polymer papers

Apparent reversal of physical ageing in amorphous glassy polymers by electron beam irradiation

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(Received 24 February 1992)

It has been found that electron beam irradiation of physically aged, glassy polymeric films results in an apparent reversal of physical ageing (i.e. 'deageing') as determined by differential scanning calorimetry and yield stress behaviour. This is the first reported observation of 'deageing' in glassy polymers that does not involve heating above the glass transition or an imposed deformation process. Effects of dose level and dose rate on the physically aged state of polystyrene, poly(methyl methacrylate) and polycarbonate have been determined. The specific deageing behaviour has been found to be material-dependent and the extent of deageing is proportional to the total absorbed dose. The experimental results support a proposed hypothesis that this deageing phenomenon is the result of radiation-induced internal gas evolution, which produces an increase in free volume and corresponding reversal of physical ageing.

(Keywords: physical ageing; glassy polymers; electron beam irradiation; deageing; differential scanning calorimetry; yield stress; polystyrene; poly(methyl methacrylate); polycarbonate)

INTRODUCTION

Physical ageing is a phenomenon that occurs over time in glassy polymers that are maintained at some temperature below the glass transition temperature (T_g) and is a manifestation of the non-equilibrium nature of the glassy state. When a polymer is cooled from the liquid state, it begins to solidify as the glass transition is approached. The development of an 'equilibrium structure' below T_g becomes limited owing to the long relaxation times of the polymer chains, and can never be completed in the timeframe typically associated with *practical cooling processes*. Hence, when the glassy state is reached, the material is in a state of non-equilibrium. Physical ageing is a process by which the equilibrium glassy state is approached over time and is characterized by the decrease in the enthalpy of the glass. This enthalpy reduction is principally associated with a reduction in free volume of the glass as the equilibrium state is approached. This study illustrates that electron beam irradiation of physically aged glassy polymers results in an apparent 'reversal' of the physical ageing process. Changes in physical ageing were monitored by differential scanning calorimetry (d.s.c.) and yield stress behaviour. This work is the first reported observation of a reversal of physical ageing that does not involve heating above T_g or some sort of deformation process. Smith *et al.* have reported that a reversal of physical ageing can be induced by imposing a strain (either tensile or compressive) on aged polycarbonate[1]. The effects of thermal processes on the physically aged glassy state have been reviewed by Struik[2]. Before proceeding with details of the radiation-induced physical ageing reversal phenomenon considered in this study, some aspects of the effects of physical ageing on polymer properties that are pertinent to this study will be briefly reviewed.

Effects of physical ageing on polymer properties

Thermal properties. Since enthalpy relaxation is associated with physical ageing, this phenomenon will affect the thermal properties of glassy polymers, especially in the temperature region near the glass transition. It is well known that physical ageing produces an endothermic peak at the glass transition, which is a result of the enthalpy relaxation. Hence, the extent of physical ageing can be followed by the area under the endothermic peak at the glass transition, as will be done in this paper. Petrie and coworkers[3,4] and Matsuoka and Bair[5] have reported on the effects of physical ageing on thermal properties of polymers, and the reader is referred to their work for a treatise on this subject.

Mechanical properties. In addition to thermal properties, physical ageing can also greatly influence the mechanical properties of polymeric glasses. This is primarily due to the increased relaxation times of the polymer chains resulting from the decrease in free volume during ageing. Since the effect of ageing on the yield stress will be of importance in this study, it should be noted that the yield stress of poly(vinyl chloride)[2], polycarbonate[6] and poly(ethylene terephthalate)[7] has been shown to increase with ageing time. This behaviour is expected for most glassy polymers. In addition to increasing yield stress, physical ageing generally causes a decrease in creep rate and an increase in the storage modulus[2]. Again, these changes in properties arise from a decrease in

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0032-3861/93/050915-10

segmental mobility of the polymer chains resulting from the volume relaxation associated with physical ageing. Much work has been done on the effects of physical ageing on the mechanical properties of polymeric glasses, and the reader is referred to several reviews and books for a more detailed treatise on the subject[2,7,8].

Permeation of gases. Since a decrease in free volume is associated with physical ageing, this process may affect the permeation of gases in glassy polymers. Lee[9] has shown that the logarithm of the permeability coefficient decreases linearly with the inverse of the specific free volume of glassy polymers. This suggests that a reduction in free volume caused by physical ageing will decrease the permeability of polymeric glasses. Since irradiation of polymers is known to result in the internal evolution of gases[10], this consideration will be of importance in this work.

