

Investigation of the mobility of polybutadienes: 1. Excimer fluorescence technique

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Intramolecular excimer formation of meso-2,4-di(*N*-carbazolyl)pentane dissolved in polybutadienes of molecular weight 500 and 1000 has been investigated. The probe dynamics, which follow the WLF equation, are not similar in the two matrices. The effect cannot be ascribed to the difference between the glass transition temperatures of the two polymers but to a variation of their microstructures.

(Keywords: polybutadienes; excimer; probe dynamics)

INTRODUCTION

This series of papers is part of a work in which fluorescence probe methods are used to investigate relaxation processes of macromolecular chains in bulk polymers. In these techniques, the emission properties of a probe embedded in a polymer above its T_g are analysed in order to achieve some understanding of the dynamics of the elastomeric matrix.

In this paper, we use a fluorescence technique based on the excimer formation of an intramolecular excimer-forming probe: the meso-2,4-di(*N*-carbazolyl)pentane (meso-DNCzPe). This bichromophoric molecule, where the two aromatic groups are separated by a three-atom linkage, gives rise to an intramolecular excimer. This intramolecular excimer formation involves rotational motion about the bonds of the linkage to achieve a conformation in which the two chromophores overlap in a sandwich-like arrangement. Because the excimer state arises from a conformational transition, the probe motion must be related to the mobility of the surrounding environment.

This paper reports an investigation of the mobility of two polybutadienes of low molecular weight 500 (PB 500) and 1000 (PB 1000) through the emission behaviour of meso-DNCzPe.

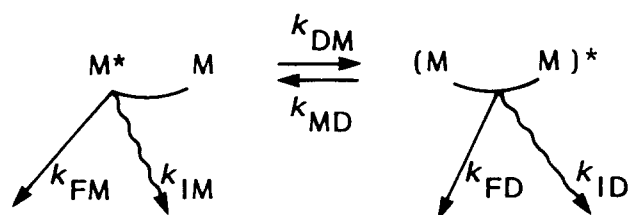
EXPERIMENTAL

Technique

Analysis of the experimental data is performed

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according to the conventional kinetic scheme¹:



where k_{DM} and k_{MD} are the rate constants for intramolecular excimer formation and dissociation respectively, 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 non-radiative decay from the monomer and the excimer. The most important parameter to characterize the efficiency of the excimer sampling mechanism and thus the mobility of the probe in the host matrix is the rate constant for intramolecular excimer formation k_{DM} determined from fluorescence lifetime measurements. k_{DM} is given by the expression:

$$(\tau_M)^{-1} - (\tau_0)^{-1}$$

where $\tau_M = 1/(k_{FM} + k_{IM} + k_{DM})$ is the excited monomer lifetime and $\tau_0 = 1/(k_{FM} + k_{IM})$ is the monomer decay (radiative plus non-radiative) in the absence of excimer formation. The latter quantity is determined by measuring the fluorescence decay time of a model compound containing only one chromophore. In the case of meso-DNCzPe, the monomeric model compound is the *N*-isopropylcarbazole (NIPCz). The rotational

motion involved in intramolecular excimer formation is characterized by a correlation time τ_c defined as the reciprocal of the rate constant of excimer formation k_{DM} .

Apparatus

The fluorescence spectra were recorded on a Fica Model 55 MK II spectrofluorimeter equipped with a 450 xenon lamp and a R 212 photomultiplier tube. Emission spectra were automatically corrected for instrumental response. The excitation wavelength was 320 nm. Fluorescence decays were performed on a single-photon-counting fluorimeter described previously². Sample fluorescence was produced by the strong 337 nm emission line of the nitrogen discharge. The monomer emission was analysed through an MTO A 2190 filter ($\lambda_{trans,max.} = 354$ nm; trans. max. = 22%; FWHM = 20 nm). The optical density of the probe was less than 0.1 at the excitation wavelength in order to avoid reabsorption effects.

Samples

The intramolecular excimer-forming probe meso-2,4-di(*N*-carbazolyl)pentane (meso-DNCzPe) was chosen on account of its high excimer sampling rate and of its good excimer stability^{3,4}. The optical density of the probe in these matrices was less than 0.1 at the excitation wavelength in order to avoid reabsorption effects.

