# Physical ageing of isotropic and anisotropic polycarbonate

## J. Bartos*, J. Müller and J. H. Wendorff†

*Deutsches Kunststoff-Institut, Schlossgartenstrasse 6, D-6100 Darmstadt, FRG*

Polycarbonate displays physical ageing when subjected to annealing in the glassy state. The ageing is considerably enhanced with oriented polycarbonate, particularly if the orientation is achieved by cold drawing. The effect of cold drawing and annealing on mobility and free volume has been investigated by means of electron spin resonance spectroscopy using the spin probe method as well as by dilatometric and X-ray scattering studies. The experimental results show that the mean rotational correlation times of the probes and the correlation time distribution depend on the mechanical and thermal history of the samples. The mobility changes are correlated with results of X-ray scattering and dilatometry and interpreted in terms of changes in the magnitude of the free volume and its distribution.

(Keywords: physical ageing; polycarbonate; annealing; drawing)

## INTRODUCTION

The macroscopic dynamic properties of amorphous polymers are known to depend strongly on the density of the molecular packing, i.e. on the free volume[1]. Physical ageing, which takes place in the glassy state due to its non-equilibrium character[2-4] and is connected with the decrease of the free volume, therefore leads to appreciable modifications of such dynamic properties. Examples are changes in the creep behaviour, a transition from a more ductile to a more brittle behaviour and a decrease of gas permeability.

It has frequently been pointed out that it may not only be the amount of free volume but also its distribution that affect macroscopic dynamic properties[5,6]. It is for this reason that, in addition to methods like dilatometry[7,8], calorimetry[9,10], mechanical and dielectric spectroscopy[1,11,12], small-angle X-ray scattering techniques[13-15] have also been employed as well as positronium annihilation spectroscopy[16], photochemistry[17-19], e.s.r.[20] and i.r.[21] spectroscopy. These methods can provide information on structural and dynamic changes at the microscopic level, such as fluctuations of the free volume, for instance.

Such studies on the mechanism of ageing in amorphous polymers and on its influence on thermal, mechanical and other macroscopic properties have so far been restricted to macroscopically isotropic systems. The deformation of amorphous polymers, on the other hand, can be expected to change both the amount of free volume available and its distribution. This in turn will have a strong impact on the ageing properties of oriented glassy polymers and its effect on macroscopic properties. This is the topic of this paper. It is concerned with a comparison of the physical ageing processes taking place in isotropic and anisotropic polycarbonate, as controlled by the characteristic values of the magnitude and distribution of free volume in these states. The experimental techniques of choice are e.s.r. spectroscopy using the spin probe method, small-angle X-ray scattering and dilatometry.

## EXPERIMENTAL

### Material

The experiments were performed with polycarbonate (bisphenol A, tradename Makrolon LS 55/102, obtained from Röhm AG, FRG). Four different types of samples were investigated by e.s.r. spectroscopy:

(1) isotropic unaged (i, u);
(2) isotropic aged (i, a);
(3) anisotropic unaged (a, u); and
(4) anisotropic aged (a, a).

The first sample (1) was prepared by quenching the material from temperatures well above the glass transition temperature to room temperature. The second sample (2) was subsequently annealed at $T_a = 125°C$ for $t_a = 12$ days. The third sample (3) was prepared by deformation of set (1) at room temperature in a hydraulic press. Finally, the fourth sample (4) was obtained from type (3) by annealing at $T_a = 60°C$ for $t_a = 12$ days.

Samples for dilatometry, X-ray scattering and dynamic mechanical measurements were drawn at room temperature with a deformation amounting to up to 80%.

### Methods of measurements and evaluation

The small-angle X-ray scattering investigations were performed with a Kratky small-angle X-ray camera, equipped with a heating cell. Absolute intensities were established by using a moving slit device. The dilatometric studies were performed in a mercury-filled glass dilatometer, which was placed in a heating bath. A cathetometer was used to measure the height of the mercury level as a function of temperature and ageing time.

The dynamic mechanical measurements were performed

---

* Permanent address: Research Institut of Rubber and Plastic Technology, CS-764 22 Gottwaldov, Czechoslovakia
† To whom correspondence should be addressed

on a Myrenne ATM 3 automatic torsional pendulum operating in automatic mode with the following parameters: heating rate $3°C\,min^{-1}$, frequency 2 Hz. Shear moduli $G'$ and loss coefficients $\tan \delta$ were evaluated as a function of temperature.

E.s.r. measurements were carried out on a ER 200D–SRC Bruker spectrometer equipped with a temperature-controlled heating cell, enabling temperature variations in the resonator cavity. Samples for e.s.r. measurements were obtained using the spin probe, 2,2',6,6'-tetramethyl-piperidine-1-oxil (TEMPO). The probe was introduced into the polymer by the vapour diffusion technique at elevated temperature for a time sufficient to cause a homogeneous distribution in the sample.

## RESULTS AND DISCUSSION

### Results on the effect of ageing on the density

We intend to analyse ageing phenomena in isotropic and oriented glassy polymers with respect to the density of the molecular packing and with respect to the relation between the amount of free volume present and the mobility of the system. It is for this reason that results concerned with the effect of ageing on the total volume will be discussed prior to e.s.r. results on the effect of ageing on the mobility.

