Effect of thermal history on secondary relaxation processes in amorphous polymers

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Shear modulus and damping at 1 Hz were measured between -170°C and the glass transition temperature T_g for a large number of amorphous polymers. Two different thermal histories have been used: (a) quenching from above T_g to -170°C; (b) cooling at 0.5°C h^{-1} from above T_g to room temperature. The data show that thermal history does not affect secondary relaxations; it only affects the tail (onset) of the glass transition.

(**Keywords: thermal history effects; annealing; quenching; secondary relaxation; amorphous glassy polymers; moisture effects**)

INTRODUCTION

There is no consensus in the literature about the effect of thermal history on secondary relaxations in amorphous polymers. Significant or even dramatic effects are reported by some authors[1–7], but only slight or insignificant effects are reported by others[8–14]. Many years ago, the present author tried to clarify this matter by studying a large number of polymers (19 different materials). The relaxational behaviour was determined with mechanical measurements at small deformations (torsional pendulum, frequency ~1 Hz). The effect of thermal history was studied by measuring the properties of a specimen first after very slow cooling (0.5°C h^{-1}) from above its glass transition temperature T_g to room temperature and subsequently after quenching the (same) sample from above T_g to about -170°C. Careful precautions were made to ensure that the test results were not spoiled by artefacts, e.g. internal stresses in the sample which relax differently during the two different thermal histories, or a moisture content that responds differently, etc. The conclusion of the work was clear: provided that the precautions mentioned above were taken, no effect of thermal history could be detected on secondary relaxations as measured at a frequency of 1 Hz. Part of the results have been published earlier[15–17], and the full set is reported now.

EXPERIMENTAL

The torsional pendulum run

The experiments consisted of a number of torsional pendulum runs. During each run the sample is heated stepwise from -170°C to T_g. At each step the temperature is raised by 10–30°C, the time intervals of constant temperature lasting from 20 to 30 min. As a result, the average heating rate ranges from $\frac{1}{3}$ to $\frac{3}{2}$°C min^{-1}. From each run we obtain shear modulus G' and damping $\tan\delta$ as functions of temperature for frequencies between 0.3 and 3 Hz. For simplicity we only consider the results interpolated to 1 Hz.

The torsional pendulum and its temperature control system operating with dry nitrogen gas have been described by van der Wal, Nederveen and Schwippert[18,19]. The instrument has an accuracy of 1–2% for the shear modulus, 1–5% for the damping and 1°C for the temperature.

It should finally be mentioned that all measurements were made on specimens of about 3.5 × 7 × 190 mm, milled from sheets (for the materials, mostly obtained from industrial firms, see later).

Procedure of the measurements

Four torsional pendulum runs were usually made on each polymer; an illustration, for rigid PVC (emulsion, no. 14), is given in *Figure 1*. The sequence of the runs was as follows.

First run, material as received. A specimen was machined from the sheet received from the supplier and the run was made after cooling the specimen from room temperature to -170°C. Results are given in *Figure 1* by the broken curves (1) (measured points are not given).

The purpose of this measurement was:

(a) to gain an impression of the course of modulus and damping in the glassy state, of secondary peaks, etc.;

(b) to obtain an estimate of T_g, which is necessary for the next three runs;

(c) to obtain a plot of G' and $\tan\delta$ for the material as received for comparison with the results on quenched and slowly cooled samples.

The accuracy of these measurements on the as-received materials may be somewhat less than specified in the previous section. At temperatures near T_g the specimens (which were not annealed) sometimes changed in shape and dimensions due to the release of frozen-in stresses. Such changes alter the stiffness factor of the sample in an uncontrolled way.

After this first measurement, strips from the sheets were annealed in a vacuum, between glass plates, for one night, and next cooled to room temperature in about 3 h. This annealing was performed to relax possible frozen-in

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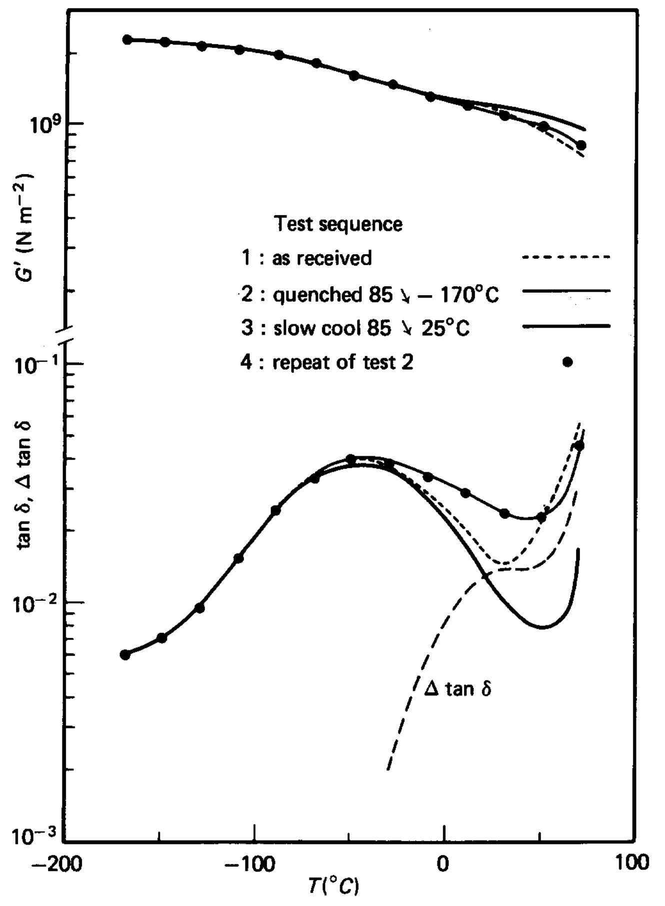

Figure 1 Modulus and damping at 1 Hz for rigid PVC, no. 14, as measured during stepped heating from −170 to 65°C at an average rate q of $\frac{2}{3}$°C min^{-1}. The tests were done on the material as received (test 1) and on materials with different thermal histories (tests 2–4). The thermal histories (quenching and slow cooling) are described in the text; the quenching temperatures and the temperature interval of slow cooling (0.5°C h^{-1}) are given in the diagram; Δ tan δ is the difference in tan δ between a quenched and a slowly cooled sample (test 4 − test 3)

stresses which would change the specimen dimensions later on (see above). The requisite annealing temperatures, T_a, given in *Table 1*, were estimated from the results of the first runs. The specimens for the other three measurements were machined from the annealed strips and were kept over P_2O_5 in a desiccator for at least two days.

Second run, properties after a quench from above T_g *to* $-170°C$. The specimen is first heated in the nitrogen atmosphere of the torsional pendulum to a temperature T_0 somewhat above T_g. Temperature T_0 was estimated from the results of the first measurement, and is given in *Figure 1*. After 20 min at T_0, the specimen is quenched to about −170°C by setting the control system of the thermostat to this new temperature. Such a quench is of course less perfect than a quench in a liquid. A time of 1–2 min is needed for the temperature to drop several tens of degrees below T_g, and another 20 min are needed to reach final thermal equilibrium at −170°C. The possibility of quenching in liquid nitrogen was rejected. The high cooling rates will produce internal (cooling) stresses in the sample[20]. These stresses may modify the mechanical properties of the material; also the torsional pendulum measurement proper may be spoiled due to dimensional and shape changes which certainly occur when liquid-quenched samples are heated to about T_g in a torsional pendulum run. Finally, liquid-nitrogen quenching may produce moisture problems since the cold sample has to be transferred from the liquid-nitrogen bath to the oven of the torsional pendulum.

After cooling to −170°C, the sample was first clamped. At T_0 above T_g, the clamping stresses will have relaxed almost completely, and during cooling from T_0 to −170°C there has been a considerable thermal contraction of the sample. After this clamping, we perform the second torsional pendulum run. The results are given in *Figure 1* by the full curves (2). No measured points are given. (The points near the curves are obtained in the fourth run.)

Third run, properties of the slowly cooled specimen. After the second run, the specimen was immediately returned to the desiccator and after some time placed in a glass tube under dry nitrogen at reduced pressure (0.1–0.5 bar). The tube was placed in an air thermostat programmed to cool at a rate of about 0.5°C h^{-1}. The cooling range is indicated in *Figure 1*. Generally the material was cooled from just above T_g to room temperature.

After cooling, the specimen was kept at room temperature for several days. Next it was removed from the tube, immediately placed in the torsional pendulum and cooled to about −170°C. After clamping, the third run was performed, and the results are given in *Figure 1* by the thick full curves (3), again without measured points.

Fourth run, properties after a second quench from above T_g *to* $-170°C$. We thought it necessary to show that the differences observed in *Figure 1* between the quenched and the slowly cooled material can be reproduced repeatedly on one single specimen and are not due to irreversible changes in the material.

To this end, the first quench (run 2) was repeated on the same specimen that was used for the second and third runs. The results of this second quench (fourth run) are given in *Figure 1* by points. No separate curve was drawn

Table 1 Materials investigated

Code no.	Polymer	Supplier	T_a (°C)	Density at 21°C (g cm^{-3})
1	PS (BASF VI)	TNO	100	1.050
4	PMMA	TNO	–	–
6	PC (Macrolon 3000 W)	TNO	155	–
7	n-Propyl methacrylate	TNO	–	–
8	tert-Butyl methacrylate	TNO	–	–
9	60 Cyclohexyl MA *co* 40 MMA	TNO	–	1.130
12	PVC, rigid, susp., Vestolit S 6557	Hüls	85	1.427
13	PVC, rigid, mass., Lucovyl GB 1150	Hüls	85	1.432
14	PVC, rigid, emuls., Vestolit P 1322 K	Hüls	85	1.423
15	PVC-VAc MA 6035	Péchiney	70	1.357
16	Post-chlorinated PVC	Montedison	120	1.561
17	SAN, Kostil AF 1542/5	Montedison	110	1.073
18	Polysulphone, P 1700	Philips	195	1.239
19	Amorph. PET, Arnite-A 200	Akzo	75	1.338
20	ABS, Cyclolac T	Philips	115	1.041
21	Impact (MBS) PVC	Solvay	80	0.977
22	Impact PS, Afcolène 492	Péchiney	100	1.041
23	Noryl 731	Philips	145	1.098
24	PPPO (Tenax)	Akzo	–	1.143

through them since they nearly coincide with the curve of the second run.

