# On the mechanical $\gamma$-relaxation modes of polycarbonate

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*(Received 10 December 1990; revised 21 February 1991; accepted 20 March 1991)*

The secondary ($\gamma$) relaxation modes of the polycarbonate of bisphenol A (PC) in the glassy state are discussed. Dynamic mechanical spectra of PC, its mixtures with plasticizers and oligomers, its blends with tetramethyl polycarbonate, as well as spectra of modified polycarbonates and of PC under stress are shown. The evidence suggests that the motions active in glassy PC are intramolecularly cooperative torsional 'local-mode' motions of backbone segments with about 5–7 monomer units. Cooperativity can be reduced or enhanced; it is controlled by the tightness of the matrix. Intermolecularly the motions are not cooperative.

**(Keywords: polycarbonate; secondary relaxations; dynamic mechanical spectroscopy)**

## INTRODUCTION

Polymer glasses are usually not totally immobilized. Mechanical relaxation spectroscopy has shown that most polymers have secondary relaxation modes in the glassy state[1]. Some of these modes are undoubtedly due to well defined molecular group motions[2,3], i.e. to changes of conformation in specific chemical groups. Other relaxation modes are not easy or are impossible to tie to group motions, simply because some polymers lack appropriate groups. In these cases, in essence, two types of motion mechanism involving backbone segments were taken into consideration.

The first type, crankshaft motions[4] (*Figure 1a*), involves cooperative rotations about two backbone bonds, which lead to *cis–trans* or anti-*gauche* conformation transitions. Undoubtedly, these processes occur in the cooperative $\alpha$-relaxation modes of polymers. It is not clear whether they also occur in glassy polymers.

The second type, local-mode motions[5,6] (*Figure 1b*), are much less elaborate. They involve oscillations of moderate amplitude in the backbone, which are damped by the surrounding matrix. Their molecular mechanism is not well known so far. Also, little is known about the cooperativity these motions may have.

*Figure 2a* shows the best example of a relaxation peak due to group motions, that of PCHMA (polycyclohexylmethacrylate)[7,8]. Its origin is known to be the transition from one of the chair conformations of the cyclohexyl ring to the other. This motion is virtually independent of the surrounding matrix. It has the same activation energy in both solid PCHMA and in liquid cyclohexane and the relaxation peak is the same in mixtures of PCHMA and in copolymers of CHMA[7–9].

*Figure 2b* shows perhaps the best example of a relaxation peak that is hard to explain with group motions, the $\gamma$-peak of PC (polycarbonate of bisphenol A)[9–11]. This paper deals with the characterization of the molecular motions causing this peak. Not much was known about the likelihood of the various conceivable motion mechanisms in glassy PC before polymers could be studied by solid-state n.m.r. spectroscopy. An analysis of PC by $^2$H-n.m.r. spectroscopy in reference 9 led to the picture sketched in *Figure 2b*. Mobility of, and in, the monomer units of PC in the glassy state proved to be surprisingly restricted[12,13].

Motions of the crank-shaft type[14] could practically be ruled out. Only two group motions were found. The methyl groups rotate at a rate higher than the frequency of the $\gamma$-relaxation modes. The phenyl rings flip over at just that frequency. The latter coincidence strongly suggests a relation between the ring flips and the mechanical relaxations. However, the rings rotate on average by $\pi$, which transfers them on average to the conformations they had before. Such phenyl motions should be, like the methyl rotations, of no mechanical consequence. In addition to the group motions, backbone wriggling motions were detected as perturbations of the phenyl flips. These by their very nature are ill-defined, so wriggling motions of the local-mode type are still under investigation.

The question remained which motions were important mechanically. Further information came from mechanical relaxation spectroscopy and from small angle X-ray scattering[9].

