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Dielectric relaxation of ball-like labels in polyisoprene

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Abstract: Ball-like molecules with strong dipoles (labels) were mixed with synthetic polyisoprene (IR305) in low concentrations ($< 1\%$) and measured dielectrically in the frequency range 10^{-2}–10^7 Hz and the temperature range -70–0 °C (glass relaxation region). Calorimetric measurements showed that this type of label has a plasticizing effect on the polymeric matrix. The dielectric measurements showed that these ball-like molecules relax through cooperative rotations with the polymeric segments and at the same relaxation frequency. In addition, the label molecules showed a high-frequency local relaxation process. The relaxation strength ratio of the local process (X_{local}) to the total relaxation strength of the label was found to be dependent on the volume as well as on the shape of the label. A comparison between the relaxation behaviors of the ball- and rod-like molecules, having the same volume, showed that the length of the label is also an important parameter for the determination of the local contribution as well as of the cooperative relaxation mechanism of the label. The label relaxation process is discussed in relation to the molecular packing of the host polymer.

Key words: Dielectric measurements – label – polyisoprene – ball-like molecules – glass process – local process – voids

Introduction

In a previous work [1], we reported about the relaxation of rod-like molecules with strong dipole in the long axis (labels) in polyisoprene. The rod-like molecules used [1] varied in length between 1.5 and 3 nm. The dipole component in the long axis of these labels showed only one symmetrical relaxation process with a narrow distribution of relaxation times. This relaxation process was found to be slower than the glass process of the matrix by a factor ranging between 10 and 100 times depending on the length of the label (The longer the label, the greater the factor). In addition, these rod-like molecules showed no contribution of the longitudinal dipole moment in the vertical direction, implying that the fluctuation of the long axis of the label is too small to be detected. This finding was attributed to the parallelism of the polymeric chains within the bundle (2–4), that could create cylindrical restrictions, which can suppress the fluctuations of the long axis of labels and thus prevents any vertical contribution of the dipole.

As a continuation of the previous work, polar ball-like molecules with different volumes and lengths (< 1.5 nm) were mixed in polyisoprene and measured dielectrically to shed more light on the relaxation mechanism of guest molecules (labels) in relation to their size and shape, as well as to the molecular packing of the host polymer.

Experimental

Ball-like molecules with different volumes (Table 1) were dissolved in synthetic polyisoprene (Cariflex IR305, $M_w = 2 \cdot 10^6$ g/mol, $M_w/M_n = 8$, kindly provided by Bayer, Leverkusen) in very low concentrations ($< 1\%$ wt). The use of low concentrations (see Table 2) was required to obtain a height of the label relaxation process, which still does not dominate the glass relaxation process, in order to detect both relaxations. The dielectric properties of the mixtures were measured using the same equipment as described before (5) in the frequency and temperature ranges, 10^{-2}–10^{7} Hz and − 70–0 °C, respectively. The samples were prepared by weighing and mixing the required amounts of the solid label and polyisoprene, then pressed between two gold-plated copper electrodes with the diameters 40 and 80 mm to get a condenser with a capacity of about 100 pF. The sample homogeneity was achieved by heating the sample at 100 °C about 6 h before the measurements and monitoring the dielectric relaxation up to steady-state. The initial inhomogeneous distribution of the label molecules resulted in a broadening of the dielectric relaxation peak and a shift of it to higher frequencies (as is usually observed in plasticized polymers). After some time, the diffusion of the label molecules led to a homogeneous distribution and their final concentration was so small that the above-mentioned effects disappeared. The polyisoprene was earlier dried in vacuum at 100 °C for about 2 h to remove any adsorbed water residues. In the case of 9-cyanophenanthrene (Phenan-CN) the mixing process was carried out by using methylene chloride as solvent. From preliminary measurements, it was recognized that a noticeable part of the additive escaped from the sample during preparation as a consequence of the high vapor pressure of the additive. For this reason the final weight of the additive in the condenser was calculated from the experimental total relaxation strength (Micro-Brownian motion as well as local relaxation), calculated from the peaks in Figs. 2–6 using Kramers–Kronig-relation, for unrestricted cyano dipoles using Fröhlich–Onsager equation (Table 2). The dipole moment used for the calculation was 4.18 D. In the case of Phenan-CN and *p*-butoxycyanobenzene (*p*-BoB-CN), the dielectrically measured concentration was identical to the weighed one. The *p*-Tol-CN was obtained from Riedel-de Haen, while Phenan-CN and Adaman-CN were supplied by Aldrich. The *p*-butoxycyanobenzene (*p*-BoB-CN) was kindly prepared by Dr. Happ in the Section of Polymers, University of Ulm, as this substance was not commercially available. The calorimetric determination of the glass transition temperatures of the mixtures was carried out, using a Perkin–Elmer DSC-2, by Dr. Höhne and his coworkers in the section of Calorimetry, University of Ulm. The heating and cooling rate was 10 K/min. The second cooling curve was used for the determination of the glass transition temperature T_g [6]. The T_g of the pure matrix was found to be 205 K. The difference ΔT_g between the glass temperature of the mixtures and that of the pure matrix is listed in Table 2. The dielectric loss curves were analyzed by using a VAX 6440 from Digital Equipments and a minimization program NAG-E04KBF from the library of the Computer Center of the University of Ulm. The program NAG-E04KBF is a comprehensive quasi-Newton algorithm for a minimization of a function of several