EXPERIMENTAL

Materials and sample preparation

The following polymers were used in this study: (a) bisphenol A polycarbonate (Aldrich Chemical), (b) poly(methyl methacrylate) and (c) polystyrene (Dow Chemical). Thin films (thickness ca. 3 mils (~76 μm)) were obtained by compression moulding between Teflon sheets at the following temperatures: (a) polycarbonate (PC) 210°C, (b) poly(methyl methacrylate) (PMMA) 180°C and (c) polystyrene (PS) 180°C. All samples were quenched to room temperature. PC was also solvent cast with methylene chloride to form thin films with thicknesses less than 1 mil (~25 μm). These solvent-cast films were used for the time delay experiment (see 'Results and Discussion'). Once formed, each film was physically aged at ca. 30°C below its glass transition temperature: 120°C for PC and 80°C for PMMA and PS. Ageing was carried out in a vacuum oven for up to one week. At this point, longer ageing times resulted in less than a ca. 5% increase in the area of the endothermic peak at the glass transition as determined by d.s.c. It must be stressed, however, that this does not imply that ageing has ceased. The rate of ageing in glassy polymers decreases nearly logarithmically with time, so at some point (depending on the material and ageing temperature) further reductions in the enthalpy of the glass may not be easily observed by d.s.c.

Radiation exposure

All films were irradiated using an Energy Sciences CB150 Electrocurtain as the electron beam radiation source. Samples were passed under the electron beam in an aluminium tray at speeds of either 20 or 40 ft/min (~10 or 20 cm s^{-1}). The beam current was varied up to 6 mA and the accelerating voltage was kept constant at 175 kV. Under these conditions doses ranging from 1 to 20 Mrads could be given in a single pass. Film thicknesses were maintained less than 5 mils (~127 μm) to ensure a uniform depth–dose profile. All samples were irradiated under a nitrogen-purged atmosphere; the oxygen content was in the range 250–350 ppm during processing. It should be noted, however, that the films were exposed to air between passes when more than one pass was necessary to achieve the required dose and dose rate.

Thermal analysis

The ageing behaviour and extent of enthalpy relaxation of all the polymers were followed by d.s.c. using a Seiko I DSC210 apparatus. The instrument was calibrated using an indium standard. Samples with weights in the range of 7 to 10 mg were sealed in aluminium pans and heated at a rate of 10°C min^{-1}. The extent of ageing was characterized by the area under the endothermic peak occurring at T_g. The baseline was taken by extrapolating the baseline established above the glass transition. It has been reported that this may result in an inaccurate value for the extent of enthalpy relaxation in the glass[5]. To determine the error associated with this analysis, second-run d.s.c. scans were made on some samples after quenching to room temperature and superimposed on the first-run scans to determine the net enthalpy difference between the aged and freshly quenched glasses. The results of this error analysis are shown in *Figure 1*. As illustrated, the error associated with this analysis of

