at infinite dilution

$$B = \lim_{\Phi_2 \to 0}\left[\frac{\Delta H_M}{N_1\Phi_2}\right] = \lim_{N_2 \to 0}\left[\frac{\Delta H_M}{N_2}\right]\left[\frac{V_1^*}{V_2^*}\right]$$
$$= \frac{V_1^*}{\tilde{v}_1}\left[P_2^*\left\{\frac{\tilde{v}_1}{\tilde{v}_2} - 1 - \alpha_1 T\left(1 - \frac{\tilde{T}_2}{\tilde{T}_1}\right)\right\}\right.$$
$$\left. - (1 + \alpha_1 T)\left\{\nu_{12} + \nu_{21}\frac{q_2/r_2}{q_1/r_1}\exp\left(-\frac{\nu_{21}v^*}{RT\tilde{v}}\right)\right\}\right] \quad \text{(B2)}$$

where α_1 is the thermal expansion coefficient of the solvent and $\tilde{T}_2$ and $\tilde{T}_1$ are the reduced temperatures for polymer and solvent.

Equation B2 is closely related to Flory's analogous expression, which is eq 42 in ref 8.

Chemical Potential. The residual chemical potential can be expressed in terms of the residual enthalpy and entropy. The residual enthalpy, calculated by the nonrandomness equation, is:

$$\overline{H}_1^R = \overline{H}_1 - H_1^0 = (\partial \Delta H_M/\partial N_1)_{T,N_2,\tilde{v}} = V_1^* P_1^*(\tilde{v}_1^{-1} - \tilde{v}^{-1}) - (V_1^*/\tilde{v})[\theta_{21}^2\nu_{21} + (\Phi_2/\Phi_1)\theta_{22}\theta_{12}\nu_{12}] \quad \text{(B3)}$$

The residual entropy is the same as that given by Flory's expression 8. The residual chemical potential is

$$(\mu_1 - \mu_1^0)^R = \overline{H}_1^R - T\overline{S}_1^R = P_1^* V_1^* \{3\tilde{T}_1 \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + (\tilde{v}_1^{-1} - \tilde{v}^{-1})\} - (V_1^*/\tilde{v})[\theta_{21}^2\nu_{21} + (\Phi_2/\Phi_1)\theta_{22}\theta_{12}\nu_{12}] \quad \text{(B4)}$$

Equation B4 is also closely related to eq 48 in ref 8.

Nonvalidity of Simplifying Assumption. An energy balance of the 1–2 interactions requires that

$$q_1 N_1 \theta_{21}\eta_{21} = q_2 N_2 \theta_{12}\eta_{12} \quad \text{(B5)}$$

It appears attractive to assume that $\eta_{21} = \eta_{12}$. However, except for the random-mixing case where local compositions are equal to overall compositions, eq B5 cannot be satisfied for all values of N_1 and N_2 when $\eta_{12} = \eta_{21}$.

The parameter η_{ij} depends not only on the potential energy between segment i and segment j but also on the distribution function. In a simple liquid mixture, distribution function i–j is the same as distribution function j–i but in a mixture of polymer and solvent, local structure differences do not allow us to assume such symmetry. One may therefore say that any à priori insistence that η_{ij} *must* equal η_{ji} follows only from a narrow interpretation, erroneously conditioned either by strict lattice concepts or by considerations valid only for simple (argonlike) fluids. These remarks in no way "prove" the model proposed here which obviously has an empirical flavor. They are intended to support the plausibility of the model and, more important, to stimulate reexamination of fundamental concepts in solution thermodynamics.

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ESR Studies of Polymer Transitions. 1[1]

Philip L. Kumler* [2a] **and Raymond F. Boyer**[2b]

Department of Chemistry, Saginaw Valley State College, University Center, Michigan 48710, and Midland Macromolecular Institute, Midland, Michigan 48640.

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ABSTRACT: The ESR spin-probe technique, using a nitroxide radical as the paramagnetic probe, has been shown to be a general method for the study of molecular transitions, especially the glass transition, in a series of polymeric materials. The technique has been applied to 19 different polymers/copolymers and an empirical correlation between the glass temperature (T_g) and an experimental ESR parameter (T_{50G}) has been established; a theoretical basis for the observed correlation is also presented. Results of the application of this method to polymers for which the T_g is a matter of controversy are also presented and discussed.

The use of electron spin resonance (ESR) techniques with nitroxide radicals to study motion in macromolecular systems was first applied to biological polymers.[3] The ESR technique is gaining increasing attention as an important tool for the study of synthetic polymers and copolymers following the pioneering work of Rabold[4] and of Stryukov and Rozantsev.[5] A recent review article by Buchachenko et al.[6] gives a good overview of the theory and scope of the technique, as well as a summary of prior experimental results.

The ESR work performed thus far falls into two different categories, "spin-probe" experiments or "spin-label" experiments. In the "spin-probe" experiment the paramagnetic molecule is present as a "free" or "guest" molecule in the polymer matrix at concentrations of 10–100 ppm;[6–11] in the

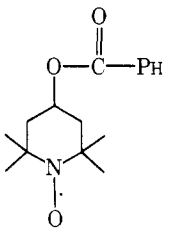
"spin-label" experiment the paramagnetic center is incorporated into the polymer chain by covalent bonding.[11-16] A few of the studies[11,14,17] have included both spin-probe and spin-label results and a comparison of the two distinct methods. The work to be reported here is exclusively of the spin-probe type.

Other magnetic resonance techniques, especially wide-line NMR experiments, empirically exhibit the same type of temperature dependency as ESR spin-probe experiments.[18] It is well established that NMR line-width parameters do correlate with glass temperatures but no direct comparisons of the NMR and ESR methods have been made. Both of these methods are high-frequency test methods and we expect the results from these two types of experiments to be complementary. Whereas the NMR method "observes" the host polymer directly (signals from protons or other nuclei covalently bonded to the polymer itself), the ESR spin-probe method "observes" the dynamic properties of a "guest" paramagnetic mlecule.