Table 1. Some physical data of labels

Label	Abbreviation	Volume Å^3	Length Å
p-cyanotoluene	*p*-Tol-CN	200	9
9-cyanophenanthrene	Phenan-CN	301	9
1-adamantancarbonitrile	Adaman-CN	238	7
p-butoxycyanobenzene	*p*-BoB-CN	292	12

The volume was determined from the density values

Table 2. Results obtained for different labels in polyisoprene

Label	C %wt	ΔT_g	Temp °C	$\Delta\varepsilon \cdot 10^2$	$(1-\alpha)$	X_{local}
				main process		
p-Tol-CN	0.5	− 2.5	− 60.7	7.2	0.6	0.41
p-Tol-CN	1	− 4.5	− 55.5	16	0.61	0.47
Phenan-CN	0.6	− 1.5	− 50.6	8.2	0.55	0.17
Adaman-CN	0.6	− 1.5	− 55.6	10.8	0.55	0.08
p-BoB-CN	0.9	− 2	− 50.4	13.7	0.76	0

C % wt is the weight concentration of the label in polyisoprene
$(1-\alpha)$ is the Cole–Cole distribution parameter
X_{local} is the dielectric relaxation strength of the local process of the label, divided by the total relaxation strength of the label

variables, and was optimized for our analysis by W. von Soden in the department of Applied Physics, University of Ulm.

Results and discussion

The logarithm of the dielectric loss parameter of the pure polyisoprene IR305 (matrix) over the logarithm of the frequency is presented in Fig. 1. The dielectric constant was found to be about 2.5 and almost independent on the frequency (is not presented). The observed relaxation process in these frequency and temperarture ranges is the glass relaxation process (called "segmental mode" in the literature [7]) which is due to the cooperative reorientations of the polymeric segments. The glass relaxation process of the used polyisoprene IR305 ($M_w = 2 \cdot 10^6$ g/mol) is completely separated from the relaxation of the longitudinal dipole component of the chains (normal mode or reptation process [7, 8]) by about eight decades, where the reptation process appears only at temperatures higher than 0° C in our frequency window. It can be seen that the shape as well as the width of the glass process in polyisoprene is almost independent of the temperature.

The dielectric loss measurements of the mixtures of the ball-like molecules in IR305 are represented in Figs. 2–5, and for an ellipsoidal label in Fig. 6. The measurements of the mixtures were carried out in the same frequency and temperature ranges as those for pure polyisoprene.

Figures 2 and 3 represent the measurements of the mixtures of 0.5 and 1% wt *p*-cyanotoluene (*p*-Tol-CN) with polyisoprene IR305. It can be seen that the height of the observed relaxation process is dependent on the dissolved amount of the *p*-Tol-CN molecules (compare Figs. 1–3). The position and the temperature dependence of the main peak of the mixtures are very similar to that of the pure polyisoprene. This means that the *p*-Tol-CN molecules relax cooperatively with the glass process of the matrix. It can, however, be observed that the *p*-Tol-CN molecules exhibit an additional high-frequency relaxation process which is better resolved at low temperatures.