We thus observe that the short heating to above T_g at the beginning of the fourth run completely erases all previous thermal histories and that the thermal history effects observed in the glassy state can be repeated on one and the same specimen[17].

The careful experimental procedure described above was generally followed for all materials. Exceptions are mentioned explicitly in the section on 'Experimental results'. Some of the precautions made, such as annealing in a vacuum, drying, slow cooling under nitrogen gas at low pressure, etc., may not have been necessary for all materials, though for some of them they were. It will be shown later that for two materials (PC and polysulphone) the precautions described above were not sufficient.

Materials

A survey of the materials investigated is given in *Table 1*. For each test material it shows the code number, the (trade) name, the supplier, the annealing temperature to release frozen-in stresses (cf. earlier section) and the density at 21°C (after annealing) as measured by hydrostatic weighing in air and in silicone oil MS 200. The code numbers differ from those used in Appendix B of ref. 17. The PPPO material has not been annealed; the reasons are given in the next section.

The methacrylate polymers (nos. 4, 7, 8 and 9) were (plate) polymerized at TNO; the PS and PC samples (nos. 1 and 6) were obtained by compression moulding of commercial granulate. The samples 12–23 were received as compression moulded sheets from the suppliers; details about material 24 (PPPO) will be given in the next section.

EXPERIMENTAL RESULTS

The results for the 19 polymers are presented in *Figures 1–19*. Each figure is composed in exactly the same manner as in *Figure 1*. Detailed figure captions are omitted; these are the same as in *Figure 1* and the pertinent details about average heating rate q, quenching temperature T_0, slow cooling range, etc., are given in each figure.

The following departures from the standard procedure of measurement described in the earlier section should be mentioned:

(1) The first torsional pendulum measurement (run 1) to determine the properties of the material as received was omitted for all TNO materials (nos. 1–9) because sufficient data were already available. It was also omitted for impact PVC, no. 21.

(2) The annealing to relax frozen-in stresses was omitted for the methacrylates polymerized at TNO; these materials never gave problems arising from frozen-in stresses.

(3) The first quench (second run) was omitted for polystyrene (no. 1).

(4) For the three PVC samples (nos. 12, 13 and 14) and for SAN (no. 17), the third and fourth runs were made on other samples than those used for the second run, the latter having been spoilt by accidental heating to 220°C. The repeatability of the thermal history effects could still be verified because slow cooling (run 3) and final quench (run 4) were performed on the same specimen.

(5) The same applies to amorphous PET (no. 19); the third and fourth runs were made on another specimen than that used for the second.

(6) With PPPO (no. 24) we encountered a number of problems. First, this material rapidly crystallizes when it is heated slightly above its T_g (220°C). We therefore did not anneal PPPO and consequently the samples were not free of internal stresses. This spoiled the measurements on the 'as-received' material. The sample warped and its dimensions changed considerably during the torsional pendulum run and consequently no G' data could be presented in *Figure 19*. For the measurements after slow cooling and quenching, the results were much better; the short heating period to above T_g preceding these tests served as an annealing period and guaranteed that sufficiently reliable G' measurements could be made (see *Figure 19*).

The second problem with PPPO was that the supplier (Akzo) could not deliver the sample sheet when the tests were in progress. We therefore prepared (compression moulding) a sample from powder separately supplied by Akzo. The results of this sample are shown in *Figure 19*. After the work has been finished, we received the Akzo sheet and could complete the data of *Figure 19* with a curve on this sheet 'as received'.

DISCUSSION

The insensitivity of secondary relaxations to thermal history

By inspection of *Figures 1–19* we can draw the following set of conclusions.

(a) *Thermal history effects can be produced repeatably on a single specimen; previous thermal histories are erased by a short heating slightly above* T_g. In all cases the first quench (run 2) gives the same results as the final quench (run 4), in spite of the fact that the specimen had rather different properties in between the quenches (run 3).

(b) *Thermal history may strongly influence the damping (changes of up to a factor of 4) and slightly influence the modulus (changes of 0–20%)*. The changes in damping are so large that thermal history effects obviously can (should) not be ignored in practice or damping measurements. It is also of interest to see that the effects may persist down to very low temperatures (50–250°C below T_g, see e.g. *Figures 2, 4* and *13*).

(c) *Changes in thermal history (quench vs. slow cooling) never give rise to new damping peaks, to disappearance of damping peaks, or to changes in the location of the peaks on the temperature scale.* We observe that in all cases damping peaks shown by the quenched material are also shown by the annealed material, even the very weak ones (compare *Figures 2, 6, 10* and *12*). Only n-propyl methacrylate (*Figure 5*) seems to be an exception to this. The annealed polymer shows a weak peak around -100°C, between the β-peak at about 0°C and the n-alkyl peak[21] at about -180°C. We think, however, that this peak is due to moisture. As will be shown under point (d), our precautions against moisture were not sufficient for the slow-cool tests. It is further known that moisture in methacrylate polymers gives rise to a peak around -100°C[22].

We further observe that well pronounced peaks (see *Figures 1, 3, 4, 7, 8, 9, 14–18*) hardly change their location on the temperature scale. For materials showing weak peaks (*Figures 2, 6, 10–12*), the secondary peak is

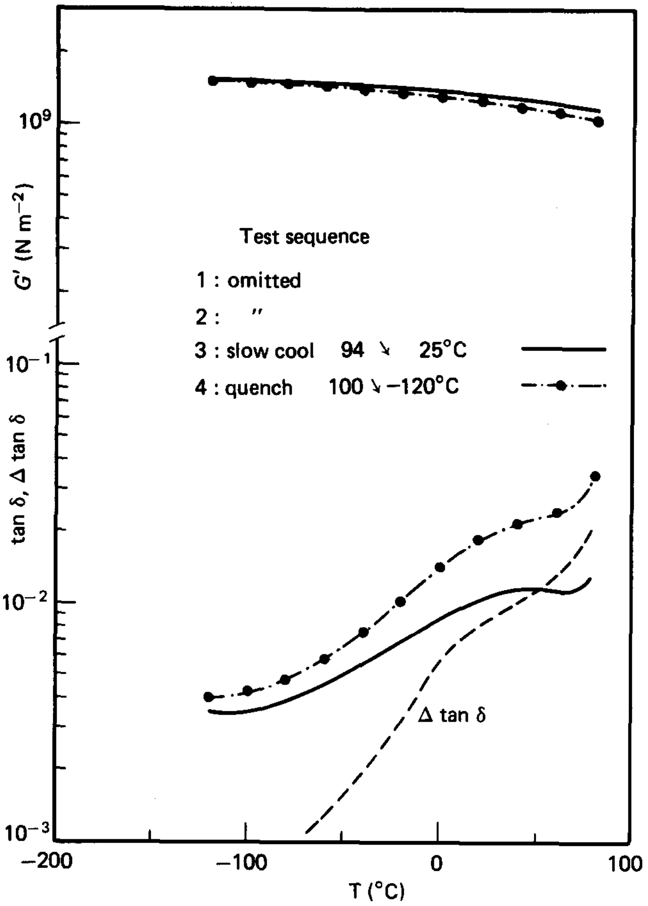

Figure 2 As *Figure 1*, for PS, no. 2, $q{\sim}\frac{2}{3}$°C min^{-1}

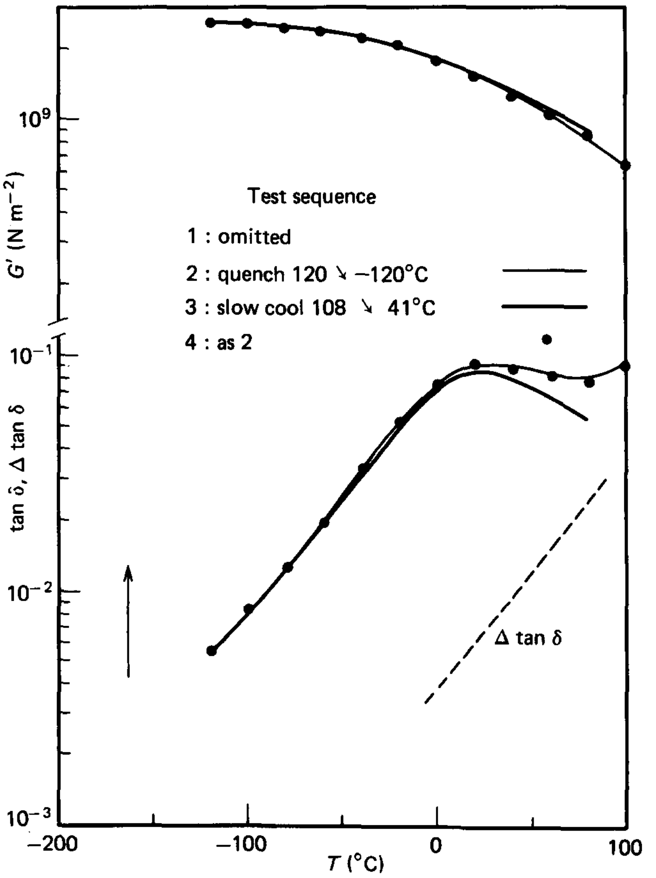

Figure 3 As *Figure 1*, for PMMA, no. 4, $q{\sim}\frac{2}{3}$°C min^{-1}

overlapped by the tail of the α-peak (glass–rubber transition) and an unambiguous conclusion cannot be drawn. Yet, there are no indications for large changes in the (temperature) location of even the weak peaks.

