polymer papers

Physical ageing of polycarbonate and PMMA by dynamic mechanical measurements

L. Guerdoux,* R. A. Duckett† and D. Froelich
Universite Louis Pasteur, Ecole d'Application des Hauts Polymeres, 4 rue Boussingault, 67000 Strasbourg, France

(*Received 1 October 1983*)

The physical ageing properties of polycarbonate and poly(methyl methacrylate) have been measured by dynamic mechanical experiments at different temperatures. It appears that the horizontal shift proposed by Struik to superpose the experimental curves for different ageing times is only a first approximation. The McCrum analysis has been used in the α region but cannot be applied between the α and β relaxations.

(Keywords: physical ageing; polycarbonate; poly(methyl methacrylate); mechanical properties; secondary relaxation)

INTRODUCTION

It is well known that the viscoelastic properties of polymers depend on temperature. One major aspect of viscoelastic behaviour is the strong dependence of the material relaxation or retardation times on temperature, which has lead to the concept of 'time–temperature superposition'. This means that if creep or stress relaxation data obtained at two different temperatures are displayed plotted against log(time), then the two sets of data can be superposed by shifting one set along the log(time) axis by an amount log a_T. The shift factor a_T depends *inter alia* on the temperature difference between the two sets of data[1].

Detailed studies on the creep behaviour of poly(methyl methacrylate) (PMMA) by McCrum and Morris[2] revealed that in the glassy state temperature affects not only the retardation times, but also the so-called 'limiting-compliances' at very short and very long times. Failure to recognize this results in an apparent conflict between the temperature dependence of the shift factors deduced from creep or dynamic mechanical experiments.

It has also been established that the viscoelastic properties of glassy polymers[3,4] and other materials[5] depend on their thermal histories. A polymer suddenly cooled into the glassy state is no longer in thermodynamic equilibrium and its properties, such as specific volume, change with time. This evolution in properties is reflected in the changes of viscoelastic behaviour that Struik[5] calls 'physical ageing'. By means of measurements of the creep behaviour of many polymers, Struik proposed that the primary mechanism of physical ageing arises from changes in molecular mobility of the polymer segments. This results in a proportionate increase in all retardation times, which can be represented by a shift with ageing time of the retardation time spectra along the log(time) axis towards longer times. Thus creep curves in the linear viscoelastic region, obtained at different ageing times, t_v, can be superposed by a 'nearly horizontal' shift along the log(time) axis. The shift factor log(a_v) varies linearly with the logarithm of the ageing time log(t_v), the constant of proportionality being approximately equal to unity over a large range of temperatures for most polymers. At sufficiently low temperatures, where the mechanical properties are dominated by the so called β-relaxation, physical ageing effects are no longer observed.

Although other authors[4,6,7] have proposed that a simple translation with ageing of the retardation time spectra cannot strictly be used to superpose the experimental curves, Struik has proposed that this is the primary effect of ageing and that the phenomenon is essentially universal.

The aim of our study was to see if Struik's proposals could be generalized from creep to embrace stress–relaxation and dynamic mechanical experiments. We present the results obtained on two amorphous polymers: PMMA and polycarbonate (PC).

EXPERIMENTAL

Mechanical measurements

The torsional viscoelastic properties of these polymers have been measured with a Rheometrics mechanical spectrometer, model RMS 7200[8].

The relaxation measurements are allowed by means of a step function, the time to achieve the desired strain being less than 20 ms.

The dynamic mechanical properties are measured in the frequency range from 10^{-2} to 10^2 rad s^{-1}. The temperature is controlled to ± 0.5°C.

Samples

We have studied two amorphous polymers: polycarbonate (PC) and poly(methyl methacrylate) (PMMA). PC was supplied by Bayer (extruded plates of Makrolon) and PMMA by Altulor (Altuglas).

---

* Present address: CdF Chimie, Centre de Recherches du Nord (C.R.N.P.) 62670 Maxingarbe, France.

† Permanent address: Department of Physics, University of Leeds, Leeds LS2 9JT, UK.