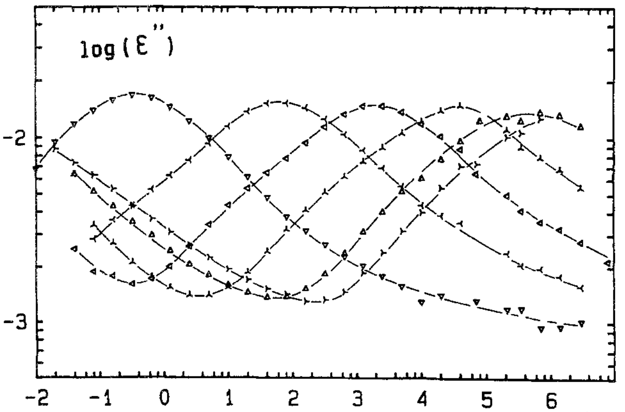

Fig. 1. Dielectric loss of technical synthetic polyisoprene (cariflex IR305) for the glass relaxation process with logarithmic scale over the frequency at different temperature (▽ − 60.3; −< − 50.2; ◁ − 40.7; ⅄ − 29.8; △ − 17.1; >− − 10.1 °C)

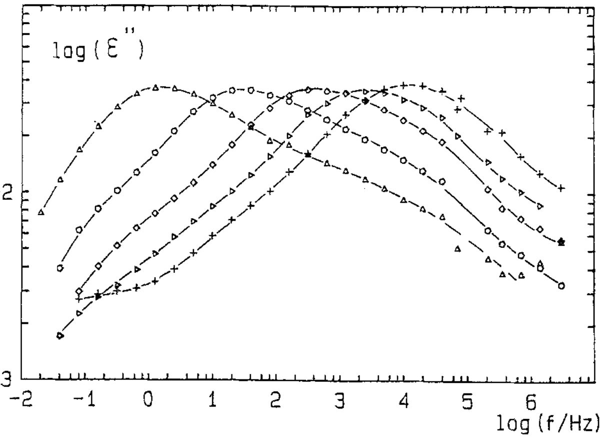

Fig. 2. Dielectric loss of 0.5% *p*-Tol-CN in IR305 (△ − 60.7; ○ − 55.5; ◇ − 49.7; ▷ − 45.3; + − 40.8 °C)

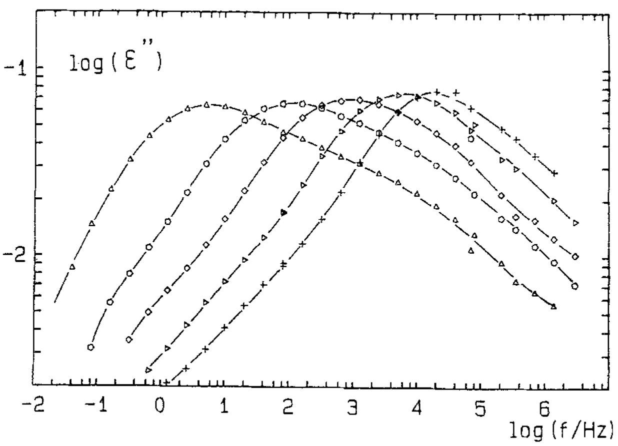

Fig. 3. Dielectric loss of 1% *p*-Tol-CN in IR305 (△ − 60; ○ − 54.9; ◇ − 50.5; ▷ − 45.1; + − 40.1 °C)

The measurements of 0.6% of 9-cyanophenanthrene (Phenan-CN) and 0.6% 1-adamantancarbonitrile (Adaman-CN) are shown in Figs. 4 and 5, respectively. These figures show also that the label molecules relax cooperatively with polymeric segments. It can also be seen that the high-frequency process in these mixtures is very small compared with *p*-Tol-CN.

Figure 6 represents the measurements of the mixture of *p*-butoxycyanobenzene (*p*-BoB-CN) in IR305. This measurement shows that the shape of the relaxation process is narrower than those in the mixtures with other labels and also narrower than that of the pure matrix. Furthermore, it is clear that there is no local process.