The motions in glassy PC are not intermolecularly cooperative, as is demonstrated in *Figure 3*. In homogeneous blends of PC and its tetramethyl derivative TMPC, which has the $\gamma$-relaxation peak at much higher

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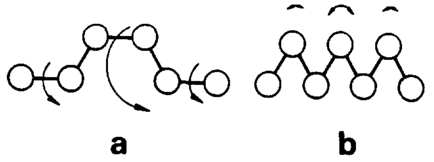

**Figure 1** (a) Crankshaft; (b) local-mode motion

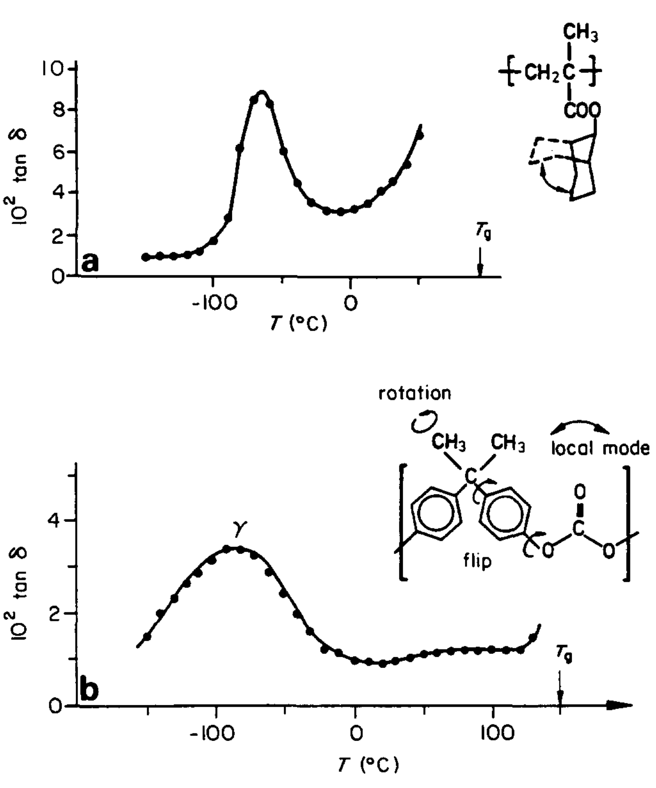

**Figure 2** Relaxation spectra of: (a) PCHMA; (b) PC (from reference 9)

temperatures[11], there is no merging of the two γ-peaks. In the blends both are found in position, with an intensity proportional to the blend composition $c_{TMPC}$. The patterns in *Figure 3* do not even indicate that the blends are homogeneous.

The γ-relaxation modes are sensitive to matrix effects. Organic plasticizers suppress the γ-peak of PC, as is seen in *Figure 4*[15–17]. The additives lower the level of density fluctuations in the glassy matrix[9], thus taking away the space for secondary motions. Group motions like those in PCHMA, in contrast, are not sensitive to such changes in the matrix packing[9].

Below, an attempt is made to characterize the mechanically active secondary motion modes of PC. This seems worthwhile inasmuch as there is statistical evidence that motions like those in PC favour ductile failure, while group motions as in PCHMA leave the polymer brittle. Dynamic spectra of glassy PC and of a number of appropriately modified systems are presented. The mechanism, the intramolecular cooperativity and the matrix sensitivity of the motions are considered.

## EXPERIMENTAL

### *Polymers*

PC ($M_w$ = 29000), TMPC ($M_w$ = 25000, formula in *Figure 3*) and oligomers of PC (formulae in *Figure 9*) were obtained from Bayer AG. The polycarbonate of bisphenol C (PCC, $M_w$ = 24000, formula in *Figure 8b*) was made as described in reference 18, and the alternating copolymer P(C–alt–TMC) ($M_w$ = 34000, formula in *Figure 7*) as described in reference 19.

The polycarbonate of 3,3′-dihydroxy-5,5′-dimethylbiphenyl (BiPC, $M_w$ = 40000, formula in *Figure 6*) was prepared by phase transfer polycondensation with phosgene[20]. The synthesis of the diol is shown in *Figure 5*.