Physical ageing is known to be accompanied by a decrease of the volume as a function of time at constant temperature. As an example, *Figure 1a* shows a characteristic result for polycarbonate in its isotropic state and *Figure 1b* for a polycarbonate that was cold drawn at

room temperature[22]. The volume is found to decrease in both cases approximately linearly as a function of the logarithm of the ageing time. The main difference between the isotropic and anisotropic samples is that the rate of volume relaxation defined as[1]:

$$r = -(1/V)[dV/d(\log t_a)]$$

is approximately twice as large for the anisotropic state if the ageing temperature is kept between room temperature and $100°C$[22]. This becomes apparent from *Figure 2*, which displays the ageing rate for both isotropic and anisotropic polycarbonate as a function of the temperature.

The interesting finding is that the volume relaxation happens faster in drawn polycarbonate despite the fact that its density has been increased relative to that of the isotropic state by about 0.3% (despite the fact that $T_g$ is not influenced by drawing). The conclusion that might be drawn is that the free volume has been increased by cold drawing, although the density has increased.

### E.s.r. spectroscopic studies on the dependence of the mobility of spin probes on the thermal and mechanical history

*Unaged samples.* In the following we will use e.s.r. spectroscopic results on the rotational mobility of small probe molecules to obtain indirect information on the free volume of the matrix[23]. Stable nitroxide radicals were used as probes because of their relatively simple spectra. These consist of three hyperfine lines, which originate from the interaction between the free electron
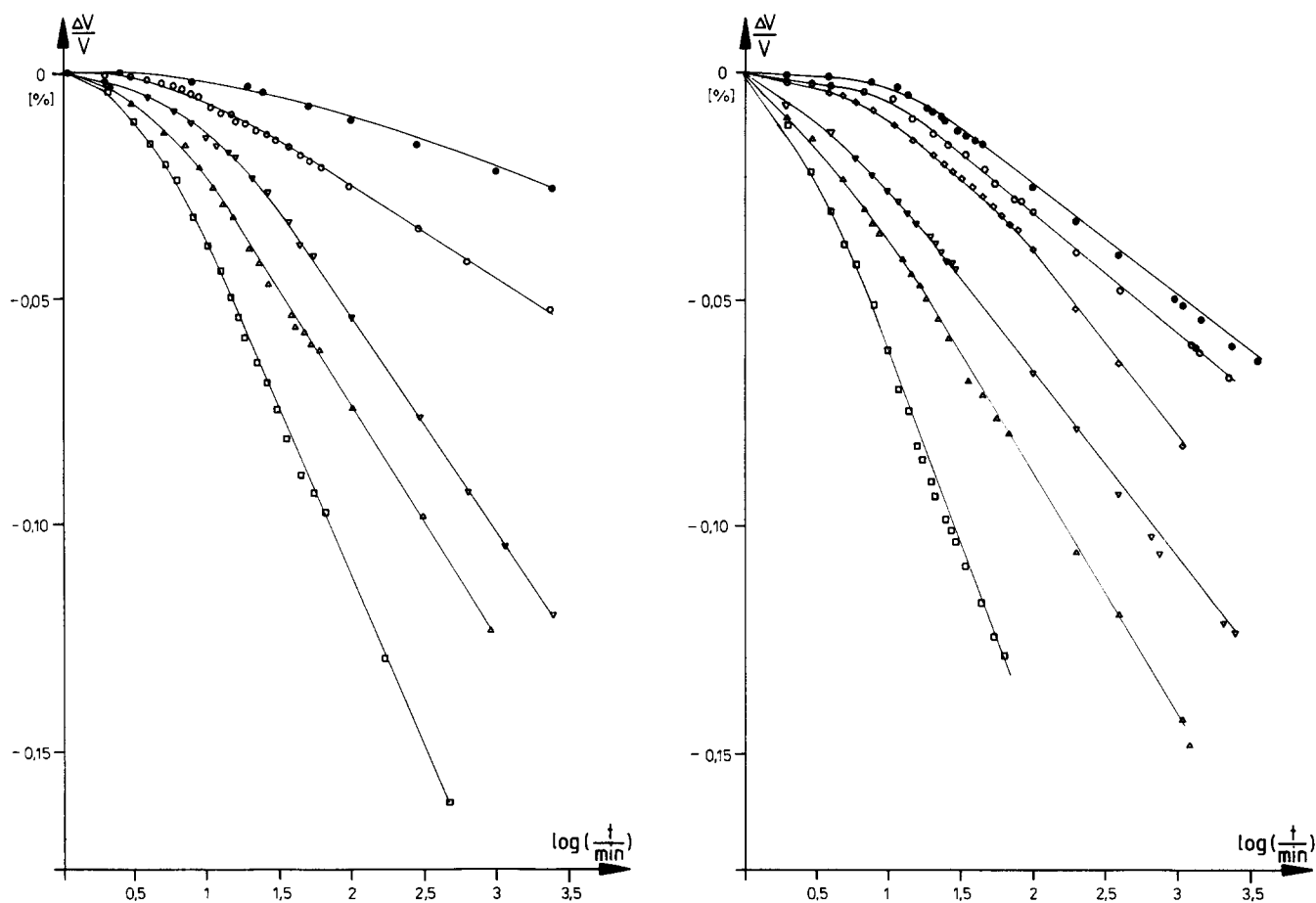


