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Piezobirefringence of PMMA: Optical and mechanical relaxations and influence of temperature

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Several optical and piezo-optical properties of PMMA have been studied and results are now presented. The refractive index shows a small dispersion for wavelengths in the visible region and decreases considerably for temperatures $T > 50°$ C. A similar behaviour is shown by the piezo-optical coefficient. Its dispersion in the visible and near ultraviolet has been analysed in the light of the models proposed by Kuhm and Grümm, and Wemple and Di Domenico. From them the influence of temperature on the molecular polarizability and on the "interband transition", energy splitting has been obtained. Several differences have been found between the optical and the mechanical relaxations. Their temporal dependence seems to obey simple logarithmic laws although they depend on temperature. At temperatures higher than the glass transition temperature T_g, the above picture is seriously modified. A qualitative explanation of this behaviour is tentatively proposed.

1. Introduction

Polymethyl-methacrylate (PMMA) is nowadays a very useful material from an optical point of view. Therefore, a better knowledge of the optical and piezo-optical properties of PMMA is desired.

The mechanical and optical properties of polymers have been extensively studied and detailed reviews have been published [1–5]. Both applied and basic information is available especially on PMMA [6]. We have applied uniaxial mechanical stresses to measure the piezobirefringence (PB) coefficient of PMMA as a function of wavelength and temperature (between room temperature and 90° C). Two alternative theories (Wemple and Di Domenico [7] and Kuhn and Grümm [8,9]) have been used to analyse the results. The refractive index of PMMA has been measured in the visible region between 20 and 70° C. Our results at room temperature show good agreement with those already published [3].

On the other hand, the time dependence of birefringence (optical relaxation) has been studied by using mechanical models and applied to organic [3, 10] and inorganic polymers [11, 12]. We have studied the optical and mechanical relaxations and their time dependence has been analysed by accepting logarithmic kinetics.

2. Experimental details

Samples used throughout this work were prepared by cutting and polishing commercial PMMA sheets. Pieces from different suppliers have been studied and only small differences have been found among them.

To measure the refractive index, an Abbe refractometer from Carl Zeiss was used. Temperatures higher than 20° C were obtained by a controlled hot-water flow through the prisms of the refractometer. With this system the sample temperature remains constant with variations smaller than ± 2° C.

We have used an intensity method [13–15] for measuring the stress-induced birefringence. The

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stress was applied and measured continuously by a Instron (Mod. 1026) machine. The sample chamber was attached to the exit slit of a windowless McPherson 0.3 m monochromator. A Hg discharge source and polaroid filters were used. The detector was a RCA 7200 photomultiplier. Before making the measurements a residual stress annealing was done.

The PB and relaxation measurements were performed in the following way: the PB coefficient (Q) was obtained by measuring the light intensity (I) versus the growing applied stress (σ) (as will be shown in Section 3). Then the strain was kept constant and the optical (δ_0) and mechanical (δ_m) relaxations were measured simultaneously.

Since PB measurements (I/I_0 versus σ) can be affected by the continuous relaxation of the sample, stresses were applied at very high rates (deformation rates $\approx 10^{-3}\,\text{sec}^{-1}$), so that the maximum stress was reached at times $\lesssim 10\,\text{sec}$. On the other hand, the time elapsed between two consecutive measurements was 10 to 15 min.

Different temperatures of the samples were obtained by attaching a cylindrical electrical furnace to the sample chamber. The temperature control was in all cases better than ± 1°C.

3. Formulation of piezobirefringence coefficients

The light intensity recorded as described above, is given by the expression:

$$I = I_0 \cos^2(\sigma/2) \tag{1}$$

where the phase shift, δ, is related to the refractive index through:

$$\delta = \frac{2\pi t}{\lambda}(n_{\parallel} - n_{\perp}) = \frac{\pi t}{\lambda n_0}(\epsilon_{\parallel} - \epsilon_{\perp}) \tag{2}$$

In this formula, $n_{\parallel}$ and $n_{\perp}$ ($\epsilon_{\parallel}$ and $\epsilon_{\perp}$) are the refractive indexes (dielectric constants) of the strained sample in directions parallel and perpendicular to the stress, the other parameters have the usual meaning.

