Correlation between β-Relaxation and α-Relaxation in the Family of Poly(*n*-butyl methacrylate-*stat*-styrene) Random Copolymers

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Received February 25, 1999; Revised Manuscript Received August 11, 1999

ABSTRACT: Previously a rough correlation between the logarithm of the most probable secondary β-relaxation time at the glass temperature T_g, $\log[\tau_\beta(T_g)]$, and the Kohlrausch−Williams−Watts (KWW) exponent, $(1 - n)$, of the primary α-relaxation correlation function $\exp[-(t/\tau_\alpha)^{1-n}]$ was found when examining a whole host of chemically different glass-forming materials including amorphous homopolymers, small molecule van der Waal liquids, plastic crystals, and inorganic compounds. This rough correlation is expected from the exact correlation between the logarithm of the primitive relaxation time of the coupling model at the glass temperature T_g, $\log[\tau_o(T_g)]$, and $(1 - n)$ and from the similarity between the β-relaxation and the primitive relaxation, both being free from intermolecular cooperativity. This correlation holds only when n in the KWW exponent $(1 - n)$ can be identified with the coupling parameter n_α of the α-relaxation in the coupling model. Now, this correlation is examined on a series of poly(*n*-butyl methacrylate-*stat*-styrene) copolymers with styrene contents ranging from 0 to 66 mol % utilizing the dielectric relaxation data of Kahle et al. [*Macromolecules* **1997**, *30*, 7214]. For the present extension, the KWW function fails to fit the dielectric data due to the presence of concentration fluctuations in the random copolymer. Instead, the most probable coupling parameter $\hat{n}_\alpha$ of the *n*-butyl methacrylate component in the copolymers is obtained indirectly through the steepness of the temperature dependences of the most probable α-relaxation time. A good correlation between $\log[\tau_\beta(T_g)]$ and $\hat{n}_\alpha$ is found to hold in this series of copolymers as well as in the poly(*n*-alkyl methacrylates). Moreover, the orders of magnitude of $\tau_\beta(T_g)$ and $\tau_o(T_g)$ are not far apart, supporting the similarity between the β-relaxation and the primitive relaxation.

1. Introduction

The secondary or β-relaxation seems to be a universal feature of glass-forming materials observed at lower temperatures or higher frequencies than the primary or α-relaxation by respectively isochronal and isothermal measurements. The most probable relaxation time, τ_β, of the β-relaxation has a Arrhenius temperature dependence

$$\tau_\beta(T) = \tau_{\beta\infty} \exp(E_\beta/RT) \tag{1}$$

In many instances, $\tau_{\beta\infty}$ corresponds to a molecular vibration time, and E_β has a magnitude that is identifiable with a real energy barrier. The magnitudes of both quantities point the origin of the β-relaxation to molecular motions[1−3] that involve no intermolecular cooperativity, in contrast to α-relaxation. This observation by Heijboer[2,3] has led him to the molecular picture that the secondary relaxation is determined by a local barrier within the molecule. However, Johari and Goldstein[4,5] have found secondary relaxation also in glass-forming systems made up of simple molecules that do not have internal molecular mode of motion. They have concluded that in some materials the potential barrier resisting the molecular rearrangement of the secondary relaxations can arise from intermolecular forces alone. Whatever the origin of the potential barriers, intramolecular or intermolecular, the experimental facts clearly indicate that the β-relaxation arises from molecular mobility which remains even in the glassy state, i.e., below T_g. The molecular motion must be quite different from the α-relaxation, particularly near T_g where the α-relaxation time, τ_α, varies rapidly with temperature according to the Vogel−Fulcher−Tammann−Hesse (VFTH) equation,[1] in stark contrast with the much milder Arrhenius dependence of τ_β (eq 1). The molecular motion of the β-relaxation could simply be the local motion of some basic molecular units that have escaped cooperativity with other units such as that experienced by the α-relaxation. Density fluctuation compatible in spatial scale with the local motion or other reasons[5] could be responsible for the large width of the β-relaxation.

Because the β-relaxation involves molecular motion that is intermolecularly noncooperative, it bears some resemblance to the primitive α-relaxation mode of the coupling model (CM).[6−9] As explained before,[10,11] in contrast to the β-relaxation, the primitive relaxation is not observable at macroscopic time scales because at those times it has already being consumed by cooperativity to form the α-relaxation. In other words, the primitive relaxation has practically no relaxation strength at macroscopic times. Therefore, the β- and primitive relaxations cannot be the same process. Although the primitive relaxation cannot be observed at macroscopic times, its relaxation time τ_o at any temperature T can be calculated from the measured α-relaxation time, τ_α, and the coupling parameter n by the much exploited CM relation,[6−9]

