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Dielectric measurements on liquid crystalline polymers derived from PETP

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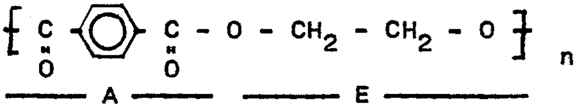
SUMMARY

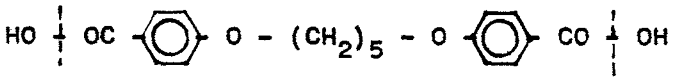
Poly(ethylene terephthalate) PETP has been modified with a difunctional alcohol and acid in the molar relation 1:1. By dielectric relaxation measurements could be shown that the modification increases the segmental mobility (α-process). The local mobility (ß-process) increases at smaller and decreases at higher concentrations of the modificators. A separation of the α-relaxation from the common relaxation process α + ß could be observed with decreasing temperature.

INTRODUCTION

Dielectric measurements are a powerful tool to study local and segmental motions of polymers (1). Such investigations are specially of interest if the respective polymers are systematically modified to improve the mechanical properties. Under this point of view 4-hydroxybenzoic acid segments have been incorporated in poly(ethylene terephthalate) PETP and liquid-crystalline random copolyesters were obtained (2). Hempel at al. (3) proposed a change of both, the di-carboxylic acid A and the difunctional alcohol E in PETP



in order to get more possibilities to vary the chemical composition and to avoid the formation of extended aromatic blocks. Therefore, n-pentane-1,5-diyl-4-oxybenzoic acid



A'

and 1,4-bis(4-acetoxybenzoyloxy)-benzene

E'

were prepared and added in the molar ratio 1:1 (A':E') to PETP. During the transesterification at T = 550 K acetic acid evaporates as indicated by broken lines. The relation between the molar fractions of building units was

$$(PETP)_x \quad A'_{(1-x)/2} \quad E'_{(1-x)/2} \qquad (x \leq 1)$$

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*To whom offprint requests should be sent for which we will use the abbreviation P(x). The melting temperature T_M found by DSC measurements decreases with respect to the T_M of the pure PETP (x = 1) as shown in Table 1.

Table 1. Melting temperatures T_M of the polymers

x	1	0,8	0,7	0,6	0,4	0,2
T_M/K	533	504	491	490	440	488

An anisotropic melt with a nematic character could be detected above T_M for $x \leq 0.8$ by a polarizing microscope. Due to the decomposition of the sample the phase transition into the isotropic melt could not be determined.

EXPERIMENTAL

For the measurements in the frequency range from 1 kHz to 1 GHz two different measurement systems were employed. From 1 kHz to 10 MHz the automatic ac-bridge HP 4192A (Hewlett-Packard) was used. The samples were pressed at about 530 K between two gold-plated stainless-steel condenser plates (Ø 20 mm) to a film of about 50 µm thickness. The distance were controlled by 50 ± 2 µm silica fibers. For the high frequency measurements from 1 MHz to 1 GHz the Hewlett-Packard Impedance Analyzer HP 4191A has been applied. In this case the cell was a part of the inner conductor (diameter 3 mm, distance 50 µm). The whole equipment including the temperature stabilization of ± 0.02 K were fully computer controlled (4). It should be mentioned here that the absolute values of ε'' show a relatively big error due to uncertainties of the cell thickness.

RESULTS AND DISCUSSION

The measurements of the dielectric constant ε' and the loss ε'' were performed after heating the sample above T_M. Then the sample was immediately cooled down to the first measuring temperature.