Conclusion (c) implies that thermal history has no effect on the activation energies of secondary loss processes, because, in general, the absolute temperature $T_{\max}$ at the top of the 1 Hz damping peak turns out to be proportional to the activation energy H[16,23]:

$$H = 0.06T_{\max} \pm 10\% \quad (H \text{ in kcal mol}^{-1},\ T_{\max} \text{ in K}) \tag{1}$$

(d) *Well pronounced secondary loss peaks are hardly influenced (location and height) by thermal history.* This conclusion is obvious from *Figures 1, 3, 7–9* and *14–18*, but polysulphone (*Figure 13*) and to a lesser extent PC (*Figure 4*) seem to deviate. A careful study, however, showed that the effects on the secondary peaks as seen in *Figures 4* and *13* are due to the extreme moisture sensitivity of these materials[24,25]. The effect of moisture is shown in *Figure 20*. For each material samples are compared which have identical thermal histories and only differ in that in the first test the sample is really dry whilst in the second it had been exposed to laboratory air (20°C, 65% r.h.) for 16 h. The moisture taken up during this period strongly changes modulus and damping at low temperatures.

We think that such moisture effects have caused the deviations seen in *Figures 4* and *13*. This implies that for PC and polysulphone, the precautions described in the earlier section were not sufficient. Possibly, the moisture has been absorbed when the samples, after slow cooling, were taken out of glass tubes and had to be exposed to laboratory air for some time, necessary to measure the sample dimensions, to install the sample in the torsional pendulum, etc. So, the slowly cooled samples cannot be

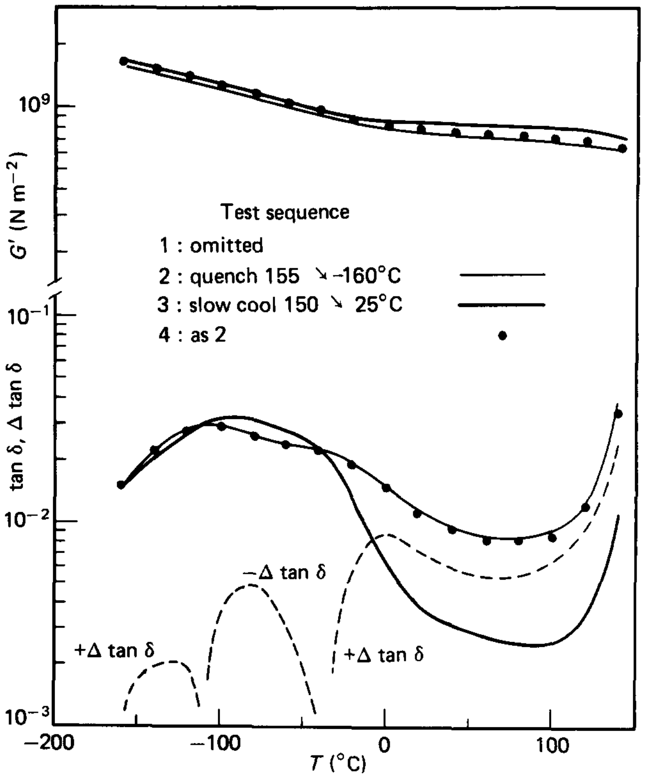

Figure 4 As *Figure 1*, for PC, no. 6, $q{\sim}1$°C min^{-1}

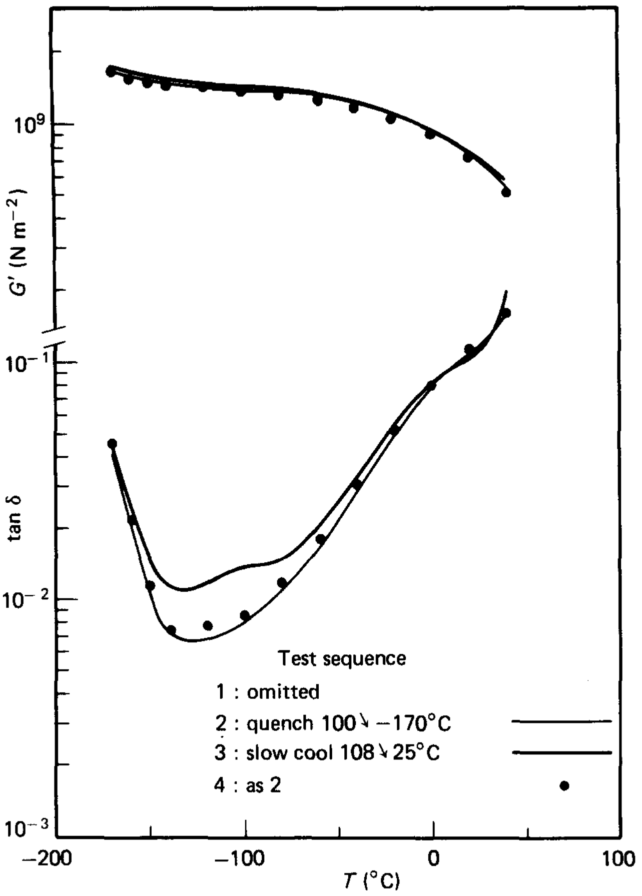

Figure 5 As *Figure 1*, for poly(n-propyl MA), no. 7, $q\sim\frac{2}{3}$°C min^{-1}

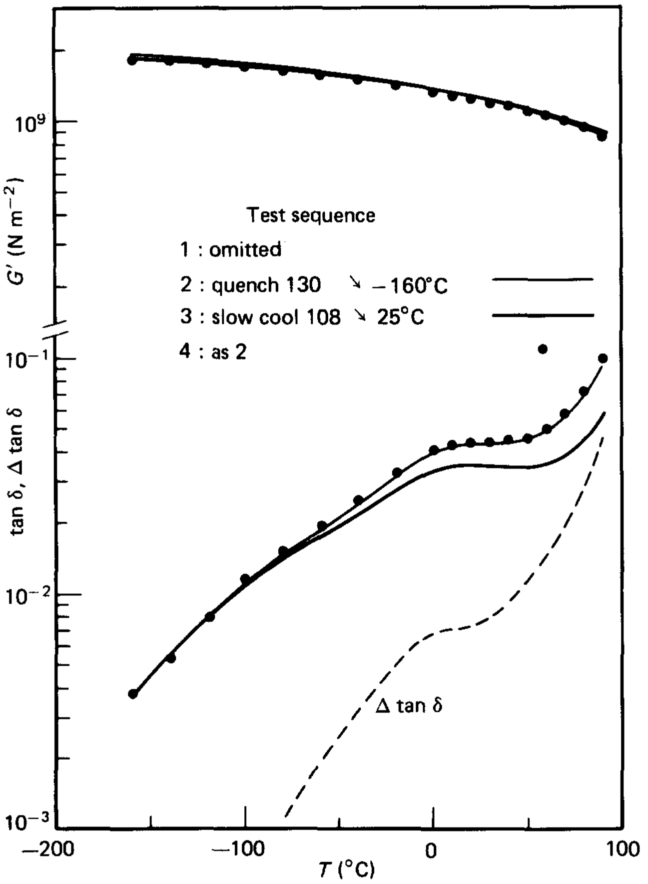

Figure 6 As *Figure 1*, for poly(t-butyl MA), no. 8, $q\sim\frac{3}{4}$°C min^{-1}

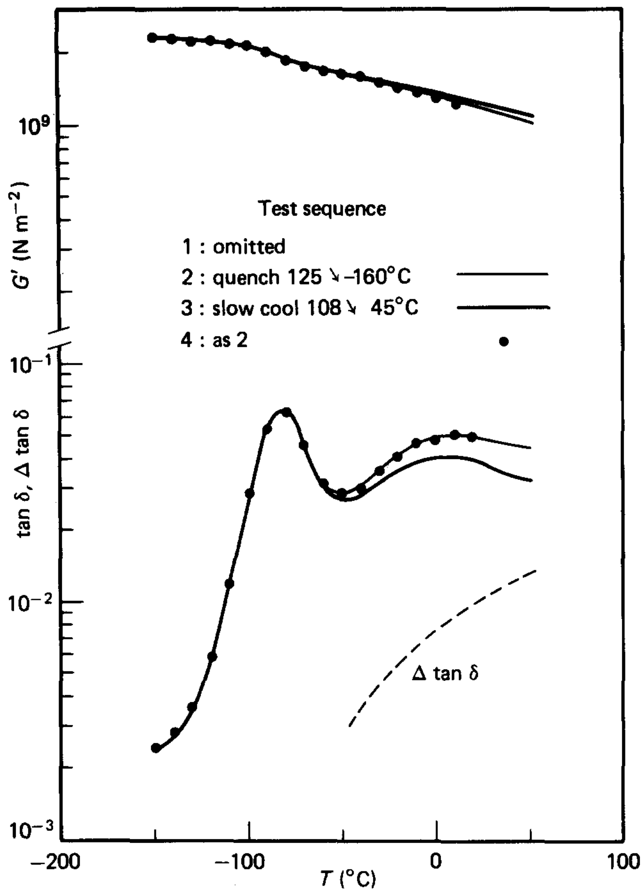

Figure 7 As *Figure 1*, for CHMA-MMA copolymer, no. 9, $q\sim\frac{1}{2}$°C min^{-1}