The polybutadienes PB 500 and PB 1000 were purchased from Pressure Chemical and were used without further purification. Their glass transition temperatures T_g , reported in Table 1, were obtained in a Dupont DSC apparatus with a heating rate of 5 K min⁻¹ and a cyclohexane calibration.

I.r. and n.m.r. spectroscopic techniques were used for the determination of the microstructure of the two polybutadienes consisting of sequences of *cis*-1,4 (*c*), *trans*-1,4 (*t*) and vinyl-1,2 (*v*) units.

In the i.r. spectrum, the amounts of *cis*-1,4, *trans*-1,4 and 1,2-additions were determined according to Binder's method⁵. The bands used for the analyses are located at 967, 911 and 680 cm⁻¹ and are essentially ascribed to the C-H out-of-plane bending mode of the *trans*, vinyl and *cis* units respectively. As can be seen in Figure 1, PB 500 exhibits a higher content of vinyl sequences.

The determination of the unit chain structure of the two polymers was also carried out by ¹³C n.m.r. spectroscopy using the assignments of the olefinic resonances reported by Van der Velden *et al.*⁶. The olefinic region is subdivided into two parts: the resonances at approximately 114 and 143 ppm assigned to the different vinyl 1,2 carbon atoms and the complex resonance pattern between 127 and 133 ppm due to the compositional splittings of the two olefinic carbons in

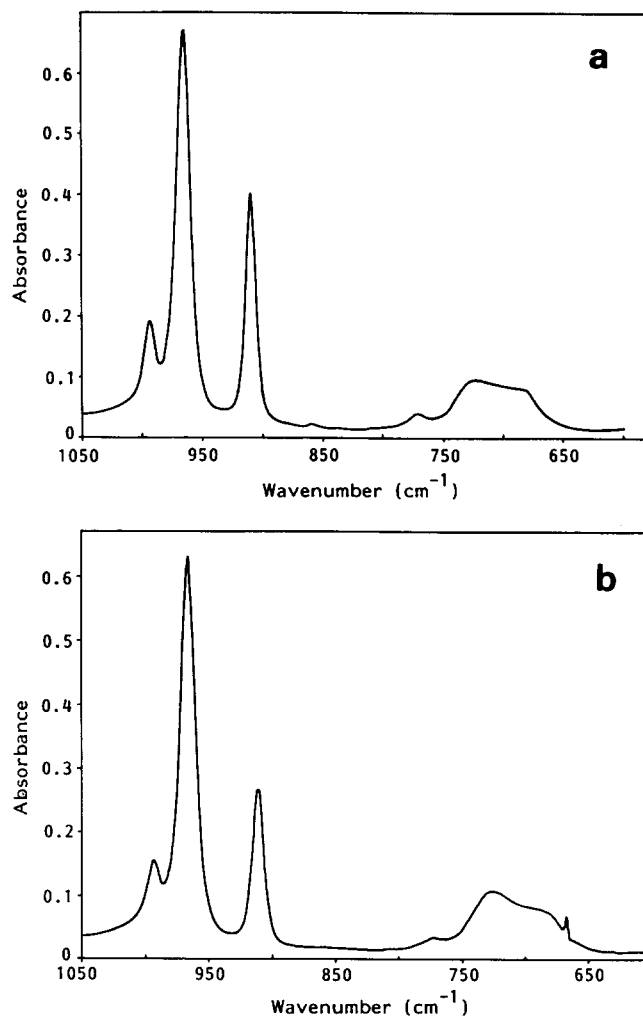


Figure 1 I.r. spectrum of the out-of-plane C-H vibrations for: (a) PB 500, (b) PB 1000

central *c* or *t* units. As is shown in Figure 2, this latter part of the spectra differs in the two polymers.

The results deduced from the ¹³C n.m.r. spectra are listed in Table 1; they are in reasonable agreement with those obtained by i.r. spectroscopy.

RESULTS

As a typical example, the temperature dependence of the excimer-monomer emission spectra of meso-DNCzPe in PB 1000 is given in Figure 3. Each spectrum exhibits, in addition to the locally excited state emission, a structureless band with a maximum around 420 nm ascribed to the fluorescence of the intramolecular excimer. The existence of an isoemissive point over the range of temperatures presented in Figure 3 shows that the non-radiative processes are not competing with fluorescence.