In Fig. 1 data of ε'' at different frequencies and temperatures of P (0.6) are presented. Whereas at T = 415.05 K (curve 1) the increase of ε'' at low frequencies is due to the conductivity, at a 100 K lower temperature a very broad dielectric absorption range has been observed. This one has been found earlier and interpreted as a β-relaxation process (5-8). Due to the strong broadening of the β-mechanism we have plotted ε'' at constant frequency over a wide temperature range. The respective data of pure PETP are given in Fig. 2. Here at low temperatures the β-mechanism and at higher one an α-mechanism could be observed. The results are in agreement with data given in the literature (6-8). It is also known that the intensity and the relaxation frequency of the α-mechanism depends on the degree of crystallization whereas the β-mechanism is not sensitive to morphologic changes (6). Therefore, we were mainly

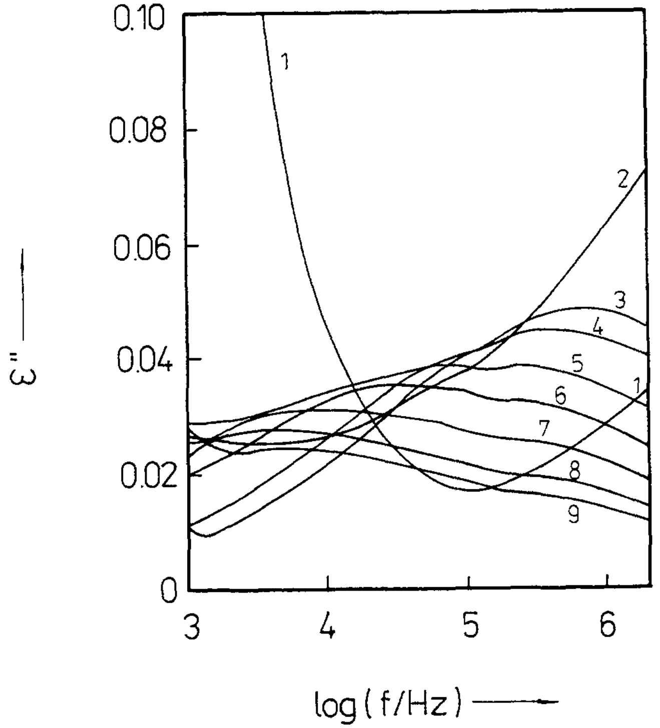

Figure 1: Dielectric absorption curves of P(0.6).
T(1) = 415.05 K, T(2) = 368.66 K, T(3) = 311.01 K,
T(4) = 301.27 K, T(5) = 284.73 K, T(6) = 271.95 K,
T(7) = 257.67 K, T(8) = 243.55 K, T(9) = 234.85 K.

interested in the change of the relaxation frequencies of the ß-mechanism due to the chemical modification because the beginning of crystallization could not be measured parallel to the dielectric data in our experiments.

The respective data of the dielectric loss versus temperature of PETP containing 40 % of modificator are given in Fig. 3. Here the intensity of the α-relaxation is decreased and the half width temperature is increased. This indicates that a higher content of A' and E' changes the energetic positions of the dipoles which are responsible for the α-relaxation. Whether this is an effect of a partial crystallization or of the variation of the PETP structure can not decided from these data.