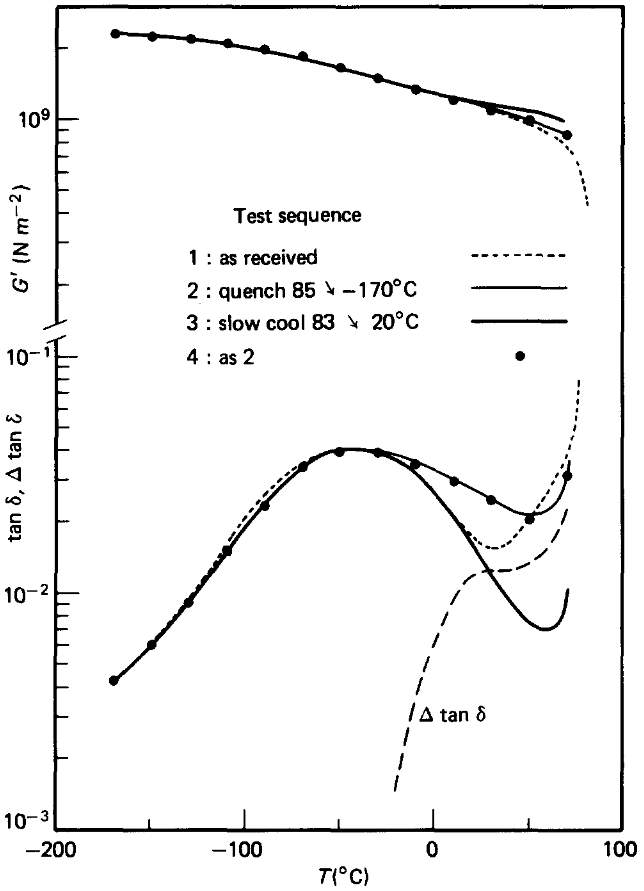

Figure 8 As *Figure 1*, for rigid PVC, no. 12, $q\sim\frac{2}{3}$°C min^{-1}

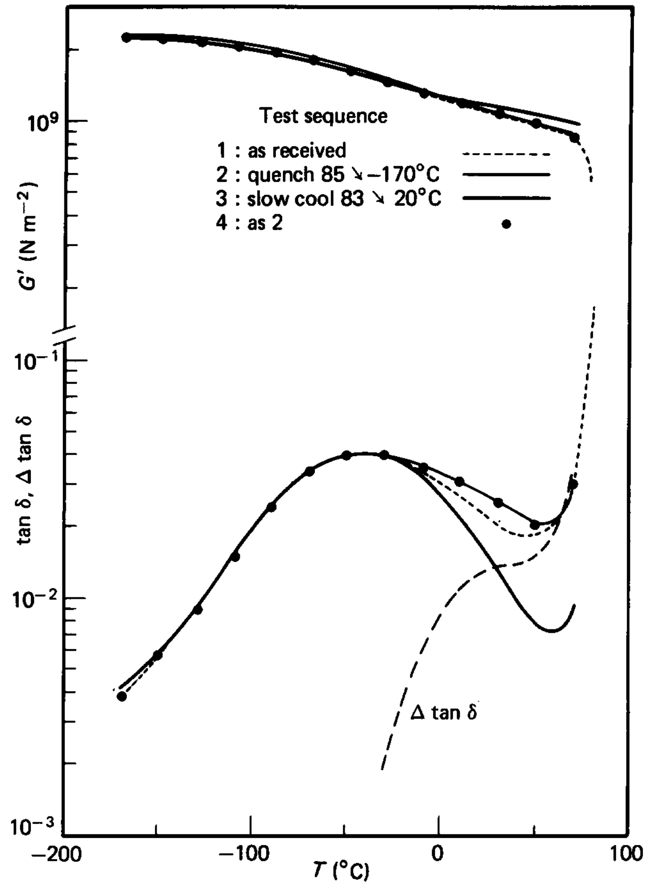

Figure 9 As *Figure 1*, for rigid PVC, no. 13, $q \sim \frac{2}{3}$°C min^{-1}

considered dry (the same was already observed for n-propyl MA (*Figure 5*)). This view is supported by the following three observations:

The low-temperature secondary loss peak of polysulphone (*Figure 13*) is almost identical for the slowly cooled sample (not dry) and for the as-received sample (not dry either).

For the quenched sample, the loss peak in *Figure 13* has the same appearance as the one for the dry sample in *Figure 20*. This is logical: in the quenching experiment, the sample will be dried during the short heating period at $T_g + 15$°C; since the sample does not leave the dry nitrogen gas thermostat of the pendulum it remains dry.

When the thermal history effects are studied under absolutely dry conditions (*Figures 21* and *22*), the irregularities seen in *Figures 4* and *13* disappear.

So we conclude that the deviations seen in *Figures 4* and *13* are artefacts which do not invalidate the general conclusion (d) that well pronounced secondary loss peaks are insensitive to thermal history, both in position and height. Of course, the measurements on the other polymers will also have suffered from the moisture effects. However, these materials are (much) less sensitive to moisture than PC and polysulphone. This was checked by experiments as shown in *Figure 20* for rigid PVC and an impact PS. It is also known that for the methacrylates the moisture effects are weak and limited to the range around −100°C.

Returning to the original data of *Figures 1–19*, we draw a final conclusion:

(e) *The material as received behaves as a quenched polymer for high temperatures, and as an annealed polymer for low temperatures, the gradual transition lying somewhat above room temperature.* There are no exceptions to this rule, at least when we disregard the data