$$\tau_\alpha = [t_c^{-n}\tau_o]^{1/(1-n)} \tag{2}$$

where $t_c \approx 2 \times 10^{-12}$ s. For neat glass-formers which are not mixtures, blends, or copolymers, the coupling parameter is the same as n that appears in the exponent of the Kohlrausch−Williams−Watts (KWW)[12,13] function,

$$\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}] \tag{3}$$

10.1021/ma990284b

for the description of the α-relaxation correlation function. It is easy to see from eq 2 that $\log[\tau_o(T_g)]$ is exactly correlated with the KWW exponent. If T_g is defined by $\tau_\alpha(T_g) = 10^4$ s uniformly for all glass-formers, then

$$\log \tau_o(T_g) = 15.7(1 - n) - 11.7 \qquad (4)$$

From the intermolecularly noncooperative nature common to both the β- and primitive relaxations, we expect at the glass transition temperature T_g the β-relaxation time, $\tau_\beta(T_g)$, and the primitive α-relaxation time, $\tau_o(T_g)$, should not be too far apart in orders of magnitude.[10,11] Thus, from eq 4 we infer that a rough correlation between $\log[\tau_\beta(T_g)]$ and $(1 - n)$,

$$\log \tau_\beta(T_g) \approx 15.7(1 - n) - 11.7 \qquad (5)$$

may exist. Equation 5 should be interpreted in the spirit of a rough correlation between $\log[\tau_\beta(T_g)]$ and n but not taken to imply an exact linear relation between the two quantities.

In earlier works,[10,11] this correlation is tested by collecting the α and β relaxations data of all sorts of glass-formers including small molecule van der Waal liquids, liquids with hydrogen bonding, plastic crystals, and amorphous homopolymers. For reasons given before in refs 10 and 11 only secondary relaxations that show a tendency to merge with the α-relaxation at some subvibrational frequency is considered as candidates for the correlation. These secondary relaxations are more comparable with the corresponding primitive relaxations. For polymers the secondary relaxation has to involve some motion of the main chain. Overall, a pattern seems to emerge; i.e., α-relaxation of a glass-former having a larger coupling parameter n or a smaller KWW exponent, $(1 - n)$, also has a shorter τ_β(T_g) or smaller $\log[\tau_\beta(T_g)]$. Furthermore, the experimental values of $\tau_\beta(T_g)$ are not far in orders of magnitude from $\tau_o(T_g)$ for many glass-formers as anticipated. However, probably because many glass-formers with diverse chemical structures are considered at the same time, there is considerable scattering of the data from a perfect correlation. The best way to test this correlation is to confine the consideration to a single family of glass-formers whose chemical structures are closely related to each other. Such an opportunity presents itself with the publication of a detailed study of the α- and β-relaxations in a series of poly(*n*-butyl methacrylate-*stat*-styrene) random copolymers with different styrene contents by Kahle et al.[14] Throughout this series the β-relaxation has the same origin. Also, the change in chemical structure from one member of the series to another can be considered as gradual or continuous. These conditions ensure that a stronger correlation should be observed in the series. The purpose of this work is to demonstrate from the experimental data that indeed such a stronger correlation exists.

2. α- and β-Relaxations in Poly(*n*-butyl methacrylate-*stat*-styrene)

Kahle et al.[14,15] made a detailed study of the α- and β-relaxations in a series of random copolymers of *n*-butyl methacrylate with styrene using dielectric relaxation and heat capacity spectroscopy. The materials, poly(*n*-butyl methacrylate-*stat*-styrene), have styrene contents ranging from 0% up to 66%, and the corresponding calorimetric glass temperature increases from 31 °C of pure poly(*n*-butyl methacrylate) to 59 °C. For each random copolymer the α-relaxation spectra and the β-relaxation spectra were obtained by dielectric measurement at temperatures above and below its glass temperature T_g. The most probable α- and β-relaxation times, τ_α and τ_β, were obtained from the reciprocal of the dielectric loss peak angular frequencies as a function of temperature. As usual, the temperature dependence of τ_α is well fitted by the Vogel–Fulcher–Tammann–Hesse (VFTH) equation, $\log \tau_\alpha(T) = A + B/(T - T_\infty)$, above T_g and that of τ_β by the Arrhenius eq 1. The parameters of the fits were given,[14,15] and they enable us to plot in Figure 1 the data, $\log \tau_\alpha(T)$ and $\log \tau_\beta(T)$, of five members of the series with styrene content equal to 0, 38, 54, 60, and 66 mol %. Some actual data of the 0% (open circles) and the 66% (open squares) styrene copolymers are also shown. As can be seen by inspection of the relaxation map (Figure 1), $\log \tau_\beta(T)$ shifts monotonically to shorter times with increasing styrene content and further away from the $\log \tau_\beta(T)$ of pure polystyrene (see Figure 9a in ref 14). Also, the activation enthalpy of τ_β of the copolymers remains nearly constant for styrene contents up to 55% and nearly the same as pure P*n*BMA. As have already been discussed by Kahle et al., these properties of the β-relaxation in the random copolymers indicate that it originates from the *n*BMA units. Another reason for this is the weak dielectric strength of the styrene unit.