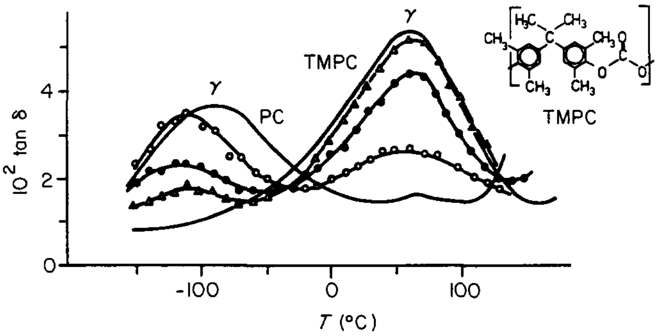

**Figure 3** Relaxation spectra of blends PC–TMPC with $c_{TMPC}$ (g g$^{-1}$) = 0.2 (○); 0.5 (●); 0.8 (△) (from reference 9)

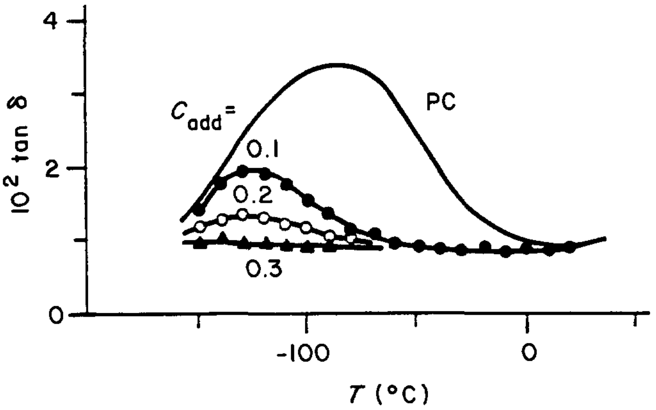

**Figure 4** Relaxation spectra of mixtures of PC with the plasticizer pentachlorobiphenyl (from reference 9)

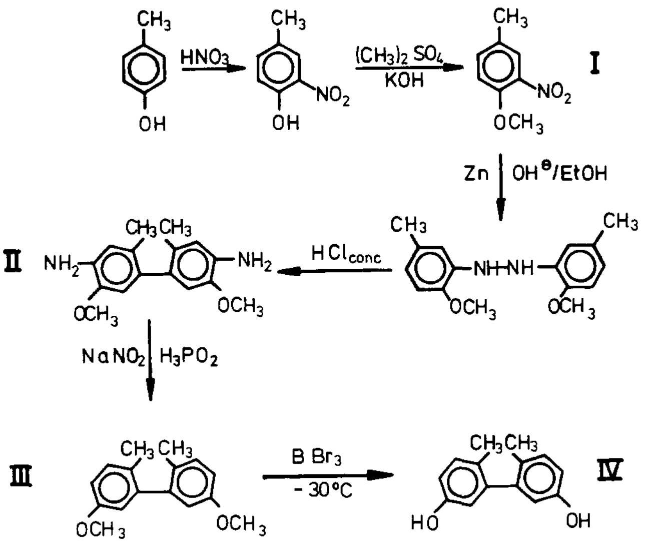

**Figure 5** Monomer synthesis of the polycarbonate BiPC

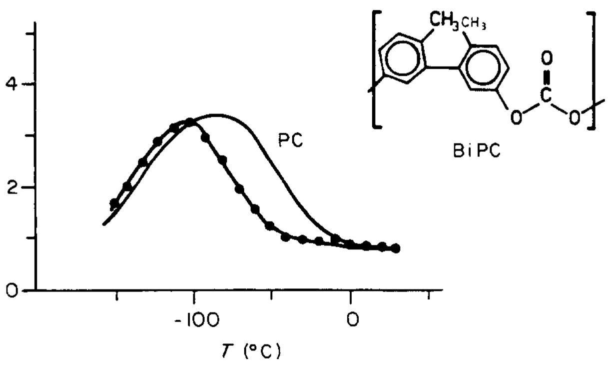

**Figure 6** Relaxation spectra of PC and BiPC (●)

*Product II.* To a solution of I (120 g) and NaOH (140 g) in ethanol (750 ml), zinc powder (80 g) was added at 80°C in portions. The solution was then diluted with ethanol[21] and cooled to 0°C, where ice-cooled concentrated hydrochloric acid[21] was added. A precipitate of the hydrochloride of II formed, which was separated after 12 h at 0°C and dissolved in water[21], from which II was precipitated in 39% yield (m.p. 155°C) by adding NaOH solution.

*Product III.* II was refluxed in dilute hydrochloric acid (500 ml). After 2 min, the solution was cooled to 0°C, and an aqueous solution of $NaNO_2$ (75 ml, 30%) was added. After 30 min an aqueous solution of $H_3PO_2$ (1.21, 30%) was added, which led to $N_2$ evolution. After 15 h at 5°C and 2 h at room temperature, a precipitate of III was separated and dried in ether, together with extracts from the aqueous phase. III was obtained by distillation *in vacuo* in 58% yield (m.p. 56°C from acetic acid).

*Product IV.* A solution of III (10 g) in $CH_2Cl_2$ (100 ml) was added at −30°C in portions to a solution of $BBr_3$ (30 g) in $CH_2Cl_2$ (100 ml) and left to stand at −30°C. After 5 h, the temperature was raised to 5°C, after another 10 h, to room temperature. After a further 2 h, the solution was poured onto ice water and stirred at pH = 5 (adjusted with dilute $Na_2CO_3$ solution) for 2 h. After phase separation, extraction with ether and drying IV was obtained in 96% yield (m.p. 233°C from $CHCl_3$).