Whereas most studies have been concerned with the onset of nitroxide motion in amorphous polymers and copolymers and in the amorphous phase of semicrystalline polymers and copolymers, recent work by both Kusumoto[8] and Woodward[10] reports observations consistent with observing motion in the fold regions of single crystals.

Our own efforts to date have been concerned with various aspects of the ESR spin-probe technique: (a) an extension of the Rabold[4] correlation of T_g with the onset of probe motion, (b) the use of this extended correlation to estimate T_g values for controversial polymers, (c) an investigation of the molecular weight dependency of T_g as determined by the ESR spin-probe method, (d) an exploration of the suitability of the ESR technique for determining T_g in multiphasic block copolymers, and (e) a systematic study of the effect of probe size and/or functionality as a tool for the study of secondary transitions in various polymers. At this time we present results directed toward (a) and (b).

In one of the earliest spin-probe studies Rabold[4] doped a series of polymers and copolymers, polystyrene, poly(vinyl chloride), polyethylene, and styrene/butadiene copolymers, with low concentrations of the stable nitroxide 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl benzoate (BzONO) and



BzONO

studied the temperature dependent ESR spectra. By plotting the separation (in gauss) of the outer-most peaks of the three-line nitroxide spectrum vs. temperature he obtained graphs of the form shown in Figure 1. An empirical parameter, T_{50G},[19] was selected and Rabold noted a linear correlation of T_{50G} with either the glass temperature (T_g) or the melting temperature (T_M). This early work, as pointed out by Rabold, suggested the potential utility of the ESR spin-probe method to gain information about molecular motion in polymeric materials, especially upon traversing the glass transition region.

The utility of the spin-probe technique to study molecular motion in polymers was extended (particularly to polyethylene) using published and unpublished data of Rabold.[20] A correlation of T_{50G} with T_g for a series of nine polymers having noncontroversial glass temperatures was made. It was noted

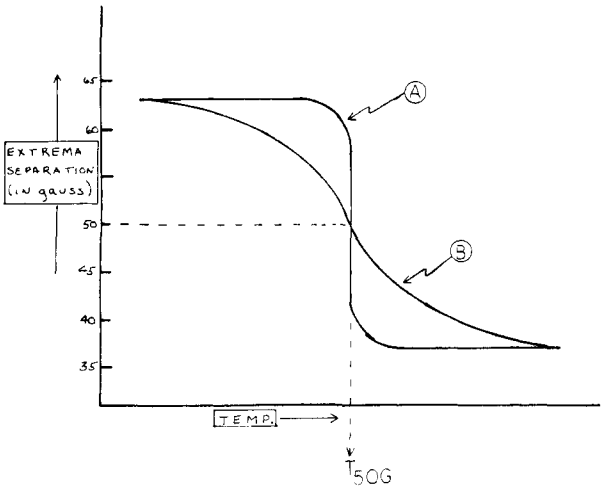


Figure 1. Plot of ESR extrema separation vs. temperature; schematic plot showing the extreme types of behavior observed.

that when T_{50G} was plotted vs. T_g the points appeared to lie on a straight line. Accepting this linear correlation of T_{50G} with T_g and using Rabold's ESR data for branched and linear polyethylenes, it was concluded that the T_g of amorphous polyethylene could be taken as 195 ± 10 K. This was the first attempt to use ESR spin-probe data to resolve conflicting opinion about the T_g of polymeric materials.

We felt it desirable to study in more detail the relationship between T_{50G} and T_g for a number of reasons. To be more useful as a technique for determining T_g, or resolving any conflicting opinin about T_g, it wa necessary to show that the linear correlation would be valid for polymers other than the vinyl type, that the linear correlation would be valid over a much greater range of T_g's than those used earlier, or that another correlation was more suitable.

Experimental Section

Materials Investigated. Whenever possible, well-characterized materials such as NBS reference materials were used. Lacking such standard materials we used: (a) materials that had been characterized to some extent by at least one other method, or (b) materials uncharacterized, except as to chemical identity, but for which T_g values could be obtained assuming the chemical identity. Except where noted, oligomers were not employed. The present work is, by intent, a survey paper designed to test the general validity of the ESR method for T_g determinations; more refined studies on many well-characterized polymers will be required later if the technique so warrants.

Polysiloxanes. All siloxanes were obtained from the Dow Corning Corp. Three low molecular weight oligomers having the general formula $Me_3Si\text{-}O\text{-}(Me_2Si\text{-}O)_n\text{-}SiMe_3$ were used: PDMS-236 (n = 1), PDMS-384 (n = 3), and PDMS-540 (n = 4–5). High molecular weight poly(dimethylsiloxane), PDMS ($\bar{M}_w$ = 305 000; $\bar{M}_n$ = 233 000), and poly(methyl ethyl siloxane), PMES ($\bar{M}_w$ = 300 000), were also used. BzONO was incorporated by method A (see below).

Polybutadiene. Commercial samples of Budene (97% *cis*-polybutadiene from the Goodyear Tire and Rubber Co.) and Diene 55 (obtained from Dow Chemical) were used; BzONO was incorporated by method D (hexane for Budene and CH_2Cl_2 for Diene 55).

Polypentenamer. This sample, of undetermined stereochemistry, was received from the Goodyear Tire and Rubber Co.; BzONO was incorporated by method D using hexane.

Poly(vinyl chloride). This was a latex obtained from within the Dow Chemical Co.; method B was used to incorporate BzONO.

Polystyrene. National Bureau of Standards reference materials were used. PS-705 had been prepared by anionic polymerization and exhibited $\bar{M}_n$ = 170 900, $\bar{M}_w$ = 179 300, $\bar{M}_z$ = 189 800. PS-706 had been prepared by free-radical polymerization and had a much broader molecular weight distribution: $\bar{M}_n$ = 136 500, $\bar{M}_w$ = 257 800, $\bar{M}_z$ = 288 100. Method D (using CH_2Cl_2) was used to incorporate BzONO into both samples.

