Macromolecules **1998,** *31,* 8291−8296

Structural Side Effects in the Use of a Fluorescent Probe for Monitoring Polymer Mobility

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Received May 6, 1998; Revised Manuscript Received August 5, 1998

ABSTRACT: Fluorescence spectroscopy using an intramolecular excimer-forming probe has been used to investigate chain mobility in various polybutadienes and copolymers of styrene and butadiene. The temperature dependence of the correlation time of the probe motion can be fitted to a Williams−Landel−Ferry equation which shows that the probe mobility reflects the glass transition phenomenon of the host matrix. However, it is obtained that the probe presents an additional mobility which depends on the polymer structure, on the existence and the nature of lateral chains.

Introduction

The fluorescence probe technique has been widely known for the study of macromolecular motions and the analysis of free volume distribution in polymeric media. The fluorescence probes are typically molecules exhibiting an excited-state formation which is expected to depend on the microviscous properties of the surrounding medium.

Bichromophoric probes consisting of two identical chromophores linked by a short flexible chain may form an intramolecular excimer. This process requires close approach of the two moieties through internal rotations during the lifetime of the excited state. Since the excimer state results from a specific intramolecular conformational change which requires a relatively large amount of free volume, an excimer-forming sensor dispersed in a polymeric medium is expected to monitor changes in the local environment induced by the segmental relaxation process of the polymeric host matrix.

The dynamics of the bichromophoric probe may be described in terms of a correlation time which is the reciprocal of the rate of excimer formation. This dynamics is expected to be dominated by the local free volume in the vicinity of the probe since polymer segments must rearrange themselves, allowing the two chromophores to reach the excimer geometry. In previous works,[1−5] we have shown that the temperature dependence of the correlation time of an intramolecular excimer-forming probe dispersed in various elastomers is described by the Williams−Landel−Ferry (WLF) equation with coefficients corresponding to the considered polymer matrix. On the other hand, on the basis of the investigated systems—polyisobutylene, polybutadiene, polyisoprene, and a copolymer of ethylene and propylene—it has been proposed that the probe's dynamics reflects the frictional environment of the host matrix.[6] The frictional effects are expected to depend strongly on the microstructure and on the intrinsic structural and conformational properties of the polymer chains.

In other words, the problem is to see if the microscopic friction felt by the probe molecule is consistent with the monomeric friction coefficient of the polymer extracted from rheological measurements. Of course, the low probe concentration allows us to assume that the probe acts as a passive participant and does not perturb the host's dynamics.

The present paper describes results on two types of polymer systems: (1) a series of polybutadienes with nearly the same cis:trans ratio but various vinyl contents as well as a polybutadiene containing 99% of vinyl configurations and (2) random styrene−butadiene copolymers with different proportions of styrene and different butadiene microstructures.

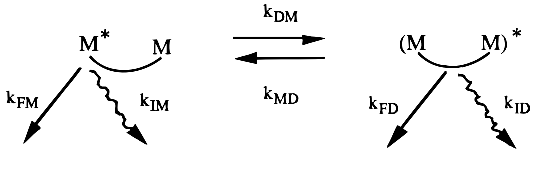
Experimental Section

Materials. All the elastomers investigated were provided by Manufacture Française des Pneumatiques Michelin (Clermont-Ferrand, France). Their microstructures, molecular weight characteristics, and glass transition temperatures are listed in Table 1.

The glass transition temperatures T_g, reported in Table 1, were determined by differential scanning calorimetry at the onset of the transition. Measurements were made at a heating rate of 5 °C·min^{-1}. As expected, the glass transition temperature increases with the content of vinyl and/or styrene configurations. Molecular weights were obtained by gel permeation chromatography (universal calibration).

Films of raw polymers were obtained by solvent casting onto a quartz plate from a cyclohexane solution containing the probe. The final probe concentration in the films does not exceed 5×10^{-7} mol·g^{-1} in the films.