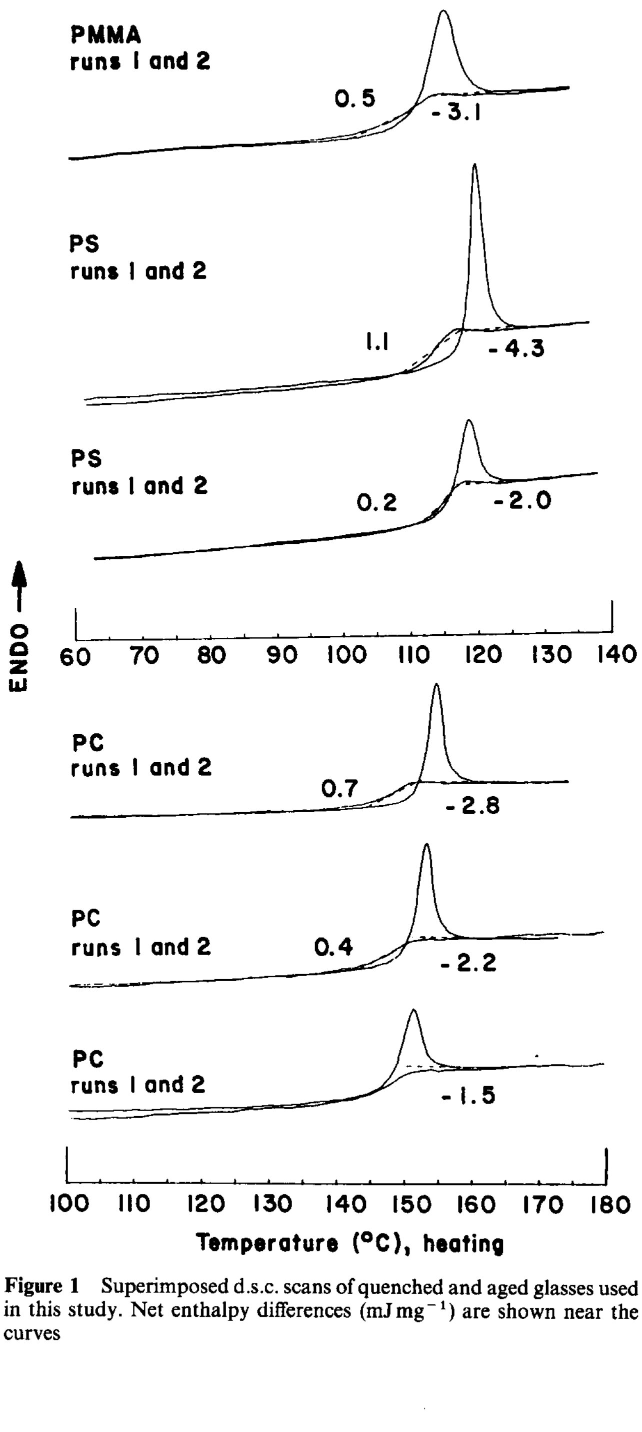

Figure 1 Superimposed d.s.c. scans of quenched and aged glasses used in this study. Net enthalpy differences (mJ mg^{-1}) are shown near the curves

enthalpy relaxation varies with the particular polymer and the extent of ageing in the sample. PS and PC have quite high errors associated with this analysis, while the error for PMMA is quite low. This level of error is of little consequence for this study since mainly trends are being established. However, to be sure that this error is not affecting the trends established, the endothermic peak areas were corrected for PS and PC based on this error analysis. As will be shown in the next section, the error has no significant effects on the trends to be discussed.

Molecular weight and gel fraction determinations

Molecular weights given were obtained using a Waters gel permeation chromatography column equipped with an ultra-violet detector ($\lambda = 254$ nm). Tetrahydrofuran (THF) was used as the solvent with a flow rate of 1 ml min^{-1}. Solutions of 50 wt% polymer were prepared for injection into the column. Only PMMA and PS standards were available, so g.p.c. was not carried out on PC.

Gel fractions on irradiated PS were obtained by extracting the films in THF with a Soxhlet extractor for 24 h. The insoluble fractions were stored under vacuum (30 inches of Hg ($\sim$760 mmHg)) at 120°C for at least 16 h prior to weighing to remove residual solvent. Longer storage times did not result in any significant weight changes. Gel fractions were obtained by dividing the insoluble weight by the initial weight, which was in the range of 80 mg.

Stress–strain measurements

The stress–strain behaviour of the PC films was studied using a model 1122 Instron tensile tester interfaced to a computer for data collection and stress calculation. A crosshead speed of 0.5 mm min^{-1} was employed. Dogbone samples (10 mm long and 3 mm wide) were cut from films with thicknesses ranging from 3 to 4 mils ($\sim$76–102 μm). Five dogbones of each sample were tested. Values reported for the yield stresses are based on the average of these five tests.

RESULTS AND DISCUSSION

Effects of radiation dose

As mentioned in the 'Introduction', it has been discovered that electron beam radiation exposure results in an apparent 'deageing' of glassy polymers. As will be illustrated, this seems to be a general phenomenon, which occurs in a variety of polymer glasses regardless of their individual intrinsic response to radiation exposure.

Figures 2–4 show the effect of dose (at 10 Mrad/pass) on the d.s.c. behaviour of PS, PMMA and PC in the glass transition region, respectively. Prior to irradiation, the former two polymers were stored at 80°C for one week, whereas PC was stored for one week at 120°C. It should be noted that the curvature in the PMMA baselines before the glass transition is due to the desorption of water on the film, but this does not seem to have any effect on the glass transition behaviour. (Well dried samples do not display this curvature.) The enthalpy values shown on the plots correspond to the area under the endothermic peak using the baselines drawn as shown. In all cases there is a steady *decrease* in the endothermic peak area and peak temperature with increasing dose. This clearly demonstrates that these polymer glasses are undergoing an apparent radiation-induced physical ageing reversal process. Furthermore, the extent of this ageing reversal is proportional to the total absorbed dose. It should be realized, however, that the decrease in peak temperature may be influenced by radiation degradation as well as a reversal of physical ageing. It is important to note that, when exposed to ionizing radiation, PS primarily undergoes crosslinking, PMMA undergoes only chain scission and PC undergoes simultaneous crosslinking and scission with crosslinking predominating at low doses (up to about 5 Mrad) and scission predominating at higher doses[11]. Hence the occurrence of this 'deageing' behaviour is not dependent on the specific radiation chemistry taking place or whether crosslinking or scission of the polymeric chains is taking place. Regardless of the specific radiation chemistry, irradiation of polymeric materials results in