Polycarbonate. The polycarbonate of Bisphenol A, poly(oxycar-

bonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene), was a commercial sample from General Electric Co.; BzONO was incorporated by method D (in CH_2Cl_2).

Polyethylene. Four different samples of polyethylene were studied. NBS-1475 was a standard reference linear polyethylene (crystallinity ca. 80%) and NBS-1476 was a standard reference branched polyethylene (crystallinit ca. 58%). High molecular wight polyethylene ($\bar{M}_w > 5 \times 10^6$; crystallinity 50–70%) was a commercial sample from Allied Chemical. An additional high molecular weight polyethylene ($\bar{M}_n = 2.6 \times 10^5$, $\bar{M}_w = 1.9 \times 10^6$) was obtained from Centre for Materials Science, the University of Birmingham, U.K. Methods of incorporating BzONO were as follows: NBS-1475 and NBS-1476, method C; Allied Chemical sample, methods C and D (xylene), T_{50G}; results identical for both doping methods; Birmingham sample, method C.

Poly(vinyl fluoride). This was a commercial sample (film) from Polysciences Inc.; BzONO was incorporated by method D (hexamethylphosphoramide).

Poly(vinylidene fluoride). Three different samples, all secured from the Pennwalt Corp., were used. One (No. 401) was a powder containing 5% head to head polymer; another (Kynar 301) was a PVF_2 homopolymer prepared by latex polymerization, mp 160 °C, containing 5.5% head-to-head; the third sample (Kynar 881), a powder prepared by suspension polymerization, exhibited mp 168 °C, $\bar{M}_n$ = 82 000, and contained 4.1% head-to-head polymer. Methods of incorporating BzONO were as follows: No. 401, method D (tetrahydrofuran); Kynar 301, method D (dimethylformamide or CH_2Cl_2); Kynar 881, method D (dimethylformamide).

Polyoxides. Poly(oxymethylene) was a commercial sample of Delrin from duPont; Celcon, the copolymer of formaldehyde containing 1–2% ethylene oxide units, was available from Celanese Corp; high molecular weight poly(oxyethylene) was a commercial sample of Polyox from Union Carbide. Methods of incorporating BzONO were as follows: Delrin, methods D (bromobenzene) or C; Celcon, method C; Polyox, method D (methanol).

Copolymers. Ethylene–vinyl acetate copolymers (88%, 72% and 55% ethylene) were obtained from Polysciences Inc.; BzONO was incorporated by either method C (88% ethylene) or method D (in CH_2Cl_2). A series of ethylene–propylene copolymers (63%, 75%, 84%, and 88% ethylene) were obtained from Exxon; their properties have been previously described;[21] BzONO was incorporated using alkane solvents (heptane to nonane) with method D. Styrene–butadiene copolymers (40% and 60% styrene content) were latexes from within the Dow Chemical Co.; method B was used to incorporate BzONO. A copolymer of vinylidene fluoride with 25–30 wt. % of tetrafluoroethylene was a commercial sample of Kynar 7201 from Pennwalt Corp.; BzONO incorporated via method D (acetone). A copolymer of ethylene and tetrafluoroethylene, believed from other evidence[22] to be an alternating copolymer similar to DuPont's Tefzel, was obtained from Polysciences; method C was used to incorporate BzONO.

Methods. Solid solutions of 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl benzoate (BzONO) in the appropriate polymer were prepared by a variety of methods: method A, crystalline BzONO added directly t a fluid polymer; ethod B, BzONO added to a latex, followed by film casting and drying; method C, mechanically mixing BzONO into the polymer sample near the polymer melting point; method D, addition of BzONO to a solution of the polymer in an appropriate solvent and subsequent evaporation of the solvent. Where appropriate the resultant samples were dried in a vacuum oven at elevated temperature for at least 24 h. The nitroxide concentration was less than 0.01% by weight in all cases. The particular method of doping used with each sample is indicated in the Materials Investigated section (see above).

The ESR spectra of the doped polymers (in 3 mm i.d. quartz tubes) were recorded using a Varian 4502 ESR spectrometer equipped with a variable temperature accesory. Samples were allowed to equilibrate for a minimum of 3 min for each 10 °C change in temperature; temperatures were determined immediately before and after the recording of each spectrum using a calibrated thermocouple with the average of these two readings used as the temperature at which the spectrum was recorded. Spectra were recorded under conditions where power saturation effects were shown to be negligible. For each doped polymer at least two complete determinations of the variable temperature spectra were recorded.

The separation (in gauss) between the outermost lines of the three-line nitroxide spectrum was measured directly from the recorded spectrum. Extrema separation was plotted vs. temperature and T_{50G} values (the temperature at which the extrema separation is equal to 50 G) were determined from this graph.

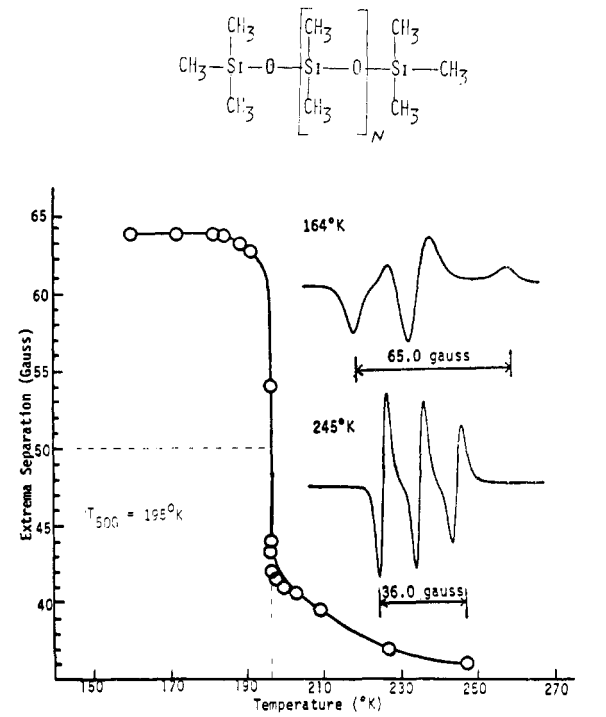


Figure 2. Extrema separation vs. temperature for poly(dimethylsiloxane); inset shows typical spectra at both high and low temperatures.

