Colloid & Polymer Science Colloid Polym Sci 272:894–902 (1994)

Dielectric relaxation of polystyrene with side-chain- and chain-end-labels

A. A. Mansour, E. Happ[1]), T. Wolf[2]), and B. Stoll[3])

Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt
[1]) Sektion Polymere, Universität Ulm, FRG
[2]) Now with DU PONT, Oestringen, FRG
[3]) Abteilung Angewandte Physik, Universität Ulm, FRG

Abstract: Polystyrenes with different concentrations of side groups with cyano groups were prepared and complex dielectric constants were measured in the range of the glass transition temperature and the frequency range of 10^{-2}–10^{7} Hz.

The GPC and DSC measurements showed that the molecular weight of these polystyrenes was about 10500 g/mole and the glass transition temperatures were 89.5 °C for all samples.

The dielectric relaxation spectra obtained for the side group polystyrene labels and also the chain-end polystyrene labels prepared before [9] were analyzed to find out the degree of coupling of the chain-end and side-group labels with the cooperative reorientation of the polymeric matrix. The analysis of the spectra was carried out using the analysis method developed by Mansour and Stoll [6].

The results obtained showed that both end- and side-group labels are strongly coupled with the segmental reorientation and relax with relaxation times longer than that of the segments.

The value of $\Delta \log f_m = (\log f_m(\text{label}) - \log f_m(\text{matrix}))$ was obtained from the recently designed comparison diagram suggested by Mansour and Stoll [6, 14]. The value of $\Delta \log f_m$ depends on the label length in the case of chain-end labels.

It was surprising to find that the side groups relax slower than the segments by only 0.9 decades. These results obtained implied that the label relaxes through a multistep relaxation mechanism of the side and end groups and not through a diffusion mechanism of the whole chain. In addition, the effective lengths of the relaxing units were determined using the empirical equation obtained before in the case of rodlike molecules in polyisoprene [7].

Key words: Labeled polymer – dielectric measurements – glass relaxation – label relaxation – glass transition temperature

Introduction

The study of reorientation of guest molecules in polymers is recognized as a method for the study of the reorientation and molecular packing of polymeric segments [e.g. 1–8]. The reorientation of guest molecules can be studied by different methods, mainly dielectric [3–7] and fluorescence [1, 2] techniques.

The dielectric technique has the advantage that the dipole relaxation of polar guest (label) can be measured for relatively longer relaxation times in the order of minutes, when compared with the fluorescence technique (1–100 ns which can be extended to some ms in exceptional cases) [8]. The dielectric technique has an additional advantage: it is possible to detect the reorientations of both label and polymeric segments simultaneously, so that the relaxation characteristics can be directly correlated with only one measurement [5, 6]. This means that all the problems of the plasticizing effect of the labels can be overcome so that a precise comparison of the relaxation times is possible [6].