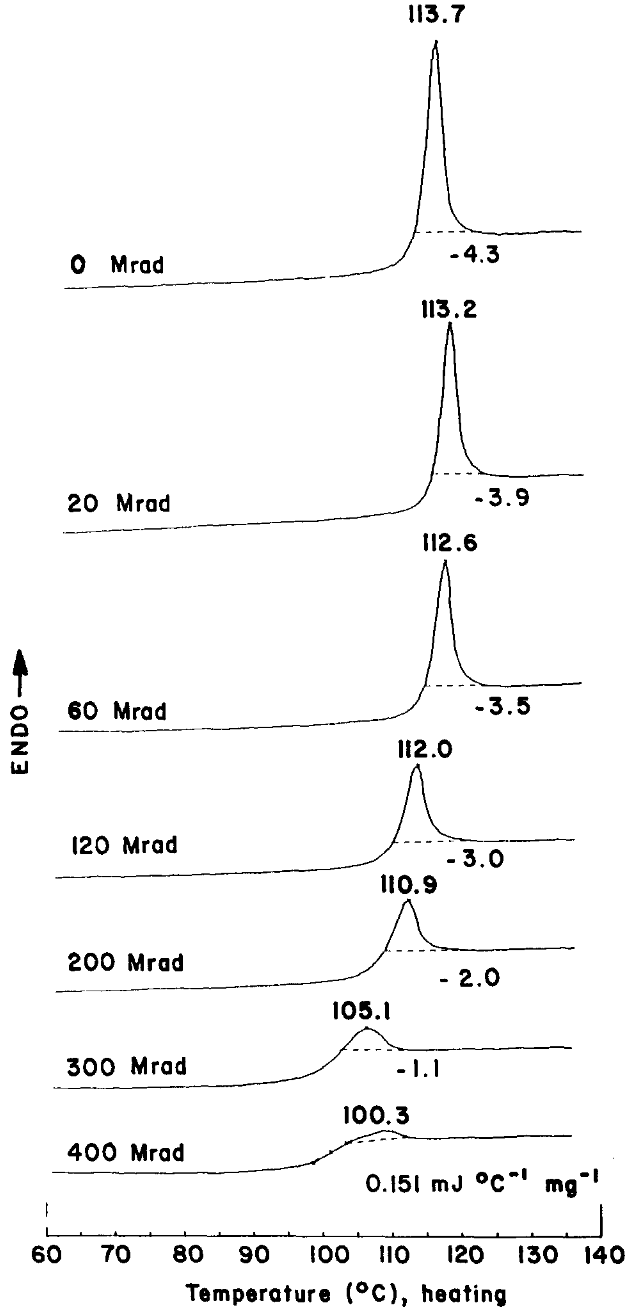

Figure 2 D.s.c. scans of aged PS after exposure to the indicated dose at 10 Mrad/pass. Peak areas (mJ mg^{-1}) and temperatures (°C) are shown

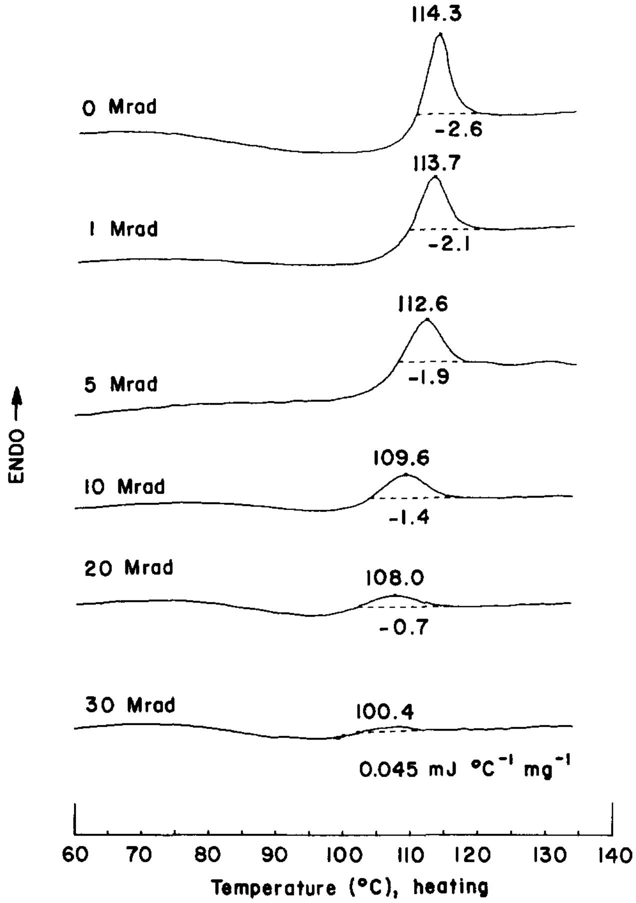

Figure 3 D.s.c. scans of aged PMMA after exposure to the indicated dose at 10 Mrad/pass (as *Figure 2*)