Fluorescence Measurements. The intramolecular excimer formation process can be represented as follows:[7]



where M, M*, and (MM)* represent respectively the unexcited chromophore, the excited monomer, and the excimer conformation. Here, k_{DM} and k_{MD} are the respective rate constants for intramolecular excimer formation and dissociation, k_{FM} and k_{FD} are the rate constants of fluorescence from the local excited state (monomer) and excimer, and k_{IM} and k_{ID} are the rate constants of nonradiative decay from the monomer and the excimer states.

An important parameter to characterize the efficiency of the intramolecular excimer formation process is the rate constant k_{DM}. k_{DM} is determined from fluorescence lifetime measure-

10.1021/ma980717v CCC: $15.00

Table 1. Molecular Characteristics of the Considered Elastomers

		butadiene microstructure, %						
polymer	sample	cis	trans	vinyl	wt % styrene	M_w	M_w/M_n	T_g (°C)
polybutadienes	PB(11v)	40	49	11		141 700	1.1	−93
	PB(24v)	38	38	24		128 900	1.1	−85
	PB(34v)	29	37	34		123 000	1.2	−75.5
	PB(54v)	21	24	54		140 900	1.6	−59
	PB(69v)	14	17	69		116 100	1.2	−44
	PB(76v)	10	14	76		158 700	2.3	−32.5
	PB(84v)	3	13	84		159 600	1.7	−23.5
	PB(99v)			99				−2
copolymers Styrene−Butadiene	SBR(10v19s)	35	55	10	19	110 000	1.2	−79
	SBR(11v24s)	38	51	11	24	128 500	1.4	−71
	SBR(24v27s)	31	45	24	27	153 100	1.2	−60.5
	SBR(33v27s)	24	43	33	27			−54.5
	SBR(25v41s)	24	51	25	41	182 300	2.3	−33

ments and is given by the following expression:

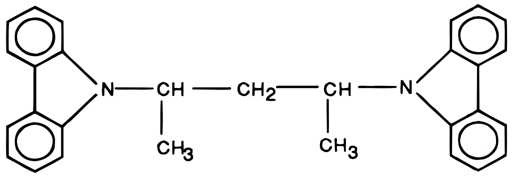
$$k_{DM} = \frac{1}{\tau_M} - \frac{1}{\tau_0} \qquad (1)$$

where $\tau_M = 1/(k_{FM} + k_{IM} + k_{DM})$ is the lifetime of the excited monomer and $\tau_0 = 1/(k_{FM} + k_{IM})$ is that of the monomer without excimer formation.

This quantity is determined by measuring the fluorescence decay time of a model compound, containing only one chromophore. This molecule which reflects the electronic properties of the probe molecule is not able to form an intramolecular excimer. Its lifetime is a characteristic of the aromatic ring.

The dynamics of the bichromophoric probe is described in terms of a correlation time τ_C defined as $(k_{DM})^{-1}$.

The intramolecular excimer-forming probe chosen for this work was meso-2,4-di(*N*-carbazolyl)pentane (called meso-DNCzPe). This molecule exhibits a single excimer conformation which is populated via a bond rotation from a single state conformer.[8,9]



The model molecule chosen for meso-DNCzPe was *N*-isopropylcarbazole.

The fluorescence lifetime measurements were made on film samples that contain either the model molecule or the excimer-forming probe molecule.

The fluorescence spectra were recorded on a Fica Model 55 MK II spectrofluorimeter equipped with a 450 W xenon lamp and a R 212 photomultiplier tube. The excitation wavelength was 320 nm.

Fluorescence decays were performed on a time correlated single photon-counting fluorimeter described previously.[10] Sample fluorescence was produced by the strong 337 nm emission line of the nitrogen discharge. The monomer emission was analyzed through a filter ($\lambda_{\text{trans.max.}} = 358$ nm, trans. max. = 30%, FWHM = 6.7 nm).