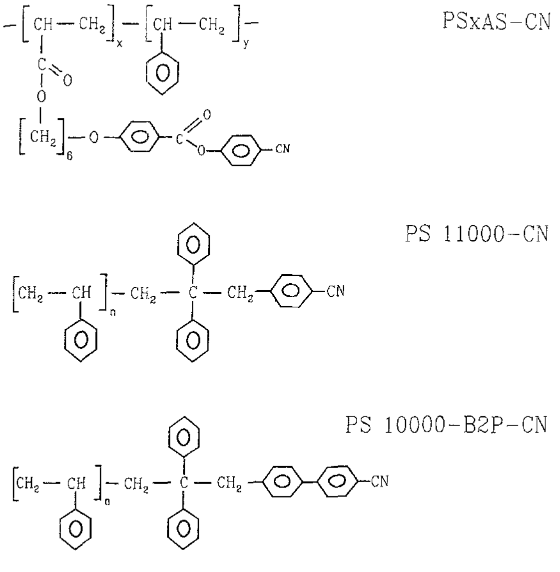

Fig. 1. Chemical formulas of the labels

The present work deals with the reorientation of labels which are chemically fixed to the polymeric chain through a covalent bond at the chain-end- or as a side chain of polystyrene. In a previous work [9], we reported on the preparation and the dielectric relaxation behavior of specially prepared polystyrene terminated with rigid groups. Two polystyrenes terminated with p-cyanophenyl and p-cyanobiphenyl groups (= labels) were prepared and characterized. In addition, their dielectric relaxation properties were measured in the glass transition region. The dielectric measurements showed that the cyano groups, which are chemically fixed as chain ends (see Fig. 1) relax cooperatively with the polymeric segments. Furthermore, the cyanobiphenyl groups were found to relax with longer relaxation times than the cyanophenyl groups. The experimental values of the relaxation strength of the label dipoles showed that there is no association of the end groups. However, an analysis for the obtained relaxation to separate the different modes of relaxation of the cyanobiphenyl or cyanophenyl groups from the glass process of the matrix was not possible. This is because the observed relaxation process is a sum of contributions of different dipoles, where each dipole has its own relaxation characteristics. The main problems of this analysis were that 1) the frequencies of the maxima of the segmental relaxation at different temperatures are unknown due to the differences in the glass transition temperatures of the different samples, and 2) the width (and also the relaxation strength) of the glass relaxation process of polystyrene is strongly dependent on the temperature. But, as a consequence of recent work, it is now possible to find out all the relaxation characteristics of the plasticized matrices for different molecular weights on the basis of the calorimetric glass transition temperature according to the method suggested by Mansour and Stoll [6].

Accordingly, the ultimate aim of the present work is to find out to what extent the cyano-groups with different lengths can relax cooperatively with the polymeric segments. In addition, it was also aimed to explore the relaxation behavior of the label molecules which are chemically fixed as side chains and to compare their behavior with those of free labels and also with the end chain labels. For this reason, an acrylic ester with rigid side groups was copolymerized with styrene with different concentrations, namely, 0, 1, and 5 wt% to produce PSxAS-CN (see Fig. 1 and Table 1). x is the weight percentage of the side groups. It is interesting to state that the pure polymer of this acrylic ester is a liquid crystalline polymer. Therefore, it is beneficial to compare the relaxation behavior of the side groups with that of the δ-process observed in the side chain liquid crystalline polymers.

Experimental

Three polystyrenes PSxAS-CN (Fig. 1 and Table 1) were prepared by free radical polymerization of the acrylate derivative and styrene monomer using benzoyl peroxide as initiator according to the method described by [10]. Their molecular weights and glass transition temperatures were determined using GPC and DSC resp. The DSC measurements were carried out by Dr. Höhne and coworkers, University of Ulm, using a Perkin Elmer calorimeter type DSC-7 with a heating and cooling rate of 10 K/min. The samples were heated and cooled twice, and only the second cooling curves were used to determine the glass transition temperatures according to the method described in [11].

The polymeric materials were dried in a high vacuum at 120 °C for about 6 h in order to expel

Table 1. Characteristics of used materials

Label	M_w g/mol	T_g/°C	Weight % of side groups: Polymerized	Weight % of side groups: From dielectric relaxation
PS 11000-CN	11000	92	–	–
PS 10000 B2P-CN	10000	97.5	–	–
PS 0AS-CN	10300	89.5	0	0
PS 1AS-CN	10300	89.5	1	1.3
PS 5AS-CN	10900	89.5	5	5.2
Host polymer PS 168 N	250000	101	–	–

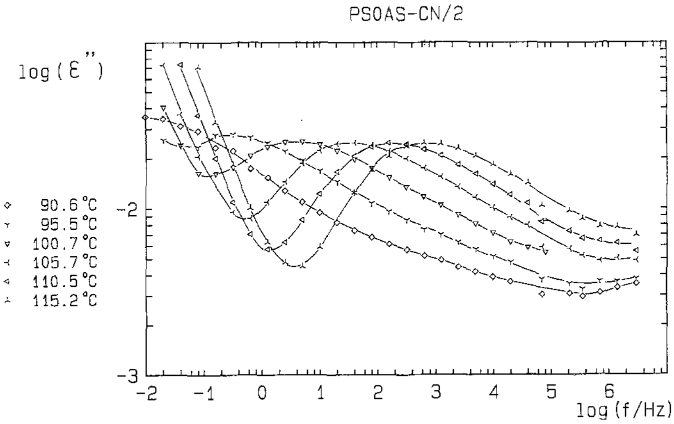

Fig. 2. Dielectric loss over frequency for the newly prepared polystyrene homopolymer PS0AS-CN at different temperatures indicated in the figure