0032–3861/84/101392–05$03.00

The experiments have been made on specimens with both cylindrical and rectangular cross-sections. The effective length of the cylindrical specimens is 40 mm and their diameter is 5 mm. The parallelepipeds had the following dimensions: length 40 mm, width 11 mm, thickness 4 mm.

The specimens, before quenching, were left for one hour at a temperature 20°C above their glass transition temperature. When the temperature of quenching was fairly high (80°C for PMMA and 120°C for PC) the rapid cooling was achieved directly in a Rheometrics oven. The specimens cooled to temperatures near ambient temperature were quenched in water at the desired temperature and then quickly introduced into the Rheometrics oven.

Linearity of experiments

Preliminary experiments confirmed that the limiting strain corresponding to the linear range is greater than 5×10^{-3}, which is in agreement with other authors. We have further shown that identical results were obtained with two values of the deformation (10^{-3} and 5.10^{-3}) and two samples having the same thermal history.

The imposed deformations were thereafter limited so that the viscoelastic behaviour of the materials can be considered to be linear. By this means the deformation did not influence the ageing process.

RESULTS AND INTERPRETATION

Polycarbonate at 30°C

Figures 1, 2 and *3* show the values of the relaxation modulus and the dynamic modulus $G'(\omega)$, $G''(\omega)$ obtained for different ageing times at 30°C. In each case the measurement times are less than one tenth of the ageing time as in the procedure of Struik. The shortest times are of the order of 20 min to be sure that the specimen had achieved thermal equilibrium.

Using only a horizontal shift, we have tried to superpose the three curves. The master curves obtained by this procedure are plotted in the same *Figures 1, 2* and *3*, and the values of a_v are given in *Table 1*. As we can see in these Figures, the superpositions are quite poor and the values for a_v for the three types of measurements are quite different.

This means that the simple hypothesis of Struik is not valid for these data.

In order to try to obtain a better superposition, we have used the model proposed by Chai and McCrum[6] which has already been used by Guerdoux and Marchal[7] to interpret their dielectric measurements.

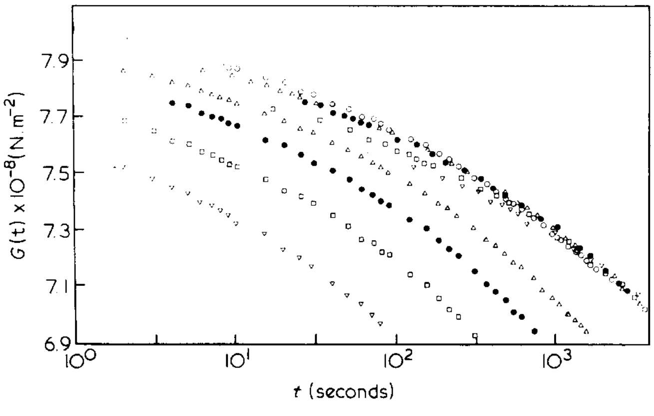

Figure 1 Relaxation modulus $G(t)$ for polycarbonate at 30°C as a function of time for different ageing times t_e. The master curve gives the results of a superposition by horizontal shifts. (▽) 20 min, (□) 60 min, (●) 130 min, (△) 292 min, (○) 808 min

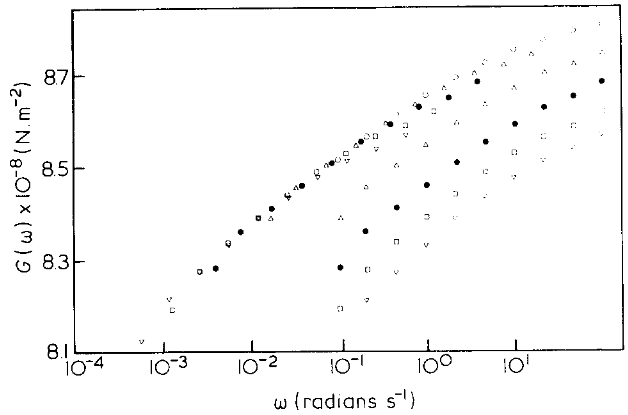

Figure 2 Storage modulus $G'(\omega)$ for polycarbonate at 30°C as a function of frequency for different ageing times. The master curve gives the results of a superposition by simple horizontal shifts. (▽) 37 min, (□) 61.4 min, (●) 110.4 min, (△) 244 min, (○) 800 min