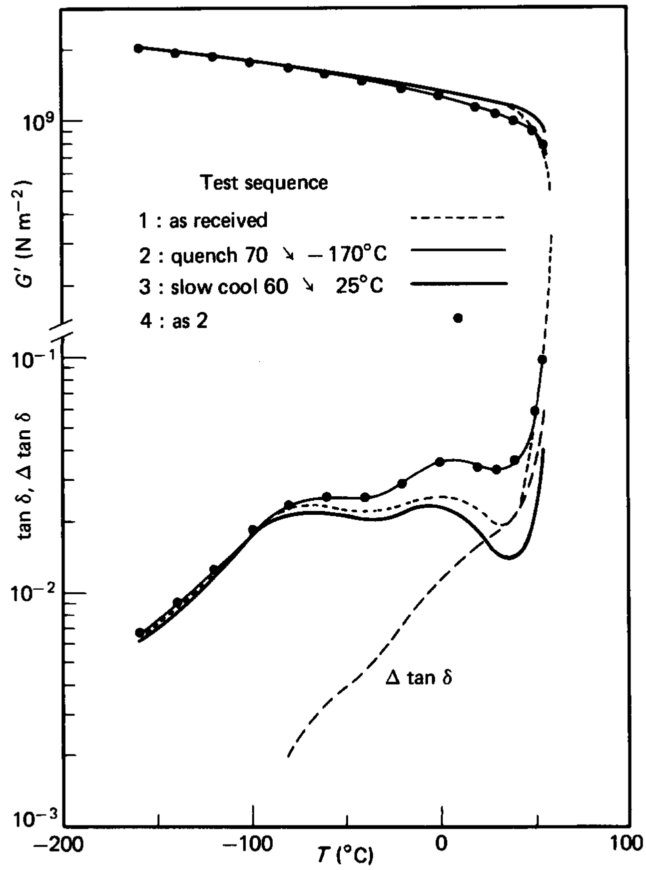

Figure 10 As *Figure 1*, for PVC–VAc, no. 15, $q \sim \frac{2}{3}$°C min^{-1}

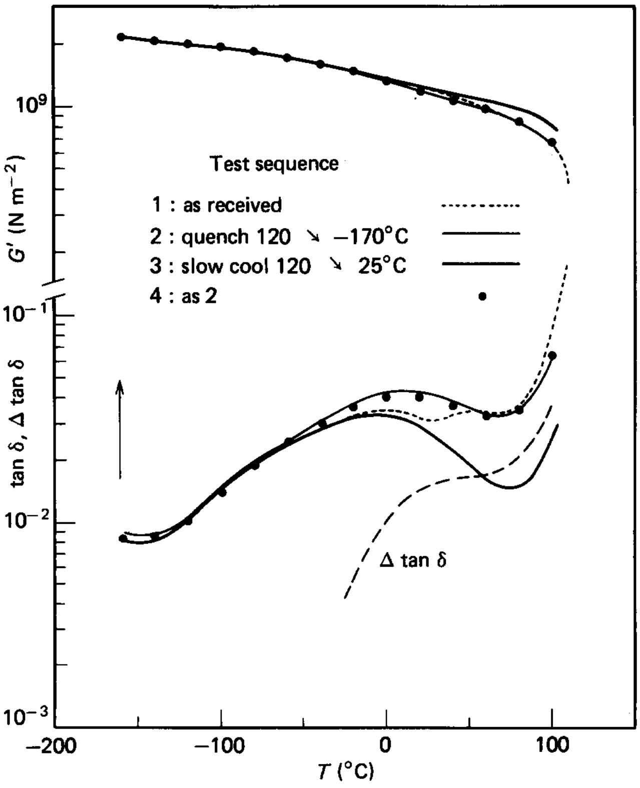

Figure 11 As *Figure 1*, for Cl PVC, no. 16, $q \sim \frac{4}{5}$°C min^{-1}

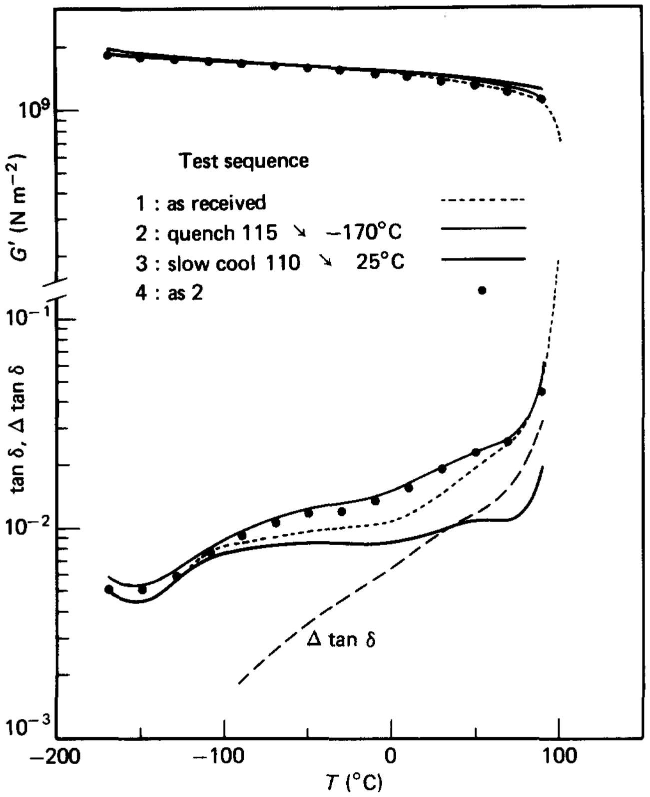

Figure 12 As *Figure 1*, for SAN, no. 17, $q \sim \frac{2}{3}$°C min^{-1}

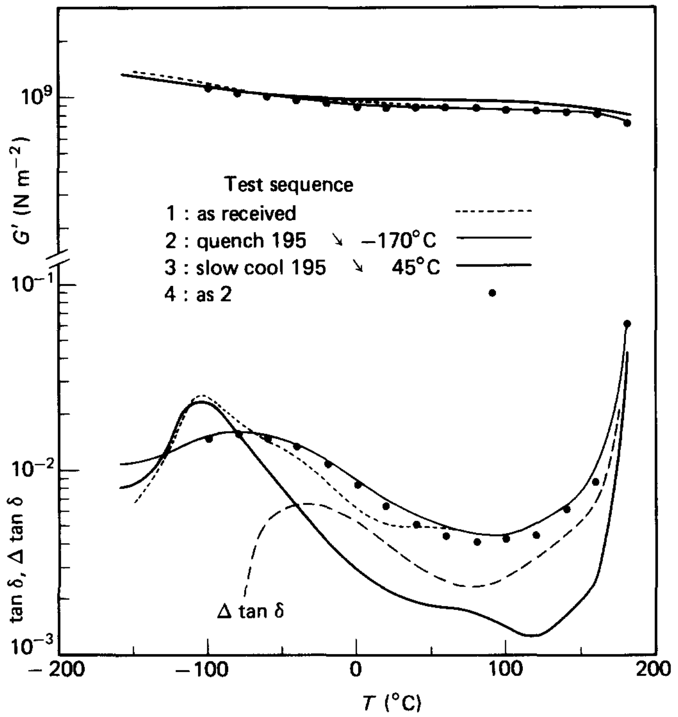

Figure 13 As *Figure 1*, for polysulphone, no. 18, $q \sim \frac{4}{5}$°C min^{-1}

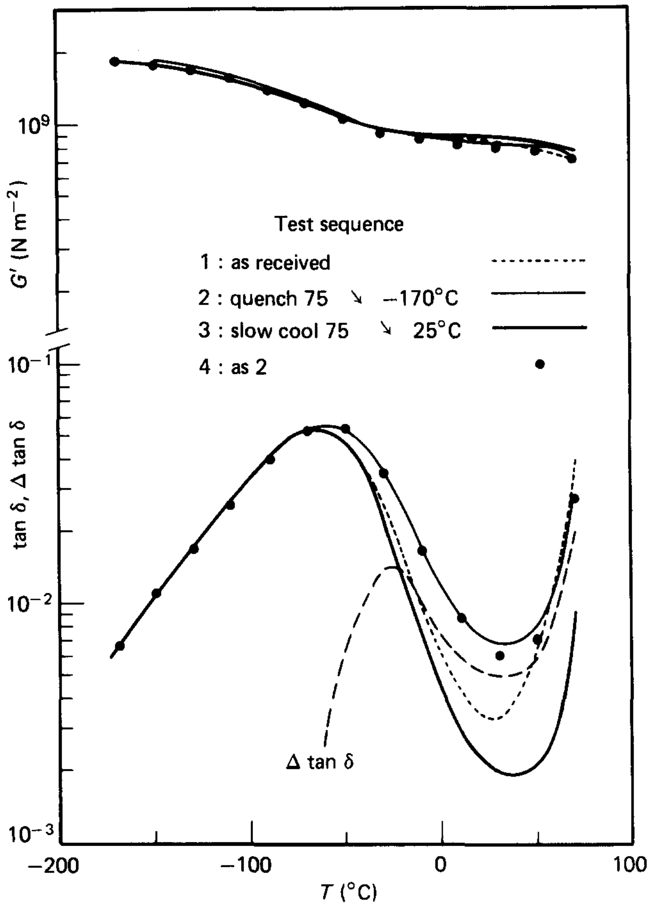

Figure 14 As *Figure 1*, for amorphous PET, no. 19, $q \sim \frac{2}{3}$°C min^{-1}

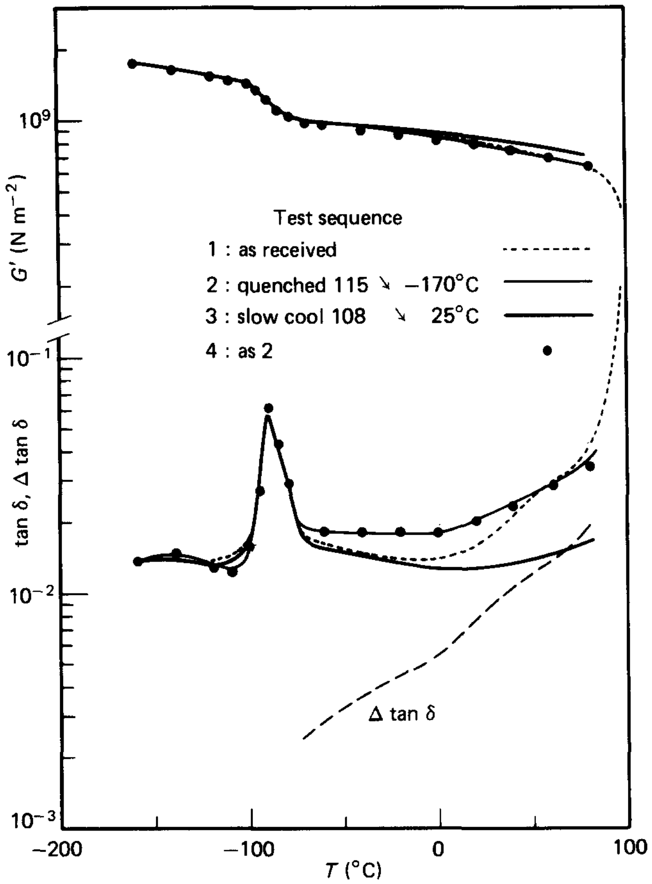

Figure 15 As *Figure 1*, for ABS, no. 20, $q \sim \frac{4}{5}$°C min^{-1}

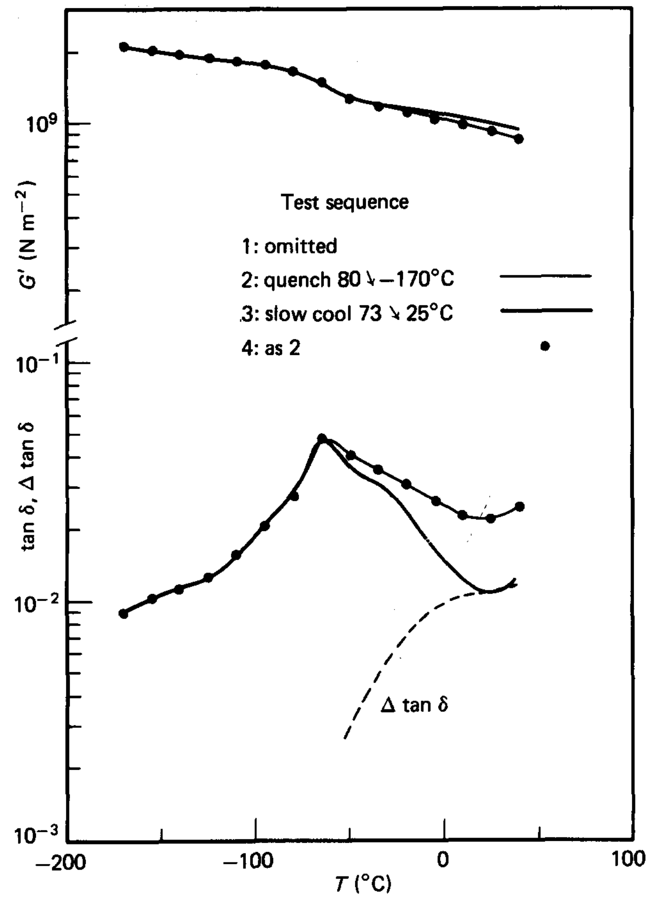

Figure 16 As *Figure 1*, for MBS–PVC, no. 21, $q\sim\frac{2}{3}$°C min^{-1}

on the 'as-received' Akzo sheet in *Figure 19* (these data were obtained on another material than those after quenching and slow cooling).

