The Very Long-Term Volume Recovery of Polycarbonate: Is Self-Retardation Finite?

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ABSTRACT: The specific volume change of Bisphenol A polycarbonate was measured at room temperature for several years. The effects of formation conditions like cooling rate and pressure, the addition of low molecular additives, and injection molding and quenching were investigated. The volume shrinkage at long times was found to be much higher than extrapolated from short term measurements. A general pattern is observed in the volume recovery curves. They start with a small constant slope on the logarithmic time scale. After about 10^7 s a transition is observed to a much steeper slope. Whereas in the first section the characteristic increase in τ_{eff} is observed, the volume recovery during the transition can be fitted quite well with a single exponential. The sharp transition suggests that there is a long retardation time, which may represent the genuine α-relaxation. It also means that the self-retardation during physical aging is finite. The slope at long times ($>10^7$ s) scales with the distance from equilibrium, as extrapolated from measurements close to T_g. The cooling rate during vitrification affects the slope in the first zone only, while the formation pressure leads to a vertical shift of the curves. Addition of low molecular weight additives leads to a dramatic densification and accelerates the volume recovery.

Introduction

Structural relaxation in glassy systems is attracting a lot of scientific interest[1] and is of great practical importance. Volume relaxation is particularly interesting as the specific volume is one of the state variables and affects all other properties.[2] The fundamentals of volume recovery of amorphous polymers were established already a long time ago by experiments of Kovacs[3] and Goldbach and Rehage.[4] A strong nonlinearity and asymmetry in the response was observed. It was realized very early that the volume recovery behavior cannot be described by a simple exponential decay. Therefore a distribution of relaxation times was introduced. The nonlinear behavior could only be described if this spectrum were to be dependent not only on the actual temperature but also on an additional ordering parameter which reflects somehow the structure. Both the fictive temperature[5,6] and the departure from equilibrium[7] are equivalent descriptions of that notion. They relate the kinetics to the average state as expressed by the specific volume. It has been shown that this concept is not sufficient to describe all the observed behavior correctly. A multi-order parameter model is required. This can be derived from the free volume distribution by discretization and alloting a certain relaxation time to each discrete free volume fraction.[8,9] In that way the spectrum will not only shift but also change shape with temperature and time. However, the predictive capability is still not much improved over other models, especially far from equilibrium.

Most work on volume relaxation has been carried out very close to the glass transition temperature, so that the time to equilibrium remained within the experimental window. For industrial applications of polymers the behavior far from equilibrium is, however, important for the prediction of a period equal to a product lifetime. Certainly no predictions can be made yet for such conditions with existing models. The goal of the present experimental investigation is to explore the very long-term volume recovery far below T_g and the effects of industrial formation conditions on it. Additionally, the influence of low molecular weight additives is investigated.

Experimental Section

Materials. All experiments on pure polycarbonate were carried out with Makrolon CD 2000 from Bayer AG (Leverkusen, Germany). This is an optical grade and has ben characterized previously.[10] PC standards from Aldrich, which have a higher molecular weight, M_w, of 48 000, were used for the experiments with diluents. The diluents used are given in Table 1.

Volume Recovery. The density was determined using a so-called gradient column (Davenport, U.K.) filled with K_2CO_3 water solution at 23 °C. Since the gradient in the column does not remain stable fo the whole period of measurement, columns were refilled regularly. During that period the samples were stored in the same solution. The density was derived from calibration spheres.

Special attention was devoted to the potential problems with th gradient column technique concerning the accuracy and reliability. In total, 33 spheres from different series of the supplier were evaluated in the range of interest. The densities of the spheres were calibrated against each other. The results are shown in Figure 1. As one can see, there is considerable scatter. The spheres from series B almost coincide with the best fit line of all spheres, also indicated in the graph. Therefore this series was eventually employed in all the recovery measurements. All samples were referred to the same calibration curve, excluding any effects from deviations in calibration spheres. The number of samples in the column was limited in order to avoid interference. The range of the columns was typically 2×10^{-2} g/cm^3 over a height of 50 cm. The reading of the position can be done with an accuracy of better than 1 mm, leading to an effective resolution of 4×10^{-5} g/cm^3 in the worst case.

