

# Effect of dissolved small molecules on the mechanical relaxation behavior of polycarbonate

I. Böhm, H.G. Brion\*, R. Kirchheim

*Institut für Materialphysik, Universität Göttingen, Hospitalstraße 3-7, 37073 Göttingen, Germany*

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## Abstract

After sorption of gas molecules (CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>) in polycarbonate, a new damping peak appears and the intrinsic  $\gamma$ -relaxation is depressed. The new peak increases in intensity and shifts to lower temperature with increasing gas concentration. This relaxation could be attributed to jumps of the gas molecules inside the polymer matrix similar to the Snoek relaxation of carbon in  $\alpha$ -iron. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Mechanical spectroscopy; Snoek relaxation; Glassy polymers

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## 1. Introduction

The relaxation behavior of polycarbonates has often been studied by mechanical spectroscopy [1,2] to get information about the dynamics of the macromolecules. Three relaxation peaks at temperatures  $T_\alpha > T_\beta > T_\gamma$  were observed. The  $\alpha$ -peak at 423 K corresponds to the glass transition, whereas the interpretation of the  $\beta$ - and  $\gamma$ -peaks remains an unsolved problem. Yee and Smith [1] associate the  $\gamma$ -peak with the motion of a whole monomer unit, whereas Varadarajan and Boyer [2] suggest a superposition of three relaxations corresponding to phenylene, phenylene-carbonate and carbonate motions resulting in one bright  $\gamma$ -peak.

In this study we focus our attention on the influence of small molecules on the relaxation behavior of polymers. Analogous to the behavior of carbon atoms in  $\alpha$ -iron [3] and hydrogen atoms in metallic glasses [4,5], one would expect an additional contribution to the loss modulus caused by jumps of the molecules inside the polymer matrix. Observations of Illers [6] in polyamide support these considerations, because he found that the  $\beta$ -peak in the loss modulus of polyamide depends on the amount of water inside the polymer matrix. The peak increased with increasing water concentration. Moreover, Fried et al. [7] performed measurements of the loss modulus of polycarbonate which was conditioned at 30 atm CO<sub>2</sub> and observed the appearance of three damping peaks in the regime of the  $\gamma$ -peak in

polycarbonate. They interpreted this observation as a support of the theory of Varadarajan and Boyer [2] about the  $\gamma$ -peak, but the cause of one of the three damping peaks could as well be jumps of CO<sub>2</sub> molecules.

## 2. Experimental

Measurements of the shear modulus were made with a torsion pendulum inside a vacuum chamber, where the samples could be exposed to gas pressures up to 1 bar. The oscillation of the pendulum was measured by a system consisting of a frequency-modulated laser, a mirror and a position sensitive detector (PSD). Because of the modulated laser system the PSD can be used in illuminated rooms. The pendulum worked at a frequency of about 0.7 Hz and could be cooled down to 133 K by liquid nitrogen. The samples were bisphenol-A polycarbonate (BPA-PC) purchased as foils of 0.25 mm thickness from Goodfellow Ltd, and cut into pieces of 100 × 10 mm.

Before the measurement, the chamber with the pendulum is evacuated and then filled up to a certain CO<sub>2</sub> or C<sub>2</sub>H<sub>4</sub> pressure at a temperature of 308 K. Samples were exposed 24 h to the gas, in order to reach equilibrium. From measurements of sorption isotherms [8] and known diffusion coefficients [9,10] the attainment of equilibrium can be calculated. After 24 h, the chamber is evacuated to a pressure of about 10 mbar and the sample area is cooled down immediately. After this treatment, where a negligible gas desorption occurs, the shear modulus is measured as a function of temperature.

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\* Corresponding author. Tel.: +49-551-39-5010; fax: +49-551-39-5012.  
E-mail address: gbrion@umpa06.gwdg.de (H.G. Brion).

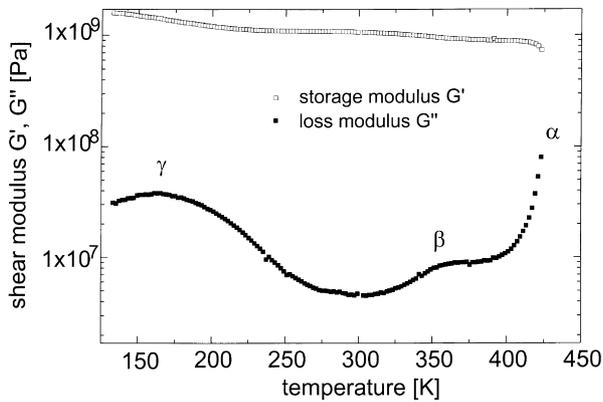


Fig. 1. Storage and loss modulus of the shear modulus of BPA-PC without sorbed molecules.