**Figure 1** Dependence of the volume on the ageing time: (a) isotropic polycarbonate; (b) cold-drawn polycarbonate. ●, 45°C; ○, 65°C; ◇, 70°C; ▽, 100°C; △, 110°C; □, 130°C
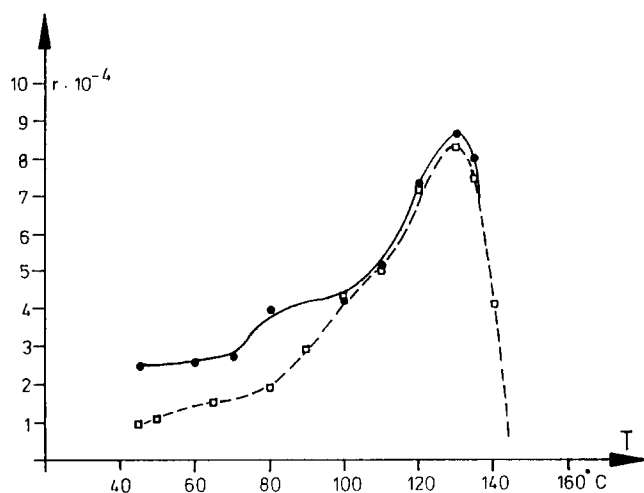
**Figure 2** Rate of volume relaxation *versus* ageing temperature for isotropic and cold-drawn polycarbonate. □, Isotropic; ●, cold drawn
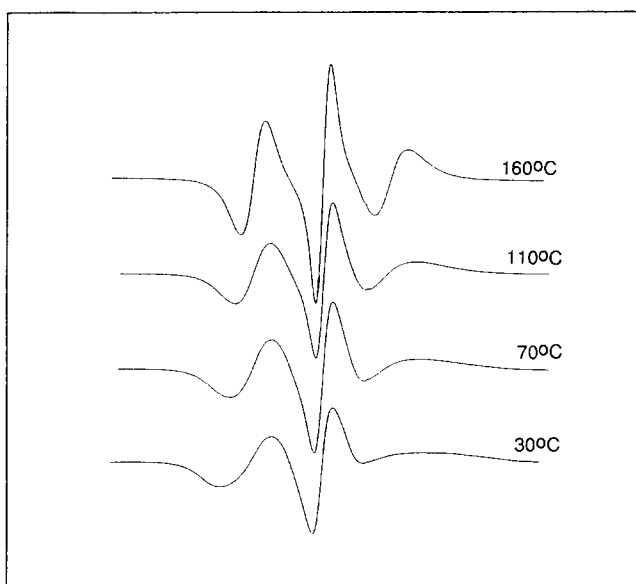


**Figure 3** E.s.r. spectra of the PC–TEMPO system for the case of an isotropic unaged sample at several temperatures

(spin $s = 1/2$) and the nitrogen nuclear spin ($I = 1$). The actual shape and the width of the spectrum depend on the rotational velocity, i.e. on the rotational correlation time $\tau_c$. The assumption is that, by using such nitroxides as dynamic probes in a polymer matrix, one is able to extract information on the environment, in particular on the free volume that is available in the matrix material and on its variation with temperature, thermal history or mechanical history, etc.[20,23,24].

*Figure 3* represents as an example the dependence of the e.s.r. spectra of the probe TEMPO in unaged isotropic polycarbonate at various temperatures. It is apparent that the separation of the extrema of the spectra, $2A$, depends on the temperature: it becomes continuously smaller with increasing temperature. The reason is that the probe tumbles sufficiently rapidly at enhanced temperatures to be able to average out the anisotropy of the nitrogen hyperfine tensor $A$. A characteristic separation $2A$ of about 30 G is observed in this so-called motionally narrowed regime.

A much broader spectrum is observed at low temperatures, the separation $2A$ amounting to more than 60 G.

The reason is that the rotational motion of the nitroxide probe has become so slow at these temperatures that the anisotropy of the hyperfine tensor is no longer averaged out. In this case the separation is controlled by the largest component of the tensor $A$—which is $A_{zz}$—and lies in the range between 60 and 70 G.

We will discuss, in the following, what kind of information can be derived from such spectra. One usually divides the dynamic range accessible to the e.s.r. technique into the range of rapid rotations ($10^{-11} s < \tau_c < 10^{-8} s$), in which the motionally narrowed spectrum is observed, and the range of slow rotations, in which the broad spectrum is observed.

