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Mobility of Macromolecular Chains As Studied by means of Excimer Fluorescence

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ABSTRACT: Intramolecular excimer formation of 10,10′-diphenylbis(9-anthrylmethyl oxide) (diphant) dispersed in bulk polybutadiene, polyisoprene, and their respective copolymers with styrene, as well as in poly(dimethylsiloxane) and a poly(dimethyldiphenylsiloxane), has been investigated through steady-state and time-resolved measurements. The dynamic behavior of the fluorescence probe is related to the mobility of the host matrix. The rate of conformational change appears to reflect the segmental chain motions occurring at the glass–rubber transition. The temperature dependence of the correlation times of the rotational motions involved in the excimer sampling mechanism can be described by the WLF equation with the appropriate set of parameters.

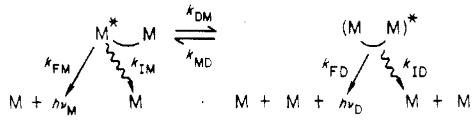
Introduction

Photoluminescence involving excimers has proved to be a powerful tool for studying a large variety of phenomena in polymer science. The fluorescence emission of intramolecular excimers provides information on the rate of conformational transition and thus on the dynamic behavior of a polymer chain.[1] Excimer fluorescence of a guest aromatic vinyl polymer dissolved at low concentration in a polymer host matrix has been used by Frank[2] to monitor relaxation processes near the glass transition region. Recently, Frank et al.,[3] Morawetz,[4] and Johnson et al.[5] have shown that excimer fluorescence is a valuable molecular probe of polymer blend compatibility. As it is very sensitive to the local viscosity and the polarity of the surrounding medium, intramolecular excimer fluorescence has developed into a method of great interest for investigating microscopic properties of the environment, such as the surfactant aggregation number in microemulsions and the polarity at micelle–solvent interfaces.[6]

In previous papers,[7,8] we have shown that the excimer fluorescence technique may afford a way to probe molecular motions in bulk polymers. 10,10′-Diphenylbis(9-anthrylmethyl oxide) (diphant) was chosen as the intramolecular excimer-forming probe for our investigations, on account of its high fluorescence quantum yield and the relatively high stability of its excimer. The emission behavior of diphant dispersed in two elastomers, polybutadiene (PB) and polyisoprene (PI) has been examined under steady-state conditions.

In the present work, both time-resolved and photostationary-state measurements were carried out on the two polydienes cited above and on copolymers of styrene–butadiene (SBR) and styrene–isoprene (SIR), as well as on a poly(dimethylsiloxane) and a poly(dimethyldiphenylsiloxane) copolymer. This study was performed in order to gain further insight into the emission properties of diphant embedded in polymer matrices. The aim of this work was to analyze the local mobility of the macromolecular chains and to determine whether the rate of conformational change required for excimer formation depends on the free volume induced by the segmental motions occurring at the glass transition and described by the WLF equation.[9]

The phenomenon observed was the intramolecular excimer formation of a low molar mass compound dispersed at a very low concentration in a medium so that neither excitation migration nor energy transfer between probes and matrices can occur. The formation and deactivation of the intramolecular excimer state can be described by the conventional kinetic scheme proposed by Birks:[10]



where k_{FM} and k_{FD} are the rate constants for the excited monomer M* and the excimer D* emission. k_{IM} and k_{ID} represent the nonradiative decay constants of these species, and k_{DM} and k_{MD} are the excimer formation and dissociation rate constants, respectively. The excited monomer and excimer lifetimes are defined by the following relations:

$$\tau_M = 1/(k_{FM} + k_{IM} + k_{DM})$$

and

$$\tau_D = 1/(k_{FD} + k_{ID} + k_{MD})$$

Under photostationary conditions, this scheme provides the ratio of excimer to monomer fluorescence intensities

$$\frac{I_D}{I_M} = \frac{k_{FD}}{k_{FM}} k_{DM} \tau_D \qquad \text{(A)}$$

Application of the kinetic scheme to the monomer and excimer fluorescence emission decay in response to a δ-function excitation pulse allows $I_M(t)$ to be described by a sum of two exponentials while $I_D(t)$ should decay as a difference of two exponentials.[11,12]

$$I_M(t) = k_{FM} \frac{X - \beta_1}{\beta_2 - \beta_1} \left[e^{-\beta_2 t} + \frac{\beta_2 - X}{X - \beta_1} e^{-\beta_1 t} \right] \qquad \text{(B)}$$

$$I_D(t) = k_{FD} \frac{k_{DM}}{\beta_2 - \beta_1} [e^{-\beta_1 t} - e^{-\beta_2 t}] \qquad \text{(C)}$$

where

$$\beta_1 = \tfrac{1}{2}\{(X + Y) - [(X - Y)^2 + 4k_{DM}k_{MD}]^{1/2}\} \qquad \text{(D)}$$

$$\beta_2 = \tfrac{1}{2}\{(X + Y) + [(X - Y)^2 + 4k_{DM}k_{MD}]^{1/2}\} \qquad \text{(E)}$$

$$X = 1/\tau_M$$

and

$$Y = 1/\tau_D$$

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Table I
Characteristics of the Polybutadiene, the Polyisoprene, and Their Respective Copolymers with Styrene

polymer	% styrene, in mass	microstructure of the PB or PI phase % cis	% trans	% vinyl	no. of consecutive styrene units ($n \geq$ 10), %	T_g, °C
PB 45 NF	0	37	51	12		-91
Solprene 1204	27	24	43	33	17	-48
Stereon 704	19	35	55	10	17	-72
Stereon 705	26	33	57	10	16	-64
Stereon 720	11	35	55	10	67	-90
PI IR 307	0	92	5	3		-58
SIR	20	50	31	19	0	-27

Table II
Characteristics of the Poly(dimethylsiloxane) and of the Poly(dimethyldiphenylsiloxane)

polymer	$\bar{M}_w$	% diphenylsiloxyl groups	T_g, °C
PDMS	5000	0	−124.5
PDMPS	600000	11.1	−96.0

Experimental Section

Diphant was synthesized according to the published procedure.[13] The 9-(methoxymethyl)-10-phenylanthracene was used as the monomeric model compound of diphant.

