

Spin probe investigation of molecular motions in polyepichlorohydrin: 1

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Spin probe investigations on the molecular motions in the glass transition range are reported. Within the free volume approximation, a Fox–Flory dependence of the narrowing temperature on the molecular masses is derived. The experimental results support this theoretical prediction. The glass transition temperature is estimated from the spin probe data, within various approaches, and compared to the results obtained by differential scanning calorimetry.

(Keywords: spin probe investigation; molecular motion; epichlorohydrin)

Introduction

The spin probe method involves the introduction of a small amount (10^1 – 10^3 ppm in weight)^{1–14} from a stable free radical whose electron spin resonance (e.s.r.) spectrum exhibits a resolved hyperfine structure (usually nitroxide-like free radicals), within the diamagnetic matrix of a polymer. In the glass transition range, a correlation between the narrowing temperature T_N (defined as the temperature at which the extreme separation parameter W equals 5 mT) and the glass transition temperature, T_g , has been suggested by several authors^{4–11}, using various approaches.

1. The polynomial method^{3,4,6,7}. According to this empirical method, developed in the earlier stages of spin probe investigations on the glass transition process, the relation between T_N and T_g may be written as follows:

$$T_N = \sum a_i (T_g)^i \quad (1)$$

where a_i are the polynomial coefficients.

2. The graphical method^{6,7} is another empirical approach, in principle reducible to the previous one, allowing the estimation of T_g , if T_N is known, from a graph of T_g versus T_N .

3. The activation energy approach has been suggested by Kumler and Boyer⁷ supposing an Arrhenius-like dependence of the relaxation times on temperature, in the glass transition range. Within this description, the

relation between T_g and T_N is expressed by the relation⁷:

$$T_N = \frac{T_g}{1 - RT_g(\ln a_T/H_a)} \quad (2)$$

where

$$a_T = \frac{\phi(T_g)}{\phi(T_N)} = \frac{\phi_0}{\phi_5} \quad (3)$$

$\phi(T_N)$ is the segmental jump frequency at T_N (corresponding to $W = 5$ mT), $\phi(T_g)$ is the segmental jump frequency T_g and H_a is the activation enthalpy.

Usually, in the case of the spin probe method, if nitroxide-like free radicals are used, it is supposed that $\ln a_T = 13.816$ (ref. 9).

The main weakness of this approach is associated with the hypothesis of an Arrhenius-like dependence of the relaxation times on temperature, within the glass transition range. This assumption is at variance with both theoretical and experimental data, which are consistent with a Williams–Landel–Ferry (WLF) dependence of the relaxation processes on temperature, in the glass transition range^{15–20} (or with a temperature dependent activation energy¹⁹).

4. The Braun–Tormala–Weber (BTW) approach⁸ is in fact an improvement of the activation energy approach, in which a new empirical parameter, the critical temperature T_c , is introduced by the relation:

$$T_N - T_g = \frac{T_g}{\exp(T_g/T_c)} \quad (4)$$

Accordingly, the activation enthalpy may be estimated

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using the equation:

$$H_a = RT_g [1 + \exp(T_g/T_c)] \ln a_T \quad (5)$$

However, the physical significance of T_c remains obscure.

As in the previous case, the Arrhenius-like dependence of the relaxation processes on temperature in the glass transition range remains the most important weakness of this description.

5. Kusumoto *et al.*'s⁹ description is the first tentatively to explain the relation between T_g and T_N within the free volume approximation:

$$T_N = T_g + C_{2g} \left[\frac{C_{1g} f}{\ln a_T} (1 - \ln f) - 1 \right] \quad (6)$$

where C_{1g} and C_{2g} are constants related to the WLF equation and f is the ratio between the spin probe volume and the segmental one.

6. Bullock and co-workers^{10,11} approach has also been developed within the free volume approximation, leading to the following relation between T_g and T_N :

$$T_N = T_g + C_{2g} \left(\frac{C_{1g} f}{\ln a_T} - 1 \right) \quad (7)$$

Bullock *et al.* have derived a formula in which appears a factor equal to 2.303 as they used the logarithm to base 10, whereas in equation (7) the natural base is utilized. Analogous equations have also been reported in refs 12 and 13.