The temperature dependence of the monomer lifetime of the probe in each matrix as well as that of the model compound, the *N*-isopropylcarbazole, is given in Figure 4. The data show that, at a same temperature, the monomer lifetime and consequently the rate of conformational change of the probe is affected by the host matrix. The onset of mobility detected at the beginning of the decrease of the monomer lifetime occurs at about 248 K in PB 1000 and around 233 K in PB 500. In PB

Table 1 Characteristics of the polybutadienes

| | T_g (K) | Microstructure | | | | | |
|---------|--------------|----------------|--------|----------------|--------|---------|--------|
| | | % <i>cis</i> | | % <i>trans</i> | | % vinyl | |
| | | I.r. | N.m.r. | I.r. | N.m.r. | I.r. | N.m.r. |
| PB 500 | 157 | 18 | 21 | 56 | 57 | 26 | 22 |
| PB 1000 | 167 | 22 | 29 | 60 | 59 | 18 | 12 |

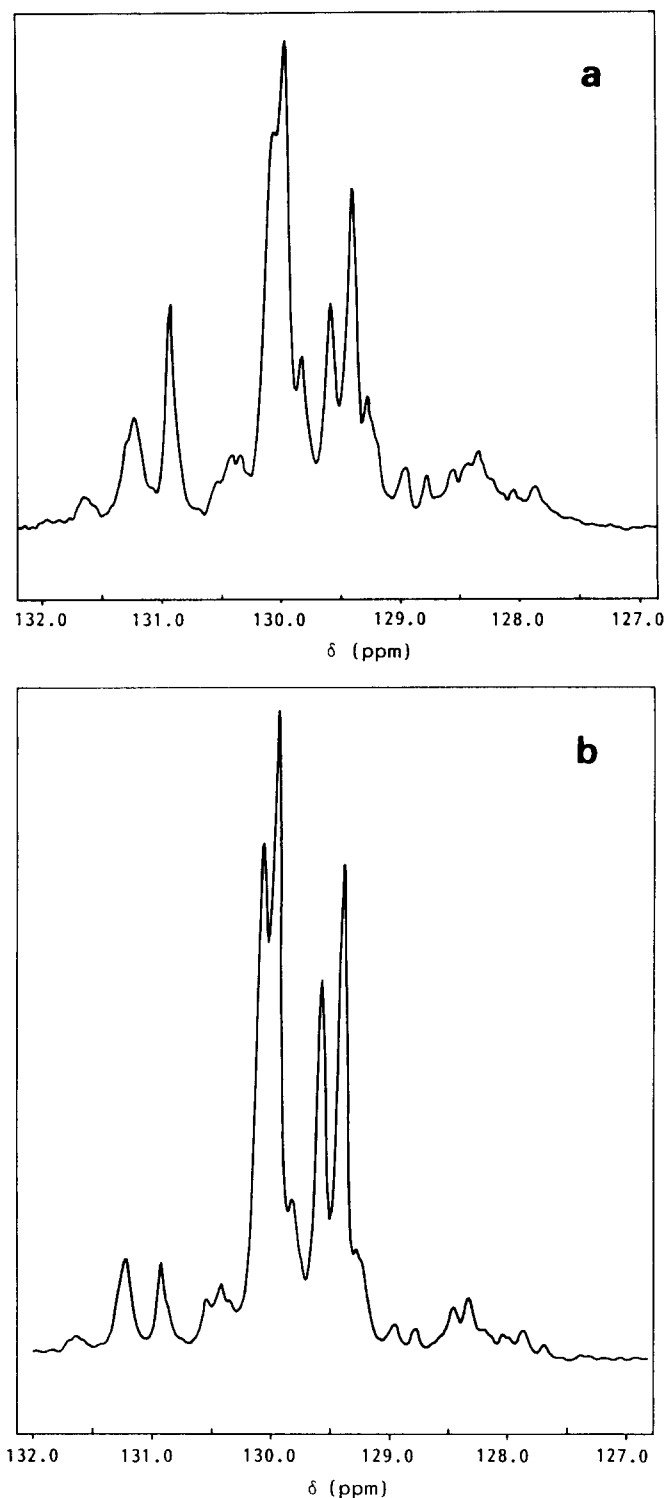


Figure 2 Expanded ^{13}C n.m.r. spectra (62.90 MHz) of the 127–132 ppm region for: (a) PB 500, (b) PB 1000