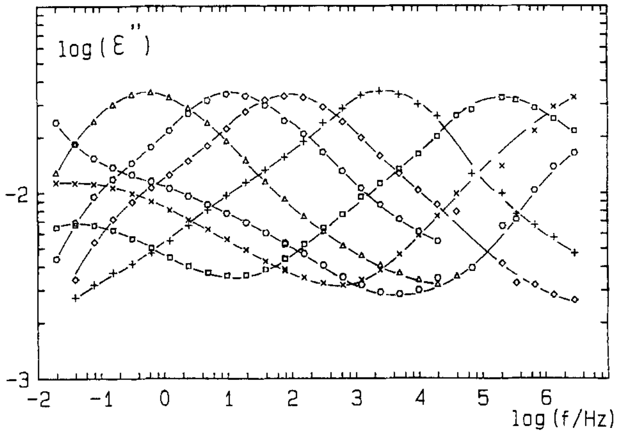

Fig. 4. Dielectric loss of 0.6% Phenan-CN in IR305 (△ − 60; ⬠ − 54.9; ◇ − 50.6; + − 40.7; □ − 21.5; × 0; ⬡ 20°C)

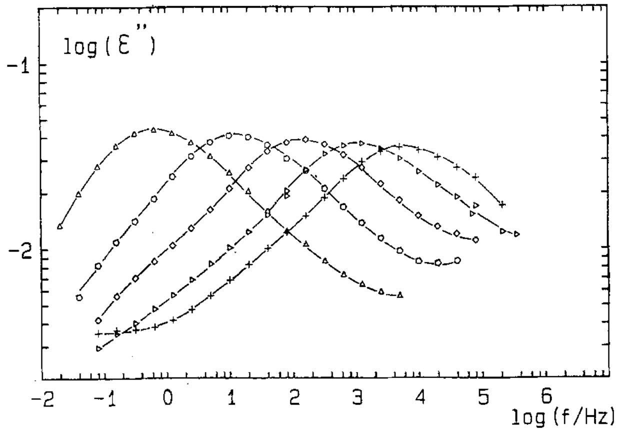

Fig. 5. Dielectric loss of 0.6% Adaman-CN in IR305 (△ − 60.9; ⬠ − 55.6; ◇ − 50.5; ▷ − 45.3; + − 40.2 °C)

Although the *p*-butoxycyanobenzene is ellipsoidal in shape and not a spherical molecule, as are the other molecules, its mixture in polyisoprene was measured. The reason for performing the measurements was to answer the question: are the characteristics of the relaxation process of the label in the polyisoprene dependent only on the volume or also on the shape of the molecule? The *p*-BoB-CN was selected because it has nearly the same volume as the disc-like phenan-CN.

Figure 7 represents the activation energy curves of the different mixtures in comparison with the

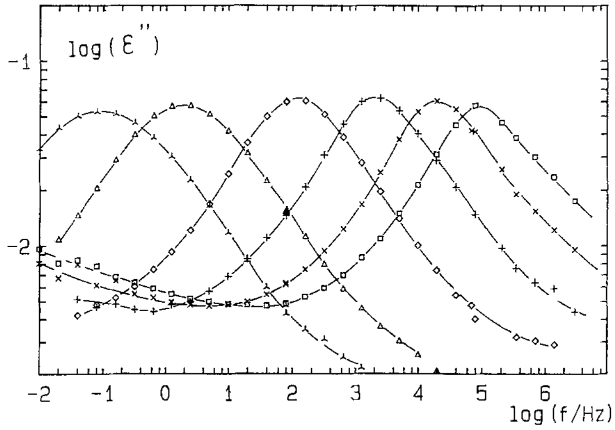

Fig. 6. Dielectric loss of 0.9% *p*-BoB-CN in IR305 (⅄ − 66.1; △ − 60.5; ◇ − 50; + − 40.2; × − 29.8; □ − 20.9° C)