When high strain rates are applied, it is assumed that the phase difference, δ, is linear with the stress, σ. So that we can write:

$$[\epsilon_{\parallel} - \epsilon_{\perp}] = Q\sigma, \tag{3}$$

where Q is the piezo-optical coefficient and σ is defined positive for tensile stresses.

By combining Equations 1 to 3 we obtain:

$$I/I_0 = \cos^2\left[\frac{\pi t}{2\lambda n_0} Q\sigma\right]. \tag{4}$$

From experimental data of I/I_0 versus σ, Q can be obtained.

4. Results and discussion

4.1. Refractive index of PMMA

As far as we know, the influence of temperature on the PMMA refractive index has not yet been published and data are not available in the current literature. The variation of n with λ at room temperature has been reported in [3]. In order to obtain values of Q, it is necessary to know the variation of n with λ and T. The obtained results are shown in Fig. 1. Data from [3] are shown by the dashed line and the symbols represent the experimental points. As expected, a small dispersion appears on changing λ from 650 nm to 400 nm.

The influence of temperature on n is more clearly displayed in the small insert of Fig. 1, where values of n for λ_D (the sodium yellow line) and 450 nm are shown. One sees that n remains practically constant between room temperature and $T \approx 50°$ C. At higher temperatures, n decreases continuously. As will be discussed later, this behaviour may be associated with the proximity of the glass transition temperature of PMMA.

Some relevant microscopic information can be obtained by fitting the experimental points of Fig. 1 with the phenomenological expression proposed by Wemple and Di Domenico [7]. These authors suppose that the refractive index of a very wide group of materials can be written as a Sellmeier oscillator:

$$n^2(\omega) - 1 = \frac{F}{\omega_0^2 - \omega^2} \tag{5}$$

where ω represents photon energies and F the "mean oscillator strength" of "mean interband transition energy" ω_0 giving place to the dispersion of n. The solid lines of Fig. 1 show the fitting of the experimental results by using Equation 5. Values of ω_0 and F obtained from those fittings are displayed in Table I. The dispersion energy, $\omega_d(\omega_d = F/\omega_0)$ is also listed in Table I. This parameter, ω_d, allows for the grouping of different materials according to their electronic

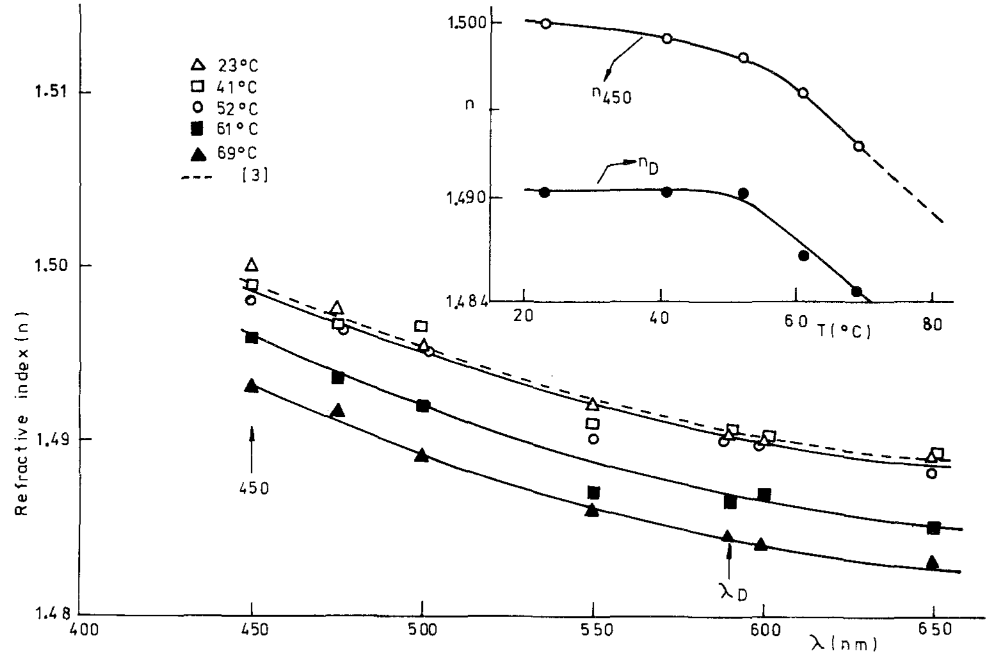

Figure 1 Refractive index of PMMA as a function of λ and *T*. The small inset shows the influence of temperature on n_D and n_{450}.

characteristics [7]. Values of ω_d for amorphous and plastic materials are not known and a classification of these solids is not possible now.