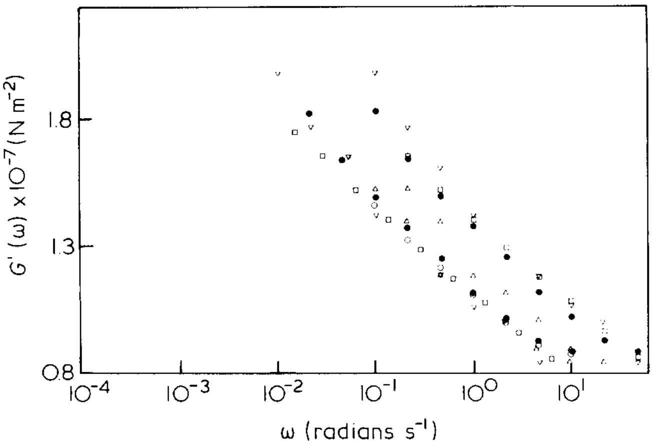

Figure 3 Loss modulus $G''(\omega)$ for polycarbonate at 30°C as a function of frequency for different ageing times. The master curve gives the results of a superposition by simple horizontal shifts. (▽) 37 min, (□) 61.4 min, (●) 110.4 min, (△) 244 min, (○) 800 min

In this model we suppose that the limiting values of the viscoelastic functions vary with ageing time. This hypothesis gives directly by a simple calculation the three following equations:

$$G'^{t_{v_0}}(t) = C_v . G'^{t_v}(t . a_v) + B_v \qquad (1)$$

$$G'^{t_{v_0}}(\omega) = C_v . G'^{t_v}(\omega / a_v) + B_v \qquad (2)$$

$$G''^{t_{v_0}}(\omega) = C_v . G''^{t_v}(\omega / a_v) \qquad (3)$$

where t_{v_0} is the reference ageing time, B_v and C_v describe changes in the relaxed and unrelaxed moduli as described in ref. 7.

These equations imply that to superpose the experimental curves it is necessary to make a vertical shift and a rotation, as well as the horizontal shift a_v. For reasons of precision, the analytical solution of the three equations (1), (2) and (3), with three unknowns a_v, C_v and B_v does not give satisfactory results. We therefore used the regression technique which has already been used for the dielectric measurements by Guerdoux *et al.*[7].

An analytical form $G'^{t_{v0}}(\omega)=A_0+A_1\log\omega+A_2\log^2\omega+A_3\log^3\omega$ is assumed for $G'^{t_{v0}}(\omega)$ in the reference state where the most extensive data is available, and the parameters A_0 to A_3 obtained by least squares optimization. For each of a set of assumed values of $v=-\mathrm{d}\log a_v/\mathrm{d}\log t_v$ equation (2) is written as

$$B_v+C_vG'^{t_v}(\omega/a_v)=A_0+A_1\log\omega+A_2\log^2(\omega)+A_3\log^3(\omega)=G'^{t_{v0}}(\omega)$$

and then B_v and C_v obtained by linear regression of $G'^{t_{v0}}(\omega)$ on $G'^{t_{v0}}(\omega/a_v)$. Values of v, B_v and C_v are chosen in such a way as to lead to a satisfactory master curve $G'^{t_{v0}}(\omega)$. The same values can then be used to obtain master curves for $G''^{t_{v0}}(\omega)$ and $G^{t_{v0}}(t)$.

The master curves obtained by this procedure are presented in *Figures 4* and *5* where the superposition is very good for the three curves. We can see that the values of a_v, B_v and C_v calculated from the $G'(\omega)$ curve also gives a good superposition for the $G''(\omega)$ curve. This is a good indication of the uniqueness of the values of a_v, B_v and C_v. *Table 2* gives the values of the superposition parameters.