any solvent or water residues before they are used for either of the dielectric or the DSC measurements. The samples used for the dielectric measurements were prepared by the same method as described before and measured by using the same instruments [9]. The samples were pressed in high vacuum at 130 °C between two gold-plated copper electrodes with 40 and 80 mm diameters for the upper and lower electrodes, respectively. The capacities of the measuring condensers were about 100 PF. The accuracy of the measuring equipments in the frequency range 10^{-2}–10^5 was better than $2 \cdot 10^{-4}$ and for higher range was better than 10^{-3} for $\tan\delta$. The software used for the analysis was kindly supplied by W. v. Soden, Department of Applied Physics, University of Ulm.

Results and discussion

The dependence of the dielectric loss parameter on the frequency at various temperatures for the newly prepared side-chain labels PSxAS-CN are presented in Figs. 2–4. The measurements were carried out in the frequency and temperature range of the glass transition temperature.

Figure 2 shows the measurements of PS0AS-CN, which contains 0% side groups. This figure can be taken as a comparison base for the results of the other concentrations presented in Figs. 3 and 4 for PS1AS-CN and PS5AS-CN, respectively. The observed relaxation process in these figures appears in the temperature and frequency ranges of the glass process of polystyrene with a similar molecular weight (9000 g/mole). In these figures it can also be seen that at high temperatures and frequencies lower than that of the glass process there is a rise in the dielectric loss values with decreasing frequency. This process can be attributed to the well known ionic conductivity process. On the other hand, at low temperatures, it can be seen that a weak relaxation process appears at the high frequency tail of the glass process, which is denoted as α (local) [14]. This

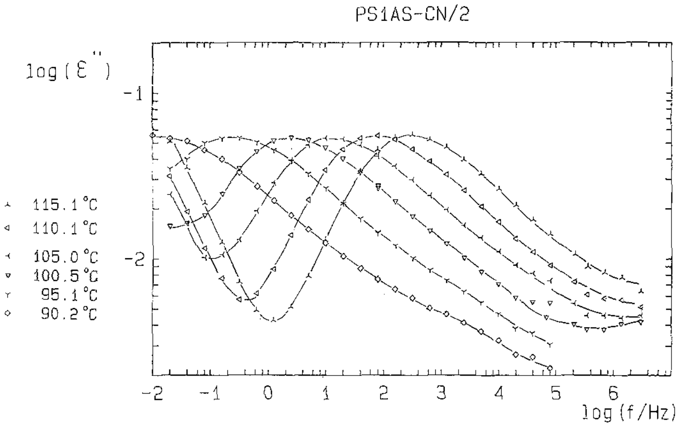

Fig. 3. Dielectric loss for the polystyrene copolymer PS1 AS-CN with 1 weight % of side groups