Viscoelastic Measurements. They were made on a Rheometrics Dynamic Analyzer (RDA II) with parallel plates of 2.5 cm diameter. The isothermal storage and loss moduli, G' and G'', were measured as functions of frequency ω. In materials which obey the time−temperature superposition,[11] the dynamic moduli at different temperatures are related by

$$G'(\omega,T) = b_{T/T_0} G'(a_{T/T_0}\omega, T_0) \qquad (2)$$

$$G''(\omega,T) = b_{T/T_0} G''(a_{T/T_0}\omega, T_0) \qquad (3)$$

in which T_0 is an arbitrary reference temperature and a_{T/T_0} and b_{T/T_0} are the frequency and modulus shift factors, respectively. The temperature dependence of the horizontal shift factors are well described by the WLF equation:[12]

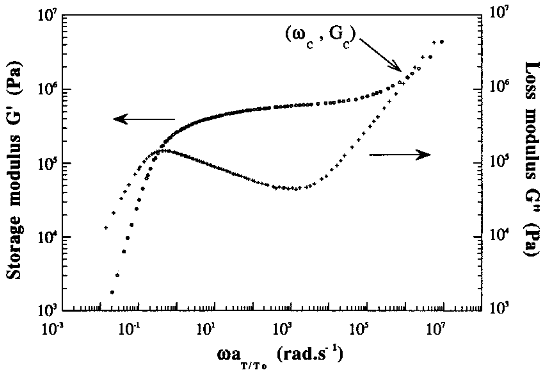


Figure 1. Linear viscoelastic behavior of PB(54v) at T_0 = 25 °C.

$$\log a_{T/T_g} = \frac{-C_1^g(T - T_g)}{C_2^g + (T - T_g)} \qquad (4)$$

where C_1^g and C_2^g are the viscoelastic coefficients at T_g, they depend on the chemical structure of the medium and are related to the free volume theory[13] by the following expressions:

$$C_1^g = \frac{1}{2.303\, f_g} \qquad C_2^g = \frac{f_g}{\alpha_f} \qquad C_1^g C_2^g = \frac{1}{2.303\alpha_f} \qquad (5-7)$$

where f_g and α_f are respectively the fractional free volume at the glass transition temperature and the thermal expansion coefficient of the free volume.

Figure 1 shows the viscoelastic behavior of PB(54v) at the reference temperature T_0 = 25 °C. The master curve represents the combination of experimental data obtained at several temperatures (ranging from 55 to −40 °C). The experimental data at different temperatures were shifted to obtain the master curve at the reference temperature. The behavior is typical for high-molecular-weight narrow distribution polymers.[11,14,15]

An important parameter is the monomeric friction coefficient, ζ_0, which represents the resistance encountered by one repeat unit moving through its environment.[16] This coefficient is determined from experimental data in the transition zone (at higher frequencies) where $G' = G'' = G_c \sim \omega^{1/2}$, according to the following equation derived from the Rouse theory modified for undiluted polymers:[11]

$$\zeta_0 = \frac{48 M_0^{\,2} G_c^{\,2}}{a^2 \rho^2 R N T \omega_c} \qquad (8)$$

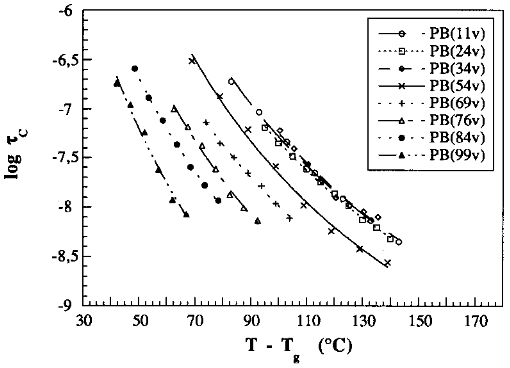


Figure 2. Plot of the correlation time τ_C of the meso-DNCzPe probe versus $(T - T_g)$ in various polybutadienes. The broken and solid lines represent the related WLF equations.

(ω_c, G_c) represents the crossover point coordinates (see Figure 1), M_0 the monomer molecular weight, ρ the polymer density, R the universal gas constant, T the temperature, N the Avogadro's number, and a the root-mean-square end-to-end length per monomer unit. The temperature dependence of ζ_0 is also described by the WLF equation.

Results and Discussion

We will first present the results concerning the polybutadienes. It was shown previously[1,2,4] that in elastomeric matrices, at temperatures well above the glass transition temperature, the temperature dependence of the correlation time of the excimer-forming probe is described by the WLF equation:

$$\log \frac{\tau_C(T)}{\tau_C(T_g)} = \frac{-C_1^g(T - T_g)}{C_2^g + (T - T_g)} \tag{9}$$

with $\tau_C(T_g)$ the probe correlation time at the glass transition temperature of the matrix.