Theory

In order to derive an equation for the dependence of the narrowing temperature on the molecular masses (numerical average M_n) within the free volume approximation, we may use the following expression for the jump frequency ϕ , of a molecule of volume V_p dissolved in an amorphous polymer built up of segments specified by the volume V_m ^{9,18,20}:

$$\phi = \phi_0 \exp\{-[\beta^* + \ln(V_m/V_p)](V_p^*/V_f) - V_p/V_m\} \quad (8)$$

where V_f is the microscopic free volume and V_m is the occupied volume.

Within the glass transition range, the temperature dependence of V_f , for a polymer characterized by the molecular mass M_n , is^{9,15-20}:

$$V_f = V_{fg} + V_{mg} \Delta\alpha(T - T_{g\infty}) + A/M_n \quad (9)$$

where V_{fg} is the free volume at T_g , V_{mg} is occupied volume at T_g , α is the difference between the volume thermal expansion coefficient, above and below T_g , $T_{g\infty}$ is the glass transition temperature for a polymer with an infinite molecular mass. A is a constant, related to the constant K appearing in the Fox-Flory equation¹⁶⁻¹⁹, concerning the dependence of the glass transition temperature T_{gn} (associated with a polymer with the molecular mass M_n) on M_n :

$$T_{gn} = T_{g\infty} - K/M_n \quad (10)$$

From these equations for a polymer characterized by M_n , we obtain the equation

$$T_{Nn} - T_{g\infty} = C_{2g} \left[\frac{f C_{1g} (\beta^* - \ln f)}{\ln a_T - f} - 1 \right] - \frac{K}{M_n} \quad (11)$$

or

$$T_{Nn} - T_{gn} = C_{2g} \left[\frac{f C_{1g} (\beta^* - \ln f)}{\ln a_T} - 1 \right] \quad (12)$$

For an infinite polymeric chain, the following relation between T_N and T_g holds:

$$T_{N\infty} = T_{g\infty} = C_{2g} \left[\frac{C_{1g} (\beta^* - \ln f)}{\ln a_T - f} - 1 \right] \quad (13)$$

where the following relations have been used:

$$V_{fg} = C_{2g} V_{mg} \quad (14)$$

$$V_m = C_{1g} V_{fg} \quad (15)$$

$$f = V_p/V_m = V_p^*/V_m^* \quad (16)$$

$$K = A/(V_{mg} \Delta\alpha) \quad (17)$$

The approximation suggested by Kusumoto *et al.*⁹ is consistent with the following assumptions:

- (a) $\ln(\phi_5/\phi_0) \gg f$
- (b) $\beta^* = 1$
- (c) $C_{2g} = 52 \text{ K}$, $C_{1g} = 40$
- (d) $\phi_0 = 10^{14} \text{ Hz}$, $\phi_5 = 10^8 \text{ Hz}$, $\ln a_T = 13.816$

leading to:

$$T_{Nn} - T_{gn} = T_{N\infty} - T_{g\infty} = 52 [2.9f(1 - \ln f) - 1] \quad (18)$$

The approximation proposed by Bullock and co-workers^{10,11} may be obtained supposing that:

- (a) $\beta^* = 1$
- (b) $\ln f \approx 0$ (or $f \approx 1.0$)
- (c) $\ln \phi_0/\phi_5 = \ln a_T \gg f$

Under these conditions the following equation is obtained:

$$T_{Nn} - T_{gn} = T_{N\infty} - T_{g\infty} = C_{2g} \left(\frac{f C_{1g}}{\ln a_T} - 1 \right) \quad (19)$$

and

$$T_{Nn} - T_{g\infty} = C_{2g} \left(\frac{f C_{1g}}{\ln a_T} - 1 \right) - \frac{K}{M_n} \quad (20)$$

From these equations, in both free volume based approaches the dependence of the narrowing temperature on the molecular masses is expressed by:

$$T_{Nn} = T_{N\infty} - K/M_n \quad (21)$$

In conclusion, the dependence of the narrowing temperature on molecular masses obeys a Fox-Flory equation and accordingly the constant K may be estimated solely from spin probe data. In a representation $T_{gn} = f_1(M_n^{-1})$ and $T_{Nn} = f_2(M_n^{-1})$ two parallel straight lines are expected. In this contribution we focus our attention on the information obtained from the temperature dependence of the extreme line separation. The connection between the narrowing and the glass transition temperature is studied in detail.