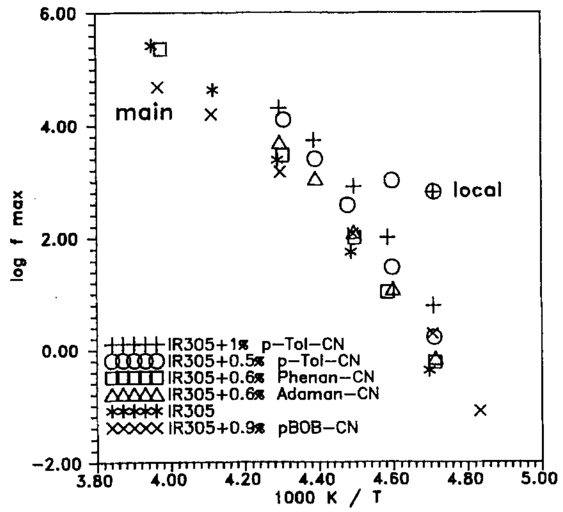

Fig. 7. The activation energy diagram of different samples

pure matrix. The relaxation maximum frequencies (f_m) of the main process were obtained directly from the peak maxima observed in Figs. 1–6, while the maxima of the local process were determined from the analysis which is described below. It can be seen in Fig. 7 that the slope in the activation diagram is the same for the pure matrix and the main relaxation of the labels (with one exception: for *p*-BoB-CN the slope is slightly smaller; this will be discussed below). This is an evidence of the strong cooperativity and coupling of the label molecules with the segmental motion. This finding is in agreement with previous measurements of additives in polymers [9–11] and low molecular weight organic glasses [12, 13] in the glass transition region. On the other hand, the temperature dependence and the position of the additional high frequency process of *p*-Tol-CN are comparable to the local relaxation of polymers [14]. Therefore, this relaxation process is attributed to the local reorientation of the dipoles. The local relaxation process of additives was detected and studied by several authors in polymers [15, 16], as well as in low molecular weight organic glasses [17].

A further analysis of the measured curves (Figs. 1–6) was required to separate the contribution of the segmental relaxation process of the IR305 (matrix) from the whole relaxation process and to evaluate exactly the difference in the position of both processes. The glass process of the polyisoprene was fitted by using two symmetrical relaxation processes, according to the formula of Cole–Cole [18], at different temperatures. We propose to describe the asymmetric shape of the glass process by two coupled relaxation modes of the same dipole. Our idea is that the faster one of both is due to the fluctuations of the "dislocation-network" (which was proposed in correlation with the glass process in polymers by Pechhold and coworkers [19]), while the other one is due to the generation of new "dislocations". These modes will be discussed in a subsequent paper. This view can be supported by the fact that the glass process at low temperatures (slightly above T_g) exhibits a curved high frequency tail which cannot be fitted by using the known empirical formula of Havriliak and Negami [20] for most of the polymers. For example, see Fig. 1 of this work for polyisoprene; this tail differs from the local relaxation process. In the literature, however, this curved, high-frequency tail is either not measured comprehensively or is neglected when applying the fitting routine for the glass process (see [21] and references cited there). It is interesting to note that Havriliak and Negami [20] have reported that the fitting of the relaxation process as two symmetrical processes can represent their data with a fair accuracy. It is not likely that the high-frequency tail of the glass relaxation process is caused by dipolar impurities, since they should behave either (if the molecules are large enough) like the label molecules which are discussed in this paper or (if the molecules are very small) their relaxation should appear as a "local" relaxation process at higher frequencies and also at temperatures below T_g. This is discussed in the following.

The analysis results of the pure matrix were used as a given parameter for the analysis of the mixtures. The contribution of the label molecules was simulated also by two symmetrical processes; one represents the low frequency cooperative process (main), while the other represents the local one. The symmetrical representation (instead of an asymmetric one) of the main process of the label was required to reduce the uncertainty factor of the analysis by decreasing the number of unknown parameters. Some representatives of the analysis diagrams are shown in Figs. 8–12 and some of the analysis data are listed in Table 2. The graphic symbols are the experimental points. The line drawn through the experimental points is the summation of the glass process of the matrix and the label relaxation. It can be seen (Figs. 8–12) that this line fits the experimental points with fair accuracy for all the analyzed curves. The analysis of the experimental data was confronted with the difficulty to position the relaxation process of the matrix. This is due to the so-called plasticizing effect of low molecular weight additives in the polymeric matrix, which leads to a shift of the relaxation maximum to higher frequencies at a constant temperature, and a decrease of the glass transition temperature [22, 23] (Table 2). For this reason, the concentrations used in the present study were selected to reveal a relaxation strength of the label being comparable with that of the glass process of the matrix, thus allowing an analysis with a fair accuracy for the determination of the relaxation maxima of both of the label and matrix processes. The analysis was carried out twice using two different conditions as follows:

The shape and relaxation strength parameters of the segmental process of the matrix were taken as known parameters (because it is unlikely that such low concentrations of the label will influence the shape or the height of the glass process of the matrix). The relaxation frequency maximum was taken once as a free fitting parameter and once as a given fixed parameter. In the second case, the relaxation frequency of the plasticized matrix was estimated by using the calorimetric glass transition [24]. It must be stated here that the two methods of analysis supplied nearly the same results. The results obtained from the second fitting method only are listed in Table 2 and presented in Figs 8–12.