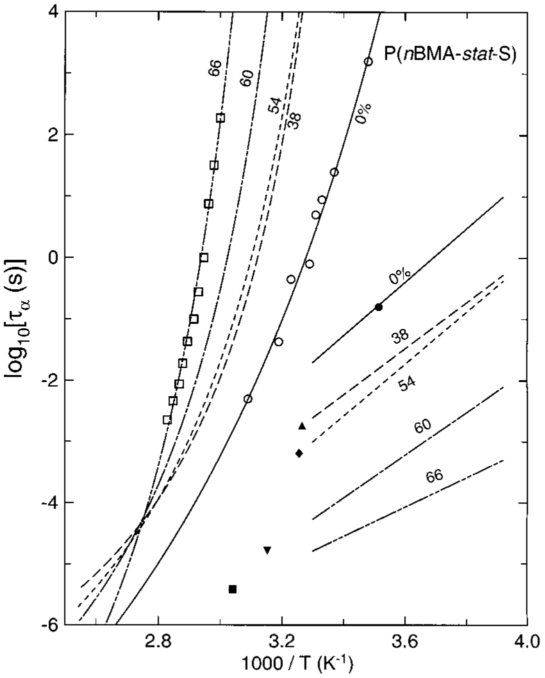

Figure 1. Relaxation map of the α-relaxation and β-relaxation of a series of P(*n*BMA-*stat*-S) random copolymers with different styrene contents. The curves are VTF fits to the temperature dependences of the α-relaxation times, τ_α. Some representative data are shown for two members of the series, 0% styrene (open circles) and 66% styrene (open squares). The straight lines are Arrhenius fits to the temperature dependences of the β-relaxation times, τ_β. Each curve and line is labeled by the styrene content of the sample it represents. The coordinates of each filled symbol are given by $(1000/T_g, \log[\tau_\beta(T_g)])$, where T_g is the temperature at which $\tau_\alpha(T_g) = 10^4$ s and $\log[\tau_\beta(T_g)]$ is obtained by extrapolation of the Arrhenius dependence of τ_β to T_g. Filled circle, triangle, diamond, inverted triangle, and square are respectively for samples containing 0, 38, 54, 60, and 66 mol % styrene.

Following the practice of earlier works[10,11] (see Introduction), we define the dielectric glass temperature T_g by $\tau_\alpha(T_g) = 10^4$ s. After the dielectric T_g is determined from the α-relaxation for each copolymer, the corresponding value of $\tau_\beta(T_g)$ is found. These values are indicated in Figure 1 by the points represented by the filled symbols (circle for 0%, triangle for 38%, diamond for 54%, inverted triangle for 60%, and square for 66%). There is experimental evidence[16] of involvement of the main chain in the β-relaxation of poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) and, by inference, also in poly(*n*-butyl methacrylate). These multidimensional NMR studies of the molecular motion in the β-relaxation of PMMA and PEMA have shown that the side group flip is accompanied by a random rotation around the local chain axis with a ±20° amplitude. Hence, we conclude that the β-relaxation of poly(*n*-butyl methacrylate-*stat*-styrene) caused by the *n*BMA units is likely a local motion that involves both the side group and the main chain *n*BMA unit. Since the primitive relaxation in the CM is also an intermolecularly noncooperative local motion that involves the main chain *n*BMA unit, the similarity with (but not identical to) the β-relaxation in poly(*n*-butyl methacrylate-*stat*-styrene) is thus clear.

3. Correct Statement of the Correlation for the Random Copolymers

It is important to point out that *n* appearing in the exact correlation (eq 4) and the rough correlation (eq 5) is the coupling parameter of the coupling model (CM). This is clear because it is the "second relation" of the CM (eq 3) that generates these results. Therefore, one should be careful with the statement of the existence of a rough correlation between $\log[\tau_\beta(T_g)]$ and the exponent, $(1 - n)$, of the KWW function $\exp[-(t/\tau_\alpha)^{1-n}]$ used to fit the α-relaxation. This statement holds only when *n* appearing in the KWW exponent is identical to the coupling parameter, such as in neat glass-formers which are not miscible mixtures of two or more components having different T_g's. All glass-formers discussed in refs 10 and 11 are of this kind, and the KWW exponent can be identified with the coupling parameter for all of them as described by eqs 2 and 3. Consequently, for the neat glass-formers it is the same whether we say that $\log[\tau_\beta(T_g)]$ is correlated with the coupling parameter *n* or with the exponent $(1 - n)$ of the KWW function that fits the α-relaxation dispersion (eq 3).