Finally, we must note that whenever necessary, values of n above 70° C and below 450 nm have been obtained by extrapolating the data of Fig. 1.

4.2. Piezobirefringence results

Fig. 2 shows Q as a function of the light wavelength for the temperatures between 20 and 97° C. Data from other authors have not been found in a thorough revision of the current literature. Absolute values of Q from PMMA appear to be higher than those corresponding to other transparent materials like alkali halides [13–15]. This quality makes the PMMA a useful material for photoelastic applications.

The results of Fig. 2 have first been analysed by applying a semi-macroscopic model. The continuous curves of Fig. 2 correspond to the best fitting obtained with the Kuhm and Grünn theory [8, 9] on natural and mechanical stress-induced birefringence. They conclude that the stress-induced birefringence can be written as:

$$\frac{\Delta n}{\sigma} = \frac{\Delta \epsilon}{2n_0\sigma} = \frac{2\pi}{45kT}\frac{(n_0^2+2)^2}{n_0}(a_\parallel - a_\perp) \quad (6)$$

where $a_\parallel$ and $a_\perp$ are the molecular polarizabilities parallel and perpendicular to the stress direction. The other symbols have their usual meanings. The calculated curves resemble quite well the experimental behaviour as shown in Fig. 2.

TABLE I Values of parameters deduced from the fitting of experimental points of Fig. 1

	T (° C)				
	20	41	52	61	69
ω_0 (eV)	12.7	12.7	12.7	12.3	12.6
F (eV)^2	192.9	19.29	192.9	178.7	187.7
ω_d (eV)	15.2	15.2	15.2	14.5	14.8

The differences in the polarizabilities, $\Delta a = a_\parallel - a_\perp$, at different temperatures are collected in the first line of Table II. Higher values of Δa are obtained on increasing temperature. However, the real physical meaning of Δa appears when the values of Table II are referred to the elastic para-

TABLE II Parameters deduced from the fitting of experimental points of Fig. 2 with [8, 9] (Δa) and [7] ($\Delta\omega_0$)

	T (° C)			
	20	52	78	97
$\Delta a \times 10^{15}$ (eV cm^2 dyn^{-1})	6.8	8.8	10.3	12.3
$\Delta\omega_0 \times 10^{13}$ (eV cm^2 dyn^{-1})	2.3	2.6	2.9	3.3

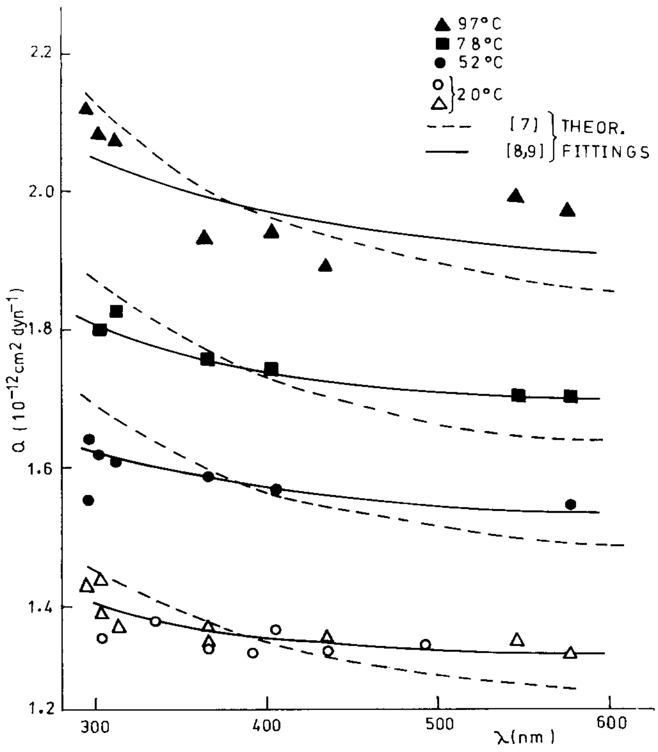

Figure 2 Piezo-optical coefficient, Q of PMMA at different temperatures and wavelengths. The continuous and dashed curves are theoretical fittings according to the models proposed in [7] and [8].