For the validity of the technique it is also essential to show that the immersion solution does not affect the volume recovery behavior. The PC samples saturate in the solution within about 2 days. The solution always leads to an increase of the density due to the saturation of the polymer with water. For the K_2CO_3 solution this is less than for pure water, typically 0.03−0.05% (w/w), as determined with a commercial humidity tester (Mitsubishi) based on Karl Fischer titration. This leads to a vertical shift of all curves of the same order of magnitude, but it should not affect the shape of the measured curves. In order to check that, samples with identical formation conditions were inserted into the column at different aging times. As will be shown below this did not affect the recovery

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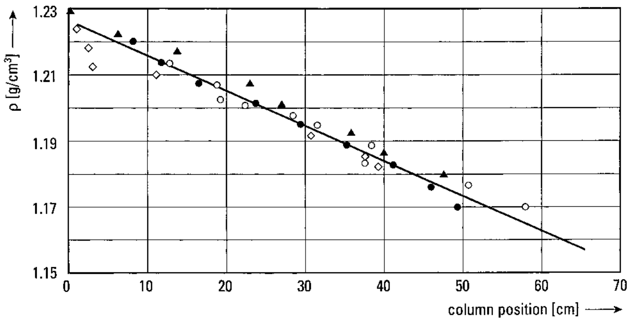

Figure 1. Calibration of various sets of calibration floats, as indicated by the different symbols: (○) A; (●) B; (◇) C; (▲) D. The solid line represents a linear regression.

Table 1. Additives

1	Bisphenol A
2	diphenyl carbonate
3	ethylene carbonate
4	*p*,*p*′-dimethoxybenzophenone
5	*p*,*p*′-dihydroxybenzophenone
6	*p*,*p*′-dichlorobenzophenone
7	*o*,*o*′-biphenol
8	dibenzofuran
9	*p*,*p*′-dimethoxybenzoin
10	*p*,*p*′-dimethoxybenzil

behavior. Additionally, samples which had been kept in the solution for several years were analyzed for their potassium concentration. Elemental analysis yielded a K concentration below the detection limit of 2 ppm, indicating that the ions from the solution were not accumulated in the samples. The samples and the calibration spheres were checked and cleaned to avoid any deposition of the K_2CO_3 salt at the surface. The possibility of crystallization of the polymer under the influence of the solution was investigated by X-ray scattering. No significant differences were observed betwen the scattering pattern of the sample that had been kept in the solution for several years and that of an as-quenched sample.

Volume recovery at elevated temperatures was determined by storing samples in an oven for various periods of time and measuring the density at room temperature in the column.

Formation Conditions. All samples were compression molded after predrying prior to the specific treatment. The cooling rate during vitrification was varied by cooling samples from above the T_g at different rates in a hot stage (Mettler) and a DSC (DSC 7, Perkin-Elmer) down to room temperature. Cooling rates of 0.1, 1, 1.6, 10, and 80 K/min were applied. In one case a constrained quench was used on a sample of 0.1 mm thickness. In that case the maximum cooling rate is approximately 6000 K/min but is not constant.[11] The pressure during vitrification was varied by compressing the samples in the molten state in a cylinder with a piston and then cooling slowly (typically 1 °C/min) to room temperature while keeping the force on the piston constant. Pressures of 1, 300, 600, and 900 bar were applied.

Inhomogeneous formation conditions were applied by quenching disk-shaped samples of typically 2 mm thickness in a stirred bath of water or ethylene glycol of varying temperatures, as described elsewhere[12] and in a constrained quench setup.[11] In these cases residual cooling stresses are built up in the sample. Injection-molded samples were obtained from the same series of experiments as have been described elsewhere.[11] Volume recovery was measured on two samples obtained with a mold temperature of 90 °C and different hydraulic packing pressures, viz. 1 and 50 bar. Pieces of approximately 1 cm^2 were cut out of the molded samples at different positions for use in the gradient column.