Experimental

Samples of polyepichlorohydrin (PECH) of different molecular masses (Table 1) were investigated using the spin probe method. The spin probe (Tempone) was

Table 1 Experimental data of polyepichlorohydrin samples

Sample	Molecular mass (M_n)	$T_{gn}^{(e)}$ (K)	T_{Nn} (K)
P1	550 000	248	291.0
P2	660 000	250	292.0
P3	1 400 000	252	294.5
P4	1 900 000	253	296.0
P5 ^a	infinite	255	297.5
K^b		3.5	3.64
COR ^c		0.98	0.99

^a Theoretical values obtained using a Fox-Flory dependence, for an infinite polymer

^b The slope of the Fox-Flory equation, in 10^6 K

^c The correlation coefficient for a linearized Fox-Flory dependence, using the least-squares approximation

dissolved in toluene and the polymer was dissolved in tetrahydrofuran, then the solutions were mixed and homogenized. The solvent was removed by evaporation in vacuum, at 50°C , for several days. The spin probe concentration was about 10^2 ppm.

The e.s.r. spectra were recorded using a JES-ME-3X spectrometer, operating in the X-band (9 GHz). The temperature dependence of resonance spectra, in the temperature range from -160 to 50°C , was investigated using a JES-VT-3X variable temperature accessory. Additional data concerning the molecular masses and the glass transition temperatures were obtained by viscosimetry, gas permeation chromatography (g.p.c.) and differential scanning calorimetry (d.s.c.), respectively (see Table 1).

Experimental data were analysed by linear regression, using a program written in BASIC within the least squares approximation.

Results

The e.s.r. spectra of doped PECH exhibit the usual triplet hyperfine structure (Figures 1a-1d), ascribed to the delocalization of the uncoupled electronic spin ($S = 1/2$) over the nitrogen nucleus ($I = 1$), corresponding to the following spin Hamiltonian²¹:

$$\mathcal{H} = g_e\beta_e\text{HS} + g_i\beta_i\text{HI} + \text{SAI} \quad (22)$$

where $g_e\beta_e\text{HS}$ is the electronic Zeeman term, $g_i\beta_i\text{HI}$ is the nuclear Zeeman term (usually neglected in the e.s.r. spectroscopy) and SAI is the hyperfine splitting term.

The resonance spectra are sensitive to the sample temperature. As may be noticed from Figure 2, the extreme line separation parameter W , has a sigmoidal dependence on temperature, from which the narrowing temperature may be estimated⁴⁻¹⁴.

Starting from the narrowing temperatures T_{Nn} , measured for samples of PECH, of various molecular masses M_n , the glass transition temperatures T_{gn} may be evaluated by various approaches⁶⁻¹².

1. The glass transition temperatures, $T_{gn}^{(1)}$ have been estimated using the polynomial approximation⁷, for samples of different molecular masses, using the relation:

$$T_N = -773.1 + 12.66 T_{gn}^{(1)} - 5.98 \times 10^{-2} (T_{gn}^{(1)})^2 + 1.306 \times 10^{-4} (T_{gn}^{(1)})^3 - 1.055 \times 10^{-7} (T_{gn}^{(1)})^4 \quad (23)$$

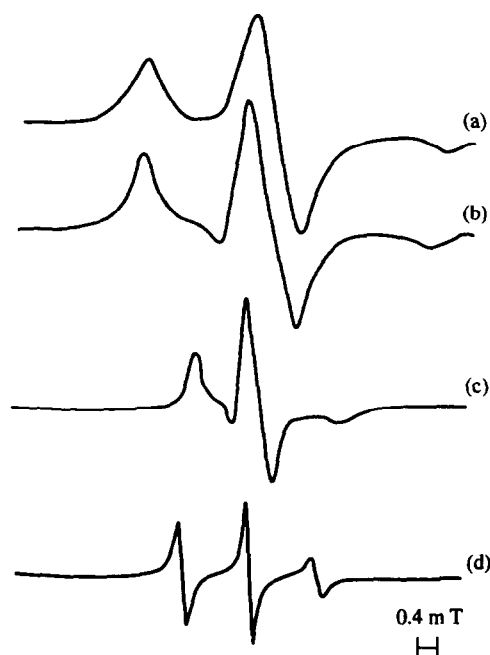


Figure 1 The e.s.r. spectra of polyepichlorohydrin doped with TEMPO, at various temperatures: (a) -120°C ; (b) -75°C ; (c) -50°C ; (d) 0°C