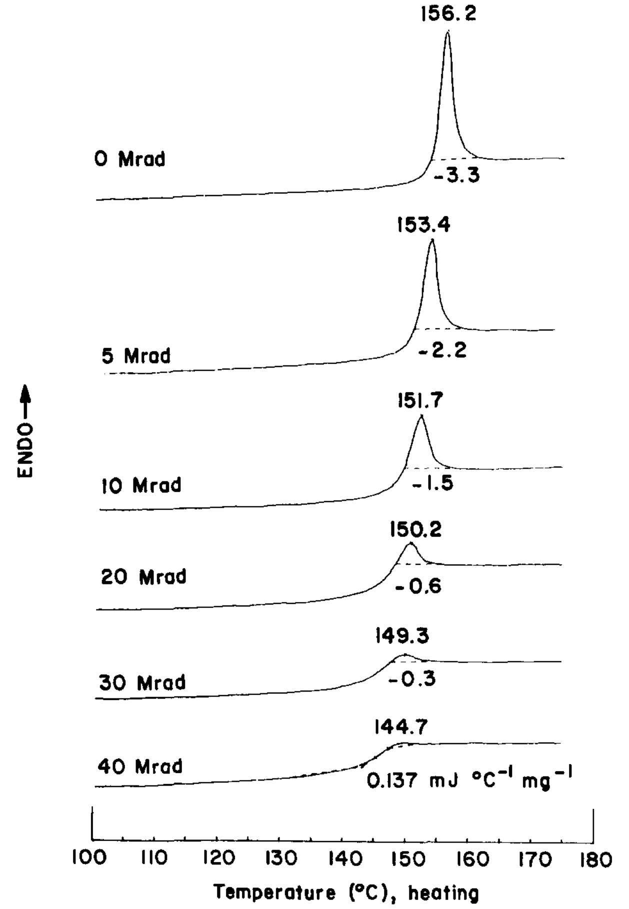

Figure 4 D.s.c. scans of aged PC after exposure to the indicated dose at 10 Mrad/pass (as *Figure 2*)

the internal evolution of gases[10]. It is therefore postulated that this radiation-induced 'deageing' phenomenon is resulting from internal gas evolution, which produces an increase in free volume and subsequently causes this observed 'reversal' of physical ageing. Furthermore, it will be clearly shown that this phenomenon is not the result of electron beam heating when the effects of dose rate are discussed. Here it is realized that the use of the word 'reversal' is limited in scope, for the process originates from chemical changes (often very small in magnitude) that are not present when considering the usual physical ageing process.

To determine the likelihood of radiation-induced gas evolution resulting in 'deageing', it is worth examining how this ageing reversal varies with dose and polymer type. *Figure 5* shows plots of the normalized endothermic peak area at T_g *versus* dose for PS, PMMA and PC, respectively. As discussed in the 'Experimental' section, using only the endothermic peak area as a measure of the enthalpy or free-volume relaxation associated with physical ageing may not always give an accurate value. To ensure that this method of analysis is not affecting the resulting *trends*, the net enthalpy differences between aged and quenched glasses were determined for PS and PC. These values are also plotted in *Figures 5a* and *5c* and, as shown, the only resulting difference is a near-horizontal shift in the enthalpy–dose curve. Hence the use of only the endothermic peak area will provide a sufficient measure of the extent of physical ageing *for the purposes of this particular study*. Having addressed this consideration, any error associated with this type of analysis will no longer be considered in this work. Furthermore, when referring to the endothermic peak area at the glass transition (or simply 'peak area'), it is implied that this is a reasonable indication of the true state of physical ageing in the material.

As shown in *Figure 5a*, the endothermic peak area decreases linearly with dose for PS. Assuming that the radiation chemistry does not change with dose (which is a reasonably good assumption for PS since it is quite resistant to radiation-induced changes in chemical structure), the amount of gas evolved will also vary linearly with dose. Hence, the results in *Figure 5a* support the postulated mechanism for 'deageing'.

PMMA also displays a linear relationship between peak area and dose. However, there is a sharp decrease in peak area up to 1 Mrad before the linearity is established (see *Figure 5b*). This sharp decrease in peak area between 0 and 1 Mrad may be the result of the consumption of highly reactive groups (possibly end-groups) at low doses in PMMA, which liberate larger amounts of gas than the rest of the polymer. Once these reactive sites are consumed, the radiation chemistry of the system will change. Hence, the *G*-value for gas evolution may decrease and remain constant above a threshold dose (i.e. less than 1 Mrad), which is consistent with the behaviour displayed in *Figure 5b*. This hypothesis could be verified by comparing the deageing behaviour of a series of PMMA with varying molecular weight and corresponding end-group concentrations, although this has not yet been done.