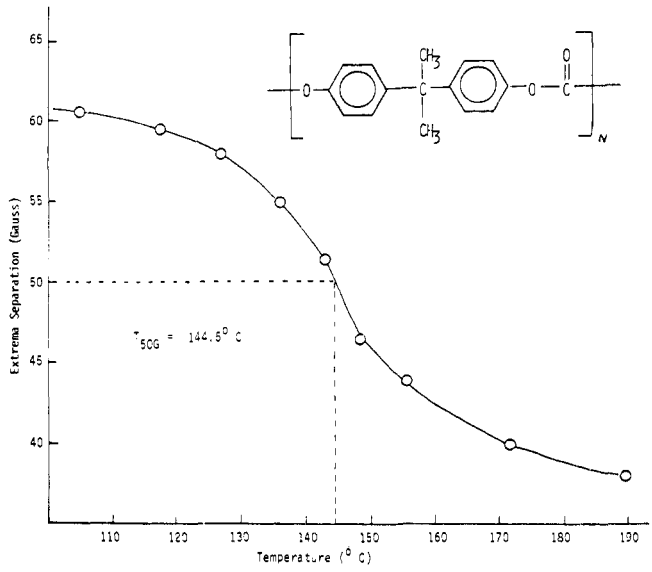


Figure 3. Extrema separation vs. temperature for polycarbonate.

Results and Discussion

We first directed our attention to extending the T_{50G} vs. T_g correlation[20] over a much wider temperature range; the T_g of polymers studied earlier[4,20] varied from −94 °C (polybutadiene) to 100 °C (polystyrene). We have now extended this range from −150 °C (PDMS-236) to 145 °C (polycarbonate). During this study it became apparent that with some polymers the extrema separation changed quite rapidly over a narrow temperature range (see Figure 1A) while with others the extrema separation changed quite slowly over a wide temperature range, leading to a broad sigmoidal curve (see Figure 1B). As actual examples of both types see Figures 2 and 3. Results for all of the polymers reported here exhibited temperature dependent ESR spectra and plots somewhere between these

two extremes. It should be noted that for either type of sigmoidal curve the upper limit of extrema separation is 60–65 G at low temperatures and the spectrum is characteristic of a "highly immobilized" nitroxide; also, with either type of curve the lower limit of extrema separation is 35–40 G at high temperatures and the observed spectrum approximates that of a "freely tumbling" nitroxide. On the basis of the two curves presented here (Figures 2 and 3) it is tempting to speculate that "sharp" curves (Figures 1A or) are typical of plymers with low T_g's and that "diffuse" curves (Figures 1B or 3) are typical of polymers with high T_g's, but such is not the case. Within the series of polymers described here, and based upon other work in progress in our laboratories, there is no obvious correlation of curve shape with T_g. It should also be noted that with either type of curve T_{50G} corresponds very closely to the inflection point on the curve; therefore, at T_{50G} the extrema separation is changing most rapidly and the rate of rotational reorientation of the probe molecule is undergoing its most dramatic change. For these reasons we feel that T_{50G} is a reasonable experimental parameter to correlate with the glass temperature.

T_g–T_{50G} Correlation. For investigating the correlation of T_g with T_{50G} we selected 19 polymers and copolymers of varying structural type encompassing a wide range of T_g's. Only polymers for which there was little or no controversy about T_g were included in this phase of the study. T_{50G} values were determined for each polymer from the smooth curve drawn through the experimental points on the extrema separation vs. temperature plot (see Figures 2 and 3, for example). A summary of the results is presented in Table I and graphically in Figure 4.

Line A of Figure 4 is a "best fit" smooth curve of the experimental points, derived by computer analysis (polynomial regression) of the nineteen T_g–T_{50G} pairs;[23] line B is the linear correlation previously suggested.[20] It is obvious from Figure 4 that the true correlation of T_{50G} with T_g deviates significantly from linearity, especially at low T_g values. It may also be noted from inspection of Figure 4 or Table I that $T_{50G} \simeq T_g$ at either very low or very high T_g values whereas $T_{50G} > T_g$ in the midranges of the correlation.

The curvature at low T_g and the approximate linearity at high T_g in our ESR results are directly understandable in terms of two characteristic features of the glass transition observed elsewhere:

(a) On plots of log f_{max} vs. $1/T$, where f_{max} is the frequency at which a mechanical or dielectric loss peak in a polymer is a maximum for temperature T, two types of behavior are possible. One observes either simple Arrhenius behavior (eq 1) where ΔH_a is an apparent enthalpy of activation in kcal/mol or a modified Arrhenius behavior (eq 2) where C is a constant and T_0 a reference temperature.

$$f_{max} = \exp(-\Delta H_a/RT) \quad (1)$$

$$f_{max} = B \exp(-\Delta H_a/CR\{T - T_0\}) \quad (2)$$

This equation represents the sharp curvature ($\Delta H_a \rightarrow \infty$) at low frequencies as the quasiequilibrium value of T_g is approached. Equation 2 is known as the vogel equation or more generally among polymer scientists as the Williams–Landel–Ferry (WLF) equation.[24] For a general discussion of the WLF equation and examples of relaxation maps the work of McCrum, Read, and Williams[25] should be consulted.