1000, the monomer decay deviates from monoexponentiality at 298 K on account of excimer dissociation; the relative amplitude of the second exponential is small (about 3%). In the case of PB 500, the dissociation process, which appears at 273 K, is more important since the second component of the monomer decay represents, at this temperature, 10% of the total signal. The difference between the two temperatures of dissociation can be understood in terms of polymer mobility. The higher flexibility of PB 500 chains tends to destabilize the excimer state at a temperature lower than in PB 1000.

Figure 5 displays a logarithmic plot of the correlation time of the intramolecular rotational motion of meso-DNCzPe against the reciprocal of temperature. The non-Arrhenian behaviour in the two matrices suggests that the probe can move only when the surrounding molecules

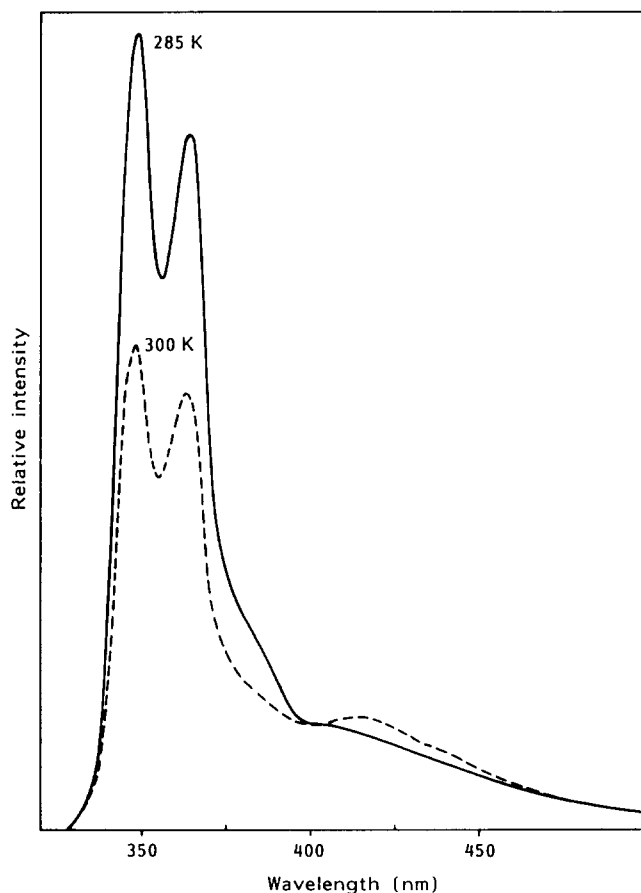


Figure 3 Temperature dependence of the emission spectrum of meso-DNCzPe in polybutadiene (PB 1000)

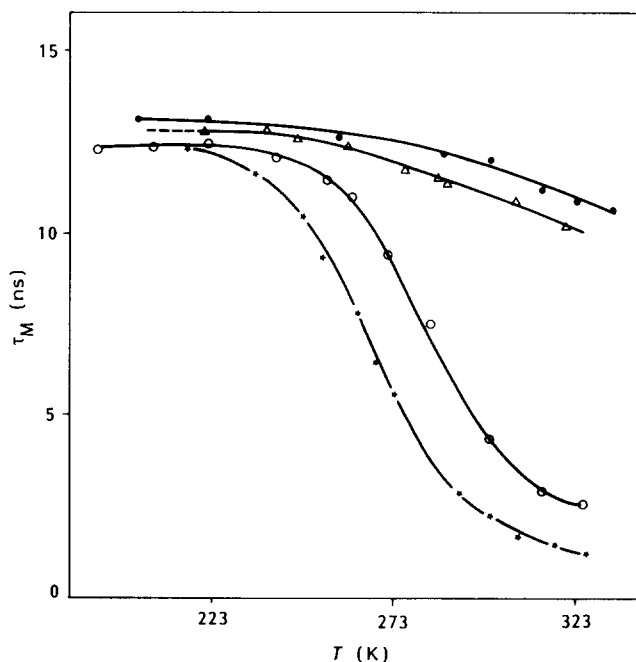


Figure 4 Temperature evolution of the monomer lifetime of meso-DNCzPe in PB 500 (★) and in PB 1000 (○) and that of the fluorescence decay time of the model compound (NIPCz) in PB 500 (△) and in PB 1000 (●)