meters of PMMA, which also change with temperature. Values of the elastic constants of PMMA have been indirectly obtained from the stress–strain curves reported by Thierry [16] at strain rates very similar to the ones used in this work. The normalized parameter, $\Delta a/s$, is shown in the upper part of Fig. 3 as a function of temperature. The most striking characteristic of the experimental curve is that $\Delta a/s$ decreases markedly once temperatures higher than ~ 50° C have been reached.

We have tried to obtain a closer view of the microscopic piezo-optical behaviour of PMMA. In this sense, results from Fig. 2 have also been fitted according to the model proposed by Wemple and Di Domenico [7]. This approach to the problem should be considered only tentative, because a knowledge of the electronic properties of PMMA which would support our treatment is lacking. On the other hand, the Wemple and Di Domenico proposals should be particularly correct for wavelengths in the proximity of the absorption edge and these only correspond to a reduced range of our results. From Equation 5 the following relation is obtained:

$$\frac{\Delta\epsilon}{\sigma} = \frac{\epsilon_{\parallel} - \epsilon_{\perp}}{\sigma} = A\left(1 + \frac{2\omega^2}{\omega_0^2}\right) \qquad (7)$$

and constant A is given by:

$$A = -2\frac{\omega_d \Delta\omega_0}{\omega_0^2}. \qquad (8)$$

$\Delta\omega_0$ represents the splitting of the "mean interband-transition energy" per unit stress. By taking values of ω_0 and ω_d from Table I the fittings shown by the dashed curves of Fig. 2 have been obtained and the evolution of $\Delta\omega_0$ with temperature deduced. This is listed in the second line of Table II. $\Delta\omega_0$ also increases markedly with temperature. The normalization of $\Delta\omega_0$ to the elastic constant is shown in the lower part of Fig. 3. Although the fittings from the Wemple and Di Domenico model are not totally satisfactory (see Fig. 2), $\Delta a/s$ and $\Delta\omega_0/s$ behave quite parallel which suggests that the polarizability variations measured in our experiments are closely related to changes in the electronic structure of PMMA. This interpretation is, in fact, in agreement with conclusions obtained in other transparent materials, where the dispersion of the piezo-optical coefficients is attributed to stress-induced modifications of the electronic energy levels [13].