Samples. A wide range of elastomers differing in chemical structure and microstructure, and thus in glass transition temperature, was kindly supplied by "Manufacture Française des Pneumatiques Michelin". Their characteristics are summarized in Table I. The samples consist of films cured with dicumyl peroxide. Experiments were also performed on a sample of polybutadiene with no cross-linking agent. The cured polybutadiene (PB) and polyisoprene (PI) samples were those used in our previous study.[7] The copolymers investigated present a random distribution except one compound (Stereon 720) which is a block copolymer enclosing styrene microphases. The cross-linked films were swollen with a solution of diphant in cyclohexane (Merck spectrofluorimetric grade) while the film of raw polybutadiene was obtained by solvent casting onto a quartz plate from a cyclohexane solution containing the probe. All films, about 300 μm thick, were dried by extensive pumping in vacuo.

The samples of poly(dimethylsiloxane) (PDMS) and poly(dimethyldiphenylsiloxane) (PDMPS) were provided by Rhône-Poulenc Industries. The substitution of a certain fraction of dimethylsiloxyl groups by diphenylsiloxyl groups involves an increase of, the glass transition temperature (see Table II) and prevents the crystallization occurring at −40 °C in PDMS. Diphant was dispersed in these bulk fluid polymers by addition of a solution of the probe in cyclohexane. The mixture was dried in vacuo at 60 °C for 6 h to completely remove the solvent. The final probe concentration in the samples was approximately 2×10^{-7} mol/g of polymer in the films and 3×10^{-9} mol/g of polymer in PDMS and PDMPS. It was checked that only intramolecular excimer formation can occur at these concentrations.

Fluorescence Measurements. The fluorescence spectra were recorded on a FICA Model 55 MK II spectrofluorimeter equipped with a 450-W xenon lamp and an R212 photomultiplier tube. Emission spectra were automatically corrected for instrumental response. The excitation wavelength was 365 nm. In the case of films, the spectra were obtained by front-surface excitation. The emission intensities of the monomer (I_M) and the excimer (I_D) were measured at 430 and 550 nm, respectively.

Transient fluorescence measurements were performed on a single-photon-counting fluorimeter described previously.[14] The excitation wavelength was 357 nm, and the emission was analyzed through an MTO 5068 filter for the monomer and through a Schott OG 550 filter for the excimer.

PB, PI, and Their Copolymers with Styrene

A. Results. As a first step, we will only consider the results obtained in cured PB films. The general behavior of diphant proves to be similar in all the matrices.

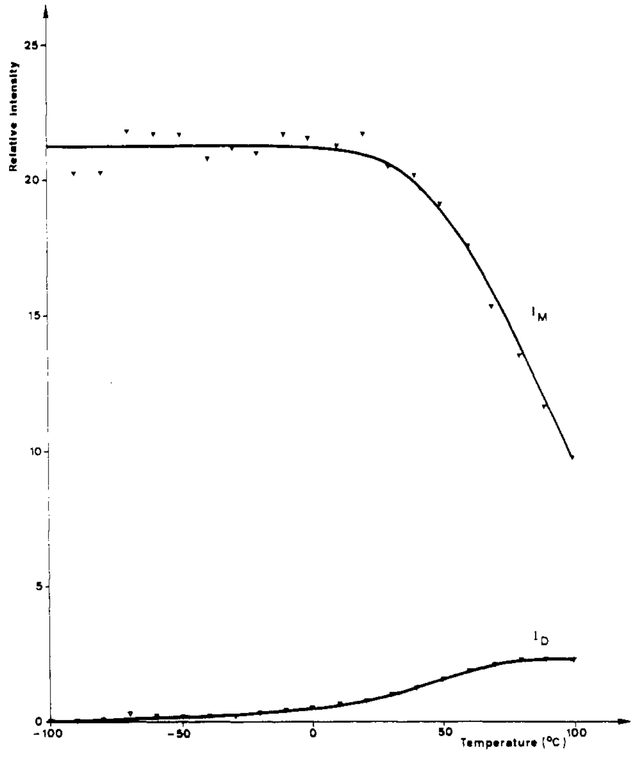

Figure 1. Temperature dependence of monomer and excimer fluorescence intensities of diphant in polybutadiene.

The evolution of the monomer and excimer fluorescence intensities as a function of temperature is shown in Figure 1. I_M remains approximately a constant between −100 and −20 °C. This fact indicates that the probe motions are still hindered in this range of temperature. Nevertheless, I_D displays simultaneously a very slight increase, which cannot result from the usual rotational process of conformational change. More likely, it arises from the excitation of a chromophore pair preformed in the ground state. The amount of probe molecules in this conformation is defined by Boltzmann's equation as a function of its energy and increases very slowly with temperature. At higher temperature, I_M is observed to decrease on behalf of I_D. The temperature-dependent fluorescence spectra of diphant in PB demonstrate the existence of an isoemissive point in this range of temperature. In the high-temperature region ($T > 80$ °C for PB), both I_M and I_D decrease, due to excimer dissociation and monomer deactivation. Nevertheless, the monotonous decrease of I_M in the range where I_D has reached a plateau indicates that k_{MD} remains smaller than k_{IM}.