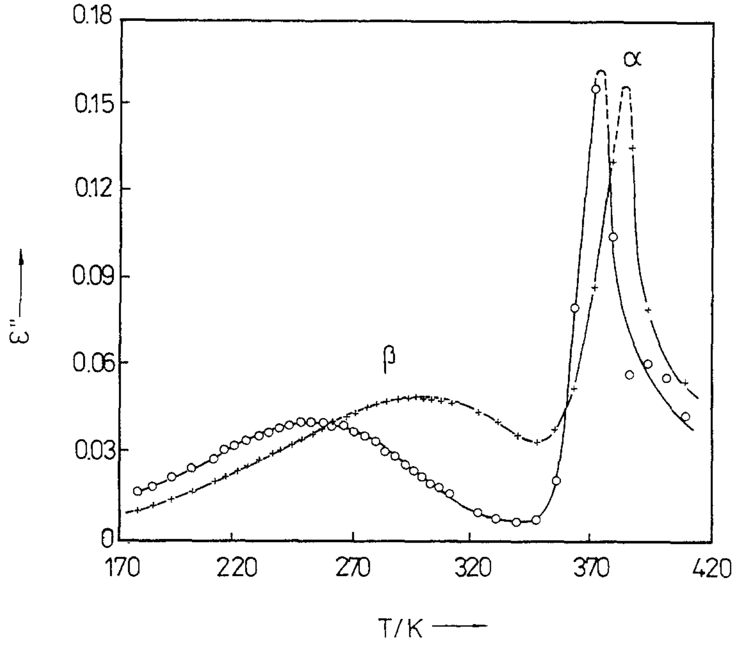

Figure 2: Dielectric absorption of PETP as function of the temperature. o: f = 1.78 kHz, +: f = 100 kHz.

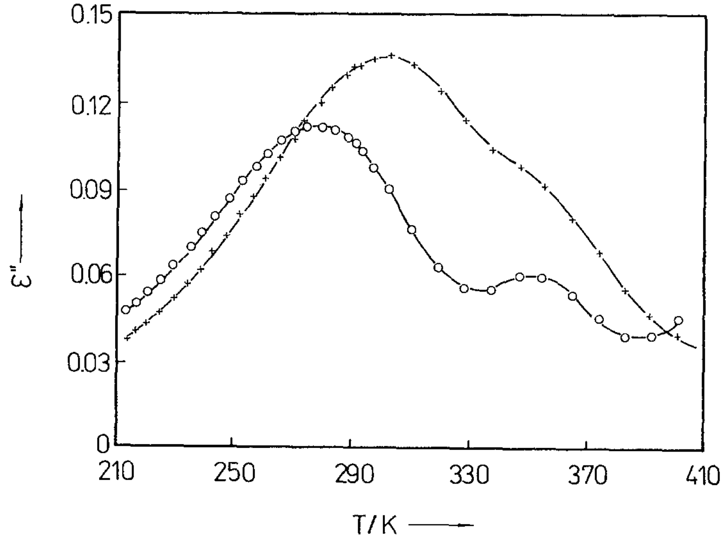

Figure 3: Dielectric absorption of P(0.6) at f = 31.6 kHz (o) and f = 0.1 MHz (+).

At high frequencies only one dielectric dispersion range could be detected. For the pure PETP the maximum of the absorption curve is outside of the experimental temperature range whereas for P (0.6) a maximum was found (Fig. 4).

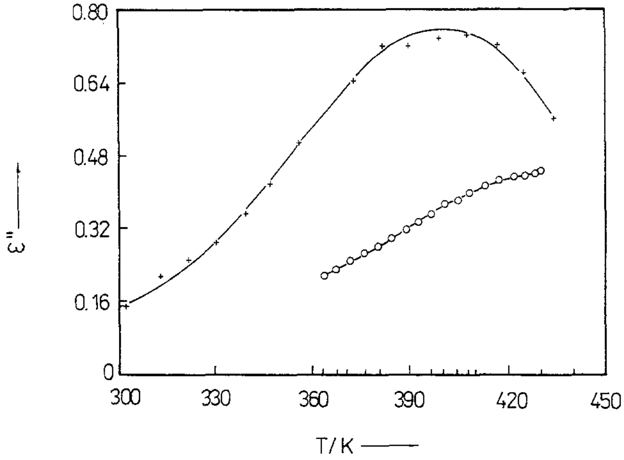

Figure 4: Dielectric loss of PETP (o) and P (0.6) (+) at 0.1 GHz.

For other samples we could also observe only one dielectric absorption peak at $f > 1$ MHz. There are no experimental hints for a cross over of the α and ß relaxation. Such an effect should be quite improbable because a local motion (ß-process) should be always faster than a segmental one. The mutual influence of both mechanisms can be seen in the summarized relaxation frequencies in Fig. 5.

For the discussion two points are of interest:
(i) How the α and ß mechanisms form only one complex relaxation process at higher temperatures (frequencies) and
(ii) how the chemical modification influences the dynamics.