We note from the Table that the values of a_v, B_v and C_v obtained independently from $G'(\omega)$ and $G(t)$, are the same for similar reference ageing times. We can also note that the parameters B_v and C_v suggest rather small vertical shifts and $v\approx1.00$, which is in agreement with the results of Struik[5].

Polycarbonate at 115°C

In order to further check the validity of the preceding analysis, we have measured the physical ageing of the polycarbonate for another temperature. We have chosen 115°C, which is approximately 30°C below the glass transition temperature. The results are given in *Figure 6* and *Table 3*.

We can see in *Figure 6* that the superposition for $G'(\omega)$ and $G''(\omega)$ is rather good. But the difference compared with the results obtained at lower temperatures is that the values for the vertical shift B_v are large as compared with the values of $G'(\omega)$. This is unexpected and difficult to reconcile.

From the Figure we can see that $G'(\omega)$ shows a minimum *versus* ω, which indicates that at 115°C and for

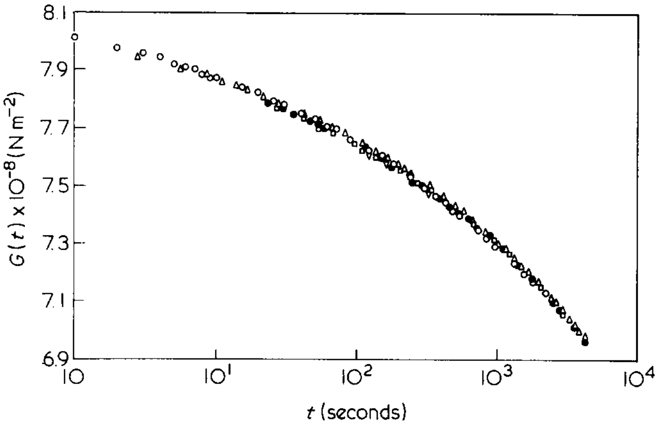

Figure 4 Relaxation modulus $G(t)$ as a function of time. Master curve for polycarbonate at 30°C. (▽) 20 min, (□) 60 min, (●) 136 min, (△) 292 min, (○) 808 min

Table 1 Values of the superposition parameter a_v for PC at 30°C obtained by horizontal shifts on the curves $G(t)$, $G'(\omega)$, $G''(\omega)$

$G(t)$	t_v (min)	20	60	136	292	808	ν
	a_v	0.02	0.06	0.17	0.32	1	1.06
	t_v	37	61.4	110.4	244	800	ν
$G'(\omega)$	a_v	0.006	0.015	0.04	0.14	1	1.66
$G''(\omega)$	a_v	0.11	0.11	0.2	0.45	1	0.718

Table 2 Superposition parameters for PC at 30°C, ν = 1.00

	t_v(mins)	37	61.4	110.4	244	800
$G'(\omega)$ and $G''(\omega)$	$B_v\times10^{-7}$ (Nm^{-2})	−9.66	−5.78	−1.52	−0.046	0
	C_v	1.130	1.074	1.027	1.005	1
	$\frac{B_v}{C_v}\times10^{-7}$ (Nm^{-2})	−8.55	−5.38	−1.48	−0.458	0
	a_v	0.046	0.077	0.138	0.305	1
	t_v(min)	20	60	136	292	808
$G(t)$	$B_v\times10^{-7}$ (Nm^{-2})	−8.08	−4.60	−0.68	−0.0294	0
	C_v	1.125	1.071	1.013	1.005	1
	$\frac{B_v}{C_v}\times10^{-7}$ (Nm^{-2})	−7.18	−4.29	−0.672	−0.0292	0
	a_v	0.0245	0.074	0.170	0.363	1

this range of frequency we are located between the main relaxation and the β relaxation.

As Struik has shown that ageing does not affect secondary relaxation processes, we can expect that the curves cannot be superposed over the entire frequency range. In this case even if the McCrum analysis allows us to superpose the G' and G'' curves, we must recognize, especially as the B_v parameter is large, that this type of superposition may not be unique and may even be physically incorrect.