For high gas concentrations of CO<sub>2</sub>, some foils were also loaded with gas in a separate chamber where sorption pressures of 30 bar could be realized. These samples were quickly mounted into the pendulum after the gas sorption and cooled down immediately, in order to avoid losses of dissolved gas molecules. Again an estimation of possible out gassing by diffusion showed that the corresponding losses of CO<sub>2</sub> were negligible.

The complex shear modulus  $G^*$  which is needed to describe the anelastic behavior of polymers in Hooke's law

$$\tau = G^*(T, c)\gamma = [G'(T, c) + iG''(T, c)]\gamma \quad (1)$$

can be calculated from the logarithmic decrement  $\Lambda$  and the pendulum frequency  $\omega$  as described by Illers and Breuer [11]:

$$\text{storage modulus } G' = a \frac{I}{F} \omega^2 \quad (2)$$

$$\text{loss modulus } G'' = a I \omega^2 \frac{\Lambda}{\pi} \quad (3)$$

where  $a = 3l(bd^3(1 - 0.63d/b))$  for rectangular samples with  $b/d > 3$  (width  $b$ , thickness  $d$ , length  $l$ ),  $F = \omega^2 / (\omega^2 - \omega_{\text{App}}^2)$  for low damping of the apparatus (frequency of

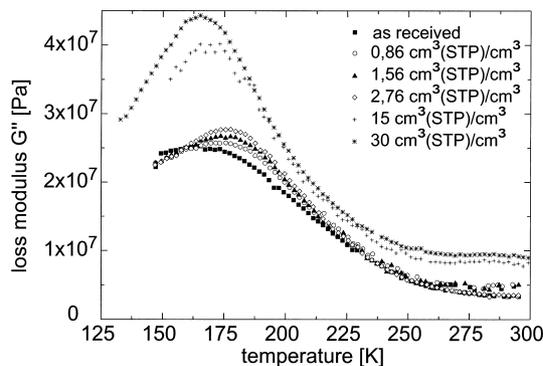


Fig. 2. Loss modulus of BPA-PC with sorbed CO<sub>2</sub> molecules. The samples with 15 and 30 cm<sup>3</sup> (STP)/cm<sup>3</sup> CO<sub>2</sub> were loaded in an external chamber.

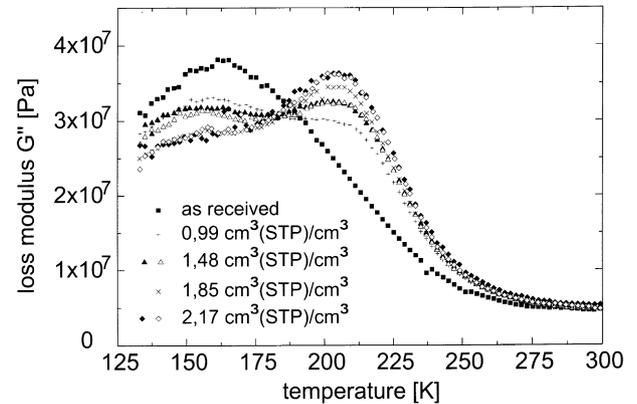


Fig. 3. Loss modulus of BPA-PC with sorbed C<sub>2</sub>H<sub>4</sub> molecules.

pendulum without sample  $\omega_{\text{App}}$ ) and  $I$  is the momentum of inertia of the pendulum.

### 3. Results

The measured shear modulus of BPA-PC without sorbed gas is shown in Fig. 1. The  $\alpha$ -,  $\beta$ - and  $\gamma$ -relaxations were observed in agreement with previous measurements [1,2]. Differences in the absolute values of the loss modulus as seen in Figs. 2 and 3 in the “as-received” measurements arise, if the samples series were taken from different foils or cut in different directions.

Sorption of CO<sub>2</sub> molecules in BPA-PC leads to changes in the loss modulus in the neighborhood of the  $\gamma$ -peak (Fig. 2). At low concentrations, the  $\gamma$ -peak seems to shift first of all to higher temperatures and then with increasing concentration of gas molecules to lower temperatures. The intensity of the damping peak also increases with the concentration. This behavior can be interpreted in different ways. The CO<sub>2</sub> molecules affect the  $\gamma$ -relaxation directly or a new damping peak nearby caused by stress induced jumps of the gas molecules inside the polymer matrix is