To give answer to the first question the dielectric loss of P (0.2) is plotted in Fig. 6 versus temperature and frequency. Two maxima can clearly be seen at low temperatures and frequencies respectively. The α-mechanism separates from the common relaxation process due to the influence of the impending glass transition connected with an increase of the activation energy.

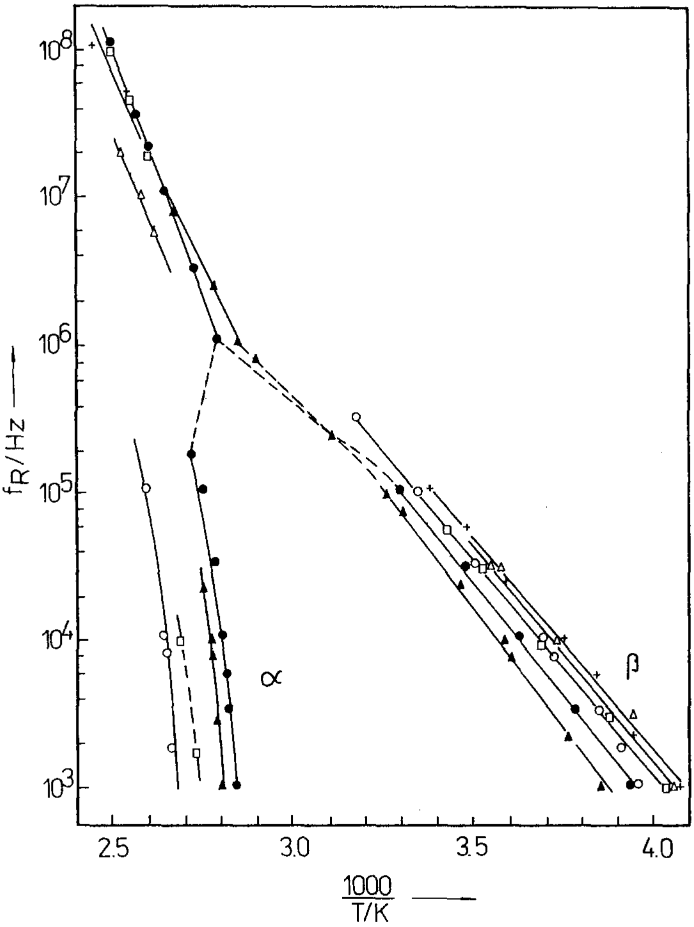

Figure 5: Arrhenius plot of the relaxation frequencies of PETP (o), P (0.8) (+), P (0.7) (Δ), P (0.6) (□), P (0.4) (●) and P (0.2) (▲).

The influence of the concentration of A' and E' on the dynamics of the α and ß relaxation at $f_R = 10^4$ Hz is illustrated in Fig. 7.
For the segmental motion (α-process) only a tendency to a higher mobility due to the modification can be detected. May be that the strong scattering of the experimental points is a result of different degree of crystallization (6). On the other hand the local ß-process which is caused by the reorientation of the -COO- and C-O-C dipoles shows a systematical behaviour: small concentrations of the modificator results in a higher mobility and starting from x < 0.8 to lower values; the motion is more and more hindered. Obviously, the incorporation of the more stiff part E' gives a stronger hindrance for the dielectric reorientation of the dipoles around the para axis of the benzene units.