The time-resolved fluorescence curves $I_M(t)$ and $I_D(t)$ were recorded between −90 °C and +80 °C, covering the range of existence of the isoemissive point. The monomer decay function was found to be monoexponential over the whole temperature interval studied. This indicates that $\beta_2 = X = 1/\tau_M$ in eq B. Thus the $k_{DM}k_{MD}$ factor in eq D and E can be neglected. The efficient excimer formation implies a nonzero value of k_{DM}, giving evidence of the unimportance of the dissociation process, as pointed out

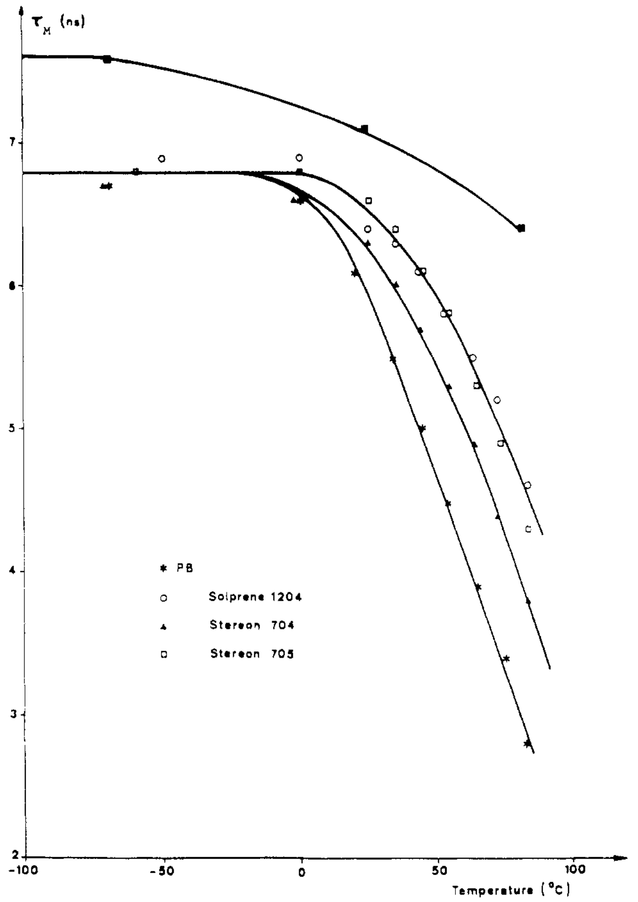

Figure 2. Temperature evolution of the monomer lifetime of diphant in polybutadiene and styrene–butadiene copolymers and of the model compound (■) in polybutadiene.

in the steady-state results. In such conditions, eq D and E gives $\beta_1 = Y = 1/\tau_D$. As β_2 is always greater than β_1,[12] it follows that τ_D is represented by the decay constant at long time in $I_D(t)$.

The excited model compound lifetime τ'_M was also measured under the same experimental conditions. The values obtained for τ_M, τ'_M, and τ_D in PB are displayed vs. temperature in Figures 2 and 4, respectively. Below −20 °C, τ_M is observed to be a constant, which means that the rotational motion of the probe is completely prevented ($k_{DM} = 0$). At these temperatures, τ'_M remains slightly longer than the monomer lifetime of diphant τ_M. A similar result was noted by De Schryver et al.[15] in solution and explained as due to an intramolecular interaction between the chromophores of diphant in the ground state. This implies that the rate constants k_{FM} and k_{IM} are not exactly identical in the mono- and bichromophoric molecules. At higher temperatures, τ_M decreases faster than τ'_M; this is ascribed to the increasing efficiency of the excimer sampling mechanism. These results corroborate those from the steady-state measurements. τ'_M was only measured in PB and PI and assumed to have the same values in their respective copolymers.

According to several authors[16] the existence of an isoemissive point over a range of temperature indicates that the radiative rate constants k_{FM} and k_{FD} are independent of temperature and that the nonradiative decay constants are negligible with regard to the former: $k_{IM} \ll k_{FM}$ and $k_{ID} \ll k_{FD}$. Furthermore, the increase of I_D implies that excimer dissociation is not competing with excimer fluorescence in this range. Thus, τ_D should be a constant, and the I_D/I_M ratio should provide an approximate measure of the efficiency of the rotational process and hence of the mobility of the probe in the host matrix. It is obvious from Figure 4 that τ_D is temperature-dependent despite the existence of the isoemissive point. Thus, the I_D/I_M ratio is not directly proportional to k_{DM}. In a previous paper,[7] in which only photostationary-state experiments were performed, we missed the temperature dependence of τ_D and were therefore led to incorrect conclusions about the matrix mobility. For these reasons, we only consider transient measurements in the present paper.