E.s.r. spectra in the fast motion region have the advantage that they can be evaluated with respect to the correlation time relatively easily, on the basis of the Freed–Fraenkel equation[25] (assumption of isotropic rotation):

$$\tau_c(T) = 6.7 \times 10^{-10} \Delta H_+ [(I_+/I_-)^{1/2} - 1]$$

where $\Delta H_+$ is the width of the low-field component of the triplet spectrum, and $I_+$ and $I_-$ are the intensities of the low- and high-field lines of the triplet signal. The rotational frequencies of the probe are thus given by:

$$\Phi(T) = 1/[2\pi\tau_c(T)]$$

and one can determine them in the rapid rotation range as a function of temperature, thermal and mechanical history, as will be shown below. *Figure 4* illustrates the dependence of the rotational frequency of the isotropic unaged sample as a function of time in terms of an activation diagram. This diagram can be used to determine the activation energy for the rotational motion of the probe in the matrix and to relate it, for instance, to relaxation processes taking place in the matrix material itself. This topic will be discussed in more detail below.

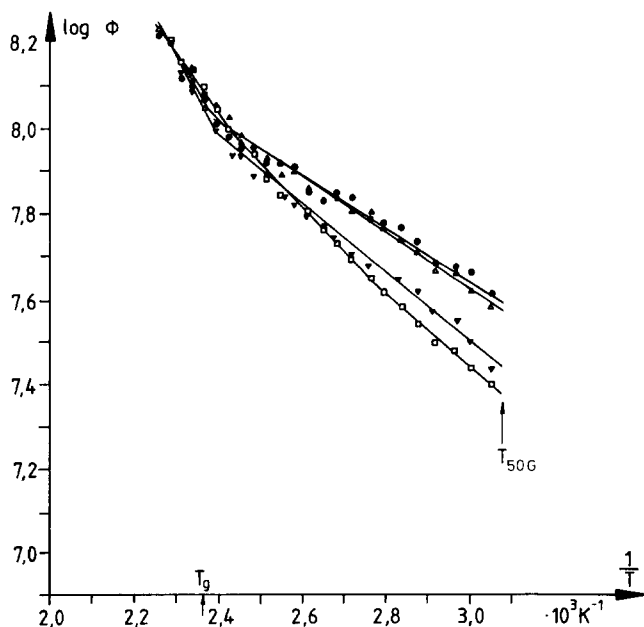No such simple direct analysis is possible outside the rapid rotation range. The spectra can, however, be



**Figure 4** Arrhenius plot of rotational correlation frequencies of the probe TEMPO in polycarbonate for various thermomechanical histories. ●, Isotropic, unaged; ▼, isotropic, aged (12 days, 125°C); △, anisotropic, unaged; □, anisotropic, aged (12 days, 60°C)
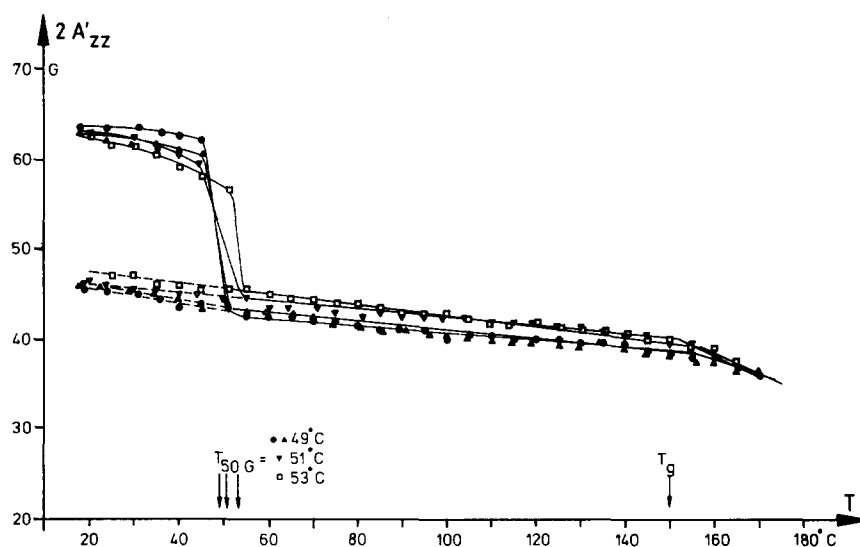
**Figure 5** Temperature dependence of the spectral parameter $2A_{zz}$ for the PC–TEMPO system for various thermomechanical histories. Symbols as for *Figure 4*

analysed to yield another piece of information on dynamic properties. An increase of the rotational correlation time gives rise to a very strong increase in the width of the spectra and the separation becomes most sensitive to changes in the correlation time in the range of 50 G where the transition from the rapid to the slow motion regime takes place. The temperature $T_{50G}$ has thus been used as a characteristic dynamic transition temperature, which in turn depends on the volume of the probe used. *Figure 5* displays the dependence of the width of the separation of the extrema of the spectra, $2A_{zz}$, on the temperature. The strong variation of the width in a narrow temperature range around 50°C is apparent. $T_{50G}$ is thus about 50°C in this particular case. If we assume that such a rapid rotation of the probe can only take place if the size of the free-volume entity in which the probe is located is larger than the probe volume, we have to conclude that the free volume may become larger than $170 \, \text{Å}^3$ due to volume fluctuations (which corresponds to the probe volume) at temperatures above $T_{50G}$. This is a rather large value in view of data published in the literature, for instance, based on positron annihilation studies, which gave values of less than $100 \, \text{Å}^3$ for polycarbonate in the temperature range considered here[16]. This aspect will be reconsidered below.