It can be seen in Figs. 8 and 9 that the *p*-Tol-CN relaxation consists of two relaxation processes and the maximum of the low frequency process lies at the same position as the segmental relaxation of the matrix. Table 2 shows that the local contribution (X_{local}) of the label molecules is about 45% of the total relaxation strength of that dipole. On the other hand, the local contribution of phenan-CN (Fig. 10) is merely about 17%, while the relaxation maximum of the low frequency process is still located at the same position as the segmental relaxation. Similar results are obtained for the mixtures with adaman-CN (Fig. 11), but the local contribution is about 8%. It is important to state that measurements at temperatures lower than T_g showed that the mixture with

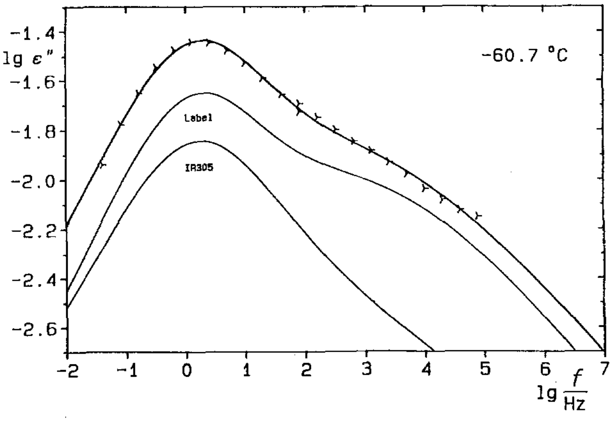

Fig. 8. An Analysis plot of 0.5% *p*-Tol-CN in IR305 at temperature − 60.7 °C. Each of both contributions (label and IR305) is represented as a sum of two relaxation processes after Cole and Cole [18].