(b) In the temperature region above T_g [$T \geq (T_g + 50$ K)] ΔH_a tends to be constant. When thus defined, ΔH_a increases with T_g with a dependence much higher than simple proportionality;[26] this also follows from the WLF treatment.[24]

We have elected to use eq 1 for two reasons: (a) It is simpler and usually valid for T_g in the frequency range from 1 to ~10^7 Hz. The lower f_{max} is reasonably common for a T_g determination with equipment such as a torsion pendulum while the higher frequency is typical for T_{50G} as measured by ESR. (b) Secondary relaxations frequently follow eq 1 exactly over an even broader frequency range than does the glass transition.[18,25]

Making the assumption that there is a correlation between T_g (1 Hz) and T_{50G} (~10^7 Hz) and that the preexponential term is a constant, it follows from eq 1 that:

$$T_{50G} = T_g/(1 - 0.03T_g/\Delta H_a) \quad (3)$$

At high T_g the semiexponential increase of ΔH_a with T_g[26] causes the denominator to approach unity and T_{50G} to ap-

Table I
Correlation of T_g with ESR Data

Polymer	T_{50G}, °C	T_g, °C[a]	Ref for T_g
PDMS-236	−121	−150	40
PDMS-384	−111	−140	40
PDMS-540	−116	−137	40
PDMS	−77	−125	34
Budene	−27	−105	41
Diene 55[b]	−24	−94	42
Diene 55[c]	−18	−94	42
Polypentenamer	−14	−100	41
Ethylene/propylene (50/50 by wt)	16	−56	44
Polypropylene	42	−20	34
Styrene/butadiene			
42 wt % styrene	39	−33	46
52 wt % styrene	52	−20	46
57 wt % styrene	47	−11	46
60 wt % styrene	54	−5	46
62 wt % styrene	64	−1	46
Poly(vinyl chloride)	120	77	34
Polystyrene-706	114	100	34
Polystrene-705	110	100	34
Polycarbonate	145	145	34

[a] Values taken from the literature. [b] Data from ref 4. [c] This work.

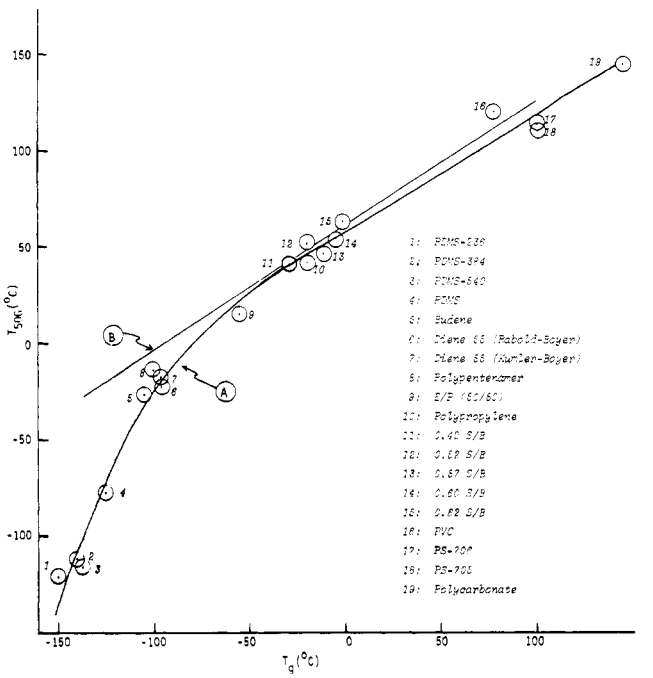


Figure 4. Experimental correlation of T_g with T_{50G}. Line A is the correlation reported here; line B is the linear correlation previously suggested by Boyer.[20]

Table II
Calculated T_g Values

Polymer	ΔH_a, kcal/mol[a]	T_g, °C[b],	T_{50G}, °C[c]
Poly(dimethylsiloxane)	20.0	−125	−84
Polyethylene	18	−85	−1
Hevea Rubber	30	−73	−23
Polyisobutylene	33	−73	−29
Polypropylene	28	−13	78
Poly(methyl acrylate)	35	10	81
Poly(vinyl acetate)	44	32	102
Poly(chlorotrifluoroethylene)	67	52	109
Poly(ethylene glycol terephthalate)	83	69	113
Poly(vinyl chloride)	70	81	131
Polystyrene	101	100	146
Poly(methyl methacrylate)	100	105	152
Polycarbonate of Bisphenol A	115	145	196

[a] Values taken from Boyer[26] except for poly(dimethylsiloxane) which was taken from ref 27. [b] From ref 34. [c] Calculated from eq 3.

proach T_g. At intermediate T_g's, when $\Delta H_a \propto T_g$, the denominator is a constant less than unity and $T_{50G} = kT_g$ where k is slightly greater than unity.

As a test of this derived equation (eq 3) relating T_{50G} to T_g we have calculated expected T_{50G} values for a series of polymers of widely varying activation enthalpies and glass temperatures (ΔH_a values from 18 to 115 kcal/mol and T_g values from −125 to 150 °C) using tabulated ΔH_a values[26] except for that of poly(dimethylsiloxane) which was taken from Beatty.[27] The resultant data are shown in Table II and graphically represented in Figure 5.

It should be noted that the derived equation gives a reasonable fit to the actual correlation data (dotted line in Figure 5) and reinforces our belief that the actual correlation of T_{50G} with T_g is, in fact, not linear as was previously suggested.[4,20] The nonlinear nature of the T_{50G}–T_g correlation should not, however, preclude the use of this technique for determining T_g's of polymers which have unknown and/or controversial values for the glass temperature. Accepting the validity of the correlation line shown in Figure 4 it should be relatively easy to determine a T_g value for any polymer whose T_g lies between the temperature limits of Figure 4. The derived equation (eq 3) should also allow the estimation of apparent activation enthalpies, in our frequecy range for any polymer once the T_{50G} and T_g values have been determined.