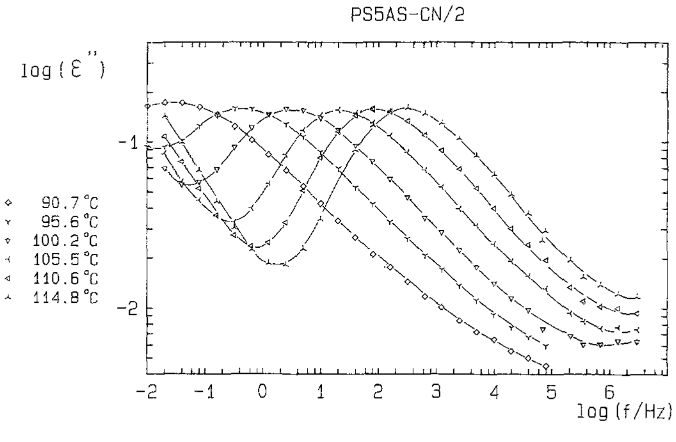

Fig. 4. Same as Fig. 3, but with 5 weight % of side groups

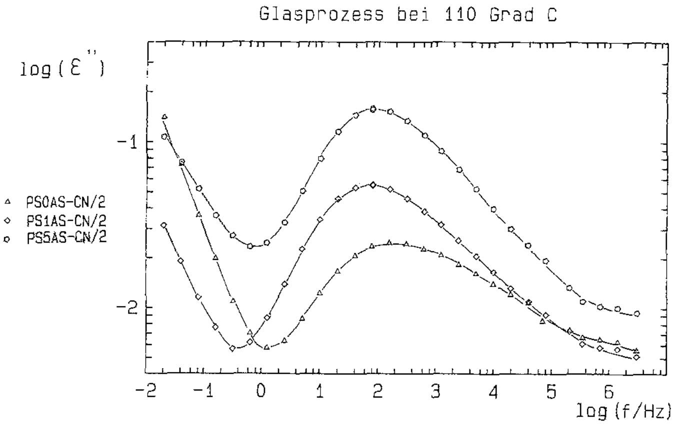

Fig. 5. Comparison of the three samples at 110 °C

process differs from the well known local processes since the activation line of the process merges with that of the glass process at a frequency of about 10^3 Hz and not at 10^6 Hz as for the typical local process. Furthermore, at frequencies higher than 10^5, the low-frequency side of a high-frequency local process appears.

Figure 5 is a comparative plot for the frequency scan of the dielectric loss of the samples with different concentrations of side groups at the same temperatures (110 °C). This figure shows that the increase in the concentration of the side groups leads to a systematic increase in the height of the observed peak. In addition, the maxima of the different samples lie at the same frequency range. These findings lead to the conclusion that the relaxation of the side groups is strongly coupled with the reorientation of the styrene segments and has similar relaxation times. Furthermore, the frequencies of the maxima of these side groups are independent of their concentration in this range (< 5 wt%).

A comparison between the height of the relaxation process of PS0AS-CN (0% side groups) and that of the pure polystyrene (see [6,9]) showed that the peak height of the earlier one is about twice as high as the latter. This finding can be explained by the fact that PSxAS-CN labels were polymerized using benzoylperoxide as initiator. This initiator remains as a fixed end at each chain. This means that some chain ends (with initiator groups) have dipoles with a dipole moment of 1.9 Debye according to the values given by Klingbiel et al. [12]. These dipoles relax cooperatively with the polymeric segments in the same way observed before in the case of the end chain labels [9]. The concentration of the initiator dipoles can be calculated on the basis of the experimental relaxation strength using Fröhlich–Onsager equation as described before [9,13]. The calculation showed that the weight concentration of the initiator groups fixed as chain ends is 2.35%. This value is equivalent to the weight concentration of the end groups contained in polystyrene with a similar molecular weight (9000 g/mole).

The concentration of the side groups can be found experimentally in the same way by using the experimental relaxation strength of the side groups. The obtained concentrations of the side groups from dielectric data are in a good agreement with the weighed values (Table 1). It must be stated here that the values given by Klingbiel et al. [12] were used for that calculation. According to these authors, the total dipole moment of the side groups is equal to 6.18 Debye.

Analysis of the curves

As was pointed out before, our aim was to find the degree of coupling of the reorientation of the side group- and end group-labels with the glass process, which originates from the micro Brownian cooperative motion of the polymeric segments. The degree of coupling can be estimated from the values of $\Delta \log f_m$, which is the difference between the relaxation frequency of the glass and the label processes. Therefore, the analysis of the curves to find out this parameter for different labels is indispensable.

The basic concept of the analysis is to subtract the contribution of the polymeric segments from the total relaxation process, i.e., the measurements presented in Figs. 2–4 in this work, and Figs. 3–7 in our previous work [9]. This is because the observed peaks in these plots represent both the contribution of the polymeric segments and that of the end group- and/or side group-dipoles. Now, according to the method suggested before [6], it is possible to find out all the required characteristics of the glass process of the matrix by using the calorimetric glass-transition temperature. The analysis was carried out for all the measured samples at different temperatures and concentrations of the labels (both the chain end [9] and side chain labels).

a) *Analysis of the measurements of chain-end-labels*

Figures 6–8 represent the analysis curves of the measurements of PS11000-CN samples with different concentrations of the end groups at the