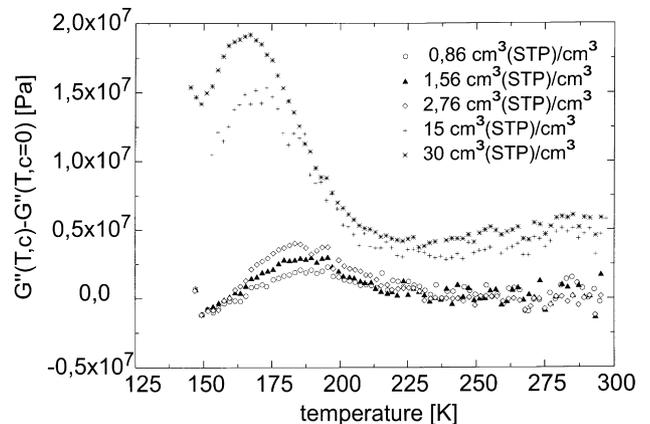


Fig. 4. Difference of the loss modulus of BPA-PC with and without CO<sub>2</sub> molecules as a function of temperature.

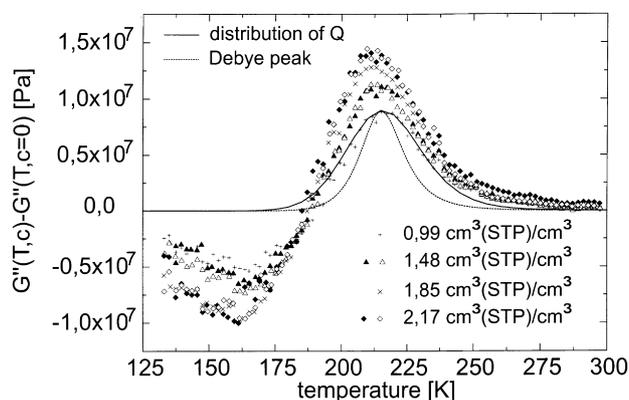


Fig. 5. Same as Fig. 4 but for  $C_2H_4$  molecules. The width of a Debye peak (see Eqs. (4) and (6)) with  $Q = 52.5$  kJ mol and  $\tau_0 = 2.2 \times 10^{-3}$  s plotted as dashed line is smaller than the one of the measured peak. In addition a peak with a Gaussian distribution of  $Q$  is plotted as a solid line (cf. text).

superimposed on the  $\gamma$ -peak. The results for sorbed ethylene molecules are less ambiguous. In these measurements (see Fig. 3) a new damping peak (Snoek peak) appears at low ethylene concentrations in the loss modulus and can clearly be separated from the  $\gamma$  relaxation. With increasing ethylene concentrations this peak increases whereas the  $\gamma$ -peak decreases. In the  $CO_2$  measurements this effect cannot be seen because  $\gamma$ - and Snoek peaks overlap.

By subtracting the loss modulus of the “as-received” sample, the results presented in Figs. 4 and 5 were obtained. For both molecules,  $CO_2$  and  $C_2H_4$ , the Snoek peak temperature shifts to lower values with increasing concentration (corresponding to a decrease of the average activation energy, see Fig. 6). This behavior is the same as observed for H atoms in metallic glasses [4,5]. The maximum values of the Snoek peak are proportional to the gas concentration (see Fig. 7).

## 4. Discussion

### 4.1. Dependence on concentration

#### 4.1.1. Activation energy

The decrease of the peak temperature of the new damping peak with increasing gas concentrations in the polymer matrix seems to be reasonable for a Snoek peak. If a distribution of site energies is assumed for gas molecules [12], they have to occupy sites with higher site energy with increasing gas concentration. Thus the average activation energy for jumps represented by the Snoek peak temperature decreases. This behavior was interpreted in the same way as for H atoms in metallic glasses [4].

From the peak temperature, an average activation energy  $Q$  for the jumps of molecules inside the polymer matrix can be estimated. If a single activation energy is assumed, the anelastic theory [3] results in a Debye function for the loss

modulus:

$$G'' = \Delta G \frac{\omega\tau}{1 + (\omega\tau)^2} \quad (4)$$

where  $\tau$  is a characteristic relaxation time.

This function has a maximum at

$$\omega\tau = 1 \quad (5)$$

and the relaxation time  $\tau$  of a thermal activated process follows an Arrhenius law:

$$\tau = \tau_0 \exp \left[ \frac{Q}{RT} \right] \quad (6)$$

Eqs. (5) and (6) lead to:

$$Q = -\ln(\omega\tau_0)RT_{\text{peak}} \quad (7)$$

with  $\tau_0 = h/k_B T_{\text{peak}}$  for a thermally activated process [13] where  $h$  is Planck's constant and  $k_B$  is Boltzmann's constant. The calculated activation energies are shown in Fig. 6. In these calculations one relaxation time is considered, but this is only an approximation compared to the assumption of a site energy distribution which also leads to a distribution of activation energies for the Snoek process. Therefore, the calculated values are average activation energies. The assumption of a distribution of activation energies is supported by the width of the measured Snoek peak (Fig. 5). The width of a Debye peak (Eq. (4)) with a single activation energy is too small in comparison with the measured one.