4.3. Optical and mechanical relaxation experiments

We have briefly outlined in Section 2 how measure-

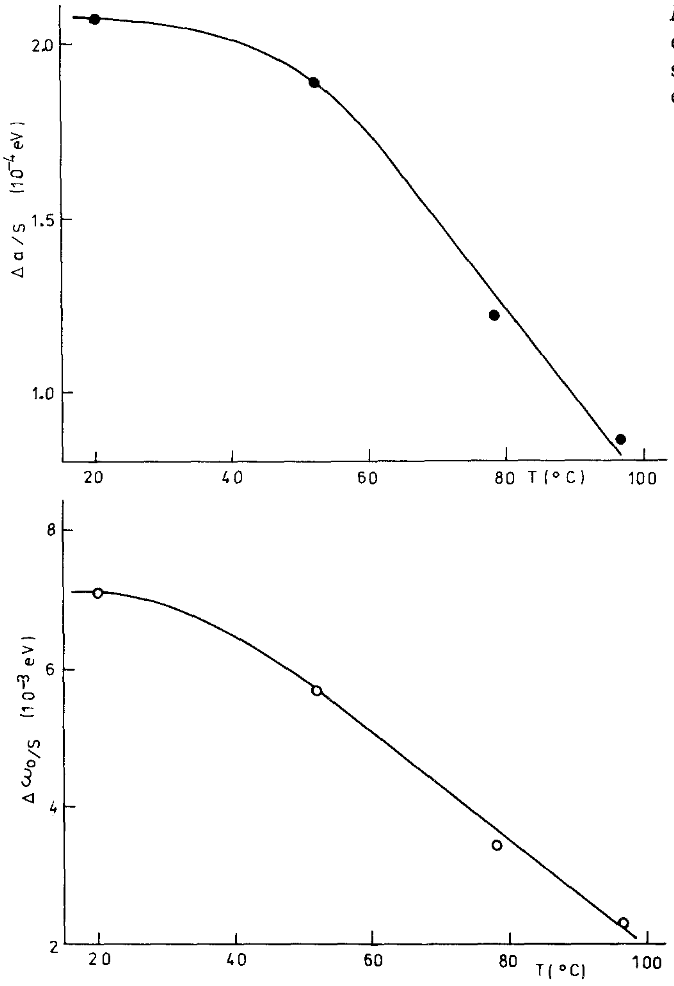

Figure 3 Influence of temperature on the molecular polarizability differences, $\Delta a/s$, and splitting of the "mean interband-transition energy", $\Delta\omega_0/s$. See text.

ments of the optical and mechanical relaxations are made. To make both relaxations comparable, we present the mechanical relaxation (δ_m) in degrees, similar to δ_0, by using Equations 2 and 3. Both parameters, δ_0 and δ_m, have been measured at different temperatures and two wavelengths. One of them ($\lambda = 2964$ Å) is close to the absorption edge of PMMA and the other ($\lambda = 5784$ Å) is far from it. By doing so, we hope that the influence of the electronic structure on the time–relaxation behaviour should be much more marked at the shorter wavelength. All the experimental results given in this section were obtained at approximately the same point of the stress–strain curve.

Results at different temperatures and at the given wavelengths are presented in Fig. 4. We must emphasize here that the mechanical relaxations at both wavelengths are identical, but on passing from σ to δ_m, different values of Q and λ are involved and, therefore, different δ_m are obtained. Both δ_0 and δ_m have different signs along the times studied in our experiments. Which may suggest a strong "optical inertia" of the deformed molecular groups of the large PMMA chains. All these results are in agreement with those published on polyethyl-acrylate [12].

At temperatures higher than T_g, results are much harder to obtain owing to difficulties in handling the samples. Fig. 5 shows a typical result of the relaxation behaviour at $T = 120°$ C and $\lambda = 5784$ Å. Both relaxations are now of the same sign. They vary strongly with time at short time and reach very high absolute values. At $t \gtrsim 100$ sec, the optical relaxation shows a trend to more positive values such as in the behaviour at $T < T_g$.

We have tried to analyse the time–relaxation curves from a kinetic point of view, in order to obtain some characteristics of the processes operating in the samples. A semi-logarithmic plot of the type