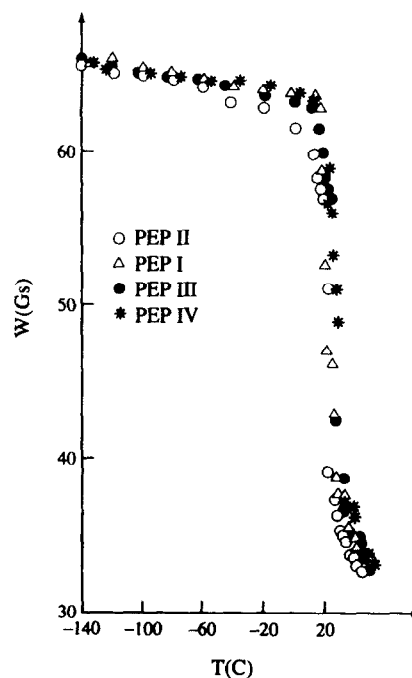


Figure 2 The temperature dependence of the extreme line separation parameter, W

As may be noticed from Table 2, this empirical method leads to higher glass/transition temperatures, $T_{gn}^{(1)}$ than the experimental data, denoted as $T_{gn}^{(e)}$. The value obtained for the slope K is significantly higher than K_e estimated from the dependence of $T_{gn}^{(e)}$ on M_n^{-1} .

2. The graphical method leads to lower glass transition temperatures, $T_{gn}^{(2)}$. The discrepancies between the glass transition temperatures estimated using these empirical methods and the experimental values are within 10%. Both $T_{gn}^{(1)}$ and $T_{gn}^{(2)}$ exhibit a linear dependence on M_n^{-1} (Fox-Flory equation¹⁶⁻²⁰) with high correlation coefficients (COR), as may be noticed from Table 2. The slope

Table 2 Glass transition temperature of polyepichlorohydrin estimated using various empirical approaches

Sample	$T_{gn}^{(1)}$ (K)	$T_{gn}^{(2)}$ (K)	$T_{gn}^{(3)}$ (K)	$T_{gn}^{(4)}$ (K)	$T_{gn}^{(5)}$ (K)	$T_{gn}^{(6)}$ (K)	$T_{gn}^{(7)}$ (K)	$T_{gn}^{(8)}$ (K)	$T_{gn}^{(9)}$ (K)
P1	265.7	228	249.0	248.0	249.0	304.4	304.2	272.5	265.3
P2	267.3	230	249.8	249.2	249.7	305.4	305.2	276.4	266.2
P3	271.5	233	251.6	252.1	251.5	307.9	307.7	278.8	268.4
P4	274.0	236	252.6	253.8	252.6	308.4	309.2	280.3	269.7
P5	276.5	238	253.8	255.5	253.7	310.1	310.7	283.0	271.0
K^b	6.04	5.47	2.67	4.19	2.65	3.11	3.64	5.24	3.20
COR ^c	0.98	0.97	0.99	0.99	0.99	0.99	0.98	0.96	0.99

^a Theoretical values obtained using a Fox–Flory dependence, for an infinite polymer

^b The slope of the Fox–Flory equation, in 10^6 K

^c The correlation coefficient for a linearized Fox–Flory dependence, using the least-squares approximation

Table 3 Activation enthalpies, critical temperatures and f ratios for polyepichlorohydrin rubbers

Sample	$H_{an}^{(1)}$ (J kmol ⁻¹)	$H_{an}^{(2)}$ (J kmol ⁻¹)	T_{cn} (K)	$f_n^{(1)}$	$f_n^{(2)}$	$f_n^{(3)}$
P1	192.7	192.7	141.5	0.2745	0.6310	0.5575
P2	199.5	196.6	140.2	0.2695	0.6244	0.5492
P3	200.5	200.6	141.6	0.2720	0.6277	0.5533
P4	199.9	202.6	142.8	0.2745	0.6310	0.5575
P5 ^a	204.9	206.7	142.3			

^a Theoretically estimated values, using a Fox–Flory equation, for a polymer with $M_n \rightarrow \infty$

of the Fox–Flory equation is $K_1 = (6.04 + 0.02) \times 10^6$ K and $K_2 = (5.47 + 0.02) \times 10^6$ K, for the case of polynomial and graphical approximations, respectively. However, these values are larger than K_c , given in Table 1.