Poly(methyl methacrylate)

We have carried out the same experiments for PMMA at 80°C. The curves $G(t)$, $G'(\omega)$ and $G''(\omega)$ are plotted in *Figures 7* and *8*.

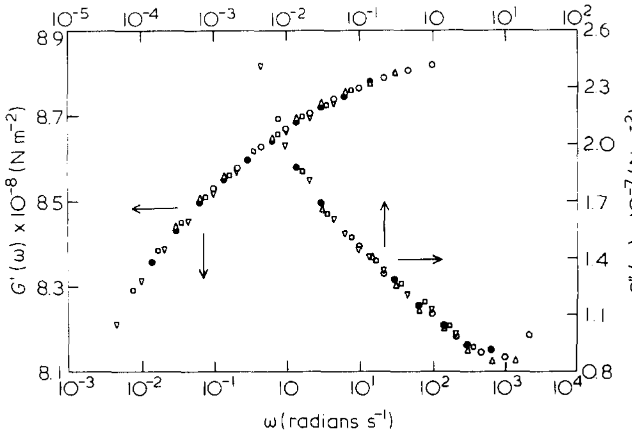

Figure 5 Storage and loss modulus $G'(\omega)$, $G''(\omega)$ as a function of frequency. Master curve for polycarbonate at 30°C. (▽) 37 min, (□) 61.4 min, (●) 110.4 min, (△) 244 min, (○) 800 min

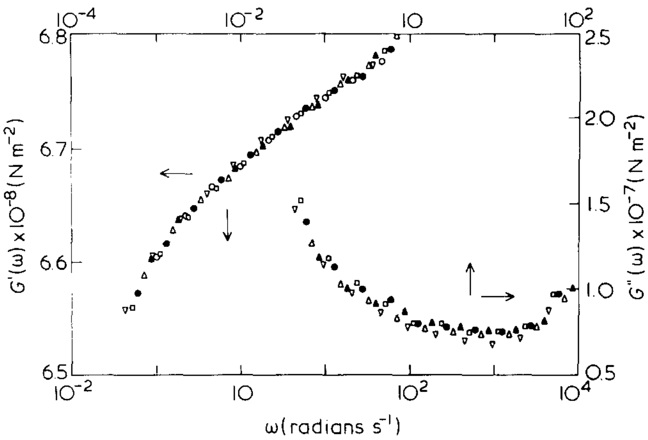

Figure 6 Storage and loss modulus $G'(\omega)$, $G''(\omega)$ as a function of frequency. Master curve for polycarbonate at 115°C. (▽) 31 min, (□) 55.5 min, (●) 104.3 min, (△) 202 min, (▲) 447 min, (○) 803 min

It is clear that the curves are impossible to superpose by a simple horizontal shift, especially for the $G''(\omega)$ curve. We can also see that at this temperature we are located between the β relaxation at high frequencies and the α relaxation which appears at the lowest frequencies.

In this case we have tried again to use the McCrum analysis and the master curves are plotted in *Figures 9* and *10*. The superposition parameters are given in *Table 4*. The master curves are good, but the B parameters are again large as compared with the values of the modulus, as was found for polycarbonate at 115°C.

The results presented here suggest that any method of superposition based on a *uniform* horizontal shift, without a vertical shift as in the simplest Struik analysis, or with a vertical shift following Chai and McCrum, is unsatisfactory. It seems necessary to recognize the occurrence of a

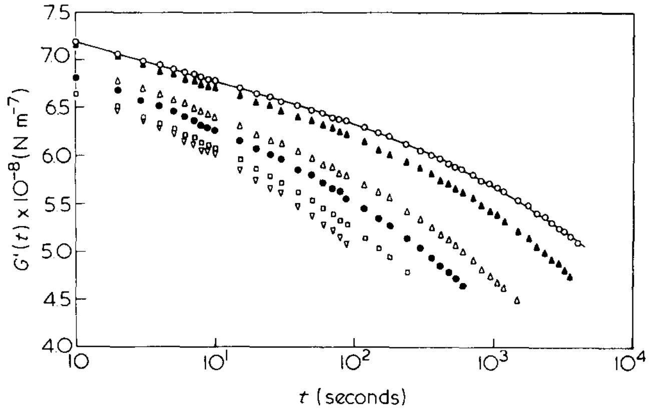

Figure 7 Relaxation modulus $G(t)$ for PMMA at 80°C as a function of time for different ageing times t_e. (▽) 30 min, (□) 64 min, (●) 135 min, (△) 282 min, (▲) 1125 min, (○) 2547 min