*Effect of ageing.* In the following we will be concerned with the effect of ageing in oriented and isotropic polycarbonate on the rotational frequency in the rapid rotation range and on the location of the transition between the rapid rotation and the slow rotation regime. The results are displayed in *Figures 4* and *5* together with those observed for the unaged isotropic samples, which have already been discussed above.

It is apparent from the activation diagram that the rotational frequencies of all kinds of samples become identical above the glass transition temperature. This is of course reasonable since both ageing effects and orientation effects relax in this temperature range so that the dynamic state of all kinds of samples should become identical.

Strong differences are, however, apparent below the glass transition temperature. The rotational frequencies

are much higher in the unaged samples in comparison to the aged samples, whereas the mobility differences between isotropic and oriented samples is small. Ageing leads, however, to a much stronger decrease of the rotational frequencies as far as the oriented samples are concerned. The rotational frequencies are much smaller in the latter case even if the ageing time was shorter and the ageing temperature was lower in comparison to the ageing parameters characteristic of the isotropic phase. These results show definitely that ageing is enhanced in oriented samples.

The shift of the characteristic temperatures $T_{50G}$, on the other hand, which is observed for aged samples and particularly for oriented and aged samples, is rather small, amounting to less than 5 K. It thus seems that the characteristic temperature is not a very sensitive tool as far as the detection of mobility changes occurring during ageing is concerned.

Finally, the specific shapes of the spectra and their variation with ageing have to be discussed. The spectra are expected to consist of three lines, as discussed earlier, and this is also what is approximately observed at elevated temperature in the motionally narrowed regime. The finding is, however, that the spectra display additional features reminiscent of composite spectra, particularly at temperatures close to but below $T_{50G}$. This becomes apparent from *Figure 6*, which displays the spectra in this temperature range for both isotropic and anisotropic samples. An additional shoulder is apparent on the high-field side of the spectra.

Such composite structures have been described in the literature for amorphous polymers in the melt and in the glassy state[23,24] and it was shown that they do not originate from anisotropic tumbling motions but rather from a rotational correlation time distribution, which in turn can be attributed to a corresponding distribution of the free volume in the matrix. A schematic diagram representing this situation is depicted in *Figure 7*. Those motions possessing correlation times shorter than that connected with $T_{50G}$ give rise to a motionally narrowed contribution and the remaining ones to the broad ones. It is for this reason that one only expects two components of the spectra, despite the presence of a broad relaxation
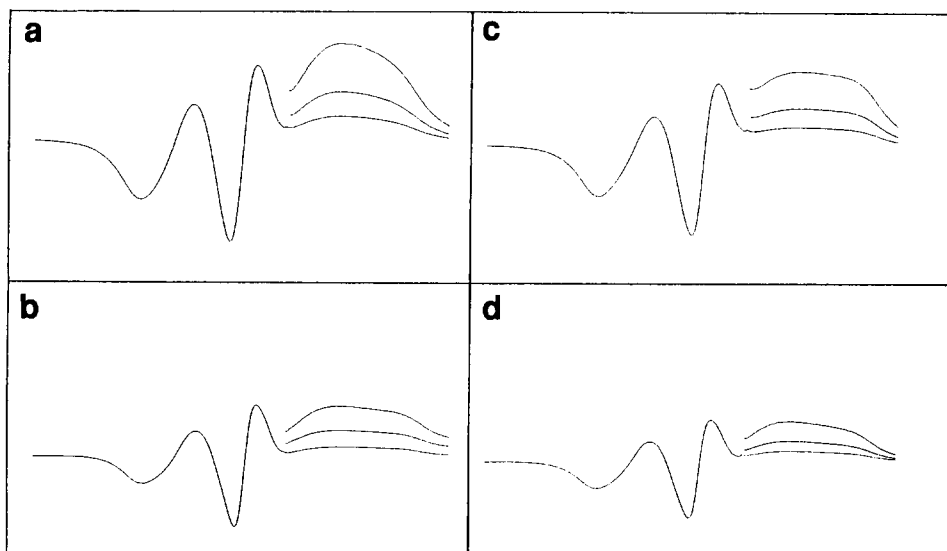
**Figure 6** E.s.r. spectra of the PC–TEMPO system for various thermomechanical histories: (a) isotropic unaged; (b) isotropic aged; (c) anisotropic unaged; and (d) anisotropic aged samples
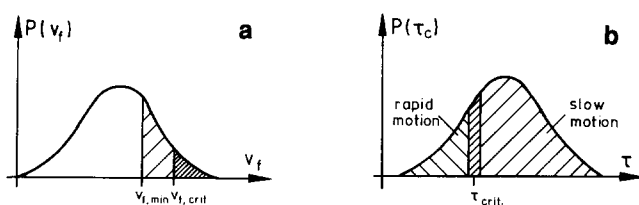


**Figure 7** (a) Scheme of free-volume distribution in an amorphous polymer. Hatched area is the region accessible to the spin probe. (b) A scheme of the correlation time distribution concept in a polymer–probe system, according to ref. 24

time distribution, and one component at high temperatures, where all motions are rapid relative to the timescale given by $T_{50G}$.