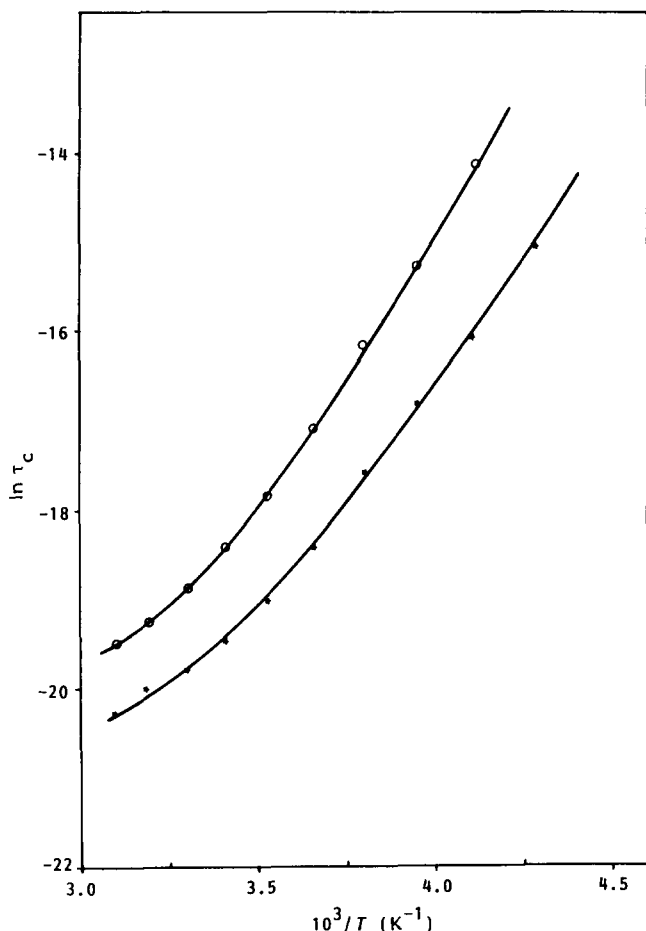


Figure 5 Temperature dependence of the correlation time of meso-DNCzPe dissolved in PB 500 (★) and in PB 1000 (○)

undergo the type of molecular motions involved in the glass transition. At a given temperature, the correlation time τ_c is shorter in PB 500 than in PB 1000.

In order to eliminate the effect of T_g shift on the mobility, we have plotted $\log \tau_c$ as a function of $(T - T_g)$ in Figure 6. The two curves do not superimpose, especially at low temperatures.

DISCUSSION

The non-Arrhenian character of the probe dynamics in the two polybutadienes suggests the use of a WLF approach⁷. According to the free-volume theory, the mobility of polymer segments should follow the WLF equation:

$$\log\left(\frac{\tau_c(T)}{\tau_c(T_g)}\right) = \frac{-C_1^g(T - T_g)}{C_2^g + (T - T_g)} \quad (1)$$

which describes the temperature dependence of the ratio of the correlation time τ_c at temperature T to its value at the glass transition temperature T_g chosen as reference. C_1^g and C_2^g depend on the chemical structure of the polymer: $C_1^g \approx 1/2.303f_g$, $C_2^g = f_g/\alpha_f$ and $C_1^g C_2^g \approx 1/2.303\alpha_f$, where f_g is the fractional free volume at T_g and α_f is the thermal expansion coefficient of the free volume.