However, a distinction has to be made when mixtures, blends, or copolymers are considered. The presence of concentration fluctuations of the components in these systems is inevitable. For example, in a miscible blend of poly(vinyl methyl ether) (PVME) with polystyrene (PS),[17,18] different vinyl methyl ether units may have environment richer or poorer in styrene units than the average. These fluctuations introduce distributions of molecular environments and coupling parameters[18,19] for the vinyl methyl ether (VME) units, which broaden the dielectric dispersion of their local segmental α-relaxation. The extra broadening from concentration fluctuation may alter the shape of the α-relaxation dispersion in such a way that it makes the KWW function totally inappropriate to be used as fitting function.[17-19] An example is the dielectric relaxation spectra of miscible blends of PVME with PS.[17,18] The dielectric loss peak coming entirely from the VME component is skewed toward low frequencies, opposite to the KWW functions, which are skewed toward high frequencies. Obviously, in these cases it makes absolutely no sense to associate a KWW exponent with the observed α-relaxation dispersion. Naturally, the extra broadening also makes the dispersion very broad compared with homopolymers as often found in polymer blends.[17-19]

These effects caused by component concentration fluctuations are seen also by Kahle et al. on the random copolymers poly(*n*-butyl methacrylate-*stat*-styrene) of our present interest. In their publication, no attempt has been reported to fit their dielectric α-relaxation to a KWW function. Even in the event that one can force fit a KWW function $\exp[-(t/\tau)^\beta]$ to the dispersion, the value $(1 - \beta)$ of the KWW exponent should not be identified with any of the coupling parameters n_α of the α-relaxations in the distributed molecular environments engendered by component concentration fluctuations.[17-19] We find it worthwhile to emphasize once more that it is the coupling parameter n_α that appears in the exact correlation (eq 4) that leads us to the rough correlation (eq 5). Therefore, for the family of random copolymers, the correct statement is **the existence of a rough correlation between $\log[\tau_\beta(T_g)]$ and the most probable coupling parameter** $\hat{n}_\alpha$. Since this is an important distinction to be made between neat glass-formers and mixtures including random copolymers, we rewrite the order of magnitude correlation for the latter differently from eq 5 as

$$\log \tau_\beta(T_g) \approx 15.7(1 - \hat{n}_\alpha) - 11.7 \qquad (5a)$$

to underscore the correct statement for the correlation when specialized to the random copolymers. In eq 5a, $\hat{n}_\alpha$ is the most probable coupling parameter in the distribution $\{n_{\alpha i}\}$ for the local environments introduced previously to describe the α-relaxation dynamics of polymer blends.[18,19]

4. Determination of $(1 - \hat{n}_\alpha)$

The change of chemical structure of the random copolymers with increasing styrene content is well-defined. The styrene unit with a bulky phenyl ring attached to one of the carbon atoms has more capacity of intermolecular coupling than the *n*BMA unit. Thus, increase of styrene content in the copolymer will enhance the intermolecular coupling of any monomer unit. Since it is a random copolymer, like in miscible binary blends, concentration fluctuation is inevitably present, and there is a distribution of different molecular environments seen by both the *n*BMA and the styrene units. Since the styrene units have weak dielectric relaxation strength compared with that of the *n*BMA units, the dielectric response comes mainly from the latter. This situation is similar to the PVME/PS blends in which the dielectric response comes from the VME units. As described in a model of miscible polymer blends based on the coupling model (CM),[18,19] the distribution of molecular environments of the *n*BMA units gives rise to distributions of α-relaxation coupling parameter $\{n_{\alpha i}\}$ and relaxation time $\{\tau_{\alpha i}\}$ that appear in the corresponding distribution of KWW response functions, $\phi_i(t) = \exp[-(t/\tau_{\alpha i})^{1-n_{\alpha i}}]$. Even for pure P*n*BMA, some degree of concentration fluctuation may be present due to internal blending with the side chain as seen clearly in higher members of the poly(*n*-alkyl methacrylates).[20] Therefore, the concentration fluctuation present in poly(*n*-butyl methacrylate-*stat*-styrene) at all styrene contents from 0 to 66 mol % contributes an additional source of broadening the dielectric dispersion. Like that seen in the PVME/PS blends,[17,18] the dielectric spectra of the copolymers change with temperature, and time−temperature superpositioning of them fails. As explained in the previous section and in refs 18 and 19, this complication preempts the determination of any of the coupling parameters, $n_{\alpha i}$, in the distribution by the usual procedure of *directly* fitting the experimental dielectric dispersion by a KWW function. This procedure not only has no meaning but also often does not even work for miscible blends and random copolymers because the shape of the α-relaxation in these mixtures usually cannot be fitted by the KWW function. In fact, Kahle et al.[14,15] did not report any attempt to fit the dielectric response of their copolymers by the KWW functions. However, in a previous application to the PVME/PS blend,[18] a method has been proposed to determine the most probable coupling parameter, $\hat{n}_\alpha$, of the assumed Gaussian distribution of coupling parameters $\{n_{\alpha i}\}$. In this method, the dielectric spectra of a PVME/PS blend at different temperatures are fitted by eq 9 of ref 18, and in the process $\hat{n}_\alpha$ as well as $\{n_{\alpha i}\}$ is determined. The method is elaborate, requiring fitting the dielectric spectra of the blend or copolymer at different temperatures. It becomes impractical for the poly(*n*-butyl methacrylate-*stat*-styrene) because dielectric spectra at different temperatures have not been reported.[14,15] Nevertheless, there is an alternative method to determine the most probable coupling parameter, $\hat{n}_\alpha$, of the distribution from the T_g-scaled temperature dependence of the most probable α-relaxation time, τ_α (see Figure 1). It was established in ref 21 for homopolymers that there exists a strong and almost linear correlation between the coupling parameter n or the KWW exponent $(1 - n)$ and the steepness[21] index S or the fragility[22] index, m, both defined by