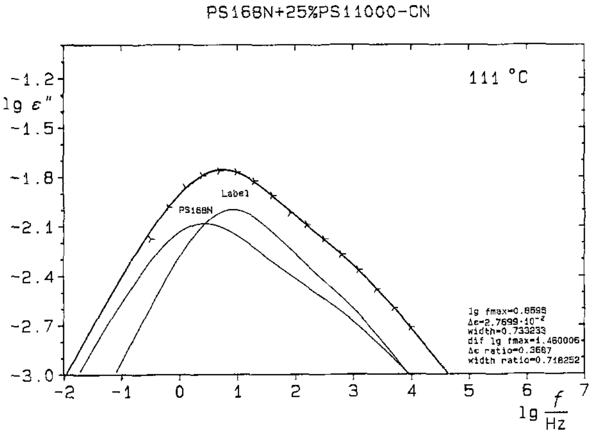

Fig. 6. Representation of the measured loss curve (for a mixture of 25% by weight of PS 11000-CN with 75% of PS 168 N) as a sum of the contributions of the two components

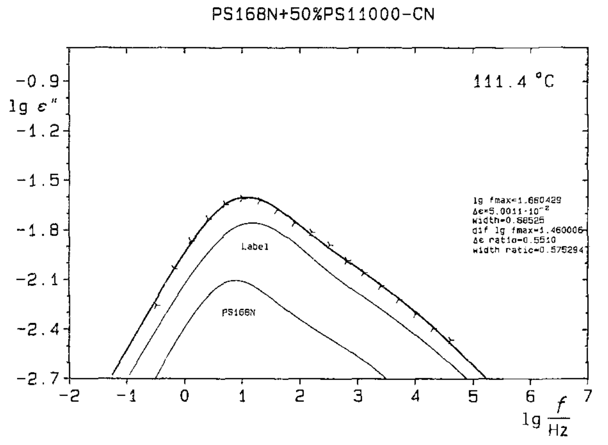

Fig. 7. Same as Fig. 6, but for 50% PS 11000-CN

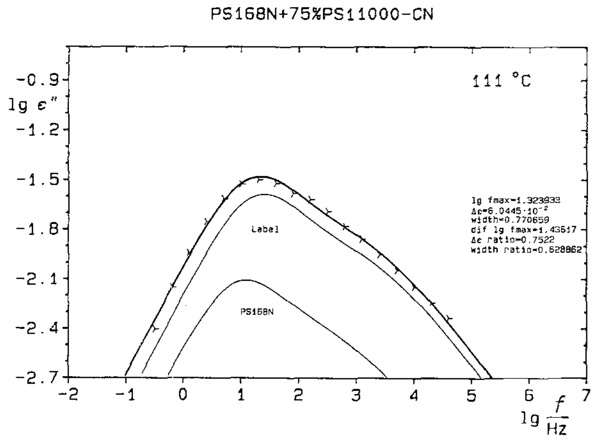

Fig. 8. Same as Fig. 6, but for 75% PS 11000-CN

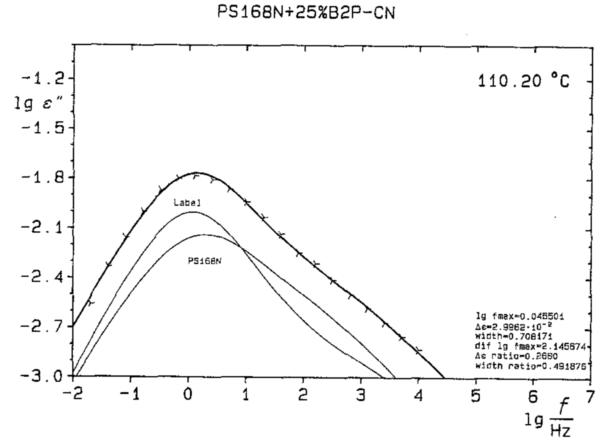

Fig. 9. Same as Fig. 6, but for 25% PS 10000 B2P-CN

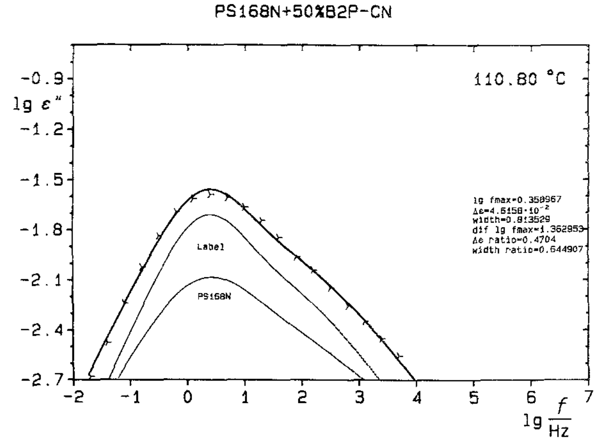

Fig. 10. Same as Fig. 6, but for 50% PS 10000 B2P-CN

same temperature. The concentration of the end groups was varied by mixing the label PS11000-CN (end group label) with PS168N (thermally polymerized high molecular weight polystyrene with $M_w = 250\,000$ g/mole, i.e., containing no dipolar end groups) by different concentrations, namely, 0, 25, 50, 75 and 100% wt [9]. It can be seen that the contribution of the label groups to the relaxation strength is proportional to admixed label concentration. The shift of the total relaxation process along the frequency axis which is observed in these figures with increasing concentration can be attributed to the plasticizing effect of the low molecular weight label PS11000-CN ($M = 11000$ g/mole) on the high molecular weight matrix (for more details see ref. [9]).

Figures 9 and 10 show the mixtures of PS10000-B2P-CN in PS168N. A comparison between the relaxation behavior of the two labels PS11000-CN and PS10000B2P-CN shows that the increase in the length of the end groups has led to a shift in the relaxation maxima to lower frequencies in relation to that of the matrix. In other words, the value of $\Delta \log f_m = (\log f_m(\text{label}) - \log f_m(\text{matrix}))$ decreases with the increase of the length of rigid dipoles fixed at the chain ends. A comparison between the values of the $\Delta \log f_m$ obtained in this case (chemically fixed) and those obtained for free labels admixed through solvents [14], shows only a slight difference. This means that the relaxation mechanism of these labels is not translatory but it is a rotational diffusion one.