PC shows significant non-linearity in the plot of endothermic peak area *versus* dose (see *Figure 5c*). At low doses (10 Mrad or less) the rate of area decrease is much faster than at higher doses. In fact, it appears as if there may be two different regimes: a linear region with a high negative slope up to 10 Mrad, and another linear region with a much lower slope beginning at 20 Mrad. This behaviour may have several origins. First, it has been shown[11] that PC undergoes simultaneous crosslinking and chain scission with the former predominating at low doses and the latter predominating at higher doses, which is unique to PC compared with the other polymers studied in this work, as previously mentioned. Hence, the radiation chemistry of PC varies with absorbed dose and therefore it is highly likely that the *G*-value for gas evolution varies with dose as well. Furthermore, for a particular polymer, it would be expected that more gaseous products would result from crosslinking than chain scission since abstraction of pendant groups (i.e. hydrogen) would be necessary to create a site for crosslinking, as opposed to chain scission. This is a speculation, of course, because unfortunately there is relatively very little reported work on the radiation chemistry of polycarbonate. However, it should be noted here that this is not the result of dose-rate effects, which will be discussed in the next section.

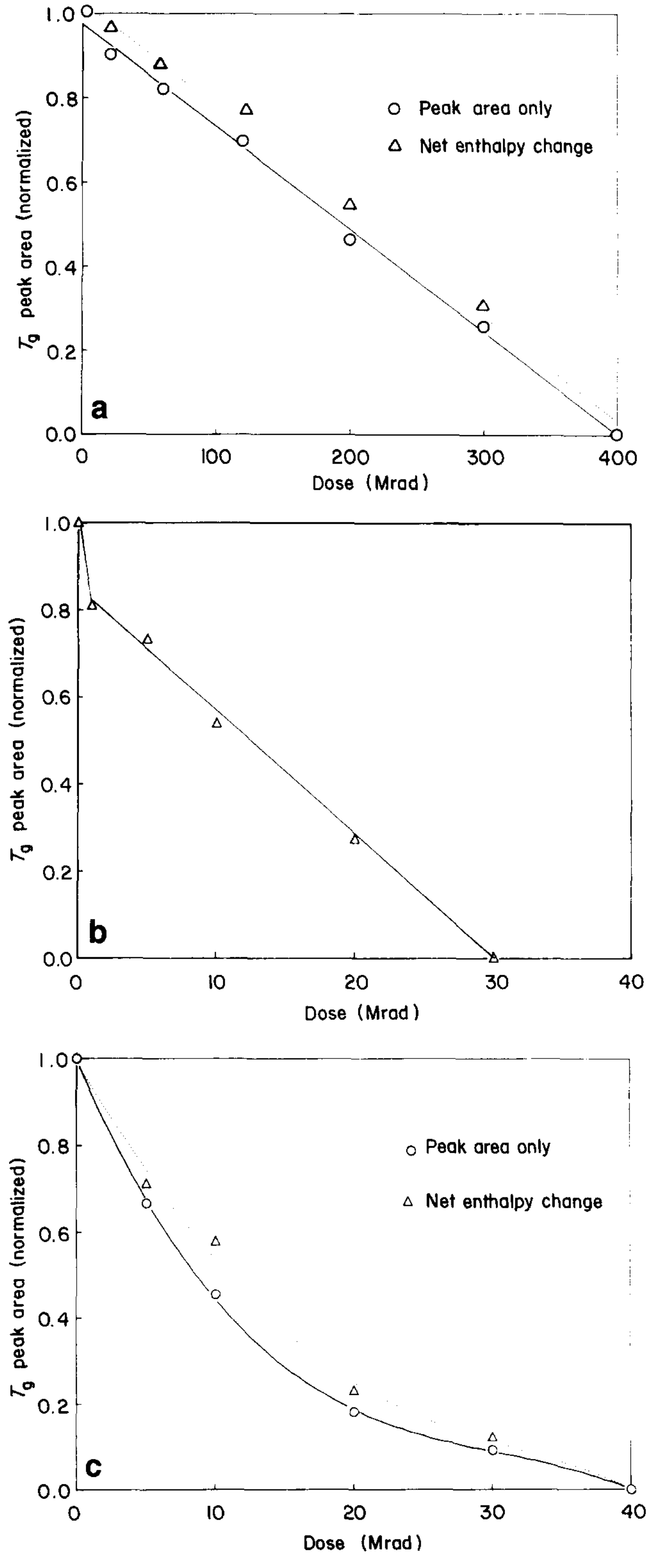

Figure 5 Plots of endothermic peak area *versus* dose for (a) PS, (b) PMMA and (c) PC