$$m,\ S = [\mathrm{d}\log\tau_\alpha/\mathrm{d}(T_g/T)]_{T_g/T=1} \tag{6}$$

Most of the results of m or S for 11 homopolymers in ref 21 were obtained by a single technique, i.e., creep compliance. In a plot of m against n the data fall almost on a straight line with little scattering (see Figure 2 in ref 21). Assuming this correlation continues to hold between m and $\hat{n}_\alpha$ for the family of the random copolymers poly(*n*-butyl methacrylate-*stat*-styrene), we use the straight line fit to the homopolymer data in Figure 2 of ref 21 to determine the $\hat{n}_\alpha$ values of the copolymers from their corresponding S values.

This procedure of determining $\hat{n}_\alpha$ from S or m is put into practice in Figures 2 and 3. For this purpose only, we follow the custom[21,22] in defining T_g to be the temperature at which τ_α is equal to 10^2 s. We point out that this definition of T_g to find m is different from that used in obtaining eqs 4 and 5, where T_g is defined by $\tau_\alpha(T_g) = 10^4$ s. To make this distinction clear, from now on we shall use T_{gm} instead of T_g whenever $\tau_\alpha(T_{gm}) = 10^2$ s. After these T_{gm}'s of the copolymers have been determined, $\log[\tau_\alpha(T)/\mathrm{s}]$ is plotted against T_{gm}/T for the several styrene concentrations in Figure 2. Also included are data of pure PMMA (filled inverted triangles),[21,22] pure poly(isobutylene),[21,22] (PIB) (filled circles) and pure poly(*n*-hexyl methacrylate) (*Pn*HMA)[23] (open triangles). The slopes of the curves at $T_{gm}/T = 1$ give us the values of the steepness index m of all materials including the copolymers. Using the linear relation between m and n represented by the continuous straight line in Figure 3 (identical to the linear fit in Figure 2 of ref 21), we have finally obtained the most probable coupling parameters $\hat{n}_\alpha$ of the copolymers from their m values (indicated by the ordinate of the horizontal lines). The results are displayed also in Figure 3 by the open circles, which lie naturally exactly on the straight line fit. The points are each labeled by the styrene content of the copolymer. Together, they show a monotonic increase of $\hat{n}_\alpha$ with m as the styrene content in the copolymer is increased. On the basis of current interpretations[18−21] of $\hat{n}_\alpha$ and m, their trend indicates an increase of intermolecular coupling or "cooperativity" with styrene content as expected from argument given in the beginning of this section. Numerical values of $\hat{n}_\alpha$ and other quantities given in the figures are tabulated in Table 1.

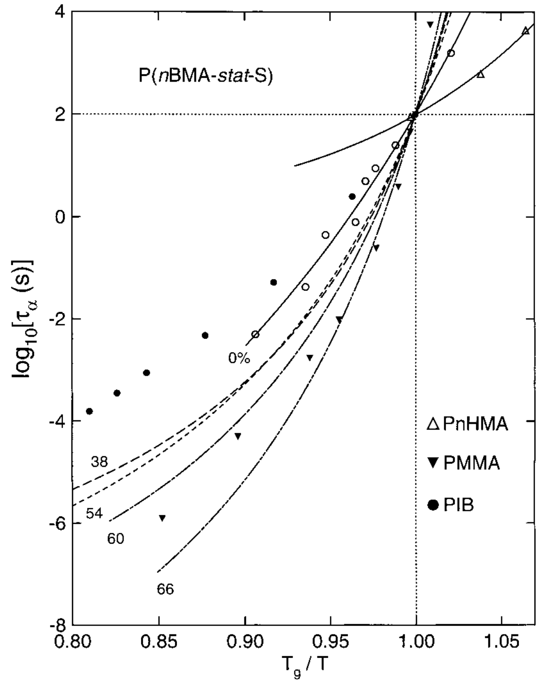

Figure 2. The α-relaxation times, τ_α, plotted against the scaled reciprocal temperature, T_g/T, for a series of P(*n*BMA-*stat*-S) random copolymers with different styrene contents. Here T_g is the temperature at which $\tau_\alpha(T_g) = 10^2$ s. Similar plots are given for the pure polymers, P*n*HMA, PMMA, and PIB, for comparison.