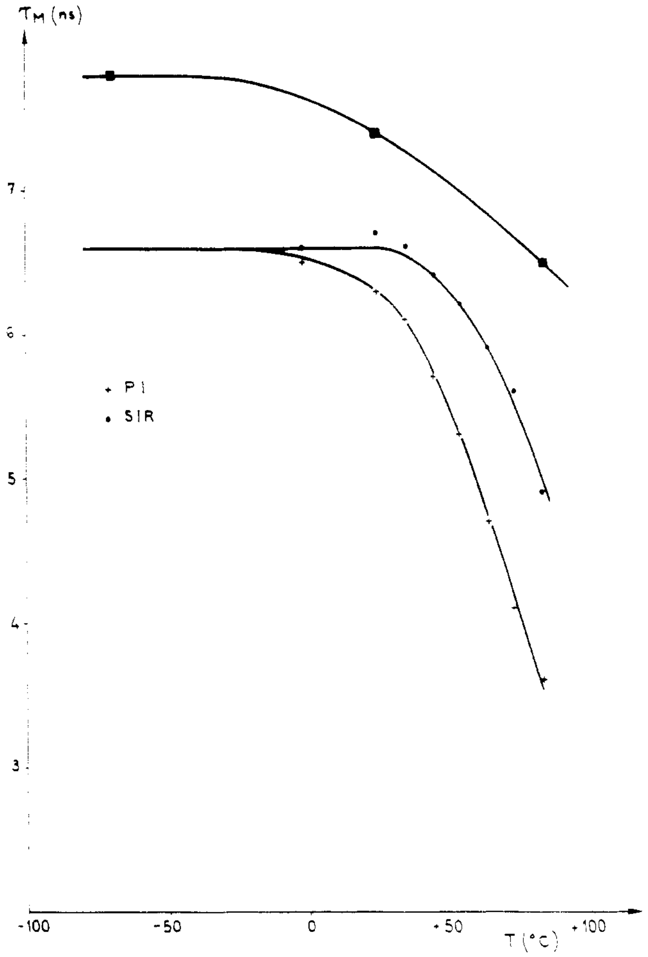

Figure 3. Temperature evolution of the monomer lifetime of diphant in polyisoprene and styrene–butadiene copolymer and of the model compound (■) in polyisoprene.

The monomer lifetime allows direct access to the rate constant for intramolecular excimer formation k_{DM}. At very low temperatures, molecular motions are completely hindered, and $k_{DM} = 0$. If we assume a similar temperature dependence for the excited monomer lifetime of diphant and its model compound, apart from the contribution of the k_{DM} factor, we can easily deduce the absolute values of k_{DM}. The temperature dependence of the monomer lifetime of diphant in PB and in its copolymers is reported in Figure 2. The results reveal that at a same temperature the monomer lifetime τ_M and thus the rate constant of excimer formation, which reflects the probe mobility, is affected by the host matrix. On the other hand, τ_M converges toward the common value 6.8 ns for all matrices at low temperatures. This is an indication of the invariability of the $k_{FM} + k_{IM}$ term in the host polymer, at least in this temperature interval. As seen in Figure 3, similar conclusions could be drawn from the study carried out in PI and its copolymer with styrene. Contrary to τ_M, the excimer lifetime τ_D plotted vs. temperature in Figure 4 exhibits little scattering within the range of polymers studied. De Schryver obtained for τ_D of diphant in methylcyclo-

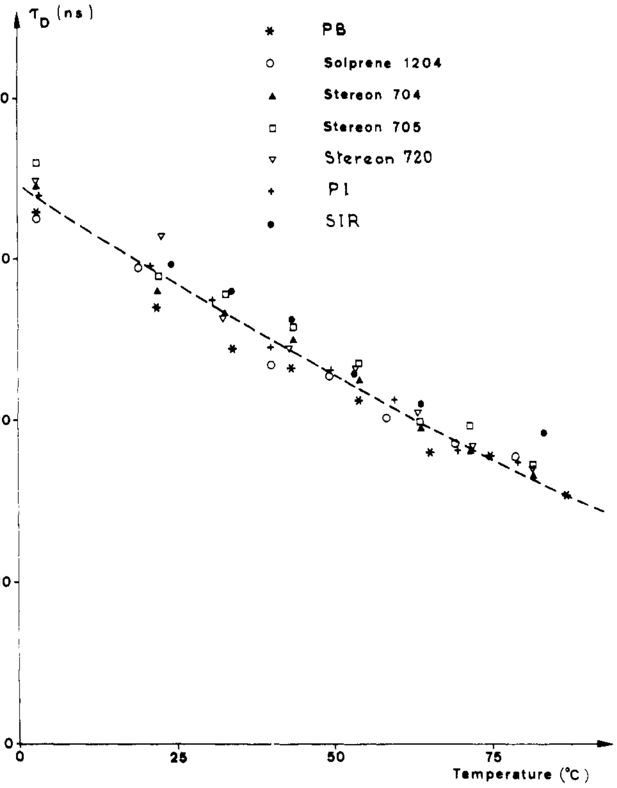

Figure 4. Temperature evolution of the excimer lifetime of diphant in polybutadiene, polyisoprene, and their respective copolymers with styrene.

hexane values close to those in all our films. τ_D is indeed an intrinsic characteristic of the fluorescence probe.

B. Discussion. Our purpose is to use the excimer fluorescence technique to probe molecular motions in bulk polymers and to identify if the rotational sampling process of diphant is controlled by segmental motions involved in the glass–rubber relaxation phenomena of the polymer matrix. From the free-volume theory of the glass–rubber relaxation, the temperature dependence of the correlation time is described by the WLF equation:

$$\log a_T = \log \frac{\tau_C(T)}{\tau_C(T_g)} = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)}$$

where a_T is the shift factor, $\tau_C(T)$ the correlation time at a temperature T, and $\tau_C(T_g)$ the correlation time at the glass transition temperature chosen as reference in rubbery polymers. The $\tau_C(T_g)$ factor is mainly determined by the experimental frequency. The set of parameters C_1 and C_2 depends upon the chemical structure of the medium. For each family of polymers, the selected values are those compiled by Ferry[9] for elastomers of microstructure similar to that of the samples investigated in the present study: for PB, $C_1 = 11.2$ and $C_2 = 60.5$; for PI, $C_1 = 16.8$ and $C_2 = 53.6$.