Another possible explanation for the non-linearity in *Figure 5c* is related to gas permeation. It has been shown that physical ageing can reduce the permeability of gases in glassy polymers. Hence, as the dose is increased and more 'deageing' occurs, the permeability of the gaseous products increases. This could decrease the efficiency of the deageing process since gas could diffuse out of the glass more readily. This would result in a lower internal pressure increase during the evolution of gas, which could cause a decrease in the amount of volume expansion. However, the non-linearity displayed in *Figure 5c* is not characteristic of PS or PMMA, and one would expect this proposed phenomenon to affect all glasses, although the extent may be material-dependent.

An interesting comparison to make in *Figure 5* is the relative rates of peak area loss with increasing dose. PMMA is the most sensitive (30 Mrad to completely reverse the initial level of physical ageing), PC is slightly less sensitive (40 Mrad) and PS is quite resistant to peak area loss (400 Mrad). The general radiation resistance of these polymers (which is indicative of the rate of chemical change and hence gas evolution) follows the same trend and relative magnitudes[12]. A more quantitative comparison would be to examine the relative differences in slopes in *Figure 5* and to compare them with the *G*-values for gas evolution of the polymers. Unfortunately, no *G*(gas) values for PC are available, but this analysis can be made for PMMA and PS. The *G*-values that will be used were obtained by gamma irradiation under an inert atmosphere at ambient conditions, which closely approximates the radiation conditions in this study. Although this study employs a much greater dose rate, *G*(gas) values have been shown to be independent of this parameter[10]. The ratio of the slopes in *Figures 5a* and *5b* is about 10:1, which corresponds to the ratio of the rate of peak area loss of PMMA to PS. The ratio of *G*(gas) values for these two polymers is about 19:1 (see *Table 1* for actual values). While these two ratios are in the same range, the agreement is not that good. However, there are two points that need to be considered. First, as previously discussed, the permeability of the polymer may affect the rate of deageing. However, the permeation coefficients of gases for PMMA in general are much less than for PS (see *Table 1*). If permeation of the material is an important variable in this behaviour, one would expect the ratio of *G*-values to be *less than* the ratio of slopes in *Figure 5* for reasons given earlier. Since this is not the case, it seems that permeability may not be an important issue. A second point to consider is what gases are being produced during irradiation of PS and PMMA. Irradiation of PS is known to result primarily in the production of hydrogen, while irradiation of PMMA results in the production of a variety of gases including hydrogen, carbon monoxide, carbon dioxide, methane and other gases. The ratio of $G(H_2)$ values for PMMA

Table 1 Some physical properties of the polymeric glasses used in this study

Polymer	Weight-ave. molecular weight	Permeation coefficient of O_2 ($cm^2 s^{-1} cmHg^{-1}$)[a]	*G*-values[b]
PS	300 000 ($M_w/M_n = 2.5$)	1.9	$G(gas) = 0.08$ $G(H_2) = 0.033$
PMMA	170 000 ($M_w/M_n = 2.0$)	0.116	$G(gas) = 1.5$ $G(H_2) = 0.3$
PC	45 000 ($M_w/M_n = 3.4$)	1.05	n.a.

[a] Values obtained at 25°C, from ref. 13

[b] Values obtained by gamma irradiation under inert atmosphere at ambient pressure and temperature, from ref. 13

and PS is 10.3:1, which is in excellent agreement with the slope ratios in *Figure 5* for these two polymers. It is therefore speculated that the production of very low-molecular-weight gases may affect the 'deageing' process more so than the production of higher-molecular-weight gases.

Effects of dose rate

To this point, only the effect of total dose on the endothermic peak area at the glass transition has been considered. It has been well established how the peak areas decrease with increasing dose. Furthermore, the behaviour displayed by the glassy polymers considered can be explained by the hypothesis relating this 'deageing' process to gas evolution. Discussion will now turn to the effects of dose rate at a constant total dose on the peak area loss of PS, PMMA and PC. Before proceeding, the term 'dose rate' as it will be used in this context should be clarified. As it applies to the electron beam source used in this study, the term 'dose rate' describes the total dose to which a film is exposed in a *single pass* under the electron beam. For example, '*X* Mrad/pass' implies that the sample was exposed to *X* Mrad in a few seconds under a nitrogen atmosphere before being removed from the conveyor system, exposed to air, and returned to the conveyor entrance for the next pass. Up to this point, all glassy films were exposed at a dose rate of 10 Mrad/pass for total doses of 10 Mrad or more. For total doses *less than* 10 Mrad, the indicated dose was given in a single pass.

