaxation data for different polymers. This can be done by calculating from the literature the temperatures at which the frequency of T_g relaxation is 3 x 10^7 and 10^2 Hz. In *Figure 9* the high frequency temperatures are plotted against the low frequency values for 12 different polymers whose relaxations have been well characterized by means of dielectric, mechanical and nuclear magnetic resonance (n.m.r.) methods over a large frequency region. Additionally the T'_{50G} values of PIB, PVF$_2$ and PA 6,10 are given as a function of T_g (10^2 Hz).

Earlier we proposed that the T_g, T_{50G} correlation can be expressed by the empirical equation[5]:

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

where T_c is a correlation temperature representing the frequency shift between T_{50G} and T_g. If this relation is generally valid it must describe the frequency shift of relaxation data within the frequency range of 10^2–3 x 10^7 Hz. The comparison between experimental and calculated (equation 1) high frequency T_g, T'_{50G} data as a function of low frequency T_g values gives a mean value of T_c = 214K for the correlation temperature by best fit method. By means of this T_c value a good agreement between measured and calcu-

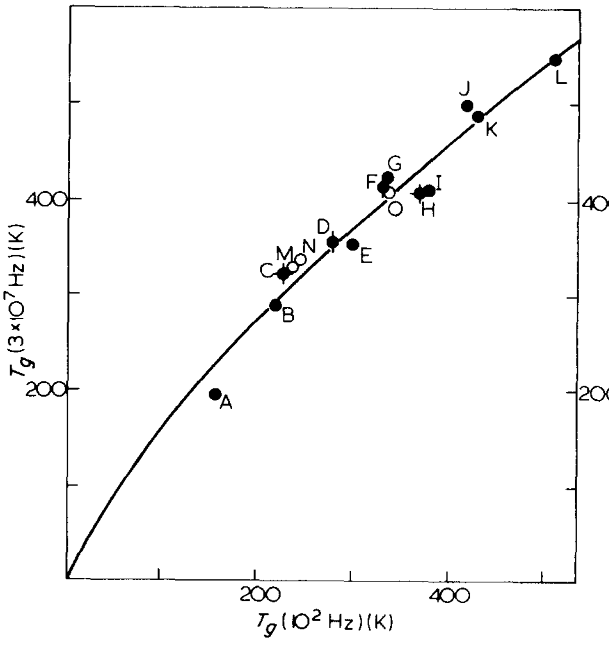

Figure 9 High frequency (3 X 10^7 Hz) glass transition temperatures vs. low frequency (10^2 Hz) glass transition temperatures. ●, A, poly(dimethyl siloxane)[34–39]; B, natural rubber[19,40–44]; C, polyisobutylene[19–21]; D, polypropylene[20,45,46]; E, poly(methyl acrylate)[19]; F, poly(vinyl acetate)[19,39]; G, polyamide 6,10[19,30]; H, poly(vinyl chloride)[19]; I, poly(ethylene terephthalate)[19]; J, poly(methyl methacrylate)[20,47]; K, polycarbonate[19]; L, poly(2,6-dimethylphenylene oxide)[23–28]. ○, E.s.r. parameter T'_{50G} from *Figure 3*. M, polyisobutylene; N, poly(vinylidene fluoride); O, polyamide 6,10. (——), Calculated according to equation (1)

lated results is obtained, as can be seen from *Figure 9*. This leads us to the following conclusions:

(A) equation (1) describes generally the temperature shift between glass transitions at low and high frequencies; and

(B) equation (1) can be applied to determine experimentally low frequency T_g values from T^{l}_{50G} values if T_g and $T < T_g$ relaxations (if any are present) are already merged at this temperature.

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