We have used the good straight line fit to the relation between m and n for homopolymers from Figure 2 in ref 21 to help us to determine $\hat{n}_\alpha$ of the copolymers. The reader may ask why similar plots for polymers such as Figure 3 of ref 22 or Figure 2 of ref 24 are not used for the same purpose. In these two plots not used here, the data that do not belong to the 11 polymers considered in Figure 2 of ref 21 were obtained by other methods than mechanical shear modulus and compliance. It has been found[25] that the widths and temperature dependence of the α-relaxation can vary significantly with the measuring techniques, including mechanical, dynamic light scattering, and dielectric relaxation. These variations contribute to larger scatter of the data from a linear relationship, making the latter less certain. For this reason we use only the homopolymer data of ref 21 that come from a single technique of creep compliance to reduce the scatters of data from a linear relationship between m and n for homopolymers. Ideally for the

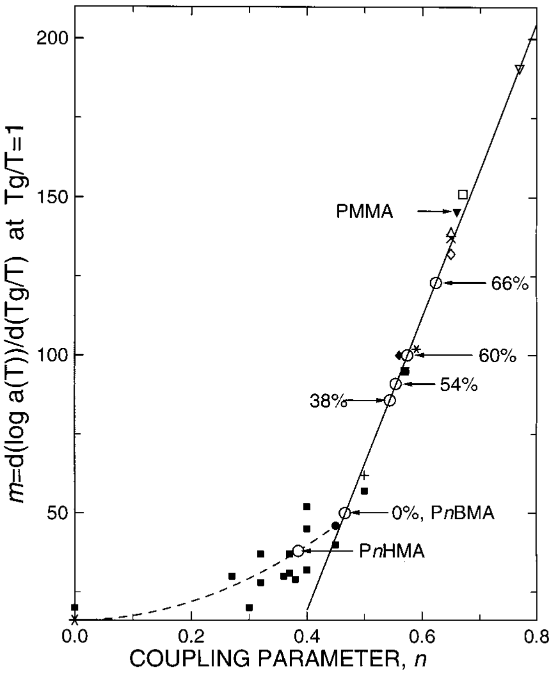

Figure 3. Coupling parameter $\hat{n}_\alpha$ (abscissa) obtained from *m* (ordinate) for a series of P(*n*BMA-*stat*-S) random copolymers with different styrene contents (open circles) and pure P*n*HMA (open circle) by using the correlation between $(1 - n_\alpha)$ and the steepness index, *m*, established in refs 21 and 22. The straight line is the fit to the data of the 11 homopolymers reproduced from Figure 2 of ref 21. The smaller solid squares are data of network glass-formers from ref 22. The dashed curve is a least-squares parabolic fit to the data of the network glass-formers. The point (0,16) correspond to the minimum value that *m* can have when $n = 0$.

Table 1. β-Relaxation Time, $\tau_\beta(T_g)$, Determined Directly from the Experimental Data of the α- and β-Relaxations of the Random Copolymers Poly(*n*-butyl methacrylate-*stat*-styrene) with Different Styrene Contents[a]

poly(*n*-butyl methacrylate-*stat*-styrene)	$n \equiv 1 - \beta(T_g)$	$\log[\tau_0(T_g)/\mathrm{s}]$	$\log[\tau_\beta(T_g)/\mathrm{s}]$
0% styrene (P*n*BMA)	0.47	−3.0	−0.80
38% styrene	0.54	−4.3	−2.74
54% styrene	0.55	−4.4	−3.19
60% styrene	0.57	−4.9	−4.78
66% styrene	0.63	−5.9	−5.41
poly(methyl methacrylate) (PMMA)	0.63	−5.9	−5.2
poly(*n*-hexyl methacrylate) (P*n*HMA)	0.38	−1.96	0.0

[a] Included are also the data of some pure poly(alky methacrylates). The primitive α-relaxation time, $\tau_0(T_g)$, of glass-formers calculated from eq 4 with the value of *n* obtained from $[1 - \beta(T_g)]$.

purpose of this paper, the single technique of choice to determine the relation between *m* and *n* is dielectric relaxation because the data of poly(*n*-butyl methacrylate-*stat*-styrene) we analyze here are obtained by dielectric relaxation. Unfortunately, at the present time dielectric data are insufficient to establish the relationship between *m* and *n* for homopolymers. Unlike creep compliance, far fewer homopolymers have been measured down to sufficiently low frequencies ($\sim 10^{-3}$ Hz) necessary for the determination of *m*. Thus, the best we can do is to use the linear relation between *m* and *n* obtained from creep compliance data of homopolymers to determine the most probable dielectric coupling parameters $\hat{n}_\alpha$ of the copolymers from their dielectric *m* values in Figure 3. The values of $\hat{n}_\alpha$ of the copolymers so obtained are approximate, but their ordering according to size should be correct because both creep compliance and dielectric relaxation give a linear relationship between *m* and *n*.