Figure 2 represents the comparison of probe mobility (represented by the logarithm of the correlation time τ_C) in the series of polybutadienes differing by the content of vinyl configurations versus $(T - T_g)$. All the curves are well fitted by the WLF equation.

The above equation can be rewritten by using the Vogel temperature, $T_\infty = T_g - C_2^g$:

$$\log \frac{\tau_C(T)}{\tau_C(T_g)} = -C_1^g + \frac{C_1^g C_2^g}{(T - T_\infty)} \tag{10}$$

When representing the evolution of log $\tau_C(T)$ versus $1/(T - T_\infty)$, as shown in Figure 3 for the different polybutadienes, the product $C_1^g C_2^g$ is merely determined from the slope of the straight line corresponding to each polymer. The values of the product $C_1^g C_2^g$ obtained by this way are in good agreement, within experimental errors, with those obtained from the rheological measurements[17] as can be seen in Table 2. These results prove that the temperature dependence of the intramolecular conformational change of the probe is mostly controlled by the segmental motions of the polymer chains involved in the glass transition phenomenon.

Despite the differences in the microstructure of the various polybutadienes, all the samples exhibit nearly the same value of the $C_1^g C_2^g$ product, and moreover, the same viscoelastic coefficients at their respective glass transition temperature,[17-20] C_1^g and C_2^g. Figure 2 shows also that, at a given value $(T - T_g)$, the higher the vinyl content, the shorter the correlation time. These results indicate that the differences in mobility at a given temperature cannot be reflected by the differences in the T_g temperatures.

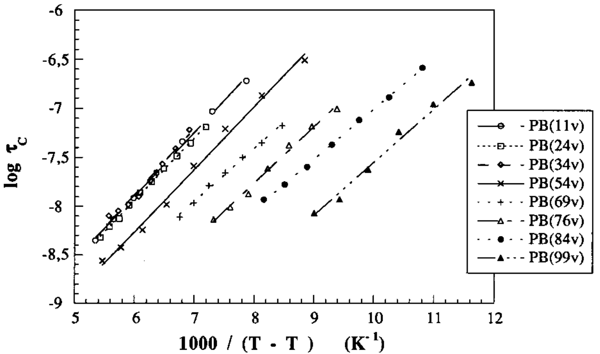


Figure 3. Vogel representation of the correlation time τ_C of the meso-DNCzPe probe versus $1/(T - T_\infty)$ in various polybutadienes.

Table 2. Values of the Product $C_1^g C_2^g$ Determined by Two Different Techniques

polybutadiene	$C_1^g C_2^g$ (K) obtained from the excimer fluorescence technique	$C_1^g C_2^g$ (K) obtained from the viscoelastic measurements[17]
PB(11v)	652	610 ± 50[a]
PB(24v)	640	
PB(34v)	673	
PB(54v)	638	
PB(69v)	538	
PB(76v)	575	
PB(84v)	512	
PB(99v)	542	

[a] Mean value calculated for all the microstructures.

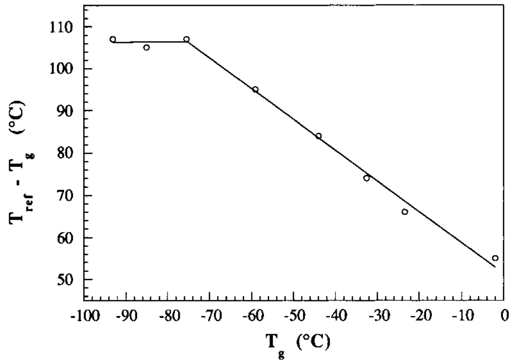


Figure 4. $(T_{ref} - T_g)$ plotted versus T_g for various polybutadienes, T_{ref} being the temperature at which log $\tau_C = -7.5$.