The correlation time τ_C of the probe motion involved in intramolecular excimer formation is defined as the reciprocal of the rate constant k_{DM} of this process. The evolution of the absolute values of $\log \tau_C = -\log k_{DM}$ in PB and PI is plotted vs. $T - T_g$ in Figure 5. At temperatures exceeding T_g + 100 °C, the experimental data agree with the temperature dependence of the WLF equation with the appropriate set of parameters. At a given $T - T_g$, the mobility in PI is higher than in PB; this reveals the important effect of the chemical structure of the matrix. The vertical translation factors correspond to $\log \tau_C(T_g)$.

Figure 6 represents the absolute correlation times calculated for PB and its copolymers. The results relating to the raw sample of PB coincide with those for the cross-linked film. The experimental data show little scattering in the fit provided by the related WLF equation for temperatures higher than T_g + 100 °C. At lower temperatures, the divergence from this curve may be attributed to a loss of accuracy of the τ_C calculation. A more refined analysis reveals that, if the correlation times precisely superimpose on the WLF curve for PB and Stereon 704 and 705, their values are smaller in Solprene 1204 and higher in Stereon 720, which is the block copolymer. This change in mobility can be interpreted by an additional effect of microstructure upon the $\tau_C(T_g)$ vertical shift factor. Indeed, Solprene 1204 and Stereon 720 differ from PB and its other copolymers by their microstructure (see Table I). Alteration of the elastomer phase in Solprene 1204, consisting of an increase of the vinyl conformations to the detriment of the 1,4 cis or trans conformations would induce a diminution of $\tau_C(T_g)$. On the contrary, the styrene content in Stereon 720, distributed in microphases, would stiffen the whole chain in comparison to PB and bring about an increase of $\tau_C(T_g)$. In other words, it appears that the vertical shift factor $\tau_C(T_g)$ relative to the WLF equation is slightly different in Solprene 1204 and Stereon 720 from its value in PB and Stereon 704 and 705. A further shift of the experimental correlation times concerning these matrices displays clearly on Figure 7 that the temperature dependence in PB and its copolymers is fitted by the WLF equation with the set of parameters suited to PB.

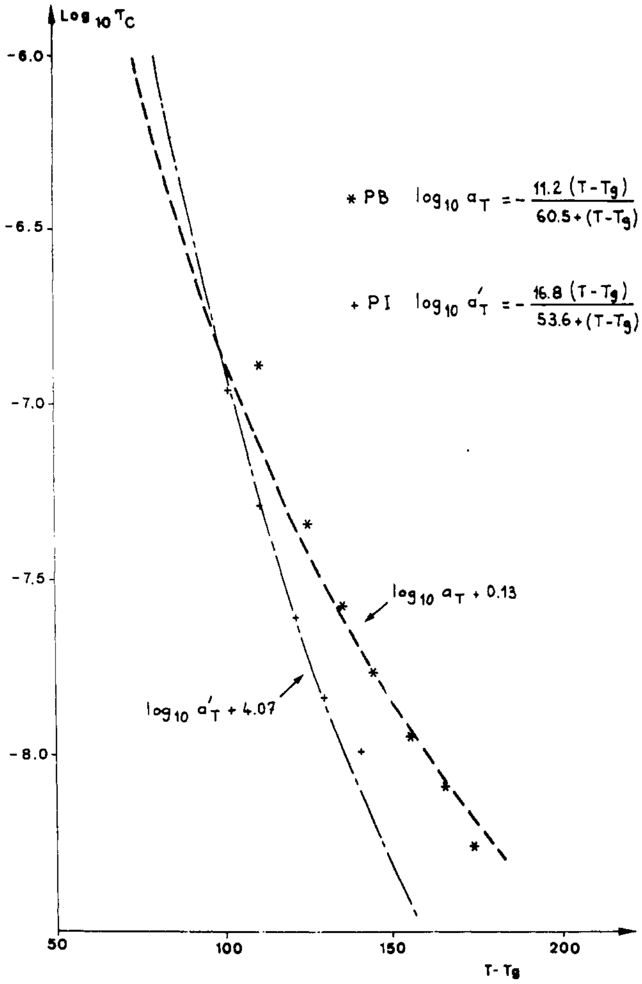

Figure 5. Logarithmic plot of the correlation time vs. $T - T_g$ for diphant dispersed in polybutadiene and polyisoprene.

The absolute values of τ_C calculated in SIR are located on the curve shown in Figure 5 for PI. No microstructure effect on $\tau_C(T_g)$ is observed.