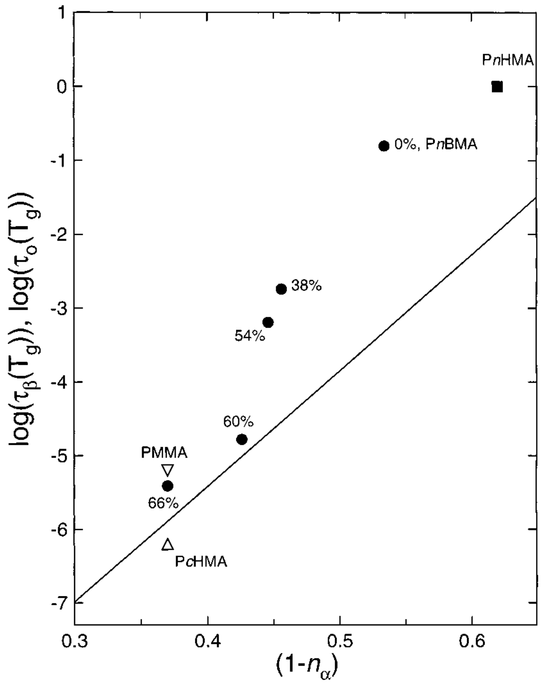

Figure 4. Correlation between $\log[\tau_\beta(T_g)]$ and $(1 - \hat{n}_\alpha)$ shown by the series of P(*n*BMA-*stat*-S) random copolymers with different styrene contents, pure PMMA and pure P*n*HMA. The straight line is $\log[\tau_0(T_g)]$ calculated as a function of $\beta = (1 - n_\alpha)$ by eq 4.

5. Correlation between $\log[\tau_\beta(T_g)]$ and $(1 - \hat{n}_\alpha)$

With both $\log[\tau_\beta(T_g)]$ and $\hat{n}_\alpha$ determined for the series of random copolymers as described in the previous sections, the moment has arrived to see whether a correlation between these two quantities holds or not. The test is made in Figure 4 where $\log[\tau_\beta(T_g)]$ of P(*n*BMA-*stat*-S) at five different styrene contents are plotted against their corresponding values of $(1 - \hat{n}_\alpha)$. The data point represented by the filled inverted triangle is for pure PMMA. The value of $(1 - \hat{n}_\alpha)$ of PMMA was determined[21] directly from the dispersion of its α-relaxation and is consistent with that can be estimated from *m* by the straight-line fit in Figure 3. The data in Figure 4 clearly show that $\log[\tau_\beta(T_g)]$ increases monotonically with $(1 - \hat{n}_\alpha)$. Therefore, when confined to the series of random copolymers, the correlation between $\log[\tau_\beta(T_g)]$ and $(1 - \hat{n}_\alpha)$ is even stronger than previously found when considering a whole host of diverse glass-forming liquids.[10,11] The straight line in Figure 4 represents the values of $\log[\tau_0(T_g)]$ calculated according to eq 4. Its proximity (in order of magnitude) to the data points of the random copolymers indicates that $\log[\tau_\beta(T_g)]$ and $\log[\tau_0(T_g)]$ are not far from each other. The orders of magnitude of $\tau_\beta(T_g)$ and $\tau_0(T_g)$ are remarkably close to each other for copolymers with 66% and 60% styrene, as well as neat PMMA. For the 54% and 38% styrene copolymers, less than 2 orders of magnitude separate $\tau_\beta(T_g)$ and $\tau_0(T_g)$. The largest difference between $\tau_\beta(T_g)$ and $\tau_0(T_g)$ of 2.5 orders of magnitude occurs in the 0% styrene sample. These differences, although large, must be considered in conjunction with the large full width at half-maximum of the β-relaxation dielectric loss peak exceeding 4.6 decades.[14,15] Since the reciprocal of $\tau_\beta(T_g)$ is the dielectric β-loss peak frequency, the largest differences between $\tau_\beta(T_g)$ and $\tau_o(T_g)$ is still within the half-width of the β-relaxation. Thus, the β-relaxation and the primitive relaxation are not far apart in order of magnitude, consistent with the fact that both relaxation processes are devoid of intermolecular cooperativity. To avoid possible misunderstanding of the reader, we reiterate that despite similarity between the β-relaxation and the primitive relaxation, they are *not the same process*. Therefore, only orders of magnitude correspondence between $\tau_\beta(T_g)$ and $\tau_o(T_g)$ can be expected, and their differences found in Figure 3 including the slopes are considered to be consistent with their similarity but not identity.