Solid solutions of low molecular weight additives in PC were made by codissolving in $CHCl_3$ and quick evaporation of the solvent in a Petri dish. The foils were dried carefully and compression molded before undergoing a quench from the rubbery state to room temperature in a water bath. Table 1 shows a list of the additives used. As can be sen, they all have some structure in common with the polymer.

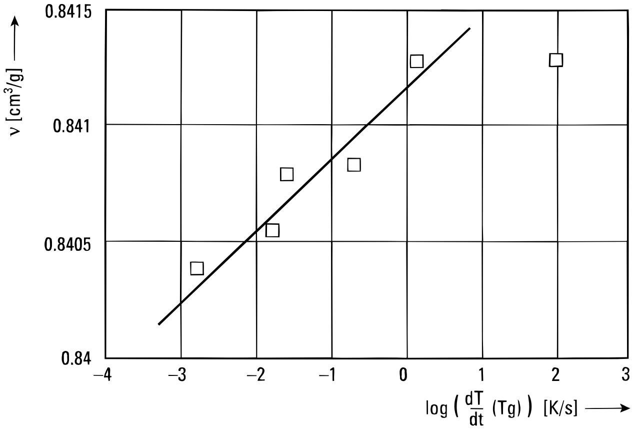

Figure 2. Initial specific volume of PC samples at RT vs the logarithm of the cooling rate during vitrification.

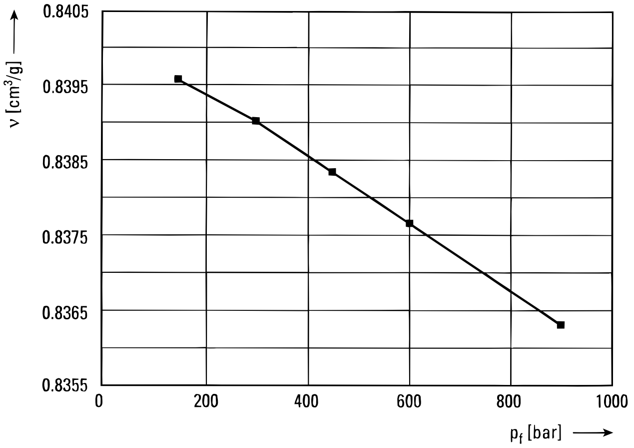

Figure 3. Initial specific volume of PC samples at RT vs pressure applied during vitrification.

Dynamic Mechanical Analysis. Dynamic mechanical analysis was performed on the plasticized systems using a DMTA MK I (Polymer Laboratories) in a single cantilever bending mode at 1 Hz at a heating rate of 4 K/min. The thermal expansivity was determined with a thermomechanical analyzer (TMA-2, Perkin-Elmer) in heating and cooling runs with rates of 5 and 2.5 K/min.

Results

Formation Conditions. First of all the effects of the different formation conditions on the initial density will be presented. "Initial" means after saturation with the solution in the column. Figure 2 shows the specific volume of samples cooled at different rates. This figure was extracted from results presented elsewhere.[13] As can be seen, a linear relation with a slope of 3×10^{-4} is observed between the specific volume and the logarithmic cooling rate. The value for the highest cooling rate does not fit this relation, probably due to an overestimation of the effective cooling rate during the quench.

The effect of the formation pressure is demonstrated in Figure 3. The residual densification per unit pressure applied during vitrification is also called pseudocompressibility, κ'.[14] From Figure 3 a value of 4.6×10^{-11} Pa^{-1} is derived. This is close to the value given by Bree et al.[15]

Figure 4 shows the initial specific volume at room temperature of solid solutions of PC with various diluents at different concentrations. The T_g (maximum in tan δ) of the mixtures of PC with one of the diluents,