3. The activation energy approach allows the estimation of the activation enthalpy H_{an} supposing that the glass and narrowing temperatures are known. From the e.s.r. and thermal analysis data, using $T_{gn}^{(e)}$ and T_{Nn} , we have estimated $H_{an}^{(1)}$ using relation (24) (see Table 3):

$$H_{an}^{(1)} = \frac{RT_{gn}^{(e)} T_{Nn} \ln a_T}{T_{Nn} - T_{gn}^{(e)}} \quad (24)$$

A slight increase of $H_{an}^{(1)}$ with M_n is noticed. Supposing that H_a is almost independent of the molecular masses, it is possible to estimate $T_{gn}^{(3)}$ using in equation (19) an average value, $H_a^{(1)}$:

$$T_{gn}^{(3)} = \frac{H_a^{(1)} T_{Nn}}{H_a^{(1)} + RT_{Nn} \ln a_T} \quad (25)$$

In this case, although there is a good correlation with the experimental data ($T_{gn}^{(e)}$) the slope of the Fox–Flory equation is too low ($K_3 = (2.67 + 0.02) \times 10^6$ K) in comparison with the experimental value.

4. Using the BTW approach⁸, the critical temperature T_{cn} has been estimated, by interpolation, from T_{Nn} and $T_{gn}^{(e)}$, using the relation:

$$T_{cn} = \frac{T_{gn}^{(e)}}{\ln[T_{gn}^{(e)} / (T_{Nn} - T_{gn}^{(e)})]} \quad (26)$$

As $T_{cn} > 0$, it becomes obvious from equation (26) that this improvement of the activation energy approach may be used solely if $T_{Nn} > T_{gn}^{(e)}$.

Because, in our case, $T_{Nn} > T_{gn}^{(e)}$, the values of the critical temperatures are collected in Table 3. It is interesting to notice that T_{cn} is almost equal to half of the glass transition temperature, T_{gn} . According to the values obtained for T_c , it is possible to suppose that T_c is almost independent of M_n and to use an average value, T_c (equal to 141.525 K) to estimate the activation enthalpy $H_{an}^{(2)}$:

$$H_{an}^{(2)} = RT_{gn} \ln a_T \left(1 + \exp \frac{T_{gn}^{(e)}}{T_c} \right) \quad (27)$$

As may be noticed from Table 3, the differences between $H_{an}^{(2)}$ and $H_{an}^{(1)}$ are within the experimental errors. In Table 2, $T_{gn}^{(4)}$ has been estimated by interpolation using the average value of T_c and T_{Nn} , according to the relation:

$$T_{Nn} = T_{gn}^{(4)} \left[1 + \left(\exp - \frac{T_{gn}^{(4)}}{T_c} \right) \right] \quad (28)$$

Supposing that $H_{an}^{(2)}$ is almost independent of M_n and using the average value $H_a^{(2)}$, $T_{gn}^{(5)}$ has been evaluated by interpolation using the relation:

$$T_{Nn} = T_{gn}^{(5)} \frac{H_a^{(2)} / (RT_{gn}^{(5)} \ln a_T)}{[H_a^{(2)} / (RT_{gn}^{(5)} \ln a_T)] - 1} \quad (29)$$

Although $T_{gn}^{(4)}$ and $T_{gn}^{(5)}$ are close to $T_{gn}^{(e)}$, we may notice from Table 2 that the slopes are different and exhibit large deviations from K_c .

5. Vogel–Fulcher-like dependences. Using the same method as Kumer and Boyer⁷, Georgescu *et al.*¹³ have derived a relation between the glass and the narrowing temperatures, supposing a Vogel–Fulcher dependence of relaxation processes on temperature. Finally, the following relation between $T_{gn}^{(6)}$ and T_{Nn} has been derived:

$$T_{gn}^{(6)} = \frac{C_{1g} T_{Nn} + (T_{Nn} + C_{2g}) \ln a_T}{C_{1g} + \ln a_T} \quad (30)$$

where $C_{1g} = 40$ and $C_{2g} = 52 \text{ K}^{9-12,15-20}$.