*Figure 6* gives a comparison of the composite spectra of isotropic and anisotropic samples and it also shows the variations to which the shapes of the spectra taken below $T_{50G}$ are subjected due to ageing. It seems that the anisotropic samples possess a smaller amount of probes, which are able to rotate rapidly compared to the isotropic samples. This is a rather surprising result in view of the fact that drawing was found to increase the rate of the volume relaxation, which seems to indicate that drawing leads to an increase of the free volume.

Furthermore, the findings show that the shoulder resulting from the motionally narrowed component becomes smaller and even vanishes with increasing ageing time. The reason apparently is, as depicted schematically in *Figure 7*, that the timescale of the total rotational correlation time distribution is shifted to larger values, so that less and less contributions originate from rapid rotations of the probes.

Next we will briefly discuss the correlation between probe rotation and the relaxations taking place in the polymer matrix. The fact that the motional narrowing takes place in a temperature region where the $\beta'$-relaxation of polycarbonate is known to take place may be taken as an indication of such a correlation. *Figure 8* displays a relaxation map of mechanical and dielectric relaxation frequencies of molecular motions in isotropic polycarbonate together with the correlation frequencies
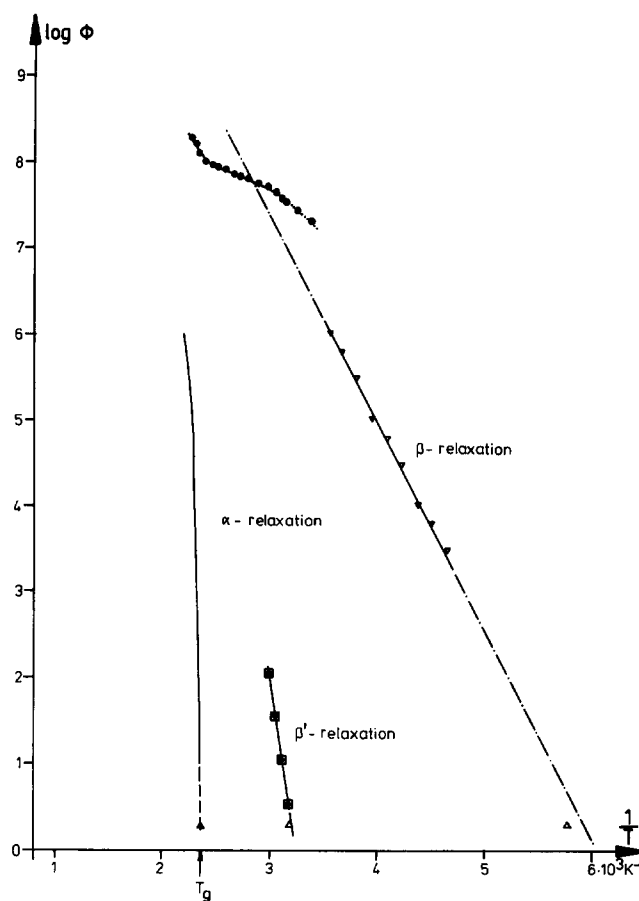


**Figure 8** Arrhenius diagram of rotational correlation frequencies of the probe TEMPO and mechanical and dielectric frequencies of molecular motions in polycarbonate. ●, ESR measurement; ▽, dielectric measurement of the $\beta$-relaxation (ref. 22); △, dynamic mechanical measurement of the $\beta,\beta'$ and $\alpha$-relaxation; □, dynamic mechanical measurement of the $\beta'$-relaxation (ref. 26); ——, dynamic mechanical and dielectric measurement of the $\alpha$-relaxation (ref. 27)

of the probe TEMPO in this polymer. By comparison it is evident that there is no direct frequency correlation between the motion of probes and the motion of kinetic units of macromolecules in the region between $T_{50G}$ and

$T_g$. This leads to the conclusion that in the glassy state of polycarbonate the probes are moving like independent kinetic entities in a given free-volume environment depending on the thermomechanical history and that their motion is only indirectly influenced by molecular mobility of the chains through the structural reorganization of the environment of probes in the polymer matrix.

### Results on density (volume) fluctuations

Finally, we intend to study the distribution of the free volume in polycarbonate and its variation during drawing and ageing. Information of the width of the free-volume distributions is available from studies on density fluctuations. The absolute small-angle X-ray intensity in the small-angle regime is directly proportional to the mean-square value of the particle density (or volume) fluctuation[13-15]:

$$I(s)/I_0 \sim \delta\bar{N}^2/\bar{N}$$

for $s = 0$; $I_0$ is primary beam intensity. *Figure 9* represents results on the mean-square value of unaged isotropic and drawn samples. The finding is that the fluctuations increase due to drawing. This increase is stable at room temperature but tends to relax at increased temperatures relatively rapidly[15]. The stable value that is approached corresponds exactly to the one characteristic of the isotropic state. Thus, the interpretation in terms of packing density and its fluctuations is that the width of the free-volume distribution is increased by the drawing and decreased by annealing. This contrasts to the case of isotropic samples, where no definite correlation between ageing effects on the absolute volume and on the absolute magnitude of the density fluctuations was observed[13].