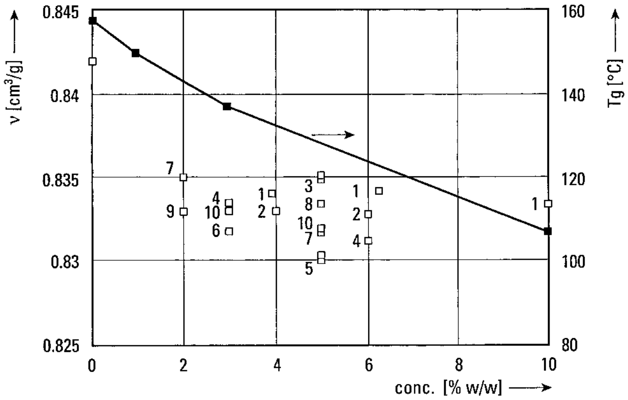

Figure 4. Initial specific volume of PC samples containing additives at RT (open symbols) and T_g of samples containing p,p'-dimethoxybenzophenone (filled symbols) vs concentration. For the meaning of numbers see Table 1.

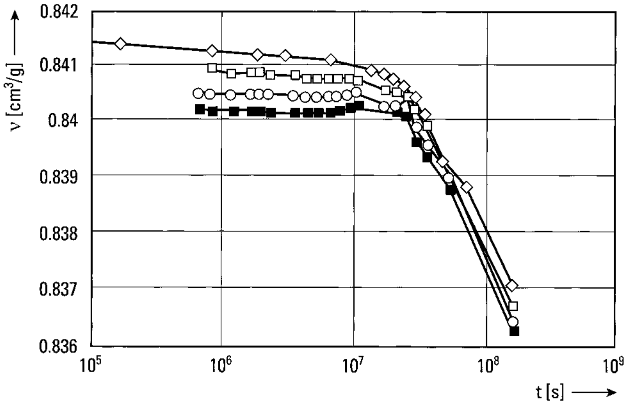

Figure 5. Volume recovery of PC samples at 23 °C obtained at different cooling rates: (■) 0.1 K/min; (○) 1 K/min; (□) 10 K/min; (◇) 80 K/min.

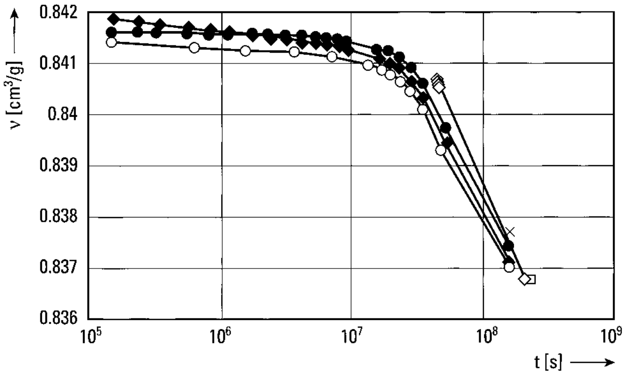

Figure 6. Volume recovery of PC samples at 23 °C obtained by quenching at different conditions and inserted into the column after different time spans after quench: (○) constant cooling rate sample 80 K/min; (●) quench from 160 to 120 °C in ethylene glycol; (◆) quench from 160 to 22 °C in ethylene glycol; (◇) quench from 160 to 22 °C in water; (□) quench between copper pistons from 160 to 25 °C; (×) quench between copper pistons from 160 to 22 °C.

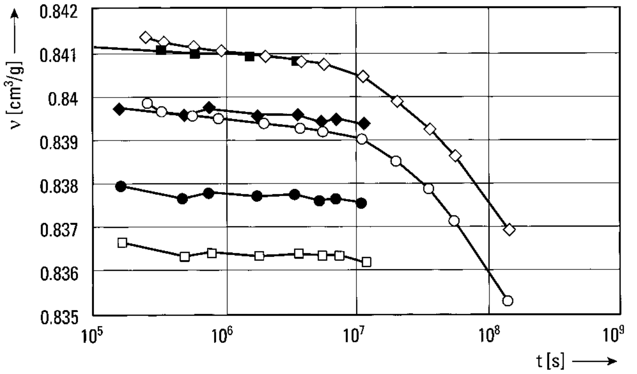

Figure 7. Volume recovery of PC samples at 23 °C vitrified under pressure and by injection molding. Injection molded: (◇) without packing pressure; (○) with packing pressure. Compression molded: (■) at 1 bar; (◆) at 370 bar; (●) at 600 bar; (□) at 900 bar.