### *Dynamic mechanical measurements*

Films 100 μm thick were cast from $CH_2Cl_2$ solution and dried in a temperature programme finishing above the glass transition temperature $T_g$. Samples 4 mm × 20 mm were cut and analysed in a set-up measuring the response to oscillating tension. The dynamic mechanical spectra in *Figures 2–4* and *Figures 6–9* refer to a frequency of 10 Hz.

For the experiments of *Figure 10*, moulded PC samples 200 μm thick were used, after annealing above $T_g$. The response to linear oscillations in tension, superposed on a constant non-linear tension $\sigma$, was measured. The non-linear tension was initially applied in a step-like manner. The linear oscillation measurements were repeated after different times $t_\sigma$ under $\sigma$. The responses to the creep induced by $\sigma$ and to the linear stress oscillations were separated by pass filters.

## MECHANICAL RELAXATION SPECTRA

### *Motion mechanism*

The only group motions possibly causing the γ-peak of PC, the phenyl flips, could not be simply declared mechanically inactive. It is known that different ring substitution shifts the γ-peak considerably (e.g. the dimethyl substitution in TMPC, *Figure 3*)[11]. This proves that some motions of the rings are mechanically active, but not necessarily the flips.

This point was studied with the polycarbonate BiPC seen in *Figure 6*. Phenyl rings can only flip if built into the backbone at the *para* positions, so that the two anchoring bonds are colinear, as in PC. In BiPC the biphenyl ring is built such that these bonds are in the *meta* positions. BiPC looks in its actual conformations very much like PC, but phenyl rotations are impossible.

*Figure 6* proves now that this does not change much. The γ-peak is only slightly reduced at higher temperatures (see below). The conclusion is that the phenyl rings participate in the mechanically active motions of PC not primarily by flipping. The flips are rather an indicator than a cause of the γ-relaxation modes. This seems to leave only local-mode motions to explain the γ-peak.

### *Intramolecular cooperativity*

The γ-relaxation modes of PC and TMPC are not intermolecularly cooperative (*Figure 3*), which leaves the question of intramolecular cooperativity.