It is of interest to define a reference state in which all the polymers are in equivalent states from the point of view of their local mobility. The temperature, T_{ref}, at which the probe undergoes its conformational change at a given frequency, for example, $10^{7.5}$ Hz, may constitute an appropriate reference state. Figure 4 represents the evolution of $(T_{ref} - T_g)$ against T_g for the polybutadienes studied. For polybutadienes with low T_g, $(T_{ref} - T_g)$ takes roughly the same value but, from −70 °C, it appears that $(T_{ref} - T_g)$ decreases regularly with T_g, showing a larger mobility of the probe in the polybutadienes with high T_g.

The frequency of the intramolecular conformational change of the excimer-forming probe is controlled by the monomeric friction coefficient of the surrounding matrix.[6,21] Indeed, for the reference temperatures, T_{ref}, the

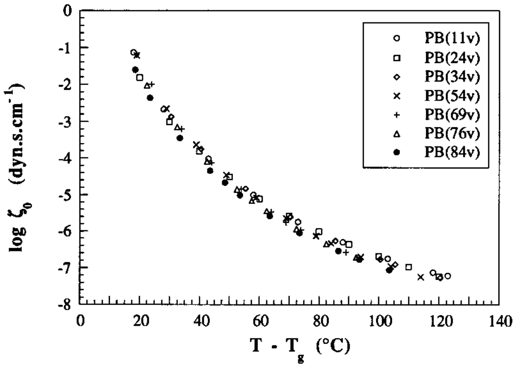


Figure 5. Plot of log ζ_0 as a function of $(T - T_g)$ for various polybutadienes.

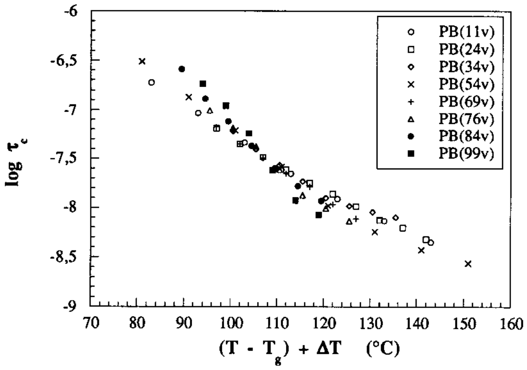


Figure 6. Plot of log τ_C as a function of $(T - T_g) + \Delta T$ for various polybutadienes, ΔT representing the horizontal shift used for each polymer to superimpose the data at log $\tau_C = -7.5$.

polymers have been shown to present a common value of ζ_0. So, we have plotted in Figure 5, log ζ_0 (obtained from the viscoelastic measurements) versus $(T - T_g)$ for all the investigated polybutadienes.[17,20] A master curve is obtained which disagrees with the results obtained from the excimer fluorescence technique where the probe does not present the same mobility in all the matrices at a constant $(T - T_g)$. These results completely different from those already obtained[3] point out the effect of the polymer molecular structure on the probe mobility.

To explain the discrepancies between rheological and spectroscopic measurements, the first idea which comes to mind is that the probe acts as a plasticizer, decreasing in its vicinity the glass transition temperature of the medium. Moreover, this effect seems to be more important when the T_g of the matrix increases. Consequently, if this assumption is true, when the curves corresponding to the polybutadienes with high vinyl contents in Figure 2 are shifted horizontally in relation to the curves of low vinyl compositions, a master curve should be obtained. As can be seen in Figure 6, by using this procedure and when taking into account experimental errors, we do not observe a unique curve for all vinyl compositions. A horizontal shift is not sufficient to justify the higher probe mobility in polybutadienes with high T_g. And what about a vertical shift? Indeed, it was shown previously that polybutadienes independently of chain microstructure present the same viscoelastic coefficient values at their own glass transition temperature,[17,18] so in the equation describing the evolution of τ_C with T, at a given $(T - T_g)$ value, the only term which differs from one polymer to another is log $\tau_C(T_g)$ and it corresponds to a vertical shift. For each polybutadiene, the experimental data shifted vertically in relation to polybutadienes with low vinyl content are presented in Figure 7. All these data lead to a master curve which is well fitted by the WLF equation with coefficients in agreement with those obtained by rheological measurements. In a matrix with higher vinyl content, the probe presents lower correlation times at a given $(T - T_g)$ value: it gets an additional mobility which depends on the polymer microstructure and increases with the content of vinyl configurations. This explains why the required vertical shift is more and more important when the glass transition temperature of the matrix rises.