b) *Analysis of the measurement of side group labels*

The analysis in this case was carried out step by step. At the beginning, the contribution of the initiator groups was obtained from the analysis of the relaxation process of PS0AS-CN (i.e., no side groups). The obtained parameters were then used as known parameters for the analysis of the measured curves of the PS1AS-CN and PS5AS-CN. The subtraction procedures of initiator and the segmental contribution from the total process was simplified by the fact that all three samples, PS0AS-CN, PS1AS-CN and PS5AS-CN, have the same molecular weight and the same glass transition temperatures as they are prepared under the same experimental conditions. This means that a direct subtraction of the PS0AS-CN curves from the PS1AS-CN and also from PS5AS-CN curves is allowed provided that the relaxation frequencies of both curves are the same, as pointed out before [6].

Figures 11 and 12 are representatives of the analysis and show, surprisingly, that the side groups relax with relaxation frequencies which are only slightly smaller than those of the segments. It was expected that the side groups would relax much slower since the rotation of the side groups should be more difficult than that of the free admixed labels.

If we compare our measurements to the relaxation of side groups with δ-processes of side chain liquid crystalline polymers, we find that the latter relax more than 3 decades, slower than the micro-Brownian motion (α-process).

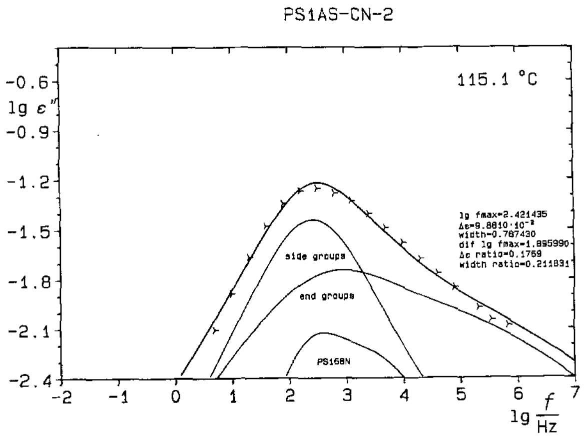

Fig. 11. Representation of the measured loss curve of PS 1 AS CN as a sum of the contribution of side groups, end groups, and styrene units