$$\delta = A + B \log T \tag{9}$$

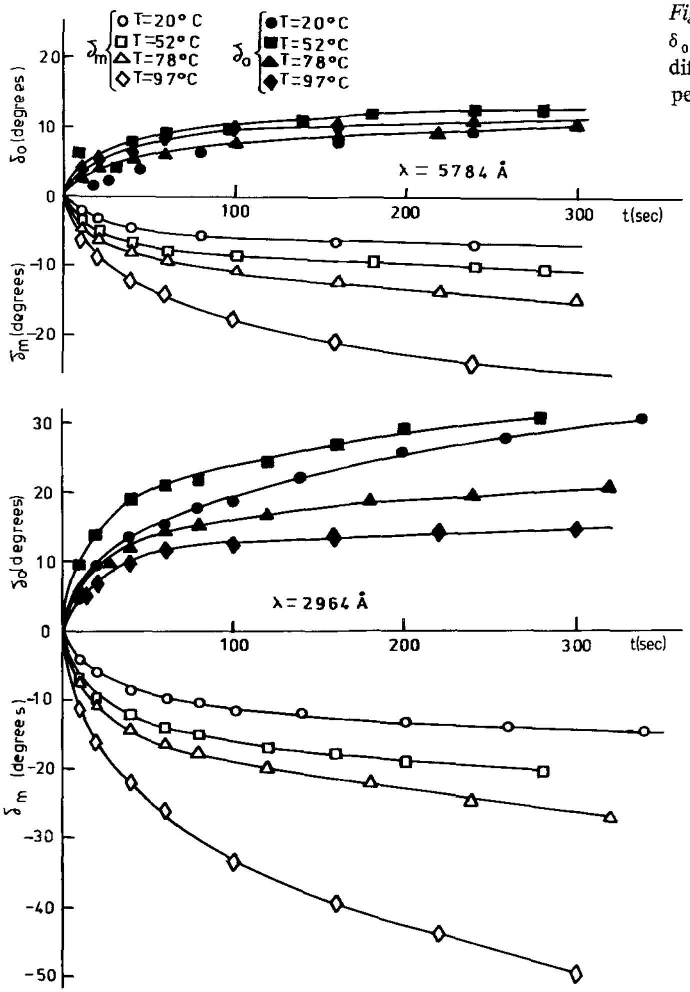

Figure 4 Optical and mechanical relaxations, δ_0 and δ_m, measured at constant strain and different wavelengths. The measurement temperature is indicated in the figure.

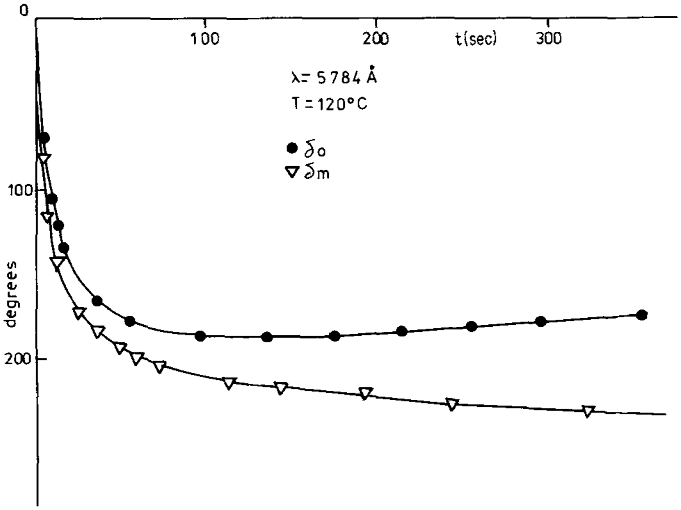

Figure 5 Optical and mechanical relaxations at 120° C.

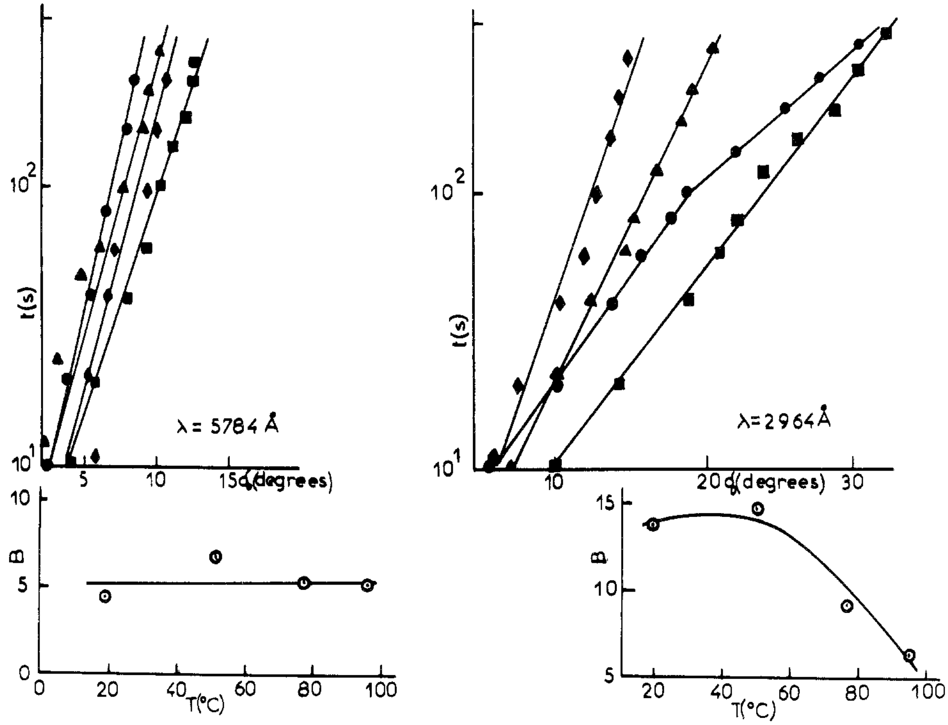

Figure 6 Upper part: logarithmic analysis of optical relaxation for ● 20° C, ■ 52° C, ▲ 78° C and ◆ 97° C. Lower part: prelogarithmic factor (see Equation 9) of the optical relaxation as a function of temperature.