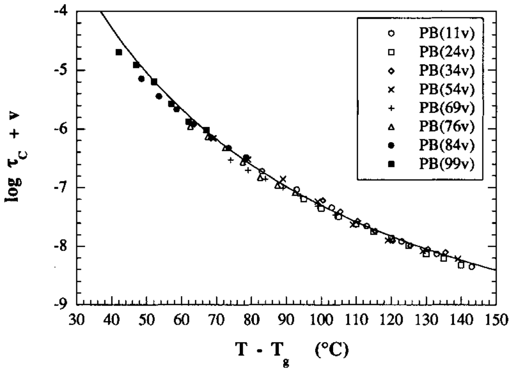


Figure 7. Plot of log τ_C as a function of $(T - T_g)$ for various polybutadienes, v representing the vertical shift used for each polymer to superimpose the experimental data; the solid line corresponds to the WLF fit of the superimposed data.

We found that log $\tau_C(T_g)$ decreases when T_g increases. Then the differences observed by the two techniques (spectroscopic and rheological) are essentially attributed to the too low values of log $\tau_C(T_g)$ in polybutadienes with high T_g. This quite unexpected result has already been presented by Inoue et al.[22] which have previously reported rotational correlation times of two probes in different polymers obtained by a photobleaching method. For the different polymers studied, they also found that probe rotation times at T_g showed a systematic decrease with an increasing matrix T_g. But they did not reach any conclusion about the origin of this effect.

From the precise analysis of the probe motion in various polybutadienes and from the comparison with viscoelastic measurements, we are able to identify that the temperature dependence of the probe motion is free-volume dependent. But the absolute value of its correlation time depends on the prefactor term $\tau_C(T_g)$ of the WLF equation (eq 10) which decreases with the vinyl content. So, the fluorescent probe giving rise to an intramolecular excimer follows the temperature evolution of the polymer fractional free volume (since the viscoelastic coefficients obtained by the two methods are the same) but with a mobility differing from that of the polybutadienes chains.

What are the results concerning the copolymers of butadiene and styrene? In Figure 8, the probe correlation time is represented versus $(T - T_g)$ for the four copolymers studied. As in the case of polybutadienes, we do not observe a unique behavior and it seems that, in copolymers with higher glass transition temperatures, the probe gets a higher mobility whereas the viscoelastic measurements lead to one curve for representing the dependence of log ζ_0 with $(T - T_g)$ in the different copolymers.[20] However, the product $C_1^g C_2^g$ determined from the Vogel representation of Figure 9, which is 582 K for SBR(10v19s) and 613 K for

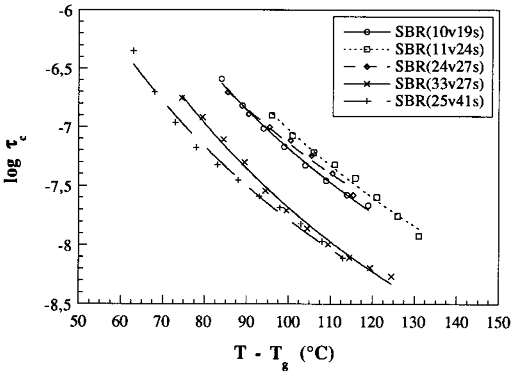


Figure 8. Plot of the correlation time τ_C of the meso-DNCzPe probe versus $(T - T_g)$ in various styrene–butadiene copolymers.

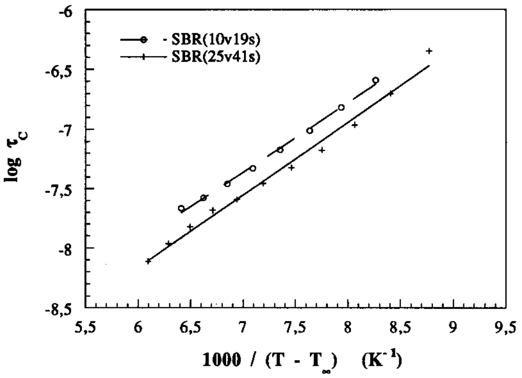


Figure 9. Vogel representation of the correlation time τ_C of the meso-DNCzPe probe versus $1/(T - T_\infty)$ in two copolymers.