An equation similar to (1) would hold for any arbitrary reference temperature T_0 :

$$\log\left(\frac{\tau_c(T)}{\tau_c(T_0)}\right) = \frac{-C_1^0(T - T_0)}{C_2^0 + (T - T_0)} \quad (2)$$

The WLF equations (1) and (2) depend on the chosen reference temperature and the following correlations can be written:

$$C_1^0 C_2^0 = C_1^g C_2^g$$

$$T_0 - C_2^0 = T_g - C_2^g = T_\infty$$

T_∞ , often called the 'Vogel' temperature, is the temperature at which the free volume in the system is zero. It represents a point of infinite viscosity and consequently of infinite correlation time.

In previous papers⁸⁻¹⁰, we have emphasized the advantages of rewriting the WLF equation as:

$$\log \tau_c = \log \tau_c(T_g) - C_1^g + C_1^g C_2^g \frac{1}{(T - T_\infty)} \quad (3)$$

T_∞ depends on the chemical structure of the polymer. Within a given family of polymers, it cannot be merely calculated only by considering the 'trivial' effect of the T_g shift since the C_2 parameter varies with the microstructure of the polymer.

I.r. and n.m.r. spectroscopic techniques have shown that the two PB matrices exhibit different microstructures which differ from those of Ferry's samples. So, application of (3) requires the knowledge of the WLF constants. They can be determined graphically by

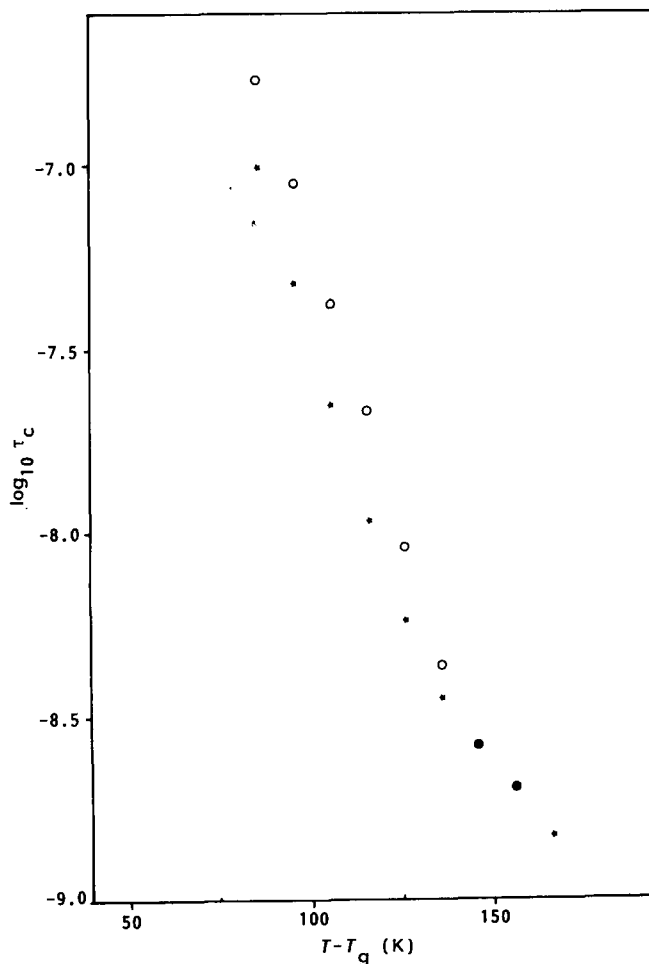


Figure 6 Logarithmic plot of the correlation time vs. $(T - T_g)$ for meso-DNCzPe dissolved in the two polybutadienes. The signs are the same as those used in Figure 5