ESR Values of T_g for Controversial Polymers

In order to demonstrate the utility of the spin-probe technique for studying the glass transition of polymers with unknown and/or controversial glass temperatures we have studied a series of polymers of this type. Our results are shown in Table III.

Polyethylene. Three distinct amorphous phase transitions have previously been observed in partially crystalline samples of both linear and branched polyethylenes at −128 ± 10, −78 ± 10, and −33 ± 20 °C.[26,28] The ESR spin-probe method has been previously used,[20] along with other data, to argue that the T_g of amorphous polyethylene is −78 ± 10 °C. It should be noted, however, that the correlation curve used in this prior work was the apparent linear correlation previously suggested (i.e., line B in Figure 4). The actual T_g that was estimated using the linear correlation was −77 °C;[20] application of the previous experimental data to the extended nonlinear correlation (line A of Figure 4) leads to an estimated T_g of −76 °C, not significantly different from the previous value. Hence, the conclusions of the earlier work stand.

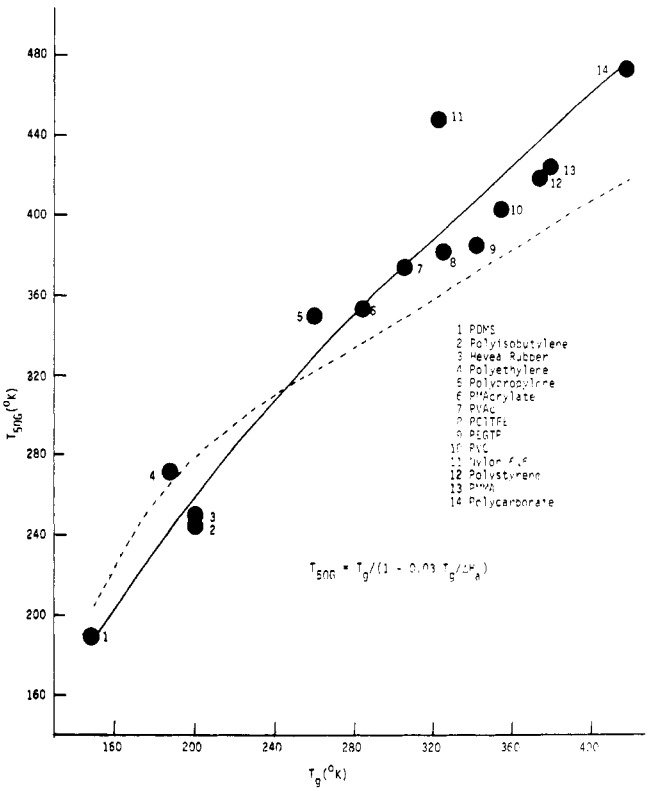


Figure 5. Theoretical correlation of T_{50G} with T_g. T_{50G} values calculated by use of eq 3 using literature values of T_g and ΔH_a. The solid line is the smooth curve drawn through the calculated T_{50G} values; the dashed line (- - -) is the actual experimental correlation.

As a further test of the method for polyethylene, a number of different polyethylene samples were investigated. Standard reference samples of both linear and branched polyethylene (NBS-1475 and NBS-1476) gave estimated T_g's by ESR of −73 and −72 °C, respectively, values quite consistent with those reported earlier.[20] A high molecular weight LPE sample ($\bar{M}_n = 2.6 \times 10^5$, $d = 0.19$) gave an estimated T_g of −53 °C while another high molecular weight ($\bar{M}_w > 5 \times 10^6$) sample from Allied Chemical gave an estimated T_g of −40 °C. The latter two samples exhibit T_g's (by ESR) consistent with an upper glass transition, T_g(U),[20] as assigned by Davis and Eby[29] as well as Chang.[30] The exact reason for this variation among the samples of polyethylene is not completely clear but may reflect a number of features such as: (a) method of synthesis, (b) degree of crystallinity, (c) variations in morphology, or (d) varying thermal histories of the samples. A thorough study of the effect of these various parameters on the ESR technique is obviously needed and should be carried out using well-characterized fractions.

Ethylene Copolymers. In view of the results discussed above for polyethylene it was of interest to apply the ESR technique to a series of ethylene copolymers of varying ethylene content. Data for a series of ethylene–vinyl acetate and ethylene–propylene copolymers are shown in Table III.

For both sereis of copolymers the T_g's were estimated from line A of Figure 4, using the observed T_{50G} values. The results for the ethylene–vinyl acetate copolymers agree quite well with the extrapolated curve of Illers[31] for high ethylene content, semicrystalline copolymers extrapolated by the Gordon–Taylor copolymer equation. The results from the ethylene–propylene copolymers also agree very well with the data of Kontos and Slichter[32] which were fitted to the Gordon–Taylor equation by Illers.[31]

The results from both of these series lend additional support to the proposition that the T_g of amorphous polyethylene

Table III
Glass Temperatures by the ESR Spin-Probe Method

Polymer	T_{50G}, °C	T_g, °C[a]	T_g, °C[b]	Lit. ref for T_g
Polyethylene (low density)[c]	4	−75	*d*	
Polyethylene (high density)[c]	5	−74	*d*	
Linear polyethylene (NBS-1475)	6	−73	*d*	
Branched polyethylene (NBS-1476)	7	−72	*d*	
LPE ($\bar{M}_n = 2.6 \times 10^5$)	24	−53	*d*	
LPE ($\bar{M}_w > 5 \times 10^6$; Allied)	33	−40	*d*	
Ethylene–vinyl acetate copolymers				
82 wt % ethylene	16	−62	−65	31
72 wt % ethylene	20	−58	−58	31
55 wt % ethylene	23	mins54	−44	31
Ethylene–propylene opolymers				
88 mol % ethylene	6	−73	−74	48
84 mol % ethylene	10	−69	−72	48
75 mol % ethylene	4	−75	−69	48
63 mol % ethylene	6	−73	−63	48
Poly(vinyl fluoride)	48	−16	−23, 41	33, 34
Poly(vinylidene fluoride)				
PVF_2 powder	74	28	−45, 13, 27	34, 36, 37
Kynar 301 (latex)	74	28		
Kynar 881 (suspension)	81	40		
Kynar 7201 (70% PVF_2/30% TFE)	67	15		
Ethylene/TFE (50/50)	89	53		
Delrin	48	−16	*d*	*d*
Celcon	47	−18	*d*	*d*
Polyox	−1	−80	*d*	*d*
Poly(methyl ethyl siloxane)	−80	−129	<−125	38

[a] Estimated from Figure 4, line A. [b] Literature values. [c] Experimental data of Rabold;[4] T_g estimated from correlation curve. [d] See discussion in text.