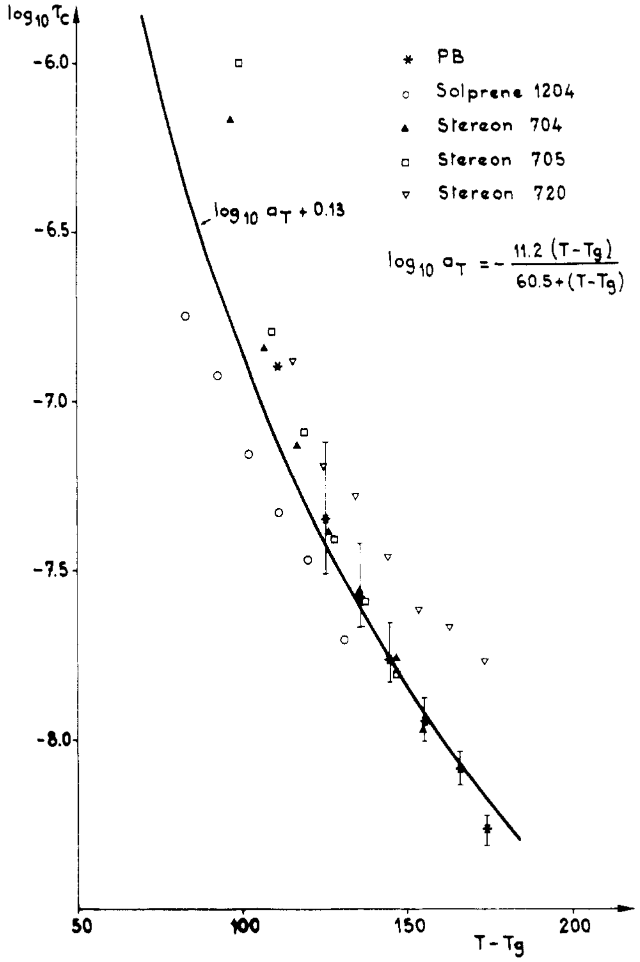

Figure 6. Logarithmic plot of the correlation time vs. $T - T_g$ for diphant dispersed in polybutadiene and styrene–butadiene copolymers.

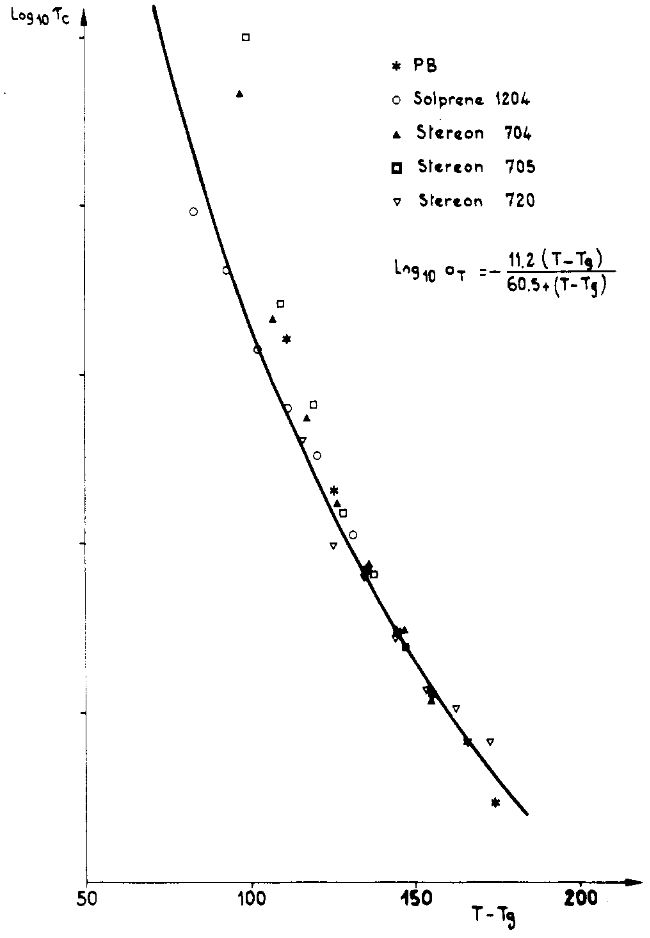

Figure 7. Master curve of the correlation time vs. $T - T_g$ for diphant dispersed in polybutadiene and styrene–butadiene copolymers.

In a medium consisting of small molecular units, the rate constant k_{DM} for intramolecular excimer formation obeys an Arrhenius temperature dependence. In the polymers studied, we have shown that the temperature dependence of the correlation time τ ($\sim k_{DM}^{-1}$) agrees with that obtained from WLF equations with the C_1 and C_2 parameters determined by mechanical measurements at low frequency. Actually, the glass transition is not an activated process. Nevertheless, in a narrow range of high temperatures, i.e., far from T_g, k_{DM} may be approximated by an Arrhenius law. Thus, the apparent activation energies for intramolecular excimer formation E_{DM} can be evaluated from Stevens–Ban plots between 40 and 80 °C. They are about 9 kcal mol^{-1} for PB and 14 kcal mol^{-1} for PI and rise to 10, 11, 14, and 6 kcal mol^{-1} in Solprene 1204 and Stereon 704, 705, and 720. These results estimate the ease of segmental motions of the host polymer in giving rise to the free volume needed by the fluorescence probe to achieve its conformational transition. E_{DM} is substantially higher in our films than in methylcyclohexane, where it was found to be 3.5 kcal mol^{-1} by De Schryver et al.[15] Thus, the results obtained in bulk polymers cannot be ascribed to the sheer rotational process but more likely reflect the molecular motions of the chains surrounding the probe. The apparent activation energy arising in the block copolymer (6 kcal mol^{-1}) is much smaller than in all other samples. In the range of temperature of our study, the styrene microphases are still in the glassy state. Consequently, the only contribution to intramolecular excimer formation is that of the probe molecules located in the elastomer PB phase. The monomer fluorescence intensity I_M is assigned to all the diphant molecules dispersed in both phases, but the excimer fluorescence intensity I_D results exclusively from those able to undergo a conformational change. This implies for I_D/I_M, and thus for k_{DM}, a slower increase with temperature than in neat PB.

The rotational mobility of the diphant probe has been shown to reflect the glass transition relaxation phenomena of the polymer host matrix, in agreement with the appropriate WLF equation above T_g + 100 °C. The correlation times of the motions involved depend mainly on the chemical structure of the medium, through the set of parameters C_1 and C_2. In addition, a slight effect of the microstructure on the $\tau_C(T_g)$ factor can be detected.