viz. dimethoxybenzophenone, is also indicated. It is interesting to note how strong the effect is. By an addition of only 2% the density increases by 1%! With increasing concentration the densification levels off. Obviously, at high concentrations the effect of dilution compensates for the improvement in packing of the polymer. No saturation is observed in the T_g. In this way the density remains more or less constant while the T_g can be varied considerably. Another observation from Figure 4 is that all diluents lead to a strong densification within the applied range. The variation of concentration is limited by induced crystallization. This is especially often the case with hydroxy-substituted diluents. Another trend which was observed is that the densification is stronger with diluents with longer distances between the phenyl rings within the applied range, e.g. from biphenol to bis(phenol) to benzoin. Ethylene carbonate, which was the smallest molecule, led to the smallest densification effect of all.

Volume Recovery. The formation conditions can affect the initial density (after thermal equilibration) in a very broad range. The question of interest is their influence on the long-term development of the specific volume. In Figure 5 the results obtained with samples of different cooling rates are displayed. The recovery curves are very similar in shape. One can clearly see the vertical shift of the curves with cooling rate, as indicated in Figure 2. Each curve is characterized by a flat first part followed by a sharp transition to a much steeper part. The transition occurs at the same aging time for all samples, at approximately 6 months. Note that the abscissa range is 30 years. This is a very interesting phenomenon which has not been described before. It will have a dramatic effect on the modeling of the long term recovery of polymer glasses.

Figure 6 shows the volume recovery of samples which were quenched under different conditions. The result with the constant cooling rate of 80 K/min of Figure 5 is included for comparison. This demonstrates the similarity of the responses. Quenched samples behave like fast-cooled ones. In the case of quenching to 120 °C the slope in the first part is much smaller. The reason for this is probably that during the residence in the quench bath at 120 °C the sample is annealed. In Figure 6 a number of samples are also included that have identical ages but that were stored outside the gradient column for a long period (1, 5, and 7 years) before they were inserted. As can be seen, they fit very well to the samples that had been continuously kept in the column after being vitrified. This is a very important point, since it proves that the presence of the water solution is not responsible for the unexpected recovery behavior.

The volume recovery responses of samples vitrified under pressure are displayed in Figure 7 together with two examples of injection-molded PC. Unfortunately, the “pressure” samples could not be followed for the same long period due to an experimental problem. But still it becomes clear that the formation pressure leads only to a vertical shift. The slopes are independent of

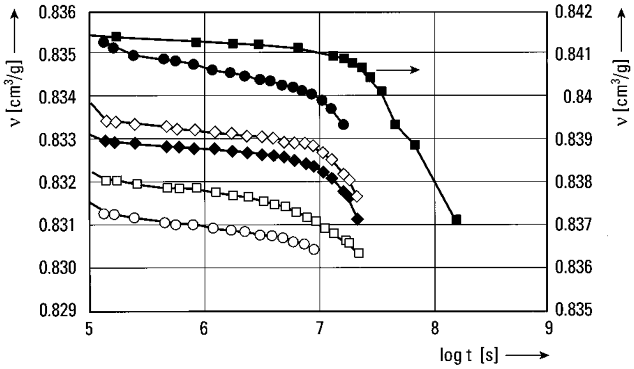

Figure 8. Volume recovery of PC samples at 23 °C containing additives: (■) cooling rate sample 80 K/min; (●) 2% *o,o′*-biphenol; (◆) 2% *p,p′*-biphenol; (◇) 3% *p,p′*-dimethoxybenzophenone; (□) 3% *p,p′*-dichlorobenzophenone; (○) 6% *p,p′*-dimethoxybenzophenone.