Somewhat related to the family of P(*n*BMA-*stat*-S) copolymers is the family of poly(*n*-alkyl methacrylates) of which P(*n*BMA) and PMMA are members. Like the copolymers, T_g changes by a large amount within this family. Naturally the reader may ask the question whether the correlation between $\log[\tau_\beta(T_g)]$ and the coupling parameter continues to hold for the poly(*n*-alkyl methacrylates) or not. Except for PMMA and maybe PEMA, the higher members containing longer methylene chains in the side groups will have the presence of concentration fluctuations due to internal blending of the main chain with the side chains. Dielectric and mechanical relaxation data of poly(*n*-hexyl methacrylate) (P*n*HMA),[23] poly(*n*-octyl methacrylate) (P*n*OMA),[26] and poly(*n*-lauryl methacrylate) (P*n*LMA)[20] show that the α-relaxation of these polymers have very broad dispersions as a result of the fluctuations in concentrations. For the same reason as discussed in sections 3 and 4, except for PMMA and maybe PEMA, the quantity of interest is the most probable coupling parameter $\hat{n}_\alpha$. It can be obtained indirectly from the steepness index *m* of the most probable relaxation time τ_α, but not from fitting the dispersion of the α-relaxation by the Kohlrausch function, which does not work for the higher members of the series. Data of τ_α as a function of temperature measured to times of the order of 100 s are necessary in order to determine *m*. Although dielectric and mechanical measurements have been made on many poly(*n*-alkyl methacrylates), only a fraction of them provide relaxation data of τ_α up to 100 s. These include PMMA,[21] P*n*BMA,[26,27] and P*n*HMA,[23] and they are plotted against T_{gm}/T in Figure 2 and their *m* values determined according to eq 6 are indicated by the horizontal arrows in Figure 3. *m* decreases with increasing length of the side chain, and P*n*HMA has the smallest $m = 38$. This value lies below the smallest *m* obtained previously,[21,22] which comes from PIB. To determine $\hat{n}_\alpha$ for P*n*HMA, we use the network glass-formers data of ref 22 in giving the guide to the correlation of *m* with *n* for $m_{\min} \le m \le m(\text{PIB})$. Here, $m_{\min} \approx 16$ is the minimum that the steepness index can have.[22] The dashed curve in Figure 3 is the least-squares fit to the data of the network glass-formers (filled squares with $m \le 57$). From this curve and its $m = 38$, we determine $\hat{n}_\alpha$ for P*n*HMA to be 0.38. The values of $\log[\tau_\beta(T_g)]$ for PMMA, P*n*BMA, and P*n*HMA obtained from experiment data[23,26,27] are plotted against *n* or $\hat{n}_\alpha$ in Figure 4. We include also the data of the poly(cyclohexyl methacryate) (P*c*HMA).[10,11,28] It is clear by inspection of Figure 4 that the correlation between $\log[\tau_\beta(T_g)]$ and the coupling parameter $\hat{n}_\alpha$ or its complement $(1 - \hat{n}_\alpha)$ holds also for the family of poly(alkyl methacrylates).

6. Conclusion

Our previous works have established the existence of a rough correlation between $\log[\tau_\beta(T_g)]$ and the KWW exponent $(1 - n)$ or the coupling parameter *n* for neat glass-formers. Such a correlation is remarkable because it is between a property of the β-relaxation and another property of the α-relaxation. However, when all the data are considered at the same time, there are large scatters from a perfect correlation. Efforts have been made[10,11] to distinguish different classes of glass-formers: small molecule van der Waal liquids, liquids with hydrogen bonding, plastic crystals, and amorphous polymers. Although the scatter of the data for a restricted class is less, it still remains. One possible cause of the scatter is the inclusion of glass-formers with diverse chemical structures even restricted to the same class. The correlation should improve when comparisons are confined to members of a closely related family of glass-formers. This expectation motivates the undertaking of the present investigation of examining the α and β relaxations in a series of P(*n*BMA-*stat*-S) random copolymers with different styrene contents. By systematically increasing the styrene content, the continuous change of the chemical structure of the copolymer leads to smooth variations of the properties of the α- and β-relaxations. This is an ideal situation to test the correlation between the logarithm of the most probable β-relaxation time $\tau_\beta(T_g)$ and the most probable coupling parameter $\hat{n}_\alpha$. The results indicate that a strong correlation indeed exists between $\log[\tau_\beta(T_g)]$ and $\hat{n}_\alpha$ for this closely related family of glass-formers. A similar conclusion can be made on the family of poly(alkyl methacrylates).

Acknowledgment. This work was supported by the Office of Naval Research.

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MA990284B