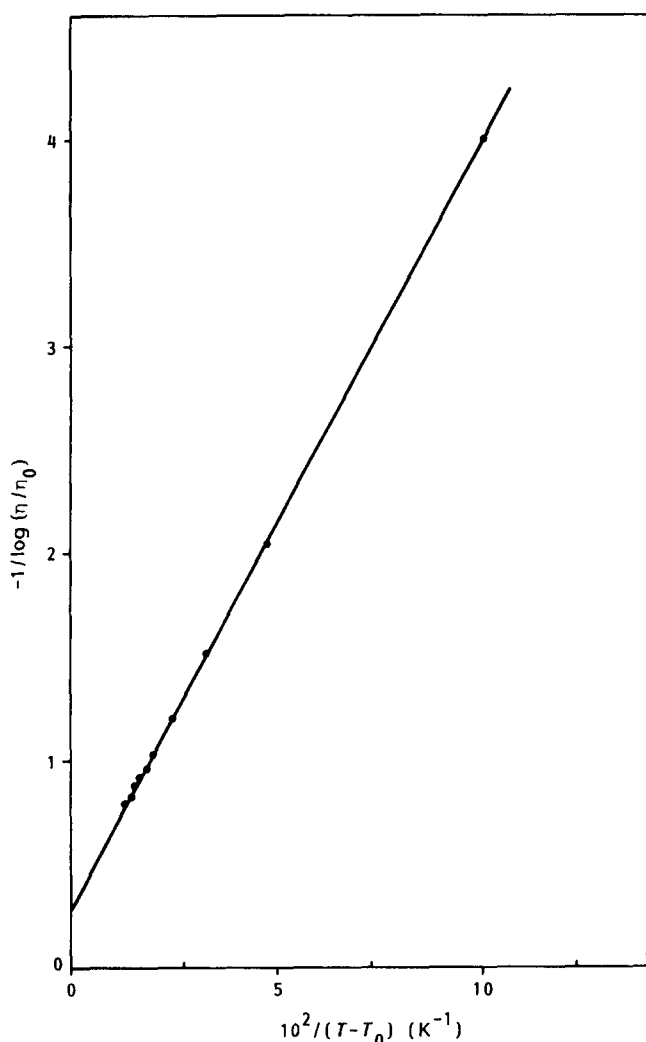


Figure 7 Determination for PB 500 of the C_1 - and C_2 -constants in the WLF equation by plotting $-1/\log(\eta/\eta_0)$ against $1/(T-T_0)$ according to equation (4)

rewriting the WLF equation (2) to a linear relationship:

$$-1/\log(\tau_c/\tau_0) = -1/\log(\eta/\eta_0) = 1/C_1^0 + C_2^0/C_1^0(T-T_0) \quad (4)$$

Therefore, a plot of $-1/\log(\tau/\tau_0)$ or $-1/\log(\eta/\eta_0)$ as a function of $1/(T-T_0)$ should be linear and should give access to the WLF coefficients.

The determinations of these coefficients have been made from viscosity measurements of each polymer between 253 and 333 K. For PB 500 (Figure 7), with $T_0 = 253$ K, we get:

$$C_1^0 = 3.5 \quad \text{and} \quad C_2^0 = 129.6 \text{ K} \quad C_1 C_2 \approx 453.6 \text{ K}$$

With the glass transition temperature T_g as a reference, these values become:

$$C_1^g = 13.3 \quad \text{and} \quad C_2^g = 34 \text{ K}$$

$$T_\infty = T_0 - C_2^0 = T_g - C_2^g \approx 123 \text{ K}$$

And for PB 1000, the WLF parameters at T_g are:

$$C_1^g = 13.1 \quad C_2^g = 41.8 \quad C_1 C_2 \approx 548 \text{ K} \quad \text{and} \quad T_\infty = 125 \text{ K}$$

These results are consistent with Ferry's data¹¹ on polybutadienes with different microstructures: an increase of the vinyl conformations leads to a decrease of the C_2 coefficient. Effectively, PB 500 exhibits a higher content of the vinyl conformations as revealed by i.r. and n.m.r. measurements.

In Figure 8 for meso-DNCzPe are reported the plots of $\log \tau_c$ against $1/(T-T_\infty)$ with the values of T_∞ found from viscosity measurements. The slopes of the curves which equal 482 and 619 respectively for PB 500 and PB 1000 are in good agreement with the $C_1 C_2$ products predicted from viscosity data. This proves that the intramolecular conformational change of the probe required for the excimer sampling process is controlled by the segmental motions of the polymer matrix involved in the glass transition phenomenon.