We can be brief about the interpretation of conclusions (a)–(e), because most has been discussed earlier, viz. conclusion (a) in Section 4.2 of ref. 17, conclusions (c) and (d) in Section 4.5 of ref. 17 and conclusion (e) in Section 9.4 of ref. 17. Conclusion (b) can be understood as follows: below T_g, we may use the following formula for the tail (onset) of the glass–rubber relaxation (pp. 34–42 of ref. 17):

$$J(t)=J_0\exp[(t/t_0)^m] \qquad m\sim 1/3 \qquad (2)$$

where $J(t)$ denotes the creep compliance, J_0 its value for $t=0$, whilst t_0 is a time parameter depending on temperature and age. This formula only describes the onset of the glass–rubber transition and not the secondary relaxations. However, the data of *Figures 1–19* strongly suggest that it is not the secondary relaxations but only the tail of the glass transition that is affected by thermal history, so we can make use of equation (2).

Linear viscoelastic theory[26] gives zero-order approximation formulae to derive G' and $\tan\delta$ from $J(t)$:

$$G'(\omega)\sim 1/J(t) \qquad t\sim 1/\omega \qquad (3)$$

$$\tan\delta(\omega)\sim\frac{\pi}{2}\frac{\mathrm{d}\ln J(t)}{\mathrm{d}\ln t} \qquad t\sim 1/\omega \qquad (4)$$

Combining equations (2)–(4) we obtain:

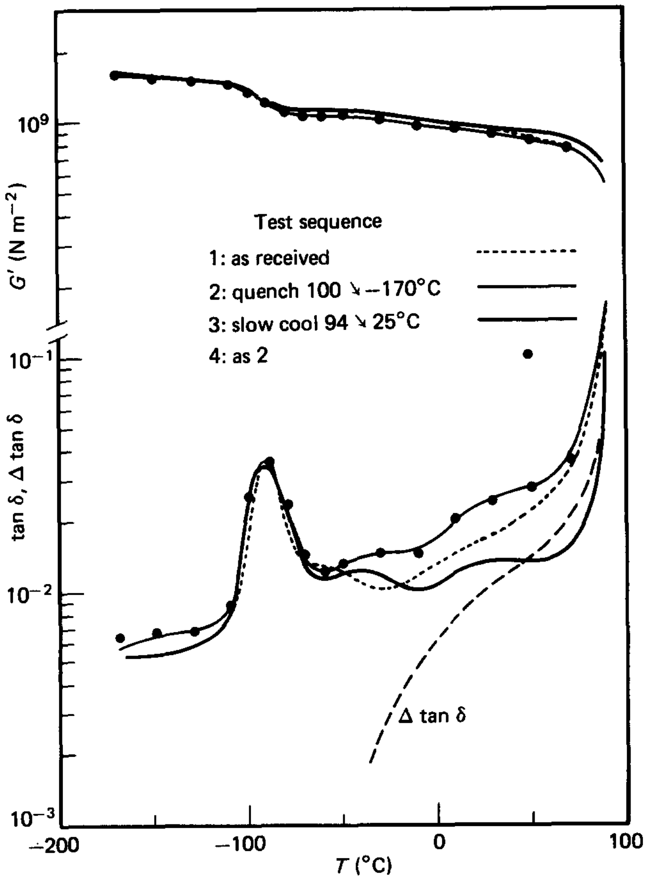

Figure 17 As *Figure 1*, for impact PS, no. 22, $q\sim\frac{2}{3}$°C min^{-1}

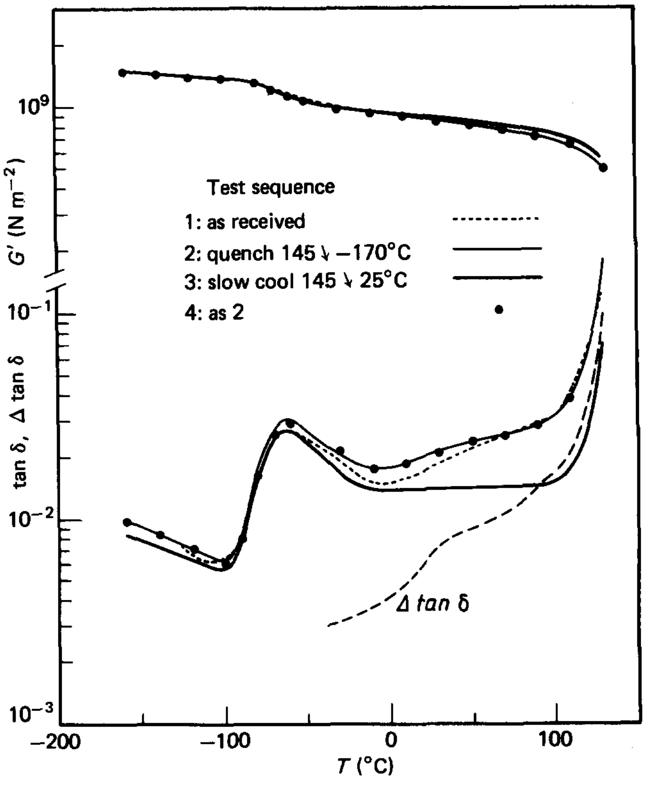

Figure 18 As *Figure 1*, for Noryl, no. 23, $q\sim\frac{2}{3}$°C min^{-1}

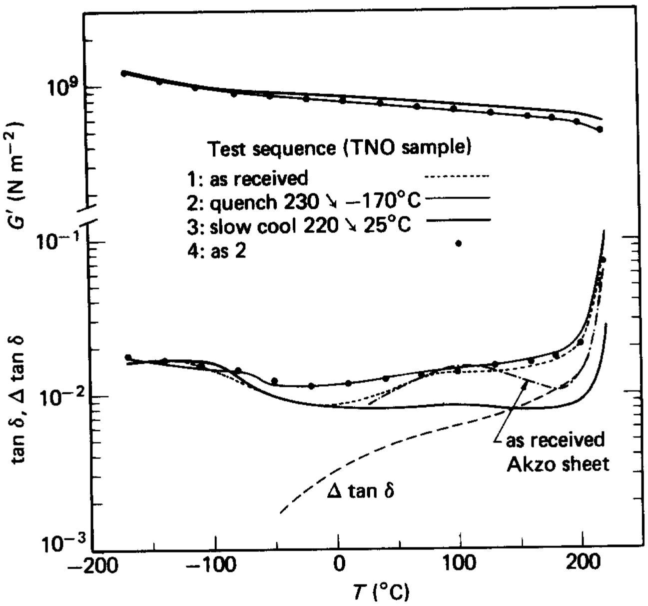

Figure 19 As *Figure 1*, for PPPO, no. 24, $q \sim \frac{6}{5}$°C min^{-1}

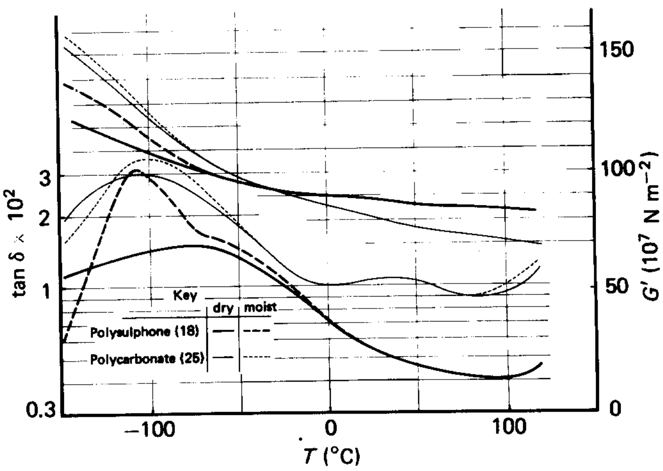

Figure 20 Effect of moisture on G' and tan δ at 1 Hz measured during stepped heating at 1°C min^{-1}. For polysulphone we used the material of *Table 1*, for PC we used another sample (Macrolon 8032, compression moulded by Philips). For both materials the following sequence of tests was done on a single sample: (1) Drying; first overnight in a vacuum oven at 155°C (PC) or 195°C (polysulphone) followed by 1 h at 130°C in the dry nitrogen gas thermostat of the torsionalpendulum. (2) Quench from $T_g + 15$°C to 20°C followed by 16 h storage at 20°C in the dry thermostat of the pendulum; next first measurement (denoted by dry). (3) Quench as above (point 2), but now the 16 h storage at 20°C is done in air of 65% RH; next second measurement (denoted by moist). After the original drying (point 1), the sample was kept continuously in the dry nitrogen gas thermostat of the pendulum, except for the 16 h exposure period (65% RH) mentioned under point (3)

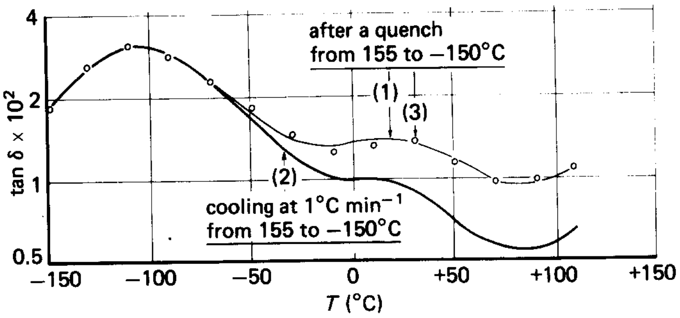

Figure 21 Damping of PC, no. 26 (Macrolon 8032), at 1 Hz as measured during stepped heating (tests 1 and 3, both after a quench) or cooling (test 2) at an average rate of 1°C min^{-1}. The sample was dried before testing and kept dry in the nitrogen gas thermostat of the torsional pendulum. Tests 1–3 were done in succession on a single sample. Reproduced with permission[17]