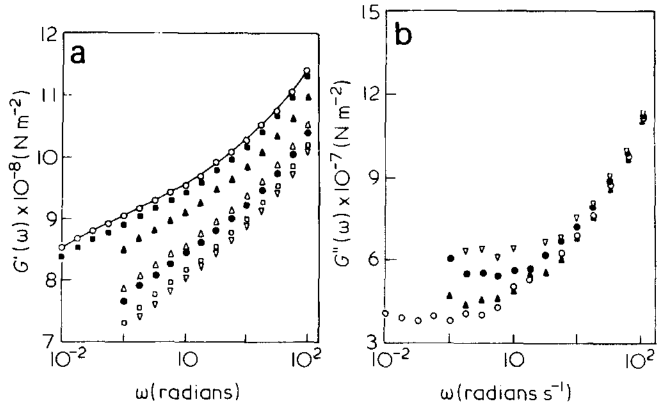

Figure 8 (a) Storage modulus and $G'(\omega)$ and (b) loss modulus $G''(\omega)$ for PMMA at 80°C as a function of frequency for different ageing times t_e. (▽) 30 min, (□) 47 min, (●) 105 min, (△) 150 min, (▲) 1045 min, (■) 2600 min, (○)3825 min

Table 3 Superposition parameters for PC at 115°C, $\nu = 0.25$

	t_V(min)	31	55.5	104.3	202	447	803
	$B_V \times 10^{-8}$ (Nm^{-2})	2.639	2.028	1.791	1.684	1.278	0
	C_V	0.656	0.749	0.777	0.785	0.820	1
$G'(\omega)$ and $G''(\omega)$	$\frac{B_V}{C_V} \times 10^{-8}$ (Nm^{-2})	4.023	2.708	2.305	2.145	1.559	0
	a_V	0.444	0.513	0.600	0.708	0.863	1

Table 4 Superposition parameters for PMMA at 80°C, $\nu = 0.50$

	t_V(min)	30	47	105	150	1045	2600	3825
$G'(\omega)$ and $G''(\omega)$	$B_V \times 10^{-8}$ (Nm^{-2})	4.375	4.143	3.499	3.234	1.513	0.485	0
	C_V	0.582	0.606	0.674	0.698	0.869	0.955	1
	$\frac{B_V}{C_V} \times 10^{-8}$ (Nm^{-2})	7.517	6.837	5.191	4.633	1.741	0.507	0
	a_V	0.089	0.111	0.166	0.198	0.522	0.824	1
	t_V(min)	30	64	135	282	1125	2547	
$G(t)$	$B_V \times 10^{-8}$ (Nm^{-2})	2.369	2.135	1.876	1.507	0.688	0	
	C_V	0.644	0.707	0.740	0.792	0.900	1	
	$\frac{B_V}{C_V} \times 10^{-8}$ (Nm^{-2})	3.568	3.020	2.535	1.903	0.756	0	
	a_V	0.108	0.158	0.230	0.333	0.665	1	

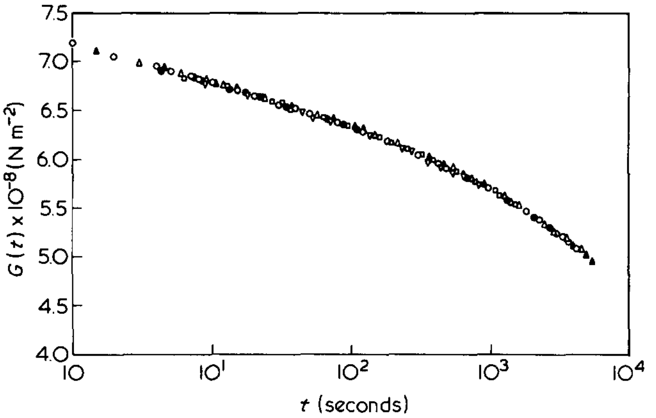

Figure 9 Relaxation modulus $G(t)$ as a function of time. Master curve for PMMA at 80°C. (▽) 30 min, (□) 64 min, (●) 135 min, (△) 282 min, (▲) 1125 min, (○) 2547 min