### CONCLUSIONS

Drawing quite obviously leads to an enhancement of ageing, as is apparent from both the increased rate of volume relaxation and the more rapid decrease of the probe mobility in the polycarbonate matrix, as found by e.s.r. spectroscopic studies. Based on the free-volume concept, the conclusion is that the amount of free volume increases due to drawing, despite the fact that drawing leads to an increase of the average density. In addition, the X-ray data reveal that the width of the distribution is increased on drawing and decreases again on ageing.
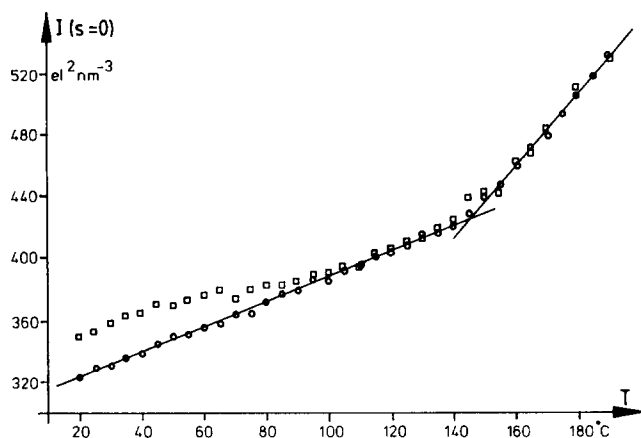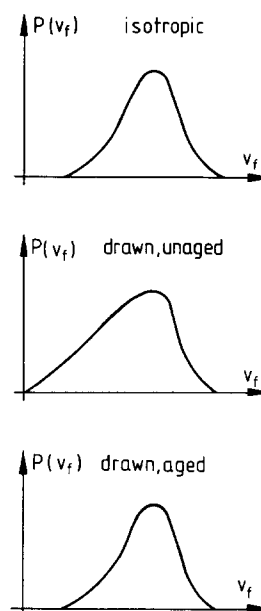


**Figure 10** Scheme of free-volume distribution in drawn, unaged and drawn, aged polycarbonate, as suggested by e.s.r., X-ray and dilatometric results

The e.s.r. data, on the other hand, indicate that the concentration of those probe molecules that are able to rotate rapidly at room temperature is reduced due to drawing, which does not seem to fit the interpretations given above. If one assumes, however, that the probe molecules have a tendency to be located in large free-volume entities (see values on the probe volume and the average free-volume size given above), one can reconcile all the results by assuming that drawing leads to additional free-volume entities on the small-scale side of the distribution, as shown schematically in *Figure 10*. This will increase the width of the distribution as well as the average magnitude of the free volume without contributing on the large-scale side. This might also explain why the relaxation of the width happens rapidly even at low temperatures as well as why the enhanced ageing is limited to temperatures well below $T_g$: smaller entities relax first. Finally, these model considerations may explain why the final width of the free-volume distributions observed for the drawn samples agrees with the one of the undrawn sample: only the additionally induced (by drawing) free-volume entities relax.

Finally, the question has to be considered whether the increased free volume and the changes in the distribution of the free volume couple to macroscopic properties of the samples. As an example, we will consider the mechanical shear modulus $G'$ and the loss coefficient tan $\delta$. They are shown in *Figure 11* for cold-drawn unaged and aged samples (12 days, 60°C) as a function of temperature. One observes, in addition to the strong $\beta$-relaxation at about $-90°C$, a shoulder for tan $\delta$ in a temperature region of $\sim 50°C$ in the case of the unaged cold-drawn samples, which is absent in undrawn samples.

Within the framework of the free-volume concept, this shoulder can be attributed to an increase in the total amount of free volume caused by the mechanical deformation process leading to an enhanced molecular mobility. Physical ageing causes changes in $G'$ and a significant drop of tan $\delta$ in this temperature region due to the relaxation of primarily those additional free-
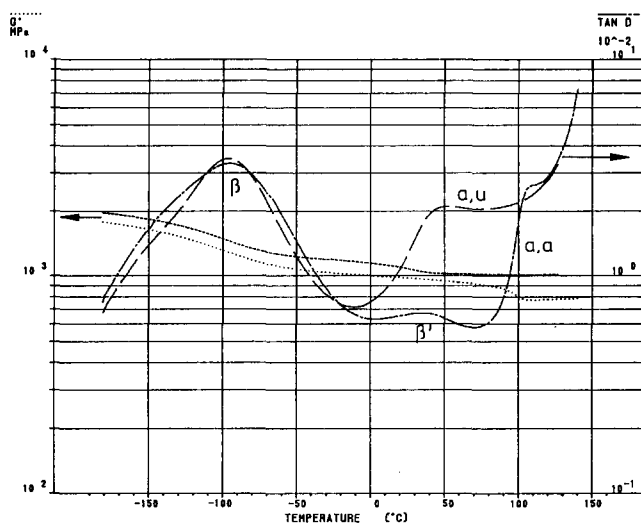


**Figure 9** Results on thermal density fluctuations of unaged isotropic and drawn polycarbonate. $\bigcirc$, PC isotropic; $\square$, PC cold drawn

**Figure 11** Shear moduli $G'$ and tan $\delta$ of cold-drawn unaged (– –) and aged (12 days, 60°C) (—·—) PC as a function of temperature

volume entities which were caused by the deformation process.