has been tried according to expected kinetics operating in polymeric and amorphous materials [3, 11]. The upper part of Fig. 6 shows log t versus δ_0 for both wavelengths at the different temperatures. Simple logarithmic kinetics seems to be obeyed.

The optical relaxation seems to obey a unique logarithmic law although, at the shorter wavelength, the existence of two processes is suggested by the experimental points obtained at 20° C. This logarithmic process may be characterized by the pre-logarithmic factor, B, which changes with temperature as shown the lower part of Fig. 6. B changes markedly at ~ 50° C for $\lambda = 2964$ Å, whereas B at the longer wavelength remains practically constant.

The following is a qualitative and simplified view of the phenomena underlying the experimental results. The mechanical relaxation behaves independently of the wavelength. It can be attributed to macroscopic (molecular) modifications of the PMMA. These modifications induce different perturbations in the electronic (microscopic) structure of PMMA giving rise to the optical relaxation. When a short wavelength is used, these electronic perturbations are clearly detected and variations in the optical relaxation are measured. On the other hand, the perturbation of the electronic structure is not "seen" by long wavelengths (far from the absorption edge of PMMA) and δ_0 remains practically constant with temperature. This schematic view is reinforced by the experimental fact that other electronic properties (n, $\Delta\omega_0/s$) vary with T as does δ_0 (at $\lambda = 2964$ Å).

At temperatures $\gtrsim T_g$, the former views seems to be seriously modified and δ_0 and δ_m may be originated by a common mechanism, probably due to drastic transformations in the PMMA structure. In this mechanism, both molecular and electronic contributions should play a role. More experimentation is needed to elucidate this point although it is already known that at $T \gtrsim T_g$ whole fragments of the molecular chains become highly mobile [17], drastically modifying the relaxations of the sample.

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References

1. A. PETERLIN, *Ann. Rev. Mat. Sci.* 2 (1972) 349.
2. P. B. BOWDEN, *J. Mater. Sci.* 7 (1972) 52.
3. "Encyclopedia of Polymer Science and Technology", Vol. 9 (Wiley, New York, 1968).
4. R. S. STEIN, S. ONOGI and D. A. KEEDY, *J. Polymer Sci.* 57 (1962) 801.
5. A. TOBOLSKI "Properties and Structure of Polymers" (Wiley, New York, 1960).
6. A. BAER, "Engineering Design for Plastics" (Reinhold, New York, 1964).
7. S. H. WEMPLE and M. DI DOMENICO Jr, *Phys. Rev. Letters* **23** (1969) 1156; *Phys. Rev. B* **101** (1942) 248.
8. W. KUHM and O. GRÜMM, *Kolloid Z.* **101** (1942) 248.
9. L. R. G. TREOLOR, "The Physics of Rubber Elasticity" (Oxford University Press, Oxford, 1958).
10. A. ANGIOLETTI, *Rubber Chem. Technol.* 38 (1965) 1115.
11. P. Y. YU, Ph.D. Thesis, Brown University (1972).
12. R. S. STEIN, S. KRIMM and A. V. TOBOLSKY, *Textile Res. J.* 19 (1949) 8.
13. A. GAVINI and M. CARDONA, *Phys. Rev.* 177 (1969) 1351.
14. F. MESEGUER, Ph.D. Thesis, University of Madrid (1976).
15. F. MESEGUER and C. SANCHEZ, *Phys. Stat. Sol. (b)* 89 (1978) 281.
16. A. THIERRY, R. J. OXBOROUGH and P. B. BOWDEN, *Phil. Mag.* 30 (1974) 527.
17. R. D. DEANIN, "Polymer Structure, Properties and Applications" (Cahners Books, Boston, 1972).

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