The glass transition temperatures $T_{gn}^{(7)}$ has been estimated supposing that $C_{1g} = 11.5$ and $C_{2g} = 24.1 \text{ K}^{22}$. As may be noticed from Table 2, the differences between $T_{gn}^{(6)}$ and $T_{gn}^{(7)}$ are negligible but the glass transition temperatures are higher than the experimental value. In general, the Vogel–Fulcher (or the equivalent WLF) equation may be extended to include an

Table 4 Glass transition temperature, estimated using various approaches, based on the free-volume approximation

Sample	$T_{gn}^{(10)}$ (K)	$T_{gn}^{(11)}$ (K)	$T_{gn}^{(12)}$ (K)
P1	248.45	248.4	304.0
P2	249.45	249.4	305.0
P3	251.95	251.9	307.5
P4	253.45	253.4	309.0
P5	254.95	254.9	310.5
K^b	3.64	3.64	3.64
COR ^c	0.99	0.99	0.99

^a Theoretical values obtained using a Fox–Flory dependence, for an infinite polymer

^b The slope of the Fox–Flory equation, in 10^6 K

^c The correlation coefficient for a linearized Fox–Flory dependence, using the least-squares approximation

Arrhenius-like term. Accordingly, $T_{gn}^{(8)}$ has been calculated using the expression:

$$\ln a_T = T_{Nn} - T_{gn}^{(8)} \left(\frac{H_{an}^{(1)}}{RT_{gn}^{(8)} T_{Nn}} + \frac{C_{1g}}{T_{Nn} - T_{gn}^{(8)} + C_{2g}} \right) \quad (31)$$

with $C_{1g} = 40$ and $C_{2g} = 52$ K.

The analogous values $T_{gn}^{(9)}$ have been derived for $C_{1g} = 11.5$ and $C_{2g} = 24.1$ K.

As may be noticed from Table 2, the agreement between the experimental data and the theoretical predictions is improved taking into account the contribution of an Arrhenius term. The constants $C_{1g} = 11.5$ and $C_{2g} = 24.1$ K lead to the best glass transition temperatures, estimated supposing a Vogel–Fulcher or WLF dependence of relaxation processes on temperature.

6. Within the description proposed by Kusumoto *et al.*⁹ it is possible to estimate the parameter $f^{(1)}$ reflecting the ratio between the spin probe volume and the segmental one from T_N and $T_g^{(e)}$, using relation (24), by interpolation (Table 4).

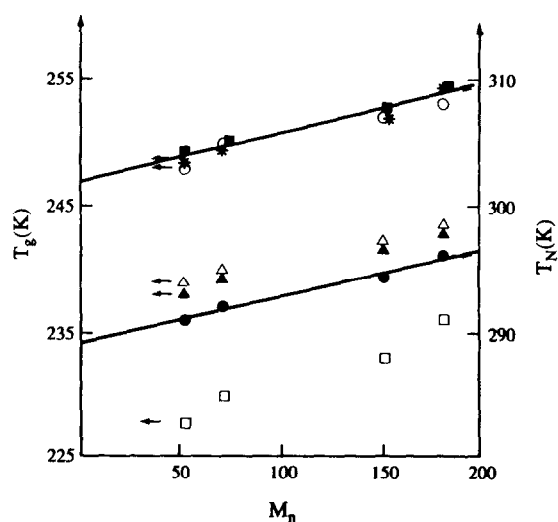
$$T_{Nn} - T_{gn}^{(e)} = 52 [2.9f_n^{(1)} (1 - \ln f^{(1)}) - 1] \quad (32)$$

We may notice that $f_n^{(1)}$ is almost independent of M_n and consequently we have estimated the glass transition temperature $T_{gn}^{(10)}$, using in relation (32) the average $f_n^{(1)}$ value ($f^{(1)} = 0.2726$) and the narrowing temperature T_{Nn} . The glass transition temperatures estimated in this manner are close to the experimental values, $T_{gn}^{(e)}$. The linear relation between $T_{gn}^{(10)}$ and M_n^{-1} is characterized by the highest correlation coefficient and K_{10} is in good agreement with the values estimated from the dependence of the glass transition temperature on M_n (K_c).

However, equation (32) has been obtained by Kusumoto *et al.*⁹ using the universal values $C_{2g} = 52$ K and $C_{1g} = 40$. Recent data suggested for PECH are $C_{2g} = 24.1$ K and $C_{1g} = 11.5$ (ref. 22). It is interesting to notice that for these values, no reasonable values ($f_n^{(1)} > 0$) have been obtained.