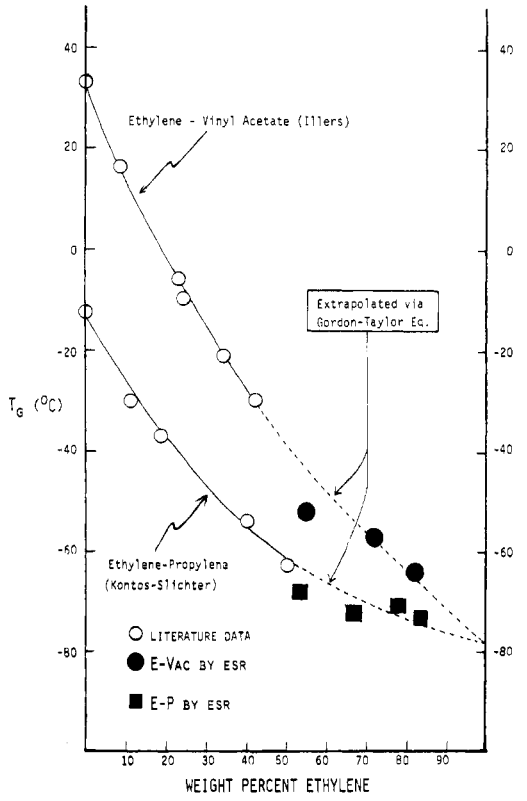


Figure 6. T_g data for ethylene copolymers by ESR; comparison with literature data.

is −78 ± 10 °C. A graphical superposition of our current ESR data onto that of Illers and of Kontos and Slichter is shown in Figure 6. The value of −78 °C supported by our present data is in contrast with values of −128 ± 10 °C occasionally reported for amorphous polyethylene[28] and with values of −33 ± 20 °C reported as the T_g for amorphous phases in crystalline polyethylene.[29,30] Our results on copolymers suggest that the nitroxide spin-probe is responding to the glass transition of an isolated, amorphous, high ethylene content phase that is essentially free from restraint by crystallites.

Fluorine-Containing Polymers and Copolymers. A series of fluorine-containing polymers and copolymers has also been studied and the results are summarized in Table III.

The current data for poly(vinyl fluoride), resulting in an estimated T_g of −16 °C, are in very good agreement with one of the two values most often cited for T_g[33] while at considerable discrepancy from the other oft-quoted (45 °C) value.[34] The question of the existence of multiple loss peaks in poly(vinyl fluoride) has been considered in some detail.[35] The current results are consistent with the assignment of the ca. −20 °C transition as a glass transition of the completely amorphous unrestrained phase and assignment of the ~45 °C transition to an amorphous phase under restraint by crystallites. Thus, the ESR spin-probe is responding to the lower T_g, that is T_g(L), rather than the upper T_g, that is T_g(U). This interpretation is also consistent with the polyethylene data reported above.

Three different samples of poly(vinylidene fluoride) have been examined in the current study. All samples gave estimated T_g's in the range 28–40 °C. Four distinct transitions of PVF_2 have been detected by many workers in the temperature range between −100 and 100 °C. The relaxation occurring at approximately −45 °C is usually assigned as T_g[34] but the relaxation observed at approximately 20 °C has also been suggested as the glass transition.[36,37] All of the data pertinent to the multiple transitions in PVF_2 have been examined critically by Boyer[35] who reached the conclusion that PVF_2 exhibits an "apparent double glass transition" with the −45 °C transition being the main glass transition, T_g(L), and the ca. 20 °C transition being an upper glass transition, T_g(U). It thus appears that the ESR spin-probe method is "seeing"

T_g(U) for PVF_2 which is in contrast to the behavior of the probe in polyethylene, various ethylene copolymers, and in PVF where it responds to T_g(L) as discussed above. No explanation for this apparent anomaly can be offered at the present time.

In addition to PVF and PVF_2, two fluorine-containing copolymers have been investigated. A copolymer of 70% PVF_2 and 30% tetrafluoroethylene (Kynar 7201) gave an estimated T_g of 15 °C and a 50/50 ethylene/tetrafluoroethylene copolymer exhibited an estimated T_g of 53 °C. For both of these copolymers there is very limited data available concerning transition temperatures and the assignment of T_g is unclear; Starkweather[22] has reported 1 Hz loss peaks at −120, −25, and 110 °C in a quenched ethylene/TFE copolymer containing 50 mol % TFE.

Polyoxides. There is considerable controversy about the glass transition temperature in highly crystalline polyoxides. In view of this controversy we have applied the ESR spin-probe technique to three polymers of this type.

Poly(oxymethylene), Delrin, exhibited a T_{50G} of 48 °C leading to an estimated T_g of −16 °C. Literature values[34] for transitions assigned as T_g vary from −85 to −10 °C. It has recently been suggested,[35] from consideration of thermal expansion data, that POM exhibits three transition ranges, tentatively assigned as follows: $T < T_g = -138 \rightarrow -78$ °C; T_g(L) = −63 → −38 °C; T_g(U) = −38 → −18 °C. The current ESR data are consistent with the spin-probe molecule responding to the upper glass transition.