The alternating copolymer P(C–alt–TMC) seen in *Figure 7* has approximately the same intermolecular contacts between monomer units C and TMC as a blend PC–TMPC with $c_{TMPC} = 0.5$ g g$^{-1}$ (*Figure 3*), but it has, in addition, also intramolecular contacts between these units. As is shown by *Figure 7*, the copolymer and the blend clearly behave differently. Both spectra have a two-peak structure, but the peaks of the copolymer overlap strongly.

Had the copolymer spectrum shown two peaks, at the positions they have in the blend spectrum, this would have indicated motions of the units C and TMC without any cooperativity. Had it shown only one peak, in the centre, this would have indicated long-ranged cooperativity along the chains. The copolymer spectrum as it is, with its two overlapping peaks, indicates that each motion process has its *centre* on a particular

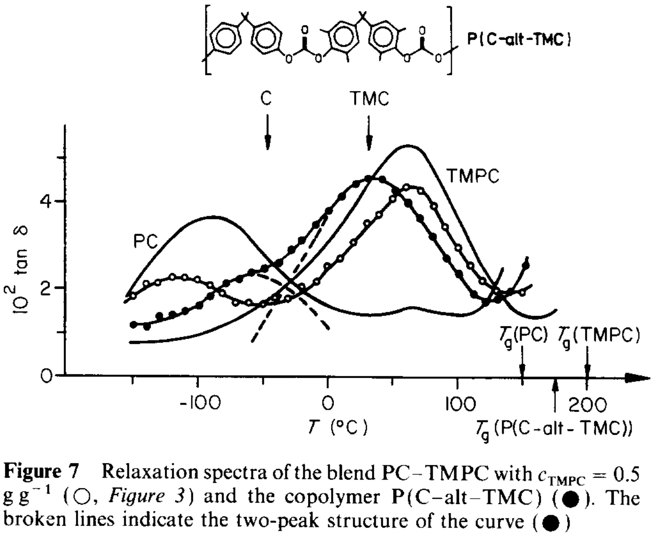

**Figure 7** Relaxation spectra of the blend PC–TMPC with $c_{TMPC} = 0.5$ g g$^{-1}$ (○, *Figure 3*) and the copolymer P(C–alt–TMC) (●). The broken lines indicate the two-peak structure of the curve (●)

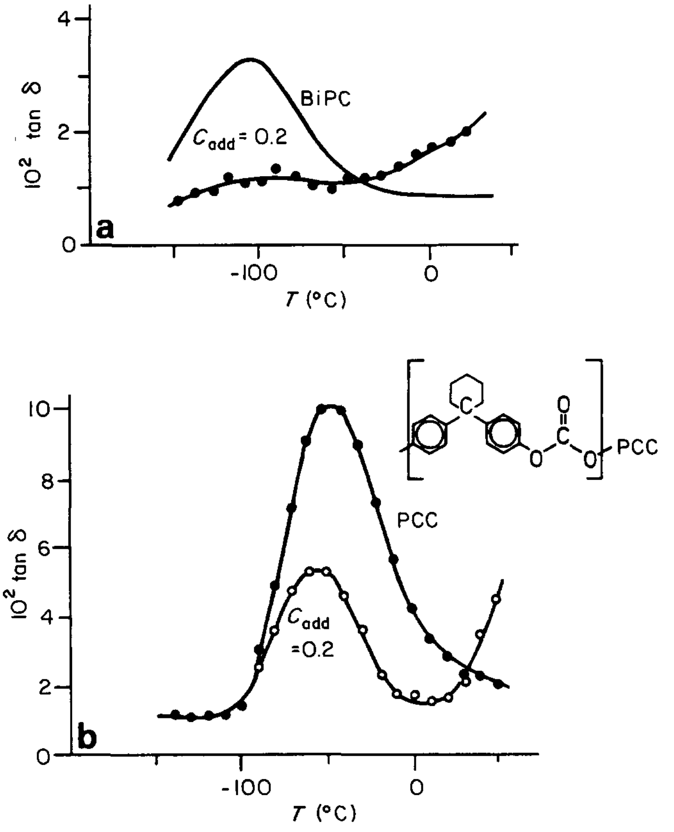

**Figure 8** Relaxation spectra of the polycarbonates: (a) BiPC (*Figure 6*); (b) PCC; and of their mixtures with the plasticizer pentachlorobiphenyl with $c_{add}$ (g $g^{-1}$)

monomer unit C or TMC, but involves, about this centre, a short-chain segment of perhaps 5–7 units.