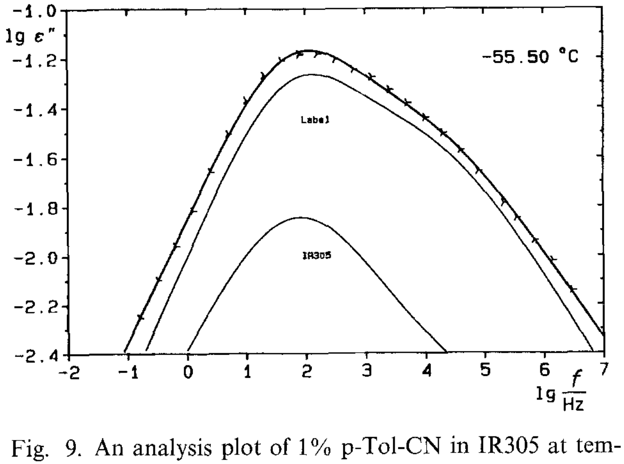

Fig. 9. An analysis plot of 1% p-Tol-CN in IR305 at temperature − 55.5 °C

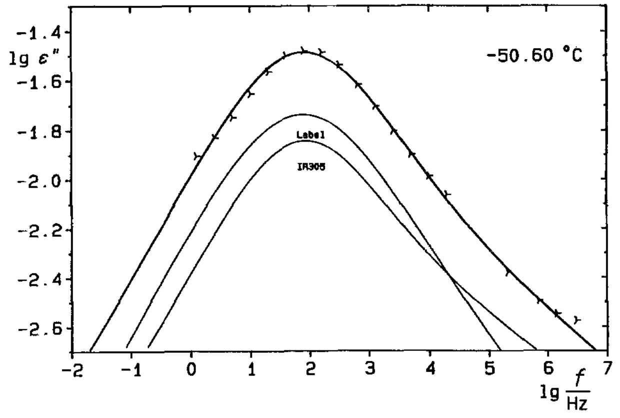

Fig. 10. An analysis plot of 0.6% Phenan-CN in IR305 at temperature − 50.6 °C

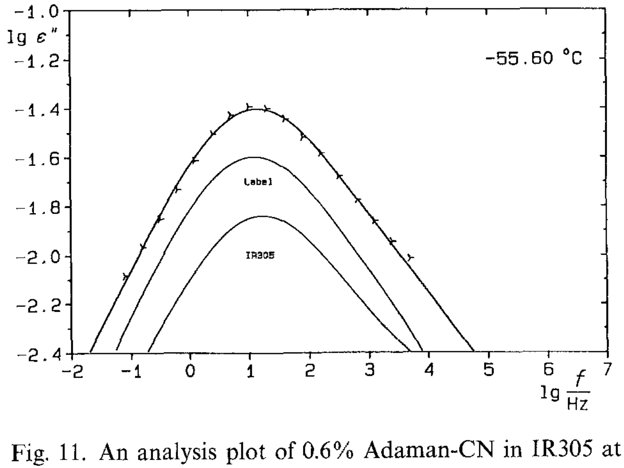

Fig. 11. An analysis plot of 0.6% Adaman-CN in IR305 at temperature − 55.6 °C

adaman-CN exhibits a local process having relaxation strength of about 6% of the total one.

The observed decrease in the local contribution can be attributed to the larger size of Phenan-CN and Adaman-CN compared with the *p*-Tol-CN. The same was observed by Williams et al. [12, 13] in their measurements of different solutes in low molecular weight organic glasses. They found that some of the solute molecules (such as fluorenone and di-*n*-butylphtalate) reorient primarily by the low-frequency cooperative process, in contrast to other solutes (such as camphor) which relax partly by a high-frequency (local) process. Their interpretation was that the ability of the fluorenone molecule to relax by the high-frequency process is very restricted, because this solute is enmeshed with the surrounding molecules due to its large size [13]. However, a comparison between the local contribution (X_{local}) of phenan-CN and Adaman-CN (Table 2) shows, surprisingly, that the local contribution of adaman-CN is smaller than that of phenan-CN, although the latter has a volume greater than the former. It seems that the fine geometry of these ball-like molecules plays a role for their local orientations. The geometrical difference between these moelcules is that phenan-CN is a more disc-like molecule, whereas adaman-CN is a more spherical one.

On the other hand, the analysis of the measurements of the mixture with the *p*-BoB-CN (Fig. 12) shows that this ellipsoidal label exhibits only one symmetrical process (no local relaxation process), although it has almost the same volume as the round, thick phenan-CN. It can also be seen in Fig. 12 that the label relaxation process of *p*-BoB-CN is slower than the glass process (segmental mode) of the matrix. These findings are in agreement with the previous measurements of different rod-like molecules with variable lengths in polyisoprene [1]. The rod-like molecules showed no contribution of the longitudinal dipole moment in the vertical direction. This fact implies that the fluctuation of the long axis is too small to be detected. This behavior of rod like-molecules was attributed to the cylindrical restrictions originating from the parallelism of the polymeric chains within the bundle [2–4]. The relaxation mechanism of the rod-like molecules was attributed to a multistep cooperative reorientation mechanism, which is controlled by the segmental motion of the matrix [1].

A plot of $\Delta \log f_m$ versus the length of the label for ball- and rod-like [1] molecules is presented in Fig. 13, where $\Delta \log f_m$ is the difference between $\log f_m$ (main label process) and $\log f_m$ (glass process of the polyisoprene). This figure shows that for lengths > 10 Å the value of the $\Delta \log f_m$ increases with increasing the label length and obeys the following empirical equation

$$\Delta \log f_m = 4 \log ((L/d) - 1),$$

where L is the length of label and d is the interchain distance of polyisoprene (5.5 Å). It can also be seen that $\Delta \log f_m$ is independent on the length