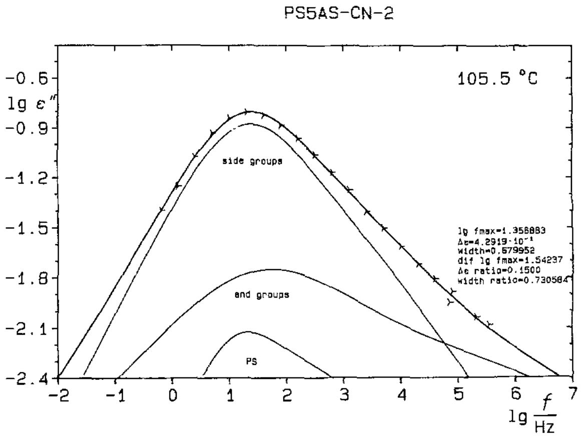

Fig. 12. Same as Fig. 11, but for PS 5 AS-CN

c) *Discussion of the analysis results*

The values of the $\Delta \log f_m$ can be found directly from the analysis curves represented in Figs. 6–12. However, it must be taken into account that the relaxation spectrum of the polystyrene segments is strongly dependent on temperature [6]. For this reason, we should consider not only an average value for $\Delta \log f_m$, but also its temperature dependence. According to Mansour and Stoll [6], it is better to use the frequencies of the relaxation maxima (instead of their temperatures) of the glass process of the matrix as the abscissa of such comparative diagrams. The design of this diagram was based on the experimental fact that the glass processes of different polystyrenes with different molecular weights and also with different contents of plasticizers, which appear at the same frequency, have the same half width and form, i.e., the same distribution of relaxation times [6].

This means that such a plot has the advantage that the relaxation behavior of different polystyrenes at different temperatures can be directly compared and correlated using one plot to find out the degree of coupling of the reorientation of the label molecules with the glass process of the matrix. Accordingly, $\Delta \log f_m$ of different labels at different concentrations and temperatures are compared in Fig. 13.

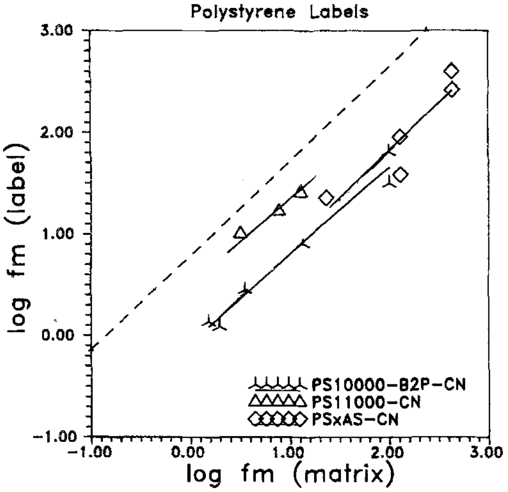

Fig. 13. Frequencies of the relaxation maxima in the dielectric loss curves: those for the label dipole reorientation plotted against those for the polystyrene segments total reorientation

The broken line in Fig. 13 represents the simple mode of relaxation of the styrene segments according to the experimental results of the relaxation of ball-like molecules in polystyrene described in ref. [15]. These results showed that the relaxation spectrum of the glass process of polystyrene consists of two main relaxation modes. The high-frequency relaxation mode is due to the orientation of the lateral dipole component of the styrene segments. On the other hand, the low-frequency relaxation mode results from the relaxation of the longitudinal dipole components after the reorientation of a limited number of segments [14, 15].

It can be seen in Fig. 13 that:

1) both chain-end- and side-chain labels are strongly coupled with the segmental reorientation;
2) both types of labels relax slower than the lateral dipoles of the polymeric segments,
3) the values of $\Delta \log f_m$ are dependent on the label length in the case of chain-end-label (the values of $\Delta \log f_m$ can be taken directly from this plot).

In addition, it can be seen that the side groups are only slower by about 0.9 decades than the segments. This finding implies that side groups must relax through a multistep relaxation mechanism very similar to that observed in the case of rodlike molecules in polyisoprene [5] and polystyrene [14] and not through a diffusion mechanism of the whole chain. Accordingly, the relaxation mechanism of the side groups can be represented schematically as drawn in Fig. 14.