In an investigation of multiblock copolymers of C and TMC, Jho and Yee[19] arrived at similar conclusions. Their spectrum of P(C–alt–TMC) looks much like ours in *Figure 7*, but is believed by the authors to exhibit only one peak. The shoulder 'C' in our spectrum appeared, however, consistently, so that the two-peak structure indicated in *Figure 7* by 'C' and 'TMC' seems justified. Jho and Yee found that a multiblock copolymer with nine units per block already has a spectrum similar to that of the blend PC–TMPC in *Figure 7*, which supports our estimate of 5–7 cooperative monomer units.

### *Sensitivity to matrix structure*

The picture so far is that, in glassy PC, short-chain segments wriggle about in damped oscillatory motions. These would, of course, turn into strongly inter- and intramolecularly cooperative α-relaxation modes of the backbone, involving crankshaft motions, if it were not for the rigid glassy matrix. Character and cooperativity of the secondary motions must thus be controlled by the structure of the 'cages' formed by the matrix around the wriggling segments.

The effect of a change of matrix structure is clearly seen in *Figure 4*. Small-angle X-ray scattering indicates that density fluctuations are subdued in mixtures of PC and plasticizer, so that the matrix cages are tighter than in PC itself. Consequently, PC segments less often have the space to move, and the γ-peak is suppressed. This suppression has been observed in many different mixtures of PC with organic additives. *Figure 8a* shows that it is also found with BiPC (*Figure 6*). *Figure 8b* shows the same for a polycarbonate with a cyclohexyl group, but suppression is not complete. A residual peak remains (not γ!), which is due to chair–chair inversions in the cyclohexyl ring, as in PCHMA (*Figure 2a*). These are *never* suppressed.

Other than mixtures with plasticizers, the blends PC–TMPC in *Figure 3* do not show peak suppression. The polymeric 'additive' TMPC does not affect the matrix like additives with small molecules.

*Figure 9* shows what happens in mixtures of PC with its own oligomers. It has been demonstrated by Pochan *et al.*[21] that these short 'homologues' of PC have already, to a degree, γ-relaxation modes. Therefore, not surprisingly, *Figure 9* shows incomplete suppression of the γ-peak.

Motions in the dimer DC1 cannot, since the molecule is too short, be as cooperative as those in PC chains. Of interest is that the γ-peak is reduced at the high-temperature side in *Figure 9*. It seems that more cooperative motions appear in the γ-peak of PC at higher temperatures. In other terms this means, quite reasonably, that the frequency of the motions depends inversely on cooperativity. This interpretation has consequences for *Figure 4*, which shows, like many other spectra in the literature, that the γ-peak of PC is suppressed by plasticizers also predominantly at the high-temperature side. Motions are obviously stopped in order of cooperativity, owing to a tightening of the matrix packing.

The question arises about whether the opposite to suppression, an activation of the γ-peak, is also observed. Indeed, this occurs in PC under non-linear stress, as is shown in *Figure 10a*. When PC is subjected to a constant non-linear stress ($\sigma$ = 300 kg $cm^{-2}$ is approximately half the yield stress), relaxation intensity is enhanced. At later times under stress, the effect fades away again. Effects of non-linear stress have been discussed by Struik[22] in terms of free volume increase and decrease, which accelerates and decelerates the α-relaxation modes of polymer glasses. *Figure 10a*, as well as data by Litt and Thorp[23], support the view that, rather than the frequency of the α-relaxation modes, the intensity of the secondary modes is affected by stress.