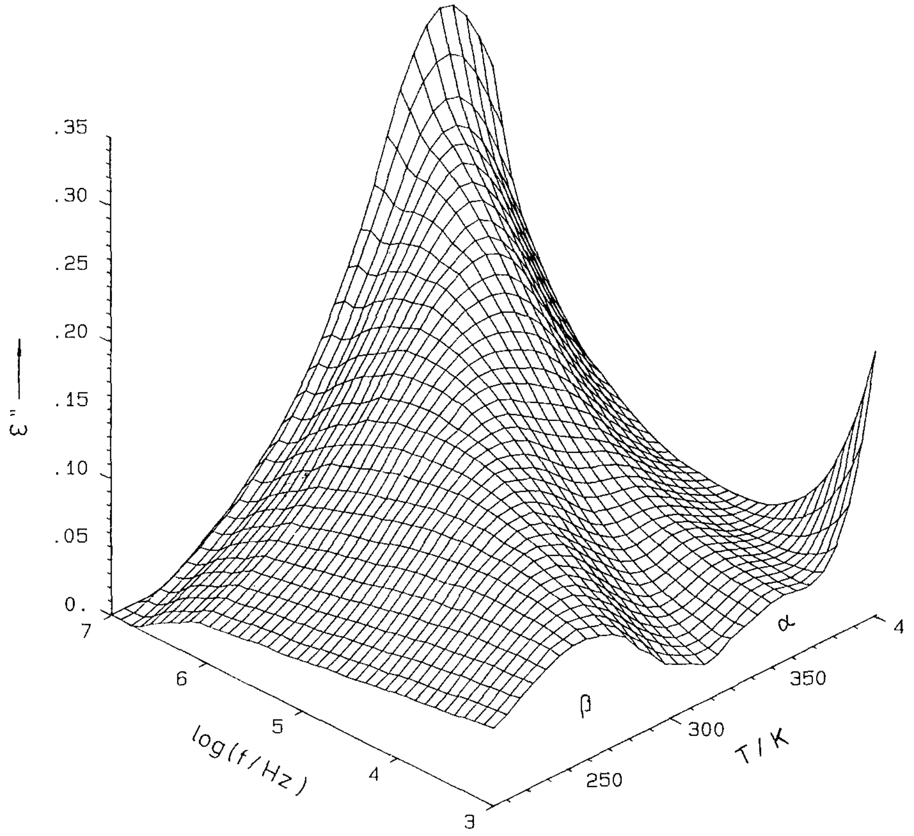

Figure 6: Dielectric loss of P (0.2) as function of frequency and temperature.

The activation energies of the ß-process are not strongly influenced by the modification as demonstrated in Table 2.

Table 2: Activation energies of the ß-process

Polymer	PETP	P(0.8)	P(0.7)	P(0.6)	P(0.4)	P(0.2)
E_A/kJ mol^{-1}	57	55	58	56	59	59

The data are in agreement with measurements from other groups on PETP (5,7) and on mixtures (6,9,10) and show that the chemical variation do not have a strong influence on the local motions. The earlier published E_A-values of P(0.4) (8) are quite more uncertain than the data of Table 2.

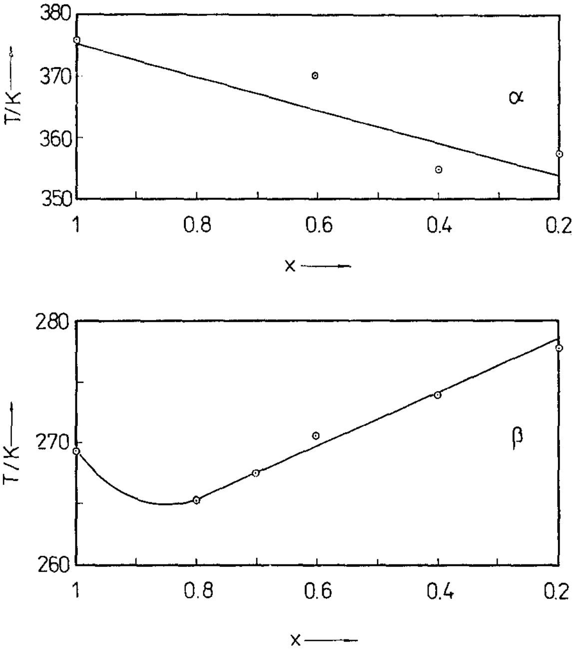

Figure 7: The influence of the modificator concentration x on the temperature of maximal dielectric absorption for f_R = 10 kHz.

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