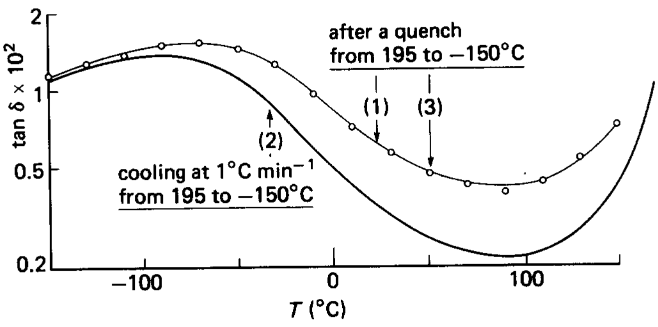

Figure 22 As *Figure 21*, but now for polysulphone, no. 18

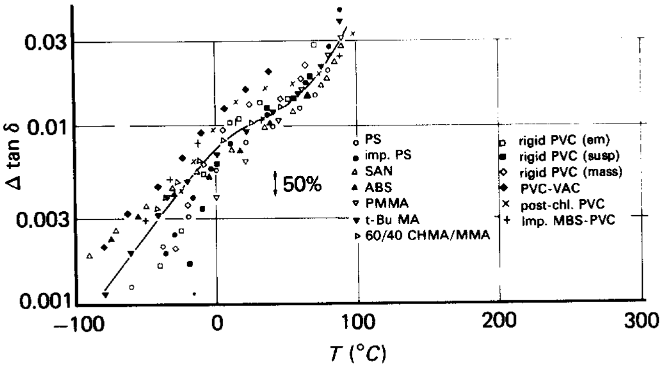

Figure 23 Effect of thermal history on the 1 Hz damping of various polymers; Δ tan δ is explained in *Figure 1*. Reproduced with permission[15]

$$G'(\omega) \sim G_0 \exp[-(1/\omega t_0)^m] \tag{5}$$

$$\tan\delta(\omega) \sim (\pi/2)m(1/\omega t_0)^m \tag{6}$$

where

$$G_0 \sim 1/J_0 \tag{7}$$

To find the ageing and thermal history effects, we consider the derivatives of G' and tan δ with respect to ln t_0 (note that according to the theory of physical ageing[17], it is primarily t_0 that changes). Equations (5) and (6) yield:

$$\mathrm{d}\ln G'(\omega)/\mathrm{d}\ln t_0 = m(1/\omega t_0)^m \sim (2/\pi)\tan\delta(\omega) \tag{8}$$

$$\mathrm{d}\ln\tan\delta/\mathrm{d}\ln t_0 = -m \sim -1/3 \tag{9}$$

Equations (8) and (9) explain conclusion (b). Ageing or slow cooling produce an increase in t_0, so G' will increase and tan δ decrease. Further, over the temperature ranges considered in *Figures 1–19*, tan δ was always much less than 1/3. This explains why the relative changes in G' were much smaller than those in tan δ.

The considerations given in Sections 4.9 and 4.10 of ref. 17 also qualitatively explain the remarkable result shown in *Figure 23*. This figure shows the Δ tan δ values from

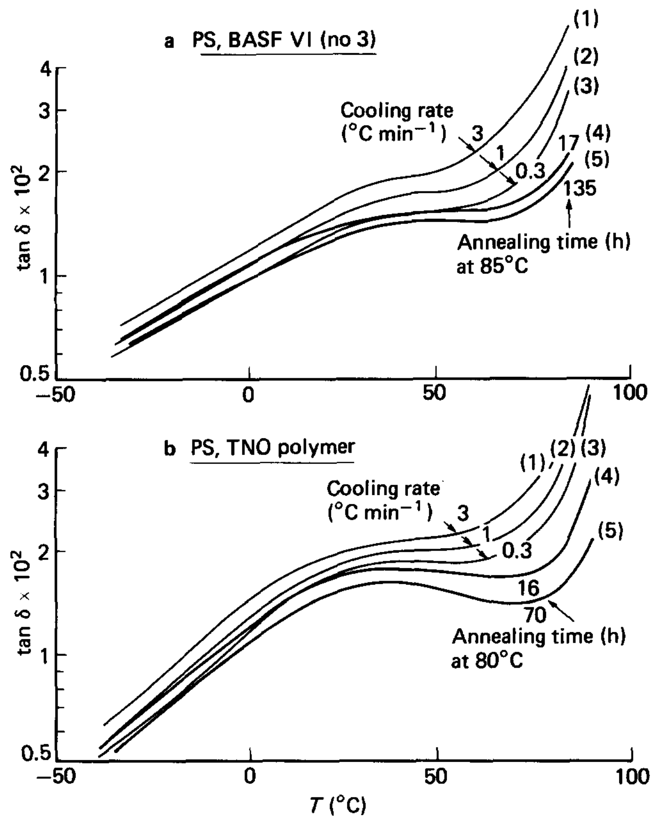

Figure 24 Effect of thermal history on the β maximum of polystyrene. Damping at 1 Hz obtained from the following sequence of measurements: (1), (2) and (3), during cooling from 110°C to −40°C at various rates; (4), (5), during heating from −40 to 90°C at a rate of about 0.5°C min^{-1} after previous annealing

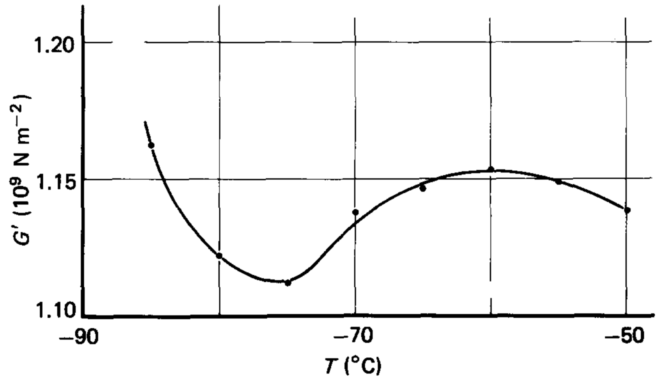

Figure 25 Shear modulus G' at 1 Hz for impact PS, no. 22, as measured during stepped heating at a rate of 6.7°C h^{-1}

Figures 1–19 for polymers with roughly the same T_g (about 100°C; only the PET data of *Figure 14* have been omitted). We observe that Δ tan δ is roughly the same ($\pm$ factor of 2) for all polymers. This is exactly what should be expected. As shown in Sections 4.9 and 4.10 of ref. 17, the viscoelastic behaviour as well as the ageing kinetics are only determined by $T_g - T$ and not by the type of polymer.

Some discrepancies with other authors

Why other authors$^{1-7}$ found effects of thermal history on secondary loss peaks remains unclear. However, we hope to have shown that severe precautions are an absolute necessity in order to get reliable results. The sample should be free of internal stresses, or such stress should be low. The direct use of injection moulded samples is highly questionable; the use of liquid (nitrogen) quenching is certainly not allowed. The samples must be dry, otherwise thermal history effects are mixed up with drying effects; even a short exposure to laboratory room conditions (20°C, 65% RH) may spoil the results. The only conclusion we can draw is that, provided such precautions are taken, the secondary loss peaks appear to be insensitive to thermal history.

Johari's paper^3 required some special comments. He proposed to consider Δtan δ as a function of temperature. If Δ tan δ shows a peak at the same temperature as tan δ itself, he concludes that the loss peak is influenced by thermal history. We come back to this criterion later on. First consider the Δ tan δ curves shown in *Figures 1, 3, 7, 8, 9, 14–18*. For all materials considered, there is a strong tan δ peak, well separated from the glass transition, but in no case does Δ tan δ peak at the same position as tan δ. So, according to Johari's criterion, these secondary peaks are insensitive to thermal history.

Johari's criterion should be treated with care, particularly when the changes in tan δ are small. To show this, consider the loss modulus $G'' = G'\tan\delta$ instead of tan δ itself. Suppose that the loss modulus can be divided into two parts, the first due to the α (glass–rubber) relaxation, the second due to the β (secondary) relaxation:

$$G'' = G''_\alpha + G''_\beta \qquad (10)$$

Suppose further that G''_β is insensitive to thermal history. We then have:

$$\Delta\tan\delta = \frac{G''_\beta + G''_{\alpha q}}{G'_q} - \frac{G''_\beta + G''_{\alpha \mathrm{sl.c}}}{G'_{\mathrm{sl.c}}} \qquad (11)$$

where q and sl.c stand for quenched and slowly cooled respectively. Equation (11) can be rewritten as:

$$\Delta\tan\delta = G''_\beta\left(\frac{1}{G'_q} - \frac{1}{G'_{\mathrm{sl.c}}}\right) + \frac{G''_{\alpha q}}{G'_q} - \frac{G''_{\alpha \mathrm{sl.c}}}{G'_{\mathrm{sl.c}}} \qquad (12)$$