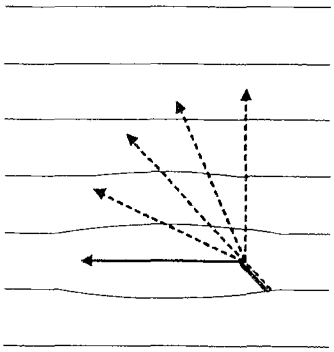

Fig. 14. Sketch of the steps of reorientation of a side-chain label in a bundle of polystyrene chains

This model implies that the relaxation of the labels must be achieved through the rotation of side groups around the carboxyl groups and/or the spacer. For this reason, it is interesting to determine the effective length of the side groups according to the experimental formula obtained before for the relaxation of rod-like molecules in polyisoprene [7].

This equation can be written as

$$-\Delta \log f_m = \log f_m(\text{segment}) - \log f_m(\text{label})$$
$$= 4 \log [(L/d) - 1] \,, \qquad (1)$$

where L is the label length, and d is the inter chain distance.

According to this equation and the experimental values obtained from Fig. 13, the effective length is found to be 22.5 Å. This value is very close to the length of the side groups. This result is in a good agreement with the above described concept for the rotation of the side groups. In this connection, perhaps, it is worth mentioning the work of Gnoth [16] about the dielectric relaxation of side-chain liquid crystalline polymers. He found, surprisingly, that the above equation is also valid for the relaxation of the admixed rod-like labels [16]. This could lead to the conclusion that the reorientation of the labels in both amorphous and liquid crystalline polymers follow the same mechanism. This finding could also be taken as an indication of the chain parallelity of the amorphous polymers in a range greater than the length of the side chain labels.

Similar calculations were carried out to find the effective length of the chain-end labels, PS11000-CN and PS10000-B2P-CN, yielding values of 19.5 and 22.5 Å, respectively. It is interesting to observe that the difference between the two effective lengths of the two labels is equal to 3.5 Å. This value is equivalent to the length of the additional phenyl group existing in the longer label. This is a good indication for the accuracy of the analysis and theory. However, the obtained lengths are longer than those of the cyano-phenyl resp. cyano-biphenyl groups. This means that some monomeric units in the chain are strongly coupled to the motion of the chain-end-groups. The number of these monomeric units is equivalent to a chain length of about 11 Å, i.e., 4 or 5 monomeric units.

Acknowledgement

The authors thank to Prof. Dr. W. Pechhold for his interest in this work and the Deutscher Akademischer Austauschdienst for financial support.

References

1. Springer H, Neuert R, Müller FD, Hinrichsen G (1983) Colloid Polym Sci 261:800
2. Fuhrmann J, Hennecke M (1989) Makromol Chem, Macromol Symp 26:209
3. Winkler G, Stoll B, Sautter E, Pechhold W (1980) Colloid Polym Sci 258:289
4. Bakule R, Heinrich W, Pechhold W, Stoll B (1986) Colloid Polym Sci 264:185
5. Mansour AA, Stoll B, Pechhold W (1992) Colloid Polym Sci 270:219
6. Mansour AA, Stoll B (1993) Colloid Polym Sci 271:834
7. Mansour AA, Stoll B (1994) Colloid Polym Sci 272:17
8. Hyde PD, Ediger MD (1990) J Chem Phys 92(2). 1036
9. Mansour AA, Junge R, Stoll B, Pechhold W (1992) Colloid Polym Sci 270:325
10. Portugall M, Ringsdorff H, Zentel R (1982) Macromol Chem 183:2311
11. Heinrich W, Stoll B (1988) Colloid Polym Sci 78:37
12. Klingbiel RT, Genova DJ, Criswell TR, van Meter JP (1974) J Am Chem Soc 96(25):7651
13. Fröhlich H (1958) Theory of dielectrics, 2nd Ed, Oxford University Press, Oxford, UK
14. Mansour AA (1992) Thesis, University of Ulm, FRG
15. Mansour AA, Stoll B (1994) Colloid Polym Sci 272:25
16. Gnoth M (1993) Thesis, University of Ulm, FRG

Received June 22, 1993;
accepted November 25, 1993

Authors' address:

Dr. B. Stoll
Abt. Angew. Physik, Universität Ulm
Albert-Einstein-Allee 11
89069 Ulm, FRG