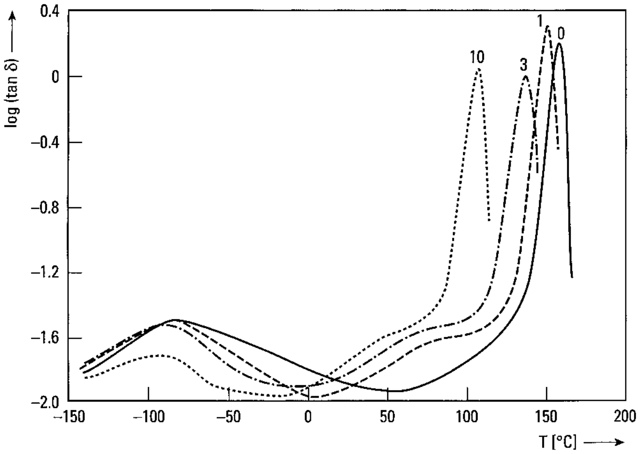

Figure 9. Damping (log tan δ) of PC samples with different concentrations of *p,p′*-dimethoxybenzophenone, as indicated, vs temperature.

pressure. The slopes of the injection-molded samples are higher in the first part. This is obviously due to the much higher cooling rate with injection molding than with the procedure followed with the formation pressure experiments. The vertical position is as expected based on the pressure trace during injection molding. The transition to the steep part starts a little earlier and is more gradual than the transition in the quenched samples. Again, the pressure does not affect the shape of the recovery curves. This is in clear contrast to, for instance, PMMA and PS, where recovery of residual compression leads to an expansion of the samples with time at room temperature.[16,17]

The volume recovery of samples containing additives is shown for a few examples in Figure 8 together with a fast-cooled sample. (Note the vertical offset.) Again the same pattern is observed. The slope in the first part is a little higher, and the transition also occurs earlier. The additive obviously leads to an acceleration of the volume recovery despite the much higher density. The mobility of the system is higher, since the distance to T_g is smaller. This increased mobility in the solid solutions is nicely demonstrated by the dynamic mechanical behavior shown in Figure 9. There the tan δ is plotted for different concentrations. One can see that with increasing concentration the γ-relaxation peak at low temperatures gets suppressed. This behavior is well-known as antiplasticization.[18] The T_g decreases and a shoulder in the damping develops (maybe a β relaxation) which leads to a higher damping at room temperature, an indication of the increased mobility.

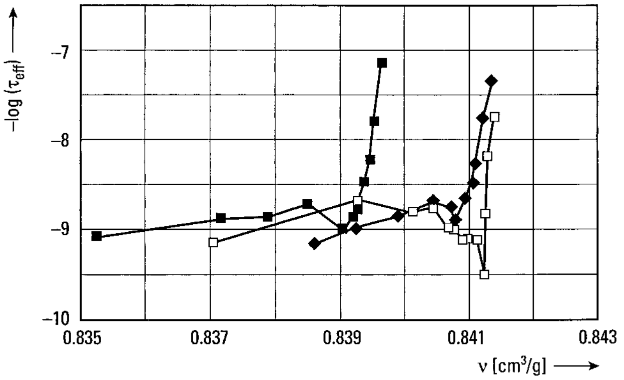

Figure 10. τ_{eff} of various samples vs momentary specific volume: (□) cooling rate 80 K/min; (◆) injection molded without packing pressure; (■) injection molded with packing pressure.