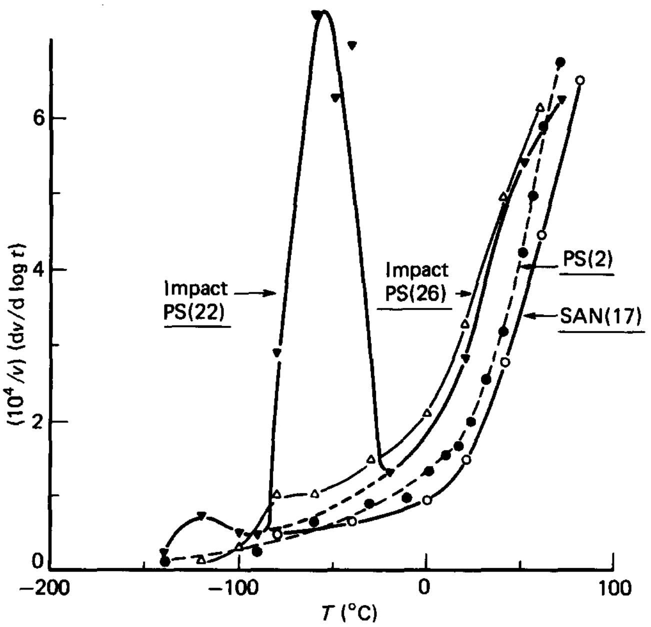

Figure 26 Rate of volume-relaxation vs. temperature for various polymers quenched from $T_g + 15$°C to the test temperature. Method: quartz dilatometer, see Appendix A2 of ref. 17

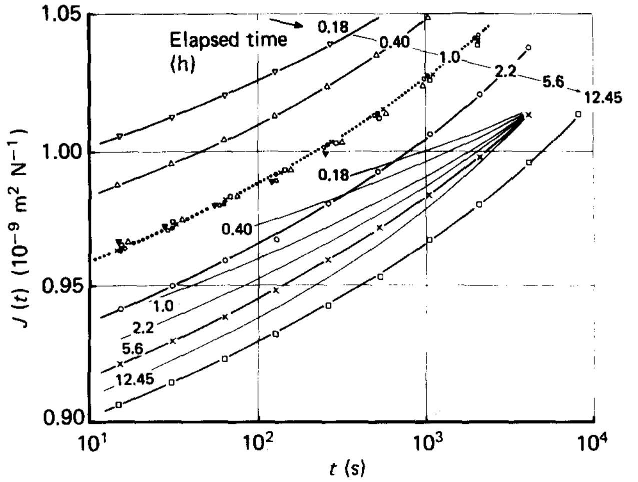

Figure 27 Impact PS, no. 22. Small-strain torsional creep curves at various elapsed times after a quench from 100 to −50°C. For methods, see ref. 17: ···○▲▽□ × ▼···, master curve obtained by vertical shifts; ———, horizontally shifted creep curves (horizontal shifting does not lead to superposition)

Slow cooling increases the modulus, so $G'_q < G'_{sl.c}$, and consequently the first contribution to $\Delta \tan\delta$ in (12) will peak at the same temperature as G''_β, even when there is no effect of thermal history on G''_β itself. So Johari's criterion is somewhat less obvious than it looks at first sight.

Discussion of some particular materials

Unmodified polystyrene. Some authors, particularly Goldbach and Rehage[27–29], state that for PS the weak secondary peak disappears after annealing. The present results (*Figure 2*) show the reverse: the peak, weak and overlapped by the tail of the glass transition, becomes more distinct (i.e. separated) by annealing. Some additional information is given in *Figure 24*. *Figure 24a* concerns the BASF VI material used by Goldbach, at least according to Boyer[29]. *Figure 24b* concerns a TNO polymer. Modulus and damping were first measured during cooling from 110 to −40°C at rates of 3, 1 and 0.3°C min^{-1} (tests 1–3). Next the materials were annealed for long times just below T_g, and modulus and damping were measured between −40°C and T_g during stepped heating (tests 4 and 5). It is quite clear that the secondary loss peak of PS does not disappear by annealing or slow cooling; moreover the two polymers behave similarly. Inspection of *Figures 2, 6, 7, 10–12* further reveals that all polymers with a weak loss peak behave like PS (cf. also *Figure 23*). Consequently, special molecular interpretations for the thermal history effects, e.g. based on the specific chemical structure of PS[27,28], seem inadequate.

Rubber-modified polymers. The impact-modified polymers, ABS (*Figure 15*), impact PS (*Figure 17*) and Noryl (*Figure 18*), show a pronounced damping peak between −60 and −100°C, which is not influenced by thermal history. This is as expected, at least when the peaks are supposed to be due to the glass transition of a rubber component. During slow cooling (0.5°C h^{-1}) from 100–150°C to room temperature (run 3), the rubber remains above its T_g. Therefore, the measurements after quenching (runs 2 and 4) and slow cooling (run 3) are identical as far as the rubber is concerned. For the rubber, both types of measurement start with a quench from above T_g (i.e. from room temperature) to below T_g (−170°C).

An anomaly in rubber-modified PS, no. 22. The behaviour of this material is depicted in *Figure 25*. Below −80°C, G' decreases on heating, obviously because of the glass–rubber transition of the rubber component. On further heating, the modulus shows a maximum, which can be attributed to crystallization and melting phenomena in the rubber component. This conclusion is substantiated by creep and volume relaxation tests on the same material.

Figure 26 shows that the volume-relaxation rate possesses an abnormally high peak at about −50°C. This peak is absent in unmodified PS, in SAN as well as in the impact PS no. 26 (Hüls, Vestyron 617). Moreover the peak occurs at temperatures considerably above the T_g of the rubber component (the 1 Hz T_g lies at −90°C, see *Figure 17;* for the volume-relaxation rate the T_g peak lies at about −115°C in *Figure 26*).

Some creep data are finally given in *Figure 27*. With amorphous polymers, creep curves measured at different times, t_e, elapsed after a quench can usually be superimposed by shifts that are almost horizontal[17]. With impact PS no. 22 this is impossible at −50°C; we need vertical instead of horizontal shifts, which suggests that the ageing at −50°C is due to a real stiffening mechanism (crystallization of the rubber component).

CONCLUSIONS

All polymers investigated show considerable effects of thermal history on shear modulus G' and damping $\tan\delta$ at 1 Hz.

These thermal history effects can be repeated reproducibly on a single specimen.

Annealing by slow cooling decreases the damping (observed changes of a factor of 4) and increases the modulus (by 0–20%).

The thermal history effects may persist over wide temperature regions below the glass transition temperature T_g.

Changes in thermal history do not influence the intensity, the location on the temperature scale and the activation energies of secondary loss peaks.

For a large group of polymers, the differences in damping between quenched and slowly cooled material are roughly equal.

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REFERENCES

1 Malpass, V. E. *Appl. Polym. Symp.* 1969, **12**, 267
2 Johari, G. P. *Ann. N.Y. Acad. Sci.* 1976, **279**, 117
3 Johari, G. P. *J. Chem. Phys.* 1982, **77**, 4619
4 Johari, G. P. in 'Relaxation in Complex Systems' (Eds. K. L. Ngai and G. B. Wright), Office of Naval Research, 1984
5 Guerdoux, L. and Marchal, E. *Polymer* 1981, **22**, 1199
6 Ito, E., Tajima, K. and Kobayashi, Y. *Polymer* 1983, **24**, 877
7 Roche, E. J. *Polym. Eng. Sci.* 1983, **23**, 390
8 Pezzin, G., Ajroldi, G. and Garbuglio, G. *J. Appl. Polym. Sci.* 1967, **11**, 2553
9 Minimi, R. M., Moore, R. S., Flick, J. R. and Petrie, S. E. P. *J. Macromol. Sci.* 1973, **B8**, 343
10 Diaz Calleja, R. and Gómez Ribelles, J. L. *Polym. Eng. Sci.* 1982, **22**, 845
11 Yee, A. F. and Takemari, M. T. *J. Polym. Sci. (Phys.)* 1982, **20**, 205
12 Bauwens-Crowet, C. and Bauwens, J. C. *Polymer* 1983, **24**, 921
13 Gómez Ribelles, J. L. and Diaz Calleja, R. *Polym. Eng. Sci.* 1984, **24**, 1202
14 Guerdoux, L., Duckett, R. A. and Froelich, D. *Polymer* 1984, **25**, 1392
15 Struik, L. C. E. *Ann. N.Y. Acad. Sci.* 1976, **279**, 78
16 Heijboer, J. *Ann. N.Y. Acad. Sci.* 1976, **279**, 104
17 Struik, L. C. E. 'Physical Aging in Amorphous Glassy Polymers and Other Materials', Elsevier, Amsterdam, 1978
18 Nederveen, C. J. and van der Wal, C. W. *Rheol. Acta* 1967, **6**, 316
19 van de Wal, C. W., Nederveen, C. J. and Schwippert, G. A. *Rheol. Acta* 1969, **8**, 130
20 Struik, L. C. E. *Polym. Eng. Sci.* 1978, **18**, 799
21 Willbourn, A. H. *Trans. Faraday Soc.* 1958, **54**, 717
22 Heijboer, J. *J. Polym. Sci. C* 1968, **16**, 3413
23 Boyer, R. F. *Rubber Chem. Technol.* 1963, **36**, 1303
24 Allen, G., McAinsh, J. and Jetts, G. M. *Polymer* 1971, **12**, 85
25 Baccaredda, M. *et al. J. Polym. Sci.* (*A*-2) 1967, **5**, 1296
26 Ferry, J. D. 'Viscoelastic Properties of Polymers', Wiley, New York, 1961
27 Goldbach, G. *Thesis, Aachen*, 1966
28 Goldbach, G. and Rehage, G. *Kolloid Z.* 1967, **216**, 56
29 Boyer, R. F. in 'Encyclopedia of Polymer Science and Technology, Section VII-B (Ed. N. Bikolas), Interscience, New York
30 Heijboer, J. *Kolloid. Z.* 1960, **171**, 7