#### 4.1.2. Relaxation strength of Snoek peak

In addition to the concentration dependence of the peak temperature the dependence of the peak height on concentration supports the interpretation of the new damping peak to be a Snoek peak. In Fig. 7, the loss modulus at the peak temperature is plotted as a function of the  $CO_2$  and  $C_2H_4$  concentration. In order to get the intensity of the loss modulus of the Snoek peak, the intensity of the  $\gamma$ -peak must be subtracted. However, as discussed in Section 4.1.3, the  $\gamma$ -relaxation is reduced with increasing gas

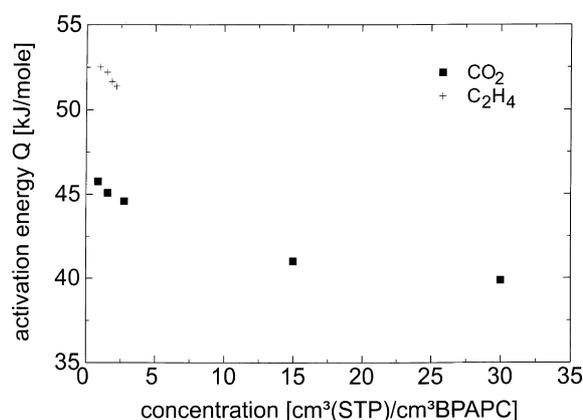


Fig. 6. Calculated average activation energies (Eq. (7)) as a function of the  $CO_2$  and  $C_2H_4$  concentration in BPA-PC.

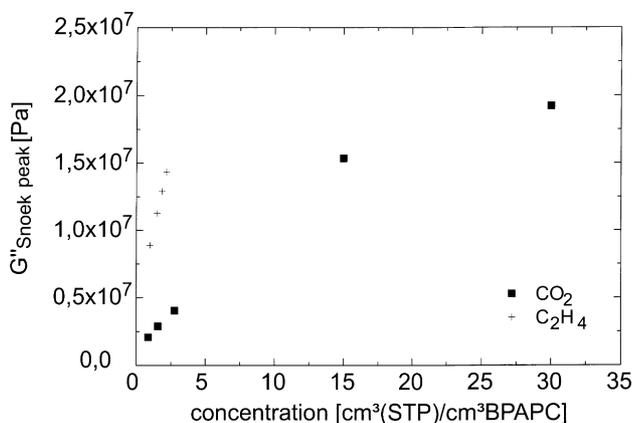


Fig. 7. Loss modulus at the Snoek peak temperature taken from the subtracted plots (Figs. 4 and 5) as a function of the CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> concentration in BPA-PC.

concentration as well. Therefore, the loss modulus of the Snoek peak obtained by subtracting the loss moduli of BPA-PC with and without gas is reduced, especially in the case of CO<sub>2</sub> sorption, where the  $\gamma$ -peak and the Snoek peak could not be separated. Nevertheless, for small concentrations a linear dependence of the peak intensity on the concentration can be seen, which is also observed in the relaxation behavior of carbon in  $\alpha$ -iron [14]. The deviation from this linear behavior at higher concentrations can be explained by a site energy distribution for the molecules inside the polymer matrix [4]. For the carbon atoms in  $\alpha$ -iron, there is only single site energy for the octahedral sites occupied by carbon atoms.

Normally the integral of the loss modulus over the temperature would be a measure of the amount of participating molecules in a relaxation process. However, the shape of the new damping peak normalized to the same maximum heights is independent of concentration, so that the loss modulus at the peak temperature can be used as an indication for the relaxation strength.

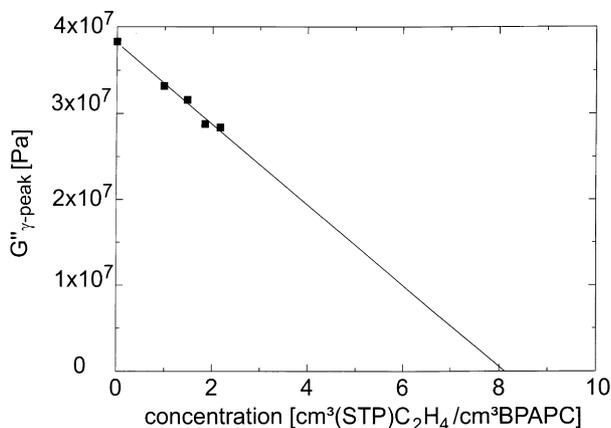


Fig. 8. Loss modulus at the  $\gamma$ -peak temperature as a function of C<sub>2</sub>H<sub>4</sub> concentration in BPA-PC.