Discussion

Effective τ. A parameter which was introduced by Kovacs[3] in order to characterize the recovery behavior is the so-called τ_{eff}. This is a retardation time which would give the same distance from equilibrium at a certain time if one dealt with a single exponential behavior:

$$\tau_{\text{eff}}^{-1} = \frac{-1}{(v - v_{\infty})} \frac{\mathrm{d}v}{\mathrm{d}t} \tag{1}$$

v being the specific volume. Typical for recovery curves following a down quench is the increase of τ_{eff} with time. It is customary to plot τ_{eff} versus the distance from equilibrium. In the present case the distance from equilibrium is not known. But since we are only dealing with one temperature, the equilibrium density is constant and we can plot versus the absolute specific volume. In Figure 10, τ_{eff} is plotted for samples of different formation histories. As can be seen, there is a characteristic slowing down on the right, i.e. at the short time end of the retardation process. In this part the expected self-retarding aging behavior is observed. The remarkable feature is the sudden leveling off of the τ_{eff} at the same level for the different samples. The retardation time becomes constant ($\approx 10^9$ s) and self-retardation ceases. This is surprising, as one is still far removed from equilibrium. Using the Tait parameters given by Zoller,[19] the equilibrium line of the specific volume can be extrapolated down to room temperature. This yields a value of 0.8087 at 23 °C, which was actually used for the calculation of τ_{eff} in Figure 10. Consequently, only a little more than the first 10% of the whole recovery has been achieved in the experiments presented so far in the case of the pure PC. As one can conclude from the injection-molded samples, pressure only leads to a shift of the curves and does not affect the kinetics. The plasticized systems are more dense, but for these systems the equilibrium specific volume could not be estimated. Therefore they are not presented in this way. But the recovery curves already showed the similarity of the responses.

It is difficult to speculate about the further course of τ_{eff}. The distance from equilibrium is still so great that it is impossible to extrapolate. The experimental time scale, however, becomes prohibitive for making a significant extension toward the left in Figure 10.

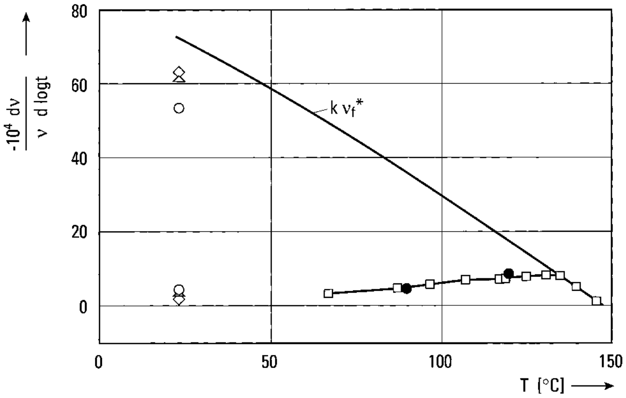

Figure 11. Logarithmic slope of recovery curves vs temperature: (□) data of Greiner and Schwarzl:[20] (●) samples aged in oven; (◇) cooling rate 80 K/min; (△) quenched; (○) injection molded.

Logarithmic Slope. Another characteristic of the recovery curves is the slope on a logarithmic time scale:

$$\beta = \max\left[\frac{-1}{v}\frac{dv}{d\log t}\right] \tag{2}$$

The maximum slope was found to scale with the distance from equilibrium. Below a certain distance from T_g the maximum slope was found to decrease.[2,20,21] This was ascribed to the increasing effect of self-retardation. A comparison of the slopes of the recovery curves of Figures 5−7 with results given by Greiner and Schwarz[20] is depicted in Figure 11. The latter represent maximum values according to eq 2. The slopes of the present recovery curves are represented as averages determined separately for the two distinct sections, viz. for times shorter and times longer than 10^7 s. For a direct comparison with the results of Greiner and Schwarzl volume relaxation experiments were also carried out at temperatures of 90 and 120 °C. As can be seen, the agreement is very good. Also, the values obtained at room temperature for the first part of the recovery curves fit very well the values determined by Greiner and Schwarzl. The different symbols represent different formation conditions. The slope of the recovery curves (on a logarithmic time scale) *after* the transition ($t \approx 10^8$ s) at room temperature is about 10 times higher and much higher than any reported in literature at elevated temperatures.