PDMS and PDMPS

A. Results. The study performed in these elastomers is similar to that described for polydienes and their copolymers with styrene. The emission spectra exhibit an isoemissive point in the range −30 to 0 °C in PDMS and −50 to +30 °C in PDMPS. At higher temperatures, the excimer fluorescence intensity is observed to decrease, which denotes the efficiency of the excimer dissociation process.

The time-resolved decay $I_M(t)$ is a monoexponential within the region of the isoemissive point. Figure 8 represents the temperature dependence of the monomer lifetime τ_M of diphant and of the model compound τ'_M, respectively, in PDMS and PDMPS. As in the films, τ_M proves to be a constant in PDMPS at low temperatures (under −50 °C). This domain could not be reached in PDMS because of its crystallization. Here again, this behavior is assigned to a complete hindrance of molecular

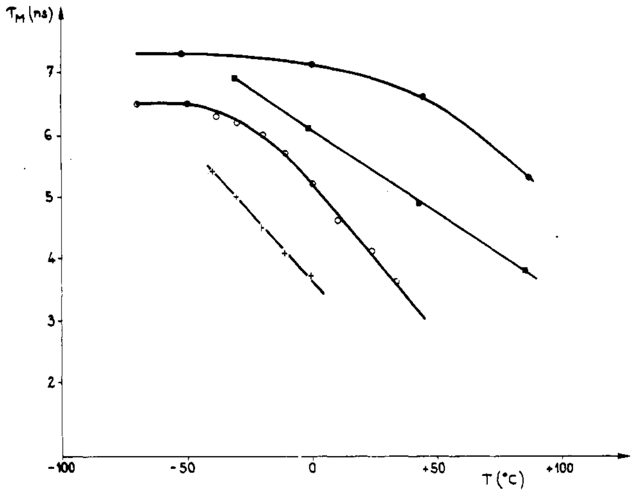

Figure 8. Temperature evolution of the monomer lifetime of diphant and of its model compound in PDMS (+, ■) and PDMPS (○, ●).

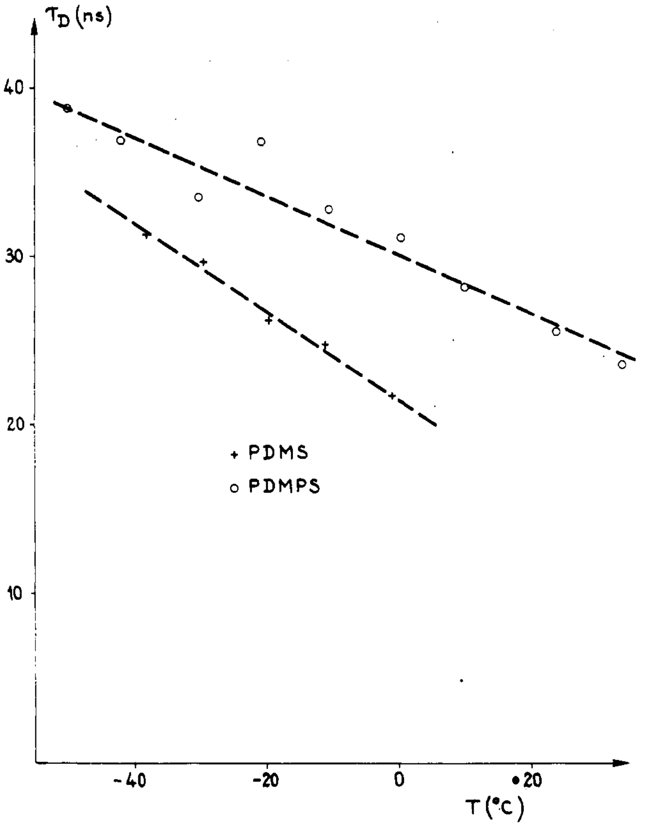

Figure 9. Temperature evolution of the excimer lifetime of diphant in PDMS and PDMPS.

motions. The remaining difference between τ_M and τ'_M at these temperatures can be pointed out and explained as already mentioned.

The values of the excimer fluorescence lifetime τ_D are displayed in Figure 9. At the same temperature, the τ_D value in PDMPS exceeds that in PDMS. This can be ascribed to a larger oxygen solubility in PDMS. This explanation does not disagree with our previous interpretation[8] in a family of PDMS, according to which oxygen quenching is equally efficient whatever the average molecular weight of the matrix. Actually, the difference displayed in the present work more likely arises from the chemical change in the polymer, with an increase of the diphenylsiloxyl content. Also, the temperature dependence of τ_D in these matrices should also be emphasized.