#### 4.1.3. Relaxation strength of $\gamma$ -peak

The decrease of the  $\gamma$ -peak intensity with increasing gas concentration can be seen in Fig. 3. This observation is evidence for an interference of the  $\gamma$ -relaxation process with sorbed molecules. If elastic distortion during the incorporation of small molecules into glassy polymers plays an important role [8,9,12], the molecules occupy large sites preferentially. These sites are part of the free volume of the polymer and, if segments involved in the  $\gamma$  process use the same free volume sections for their stress induced reconfiguration, blocking of free volume by small molecules should reduce the  $\gamma$ -peak. If one gas molecule is assumed to hinder one  $\gamma$  segment, the number of segments responsible for the  $\gamma$ -peak can be estimated from the intercept in a plot of  $\gamma$ -peak intensity versus gas concentration. In Fig. 8, the intercept is 8 (cm<sup>3</sup>C<sub>2</sub>H<sub>4</sub>(STP))/(cm<sup>3</sup> BPA-PC).

This yields:

$$\begin{aligned} n_{\gamma\text{-segments}} &= n_{\text{gas molecules}} = 8 \frac{\text{cm}^3 \text{C}_2\text{H}_4}{\text{cm}^3 \text{BPA-PC}} \frac{N_A}{V_{\text{mole}}} \\ &= 2.1 \times 10^{20} \frac{1}{\text{cm}^3 \text{BPA-PC}} \end{aligned} \quad (8)$$

where  $N_A$  is Avogadro's number and  $V_{\text{mole}}$  the molar volume (STP) of an ideal gas. This number of  $\gamma$  segments can be compared to the amount of monomer units in BPA-PC:

$$n_{\text{monomer units}} = \frac{\rho N_A}{m_{\text{mole}}} = 2.8 \times 10^{21} \frac{1}{\text{cm}^3 \text{BPA-PC}} \quad (9)$$

where the density of BPA-PC is  $\rho = 1.2$  (g/(cm<sup>3</sup> BPA-PC)) and the molar mass is  $m_{\text{mole}} = 254$  g/mol BPA-PC monomer units. Compared to the number of monomer units 8% contribute to the  $\gamma$ -process.

#### 4.2. Dependence of activation energy on temperature

As the Snoek relaxation is related to the jump frequency, their activation energy should be the same as the one for long-range diffusion in a crystalline solid. The activation energy for CO<sub>2</sub> jumps in BPA-PC from the mechanical spectra is about  $Q(T = 190 \text{ K}) = 46 \text{ kJ mol}^{-1}$  at small concentrations (Fig. 6), whereas from diffusion measurements  $Q(T = 308 \text{ K})$  is about  $37 \text{ kJ mol}^{-1}$  [15]. This difference can be explained by assuming again a distribution of site energies for the molecules inside the amorphous polymer. With a Gaussian distribution this assumption leads to a temperature dependence of the activation energy for jumps [16]:

$$Q(T) = Q^0 + \frac{\sigma_G^2(T)}{4RT} \quad (10)$$

where  $\sigma_G$  is the width of the site energy distribution, which is proportional to the storage modulus  $G'(T)$  [12]. With  $\sigma_G(T = 308 \text{ K}) = 7.8 \text{ kJ mol}^{-1}$  [8],  $G'(T = 308 \text{ K}) = 3.8 \text{ GPa}$  and  $G'(T = 190 \text{ K}) = 4.7 \text{ GPa}$  (see Fig. 1) the site energy distribution width for 190 K can be calculated

to  $\sigma_G(T = 190 \text{ K}) = 9.6 \text{ kJ mol}^{-1}$  for small  $\text{CO}_2$  concentrations in BPA–PC. This yields with Eq. (10):

$$Q(T = 190 \text{ K}) - Q(T = 308 \text{ K}) = 8.6 \text{ kJ/mol} \quad (11)$$

which is in good agreement with the difference of activation energies obtained from the mechanical spectra and diffusion measurements.

## 5. Conclusion

The appearance of a Snoek peak in BPA–PC was observed in mechanical spectra of BPA–PC with sorbed ethylene for the first time. Changes of peak position and shape with increasing gas concentration support the model of a site energy distribution.

## Acknowledgements

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