Another interesting topic is the correlation between the $\beta'$-relaxation occurring at about 40°C for isotropic and anisotropic unaged as well as for aged samples and the characteristic temperature $T_{50G}$ obtained from e.s.r. measurements. It seems possible that the molecular motions responsible for the $\beta'$-relaxation lead to changes in the amorphous polymer matrix in such a way that the mobility of the spin probes is drastically enhanced from the slow rotating regime to that of fast probe rotation. Based on the finding of different activation energies of the $\beta'$-relaxation and the spin probe jumping rates (cf. *Figure 8*), one has to conclude that the probes are more sensitive to the structural rather than to the dynamic properties of their environment.

## ACKNOWLEDGEMENTS

J.B. would like to express his gratitude to the Alexander von Humboldt Foundation for the opportunity to carry out this research. We gratefully acknowledge the financial support of the Deutsche Forschungsgemeinschaft (DFG).

## REFERENCES

1   Struik, L. C. E. 'Physical Aging in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978
2   Kovacs, A. J. C., Hutchinson, J. M. and Aklonis, J. J. in 'The Structure of Noncrystalline Materials', (Ed. P. H. Gaskel), Taylor and Francis, London, 1977
3   Kovacs, A. J., Hutchinson, J. M., Aklonis, J. J. and Ramos, A. R. *J. Polym. Sci.* 1979, **17**, 1097
4   Ngai, K. L. and Wright, G. B. (Eds.) 'Relaxations in Complex Systems', Naval Research Lab., Washington, 1985
5   Cohen, M. H. and Turnbull, D. *J. Chem. Phys.* 1959, **31**, 1164
6   Robertson, R. E. *J. Polym. Sci., Polym. Symp.* 1978, **63**, 173
7   Kovacs, A. J. *Fortschr. Hochpolym. Forsch.* 1963, **3**, 394
8   Pixa, R., Grisoni, B. and Froelich, D. *Polym. Bull.* 1986, **16**, 381
9   Petrie, S. E. B. *J. Polym. Sci. (A-2)* 1972, **10**, 1255
10  Berens, A. R. and Hodge, I. A. *Macromolecules* 1982, **15**, 756; Kung, T. M. and Li, J. C. M. *J. Mater. Sci.* 1987, **22**, 3620
11  Ricco, T. and Smith, T. L. *Polymer* 1985, **26**, 1979; Smith, T. L., Ricco, T., Levita, G. and Moonan, W. K. *Plast. Rubber Proc. Appl.* 1986, **6**, 81
12  Matsuoka, S., Williams, G., Johnson, G. E., Anderson, E. W. and Furukawa, T. *Macromolecules* 1985, **18**, 2652
13  Wendorff, J. H. *J. Polym. Sci., Polym. Lett. Edn.* 1979, **17**, 765
14  Curro, J. J. and Roe, R. J. *Polymer* 1984, **25**, 1424
15  Müller, J. and Wendorff, J. H. *J. Polym. Sci., Polym. Lett. Edn.* 1988, **26**, 421
16  Malhortra, B. D. and Pethrick, R. A. *Eur. Polym. J.* 1983, **19**, 457; *Polymer* 1983, **24**, 165
17  Lamarre, L. and Sung, C. S. P. *Macromolecules* 1983, **16**, 1729
18  Yu, W. Ch., Sung, Ch. S. P. and Robertson, R. E. *Macromolecules* 1988, **21**, 355
19  Victor, J. G. and Torkelson, J. M. *Macromolecules* 1987, **20**, 2241; 1988, **21**, 3490
20  Tsay, F. D., Hong, S. D., Moacanin, J. and Gupta, A. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 763
21  Moore, R. S., Oloane, J. K. and Shearer, J. C. *Polym. Eng. Sci.* 1981, **21**, 903; Joss, B. L., Bretzlaff, R. S. and Wool, R. P. *Polym. Eng. Sci.* 1984, **24**, 1130
22  Müller, J. Thesis, Deutsches Kunststoff-Institut, Darmstadt, 1989
23  Törmälä, P. *J. Macromol. Sci.–Rev. (C)* 1979, **17**(2), 297
24  Cameron, G. G., Miles, I. S. and Bullock, A. *Br. Polym. J.* 1987, **19**, 129
25  Freed, J. H. and Fraenkel, G. K. *J. Chem. Phys.* 1964, **40**, 1815
26  Stahl, D. Diplomawork, Institut für Physikalische Chemie, Mainz, 1971
27  McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, London, 1967