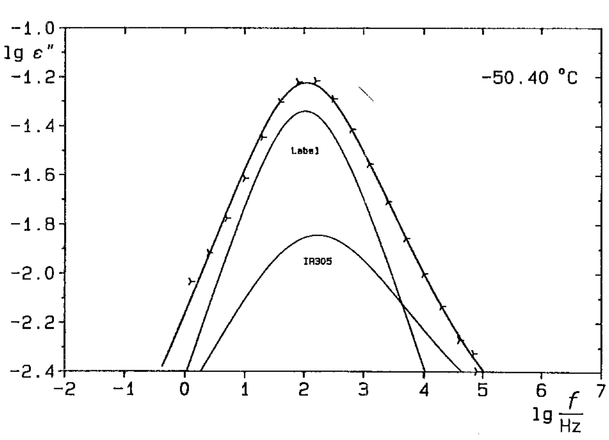

Fig. 12. An analysis plot of 0.9% *p*-BoB-CN in IR305 at temperature − 50.4 °C

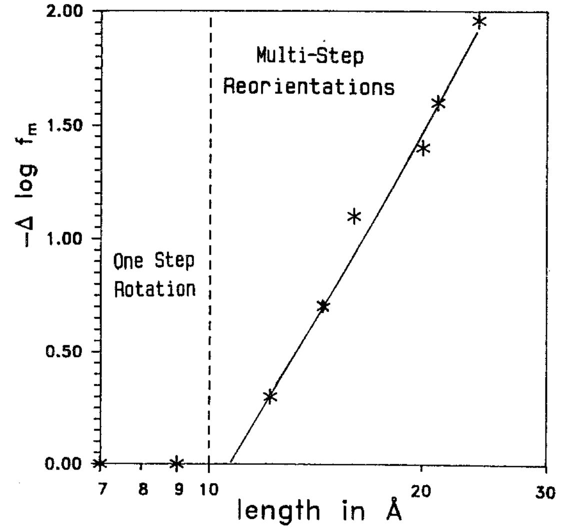

Fig. 13. A plot of $\Delta \log f_m$ versus the logarithm of the label length in Å

and equals zero for lengths < 10 Å. Furthermore, a plot of the Cole–Cole distribution parameter $(1 - \alpha)$ versus the length of the label (Fig. 14) shows that, starting from a length equal to 10 Å, $(1 - \alpha)$ increases rapidly, reaching a limiting value of about 0.85. This value corresponds to a narrow distribution of relaxation times, which is perhaps a characteristic property for the diffusion mechanism.

It is noteworthy to point out that the present measurements and analysis are in agreement with the measurements carried out by Hyde and Ediger [11] to detect the reorientation of anthracene and 9,10 dimethylanthracene (their length is about 10 Å) in cis-polyisoprene in the temperature range $T_g + 20°$ to $T_g + 120\,°\mathrm{C}$ using their sophisticated optical arrangement. They found that:

1) the temperature dependence of the rotational mobility of these labels is well described by the temperature dependence of the shear viscosity; 2) the relaxation time measured by their method is nearly the same as that measured dielectrically for the micro-Brownian reorientation of the segments (glass process); 3) there is no local contribution of these probes.

It is now clear that the length of the label is not only an important factor for the local contribution of the label, but also important for the determination of the cooperative relaxation mechanism of the label. The length of 10 Å seems to be critical length, since the longer labels relax by a multistep reorientation mechanism instead of one step rotation. Details of the possible reorientation mechanisms will be discussed in another work.

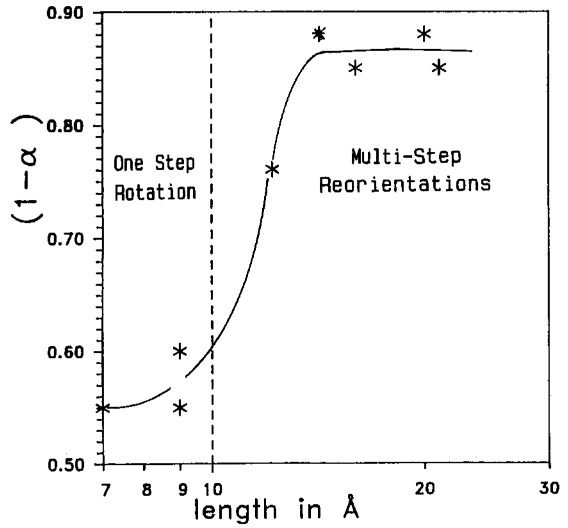

Fig. 14. The Cole–Cole distribution parameter $(1 - \alpha)$ versus the logarithm of the label length in Å

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