7. Bullock *et al.*¹⁰ have suggested an analogous relation between T_N , T_g , and f , also derived within the free volume approximation.

$$T_{Nn} - T_{gn}^{(e)} = C_{2g} \left(\frac{C_{1g} f}{\ln a_T} - 1 \right) \quad (33)$$

**Figure 3** The dependence of the glass transition temperature $T_g^{(e)}$ and narrowing temperatures on M_n^{-1}

Taking for C_{1g} and C_{2g} the same values as in the equation proposed by Kusumoto *et al.*⁹ ($C_{2g} = 52$ K, $C_{1g} = 40$), we have estimated the ratio between the spin probe volume and the segmental one, $f_n^{(2)}$, using T_{Nn} and $T_g^{(e)}$. Using the same relation, but with $C_{1g} = 11.5$ and $C_{2g} = 24.1$ K, we have estimated $f_n^{(3)}$ within the description proposed by Bullock *et al.*

As may be noticed from Table 4, the parameter f is almost independent of molecular masses. Using the same self-consistent method, we have calculated the glass transition temperatures $T_{gn}^{(11)}$ and $T_{gn}^{(12)}$ using the average values of $f_n^{(2)}$ and $f_n^{(3)}$, respectively. The agreement between the predicted values of the glass transition temperatures $T_{gn}^{(11)}$ (Table 3) and the experimental values $T_g^{(e)}$ is very good. Also, the slope K_{11} is close to K_c . However, $T_{gn}^{(12)}$ is significantly higher than $T_{gn}^{(e)}$ although K_{10} , K_{11} and K_{12} are close to K_c . Therefore, we may conclude that the descriptions based on the free volume approximation are more appropriate than the empirical models.

As may be noticed from Table 1 as well as from Figure 3, $T_{gn}^{(e)}$ and T_{Nn} obey with high accuracy a Fox–Flory equation, with the same slope, in good agreement with the theoretical predictions. The free volume based models lead to reasonable values of the slope K , whereas in the case of the empirical descriptions large discrepancies between the values predicted for the slope of the Fox–Flory equation (K_1, K_2, K_3) and the experimental value $K^{(e)}$ are noticed.

However, our experimental data suggest that the main differences between the description suggested by Kusumoto *et al.*⁹ and the model proposed by Bullock and co-workers^{10,11} are practically absorbed in the value of the ratio f .

Conclusions

From the experimental data obtained by the spin probe investigations of PECH rubbers we may conclude that both the polynomial and the graphical approaches lead to unrealistic values for the glass transition temperature. The activation energy approach improves significantly the correlation between the experimental data and the predicted values, although the constant K_3 is lower by 25% than K_c .

The improved relation proposed by Braun, Tormala and Weber reduces the discrepancies between the predicted glass temperature and the experimental values. However, in this case K_4 is overestimated by about 20%. No significant dependence of the activation enthalpy or of the critical temperature on M_n have been noticed. Consequently, we have supposed that these amounts are constants. The activation energy approach is based on the unrealistic hypothesis of an Arrhenius-like dependence of relaxation processes on temperature.

The free volume approaches lead to accurate K values and are characterized by a very good correlation among predicted glass transition temperatures and experimental data.

However, in Bullock *et al.*'s descriptions^{10,11}, using for constants the values $C_{2g} = 24.1$ K and $C_{1g} = 11.5$, an overestimation of T_g is obtained (see $T_{gn}^{(12)}$ values in Table 4).

In the description proposed by Kusumoto *et al.*⁹ it is not possible to find an acceptable value for f (positive) if $C_{2g} = 24.1$ K and $C_{1g} = 11.5$.

Although, from this point of view, Bullock *et al.*'s approach seems to be the best, the values of the ratio $f_n^{(2)}$ are too large, suggesting that the statistical segment is built up of about 2 mers^{9,23}.

The experimental data suggest that in all approaches based on the free volume approximation, the ratio f_n is almost independent of M_n .

According to the theoretical description sketched in this contribution, the spin probe method allows the direct estimation of the Fox-Flory constant, K_c , supposing that the molecular masses M_n are known, within the free volume approximation.

As may be noticed from Table 1 and Figure 3, both T_{Nn} and $T_{gn}^{(e)}$ obey with high accuracy the Fox-Flory equations. The $T_{gn}^{(e)}$ and T_{Nn} dependences on M_n are parallel straight lines, as expected.

Moreover, using the universal constants $C_{1g} = 40$ and

$C_{2g} = 52$ K, the approaches of both Kusumoto *et al.* and Bullock *et al.* are characterized by an excellent agreement between theoretically estimated glass transition temperatures and experimental data.

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