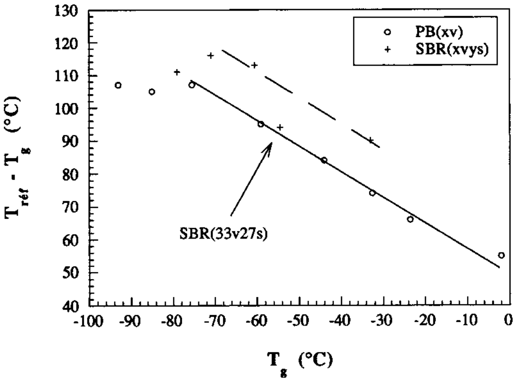


Figure 10. $(T_{ref} - T_g)$ plotted versus T_g for various polybutadienes and styrene–butadiene copolymers, T_{ref} being the temperature at which $\log \tau_C = -7.5$.

SBR(25v41s), is in agreement with viscoelastic measurements respectively 618 ± 50 K and 692 ± 50 K. The latter high value may be due to the strong polydispersity of the sample SBR(25v41s).

In Figure 10, we have plotted $(T_{ref} - T_g)$ versus T_g for all the polybutadienes and copolymers studied by the excimer fluorescence technique. A similar behavior is obtained for the two series of polymers: a constant value of $(T_{ref} - T_g)$ and then a decrease with T_g. But it appears that, for copolymers, the decrease of $(T_{ref} - T_g)$ occurs at a temperature which is higher than that in the case of polybutadienes. So it seems that the styrene groups of the polymer matrix bring less mobility to the probe than the vinyl groups.

To explain the increase of probe mobility with T_g in the different systems, one can suppose that, around the probe, the neighboring polymer chains organize themselves and build a kind of “dynamic cage”, the size of which may vary with the microstructure. In the case of 1,4-polybutadienes, with no dangling segments, the chains would contribute to creating a rather dense arrangement around the probe. On the contrary, in 1,2-polybutadienes, the presence of vinyl lateral groups would disturb this arrangement and lead to a looser environment in which the probe could perform its conformational change at a temperature closer to the T_g of the matrix, leading to a decrease of $\log \tau_C(T_g)$. This assumption would explain why, in Figure 10, a break is observed for polybutadienes: when the vinyl content increases, the probe neighborhood changes and passes from a “1,4-polybutadiene cage” to a “1,2-polybutadiene cage”. Concerning the copolymers, since the styrene group is stiffer than the vinyl group, it has a smaller effect on the cage structure. The SBR(33v27s) which behaves like a polybutadiene was already studied with another probe and was thought to be a block copolymer,[1] and then the probe will localize particularly in the polybutadienes regions and will present a greater mobility.

Conclusion

In this work, the excimer fluorescence technique is used to analyze the mobility of some elastomeric systems. It shows that the motions of the polymer chains responsible for the formation of an intramolecular excimer are those involved in the glass transition since the temperature dependence is well described by the WLF equation. While this technique has revealed to be highly sensitive for probing polymer dynamics and the frictional environment of the host matrix, a new effect is observed in this extended study devoted to an analysis of the dependence of the probe mobility on the microstructure of polymer chains. While the rate of excimer formation can be fitted to the WLF equation, it is demonstrated that an increase of the vinyl lateral groups provide an additional mobility reflected by a decrease of the absolute values of the correlation time ascribed to a decrease of $\log \tau_C(T_g)$.

This potentially perturbing influence must be considered when interpreting the data, and this finding demonstrates that the fluorescence probes for the investigation of local polymer dynamics should be used with caution.

Acknowledgment. The authors gratefully acknowledge La Manufacture Française des Pneumatiques Michelin (Clermont-Ferrand, France) for providing the samples and more especially Ph. Schill and J.-M. Favrot for useful discussions and suggestions.

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