The increase of relaxation activity in *Figure 10a* occurs at relatively high temperatures. The motions activated

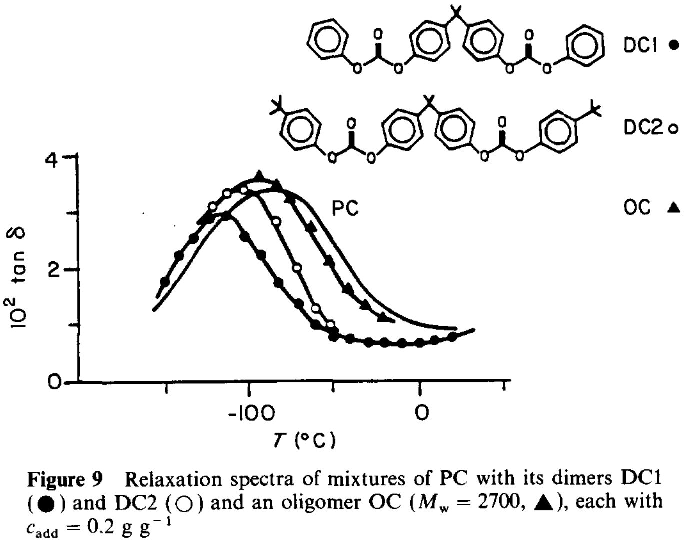

**Figure 9** Relaxation spectra of mixtures of PC with its dimers DC1 (●) and DC2 (○) and an oligomer OC ($M_w$ = 2700, ▲), each with $c_{add}$ = 0.2 g $g^{-1}$

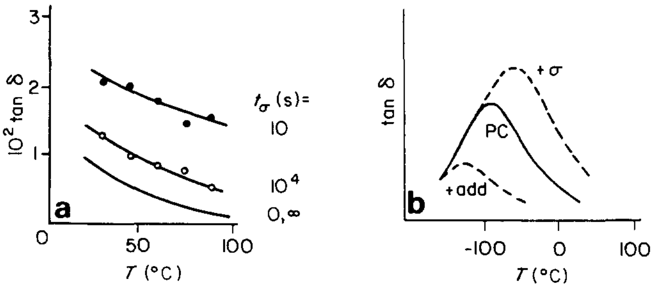

**Figure 10** (a) Part of the relaxation spectrum of PC after different times $t_\sigma$ under the constant stress $\sigma = 300\,\mathrm{kg\,cm^{-1}}$; (b) schematic relaxation spectra of PC and a mixture with an additive, both not under stress, and of PC under a non-linear stress $\sigma$

should be particularly cooperative $\gamma$-modes. Non-linear stress seems thus to have an effect opposite to that of plasticizers, as is sketched in *Figure 10b*.

## SUMMARY

The dynamic mechanical spectra in this study lead, together with other spectra in the literature and the evidence from solid-state n.m.r. spectroscopy and small-angle X-ray scattering, to the following still preliminary picture of those motions in glassy PC that cause the $\gamma$-relaxation peak.

(1) Particular group motions of the conformation exchange or the crankshaft type are not important. The mechanically active motions should, therefore, be 'local-mode' motions, i.e. damped backbone oscillations.
(2) These motions are not intermolecularly, but intramolecularly cooperative. The moving chain segments have on average 5–7 monomer units.
(3) Cooperativity is a function of the matrix packing. It is reduced in mixtures of PC with plasticizers, which form particularly tightly packed glasses, and it is enhanced in PC under stress.

PC is among the most ductile polymers. It is known that plasticizers, which suppress the $\gamma$-peak, also embrittle PC. The above point (3) therefore invites a speculative conclusion. The conditions for ductile behaviour may be that a polymer has secondary relaxation modes *and* that these modes are further activated by non-linear stress.

## ACKNOWLEDGEMENT

Financial support from the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

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