A less crystalline POM sample (Celcon; POM containing 1–2% ethylene oxide units) exhibited behavior essentially identical with the pure highly crystalline homopolymer and is again consistent with detection of T_g(U).

Poly(oxyethylene), Polyox, exhibited a T_{50G} of −1 °C leading to an estimated T_g of −80 °C. In this case also there is considerable controversy about the actual T_g; literature values[34] range from −115 to −40 °C. It has been suggested[35] that PEO exhibits multiple transitions which include "an apparent double glass transition". Tentative assignments and temperature ranges are as follows: $T < T_g = <-163$, T_g(L) = −113 → −103, and T_g(U) = −68 °C. The ESR method leads to a value consistent with the observation of T_g(U).

From the data presented here on polymers of the polyoxide type it seems that the ESR method is detecting the upper of the two glass transitions.[49] It would be of obvious value to have ESR spin-probe data o a series of polyoxide polymers of much lower crystallinity; such studies are planned in our laboratories.

Polysiloxanes. As a final example of the utility of the ESR spin-probe method for various types of polymers we have applied the technique to a sample of poly(methyl ethyl siloxane). The estimated T_g of −129 °C, which is slightly lower than the −125 °C value for poly(dimethyl siloxane),[34] is in good agreement with the T_g determined by other methods[38] and suggests the utility of the current method for studying glass transitions in a variety of polysiloxanes.

Conclusions

From the data reported here we believe that the ESR spin-probe technique is a valuable addition to the arsenal of methods available for the study of molecular motions in polymeric materials. The method seems to be valid and reproducible for a wide variety of polymer types (PVF_2 may be an exception) covering a wide range of glass temperatures. The method is especially useful for studying polymers for which T_g is controversial and/or unknown; while our present results on polymers of this type cannot be considered as a solution to the controversies that exist, it is significant that the T_g's estimated by this technique are in agreement with some of the literature data that has been reported for T_g's. It is hoped that studies currently in progress (see below) will give us further insight into the actual molecular motions to which the probe molecule is responding.

Using BzONO as the spin-probe, the ESR technique consistently detects only one transition temperature, even in cases where multiple transitions have been detected by a variety of other methods. As has been previously noted[26] low-frequency test methods should have the highest resolving power when scanning a polymer for multiple transitions; transitions having different activation energies will tend to "merge" as the frequency of the test method is increased. It is perhaps not surprising that we have failed to detect multiple transitions since these other relaxations typically have activation energies much lower than that of the glass transition. This may well, however, tend to make the ESR method selective for the glass transition (or for the relaxation exhibiting the highest activation energy) in polymers with multiple transitions; this would be a favorable situation for resolving conflicting opinions about such polymers. Preliminary data from our laboratories[39] suggest that the transition detected by the ESR spin-probe studies in a polymer exhibiting multiple transitions is a function of the size and shape of the nitroxide probe molecule relative to the size and shape of the polymer segment undergoing increased motion at that temperature. The effect of free volume is also being explored.

Preliminary results (to be reported elsewhere) suggest that the method is also of value in determining the molecular weight dependence of the glass tranition, is sensitive to molecular weight distribution, and is applicable over a very wide molecular weight range. The fact that our observed parameter (T_{50G}) is normally at a significantly higher temperature than T_g is a decided experimental advantage, especially for polymers with low T_g's (such as siloxanes).

Since the current method depends upon the paramagnetic properties of an added "foreign body" or "guest" molecule to a polymer matrix, it is expected that the observed transition temperature (T_{50G}) would be dependent on the detailed nature (size, shape, polarity, etc.) of the particular spin-probe nitroxide that is utilized, as well as being dependent on the nature of the polymeric host as we have now sufficiently demonstrated. Isolated literature data[4,6,9,40] suggest such a dependency on the nitroxide utilized, but a more extensive study of these parameters is currently underway in our laboratories.

In addition to the areas discussed above a number of other questions are at various stages of investigation and will be reported at later dates. We are evaluating the method for applicability to other homopolymer types (for example polyesters, polyurethanes, polyamides, polyimides, polyacrylates, and polyanhydrides). It would be of obvious value if the method could detect two glass transitions in biphasic block copolymers and our preliminary results[39] suggest that this is, in fact, the case.

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The Elastic Restoring Force in Rubbers[1]

S. C. Sharda and N. W. Tschoegl*[2]

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125.

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ABSTRACT: The energetic and entropic contributions to the restoring force in natural rubber have been determined by measuring the force-temperature coefficient, the force-pressure coefficient, the isothermal compressibility, and the thermal expansion coefficient, all at constant length. The experimental results were compared with the predictions of several theories. Of these, an elastic potential function for compressible rubbers, recently developed by the authors, gave particularly satisfactory agreement. Published data on a chlorinated ethylene–propylene copolymer were used to show the applicability of the new potential function for predicting the internal energy contribution for the restoring force in rubberlike materials at high extensions.

The origin and experimental determination of the elastic restoring force in rubbers has been extensively studied. The subject has been reviewed in several recent publications.[3–5] In this paper we present thermoelastic measurements on natural rubber and correlate the data using an equation of state which is based on a new strain energy density function for compressible rubberlike materials.[6] Published data on a chlorinated ethylene–propylene copolymer rubber are used to demonstrate the use of the equation in predicting the relative contribution of internal energy to the restoring force at high elongations using only a few basic parameters.

The equation points out directions in which the statistical theory of rubber elasticity needs improvement.

Restoring Force

The elastic restoring force in rubbers results from deformational changes in the internal energy and the entropy of the rubber network. The internal energy changes are due to changes in the interchain and intrachain interactions in the network, whereas the entropy changes are associated with changes in the configurations of the network chains.

The elastic force f is the change in the Helmholtz free energy, A, with length in simple tension at constant temperature and volume. For derivation see, e.g., ref 7. Thus

$$f = \left.\frac{\partial A}{\partial L}\right|_{T,V} \tag{1}$$