A possible explanation for such a high slope might come from a scaling with initial distance from equilibrium, as was established close to the glass transition temperature. The solid line in Figure 11 represents such a scaling proportional to the distance from equilibrium, v^*. The latter was estimated by taking the Tait parameters of Zoller[19] to extrapolate the equilibrium line down to room temperature. The glassy line was obtained by drawing a line through the initial specific volume with a slope equal to the thermal expansion coefficient of the glassy state, as determined experimentally. The distance from equilibrium was then multiplied by a prefactor k to fit the points of Greiner and Schwarzl at high temperatures (right of the maximum in Figure 11). As can be seen in Figure 11, the extrapolated line comes close to the measured slopes at room temperature at long times. This means that the scaling with the distance from equilibrium as observed close to T_g could still be valid. However, if one keeps in mind that the second part of the recovery curves can be fitted reasonably well by a single exponential, the slopes would increase even further to a maximum at the time equal to the retardation time ($\approx 10^9$ s). In that case the maximum slope would be higher than the extrapolation in Figure 11. Unfortunately, the present data do not allow a statement with respect to the further course of the recovery curves. On the basis of all the data in the literature obtained close to equilibrium, a broadening of the spectrum, as frequently expressed by a stretched-exponential relation, seems more likely. In that case the apparent single exponential decay would only represent the transition between two clearly separated parts of the retardation spectrum.

Implications. The surprising but very consistent behavior reported here cannot be explained with existing concepts about physical aging. The transition in the volume recovery from a self-retarded to an exponential decay implies that the mobility of the system is not directly determined by its free volume. This was already evident in the literature for volume changes brought about by an applied pressure[2] in the sense that the rather large volume changes are not reflected in significant changes of the mobility. Here this is confirmed for the effect of pressure and it is also demonstrated for the densification by the addition of small molecules. In that case the densification is even accompanied by an acceleration of the recovery process. The observed finiteness of the self-retardation poses an even more severe challenge to the otherwise very appealing model of mobility linked to excess free volume.

The time to equilibrium will not be infinite. With a terminal relaxation time of the order of 1 Gs the equilibrium specific volume would be reached after approximately 300 years. This is much faster than extrapolated by a WLF[22] or VFT[23] kind of relation which diverges at some temperature below T_g. Of course it is still a long way to equilibrium, so an eventual broadening is very likely. Therefore it will be important to carry out experiments of sufficient duration at elevated temperatures to close the gap between the “short” time side of the recovery spectrum investigated here and the long time side which is usually probed in experiments close to T_g. It will be interesting to verify the extrapolation indicated in Figure 11. It will also be important to characterize the properties of the glasses in the exponential decay with respect to, for instance, density fluctuations, the positronium lifetime spectrum, and creep behavior. The question also arises whether the aging time−time superposition principle, as established by Struik,[2] remains valid in the part where the volume recovery follows exponential behavior.

Conclusions

- The volume shrinkage of PC was measured during 7 years at room temperature. It was found to be much higher than extrapolated from short term measurements.
- The recovery curves can be subdivided into two regimes. At times shorter than 10^7 s there is a self-retarded decay following a straight line on a logarithmic time scale with a slope as expected from the literature. At times longer than 10^7 s the slope increases to an at least 10-times higher value.
- Even far below T_g the maximum slope of the recovery curves seems to scale with distance from equilibrium. One only needs to measure long enough.
- After the increase in the first regime the τ_{eff} reaches a constant value at the transition to the second regime. The further recovery can be described by a single

exponential response. This means that self-retardation is finite. With a further increase in packing the mobility remains constant.

- The various formation conditions affect the volume recovery of PC in different ways but do not change the basic pattern. The cooling rate during vitrification and sub-T_g annealing change the slope in the first regime only. Quenched samples behave like fast-cooled ones. Cooling stresses have no significant effect. Formation pressure leads to a vertical shift of the curves without any effect on the kinetics of the recovery. Injection-molded samples shift vertically according to the average formation pressure during molding. Their slope in the first part is higher and the transition is more gradual than in quenched samples.
- The addition of low molecular weight additives leads to a dramatic densification (1%) and a slight acceleration of the recovery.

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