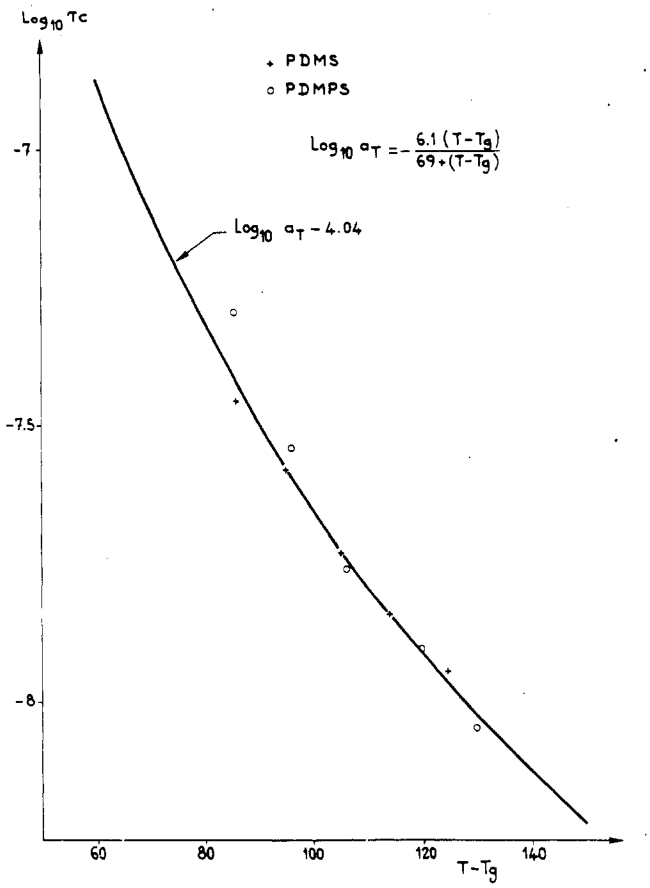

Figure 10. Logarithmic plot of the correlation time vs. $T - T_g$ for diphant dispersed in PDMS and PDMPS.

B. Discussion. The correlation time τ_C of the motion involved is calculated following the same procedure as in the films. Since τ_M and τ'_M could not be measured in PDMS at temperatures where the rotational process of diphant is hindered, we used those measured in PDMPS. In fact, the values obtained in the polydienes and their copolymers (6.5–7.0 ns for τ_M and 7.4–7.8 ns for τ'_M) and in PDMPS (6.5 ns for τ_M, and 7.3 ns for τ'_M) cause us to assume that they do not depend on these matrices. The set of parameters C_1 and C_2 of the WLF equation to be considered in the case of poly(dimethylsiloxanes) is provided by Ferry[9]: $C_1 = 6.1$ and $C_2 = 69.0$. The evolution of the absolute values of the experimental correlation times in both PDMS and PDMPS are accurately fitted by the related WLF equation, as seen in Figure 10.

The activation energies of the rotational process have been deduced between −40 and 0 °C in PDMS and −10 and +30 °C in PDMPS: the values are 3.8 and 6.2 kcal mol^{-1}, respectively. These rather low values give evidence of the considerable flexibility of the poly(dimethylsiloxane) chains. In the PDMPS copolymer, the mobility is slightly reduced by the presence of the phenyl groups distributed along the chains.

In this part of the work, we have confirmed in a completely different series of polymers that the dynamic behavior of the diphant probe is controlled by the mobility of the host medium, described by the WLF equation with the appropriate set of parameters.

Conclusion

Through this study, we have shown that the excimer fluorescence technique of a probe simply dispersed in a macromolecular medium provides detailed information about the molecular motions of the polymer. The rotational process of conformational change of diphant dispersed in a wide range of host matrices appears to be controlled by the mobility of the medium.

It is observed that the correlation times of the motions involved in the excimer sampling mechanism, and accessible only from transient measurements also follow the temperature dependence of the WLF equation using for the latter a set of parameters related to the nature and morphology of the polymer. Thus, the rotational process of the probe reflects the segmental motions which become available at the glass transition.

The analysis of the emission behavior of intramolecular excimer-forming probes of various sizes, dispersed in polymer host matrices, may afford a unique way to estimate the size of the region over which cooperative motion within the polymer must occur. Indeed, conformational energy calculations performed on the probes in order to determine the most stable conformations may allow us to estimate the volume swept out during the conformational change required for excimer formation. With the use of probe molecules of different size such as diphant, 2,4-diphenylpentane, 2,4-di(*N*-carbazolyl)pentane, etc., it should be possible to determine the lower limit of the volume from which the excimer sampling is controlled by segmental motions of the polymer host matrix.

Further investigations are in progress with other probes and other polymers.

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Registry No. Diphant, 77681-23-3; PI, 9003-31-0; PB, 9003-17-2; SBR, 9003-55-8; SIR, 25038-32-8.

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Electronic Excitation Transport as a Probe of Chain Flexibility

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ABSTRACT: The long-time divergence present in the three-body self-consistent approximation to the Green function for electronic excitation transport on ideal polymer chains (*Macromolecules* **1983**, *16*, 1456) is removed by constructing a Padé approximant for the self-energy. The resulting self-consistent approximation to the Green function is well-behaved at all times and concentrations and is shown to be in good agreement with approximants constructed from a density expansion. The approximation can be used to obtain quantitative measurements of statistical chain flexibility from fluorescence depolarization and trap fluorescence experiments on polymer chains containing a small concentration of randomly placed chromophores.

I. Introduction

In a recent paper[1] (I) we presented a theory to describe the transport of electronic excitations among chromophores attached to an isolated polymer chain. The chromophores were assumed to be randomly distributed along the chain contour and in low concentration. The theory allows fluorescence depolarization experiments on chains in rigid matrices to provide a measurement of statistical chain flexibility (i.e., a measurement of Flory's characteristic ratio, C_∞). In a subsequent paper[2] (II) the theory was extended to include both traps and intermolecular excitation transport. As a result, time-dependent and photostationary trapping experiments can also be used to probe chain flexibility, and experiments can be interpreted for any density of chains. The experimental observables in both trapping and depolarization experiments are related to a portion of the Green function for excitation transport, $G(\mathbf{r},t)$, the probability that an excitation has moved a displacement $\mathbf{r}$ in time t.

In I we investigated several types of approximations for the Green function. One of these was the class of self-consistent (SC) approximations used by Gochanour, Andersen, and Fayer[3] (GAF) for excitation transport among randomly distributed points. We extended the GAF formalism to the problem of Förster transfer on an isolated, ideal polymer chain. The two-body SC approximation was found to be well-behaved, but the next member of the hierarchy, the three-body SC approximation, was found

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