change in shape of the relaxation time spectrum, which greatly increases the complexity of the analysis. The suggestion of Struik that parts of the spectrum describing the secondary relaxations (high frequency) are not shifted horizontally is consistent with our data. It has also been supported by the dielectric data of Guerdoux and Marchal[7] who however demonstrated in addition that the strength of the secondary relaxations decreased with ageing, and so requires a simple vertical shift.

CONCLUSION

It appears that the horizontal shift proposed by Struik to superpose the $G(t)$, $G'(\omega)$ of $G''(\omega)$ for different ageing times is clearly only a first approximation and cannot be valid for the entire ranges of time or frequency.

The results obtained here agree with those of G. B. McKenna and A. J. Kovacs[9].

In the case where the mechanical measurements are taken mainly in the α region it appears that the McCrum analysis, based on the hypothesis that the limiting values of the viscoelastic functions vary with ageing time, gives a good superposition for the three functions $G'(\omega)$, $G''(\omega)$, $G(t)$ and reasonable values for a_v, B_v and C_v the three superposition parameters.

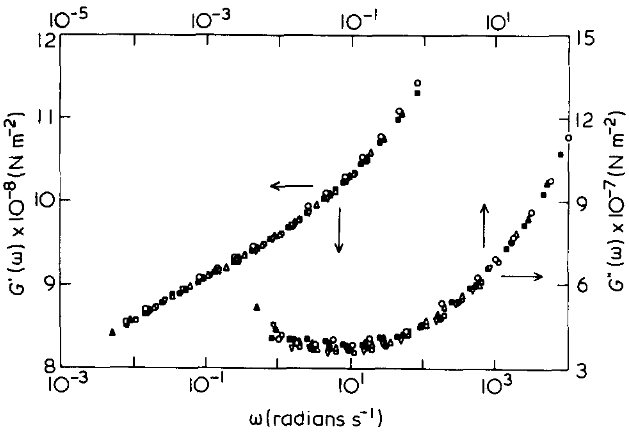

Figure 10 Storage and loss modulus $G'(\omega)$, $G''(\omega)$ as a function of frequency. Master curve for PMMA at 80°C. (▽) 30 min, (□) 47 min, (●) 105 min, (△) 150 min, (▲) 1045 min, (○) 3825 min

In the case where we stand between two transitions, it appears that the simple superposition of the curves is impossible and that the method proposed by McCrum involving changes in the limiting moduli gives values for B_v and C_v which are much too large, even if the superposition is satisfactory.

ACKNOWLEDGEMENT

We acknowledge CdF Chimie for the financial support of L. Guerdoux during the course of this work.

REFERENCES

1 Ferry, J. D. in 'Viscoelastic Properties of Polymers', John Wiley, New York, 1970
2 McCrum, N. G. and Morris, E. L. *Proc. Roy. Soc.* 1964, **281**, 258
3 Kovacs, A. J. *Fortsch. Hochpolym. Forsch.* 1963, **3**, 394
4 Kovacs, A. J., Stratton, R. A. and Ferry, J. D. *J. Phys. Chem.* 1963, **67**, 152
5 Struik, L. C. E. 'Physical Ageing in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978
6 Chai, C. K. and McCrum, N. G. *Polymer* 1980, **21**, 706
7 Guerdoux, L. and Marchal, E. *Polymer* 1981, **22**, 1199
8 Macosko, C. W. and Starita, J. M. *SPE J.* 1971, **27**, 36
9 McKenna, G. B. and Kovacs, A. J. *Polym. Prepr.* 1983, **24**, 100