An interesting value is the original coordinate of equation (3):

$$\log \tau_0 = \log \tau_c(T_g) - C_1^g$$

This value, which is a characteristic of the matrix, can be considered as the prefactor of the Doolittle equation¹² expressed in terms of correlations times:

$$\tau(T) = \tau_0 \exp(B/f_T)$$

where B is an empirical constant of the order of unity. τ_0 has been calculated for the two polymers from (3) by using the $C_1 C_2$ products obtained from viscosity measurements more precise than the fluorescence ones. It is equal to 7.58×10^{-12} s for PB 500 and to 5.50×10^{-12} s for PB

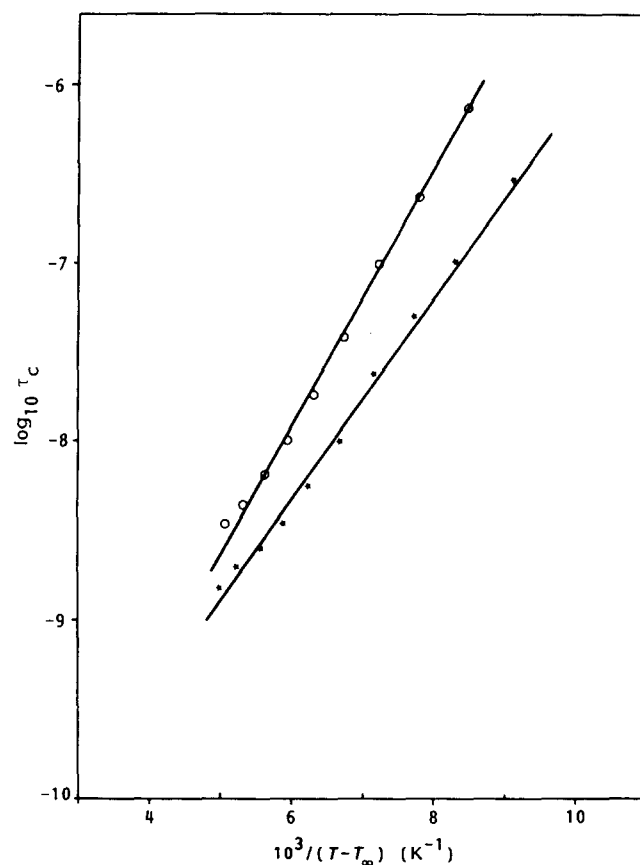


Figure 8 Logarithmic plot of the correlation time vs. $1/(T-T_\infty)$ for meso-DNCzPe in the two polybutadienes. The signs are the same as those used in Figure 5

1000. The lower value of τ_0 obtained in PB 1000 seems to be linked to a higher C_1C_2 product and consequently to a smaller thermal expansion coefficient α_f of the free volume.

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REFERENCES

- 1 Birks, J. B. 'Photophysics of Aromatic Molecules', Wiley, New York, 1970
- 2 Valeur, B. and Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* 1976, **14**, 11
- 3 De Schryver, F. C., Vandendriessche, J., Toppet, S., Demeyer, K. and Boens, N. *Macromolecules* 1982, **15**, 406
- 4 Vandendriessche, J., Palmans, P., Toppet, S., Boens, N., De Schryver, F. C. and Masuhara, H. *J. Am. Chem. Soc.* 1984, **106**, 8057
- 5 Binder, J. L. *Anal. Chem.* 1954, **26**, 1877
- 6 Van der Velden, G., Didden, C., Veermans, T. and Beulen, J. *Macromolecules* 1987, **20**, 1252
- 7 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
- 8 Pham-Van-Cang, C., Bokobza, L., Monnerie, L., Clarson, S. J., Semlyen, J. A., Vandendriessche, J. and De Schryver, F. C. *Polymer* 1987, **28**, 1561
- 9 Bokobza, L., Pham-Van-Cang, C., Giordano, C., Monnerie, L., Vandendriessche, J., De Schryver, F. C. and Kontos, E. G. *Polymer* 1987, **28**, 1876
- 10 Bokobza, L., Pham-Van-Cang, C., Giordano, C., Monnerie, L., Vandendriessche, J. and De Schryver, F. C. *Polymer* 1988, **29**, 251
- 11 Ferry, J. D. 'Viscoelastic Properties of Polymers', 2nd Edn., Wiley, New York, 1970
- 12 Doolittle, A. K. *J. Appl. Phys.* 1951, **22**, 1471