Figure 6 illustrates the effect of dose rate on the endothermic peak area at the glass transition of PS for a total dose of 120 Mrad. As shown, there is virtually no difference in the d.s.c. behaviour for films exposed at 5 Mrad/pass and 10 Mrad/pass. This is to be expected based on the proposed 'deageing' mechanism because it is well known that gas evolution is generally not dose-rate-dependent. However, at 20 Mrad/pass the endothermic peak has almost completely diminished. It is distinctly believed that this latter effect is due to thermal heating by the electron beam to some temperature above the glass transition for a short time period such that the physical ageing is almost completely erased. To illustrate this, consider that PS has a heat capacity of $1.2 J g^{-1} K^{-1}$. It should also be noted that 1 Mrad is equivalent to $10 J g^{-1}$ of energy. If no heat transfer effects are considered, the absorption of 20 Mrad in less than several seconds will theoretically result in a temperature increase of 166 K *if* all of the beam energy is converted into heat. Of course, in a real system, heat transfer effects would be operative and there may not be 100% conversion of beam energy to heat, so the temperature rise would be less than 166 K. However, after six consecutive passes (to achieve a 120 Mrad dose) an organic glass such as PS could be expected to reach a maximum temperature above 105°C (T_g of PS). In fact, it was observed that the PS film adhered to the poly(ethylene terephthalate) (PET) substrate after exposure to six 20 Mrad passes, indicating that the T_g was indeed surpassed. Hence, it is believed that the elimination of the endothermic peak at a dose rate of 20 Mrad/pass to a dose of 120 Mrad is the result of thermal heating above the glass transition of PS.

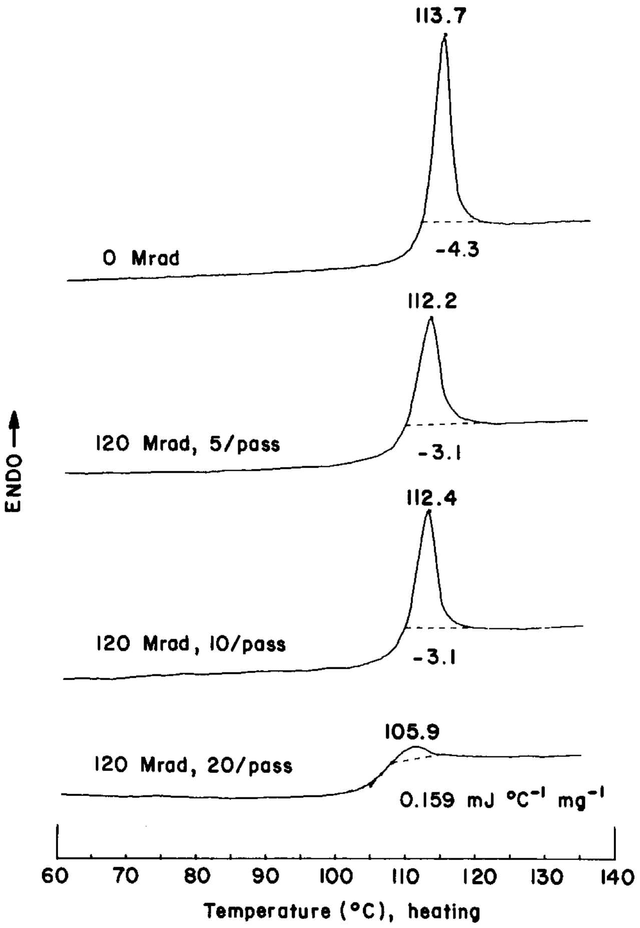

Figure 6 Effects of dose rate on the d.s.c. scan of aged PS after exposure to a total dose of 120 Mrad (as *Figure 2*)

Figure 7 illustrates the effect of dose rate on the peak area of PMMA at a total dose of 20 Mrad. This series of d.s.c. scans indicates that there is no effect of dose rate on the extent of deageing in PMMA over the dose-rate range considered. Again, this is to be expected based on the postulated deageing mechanism, since gas evolution is generally known to be independent of dose rate.

Figure 8 depicts a series of d.s.c. scans of aged PC irradiated to 20 Mrad for the dose rates indicated. As shown, there does appear to be a substantial influence of dose rate on the extent of peak area loss at this dose. This is clearly not the result of thermal heating to temperatures in the range of T_g since PC has a T_g well above the temperatures expected to be reached during radiation exposure. As the dose rate is increased from 2 to 10 Mrad/pass, the extent of peak area loss increases. There does not seem to be any difference between dose rates of 10 and 20 Mrad. This behaviour indicates that

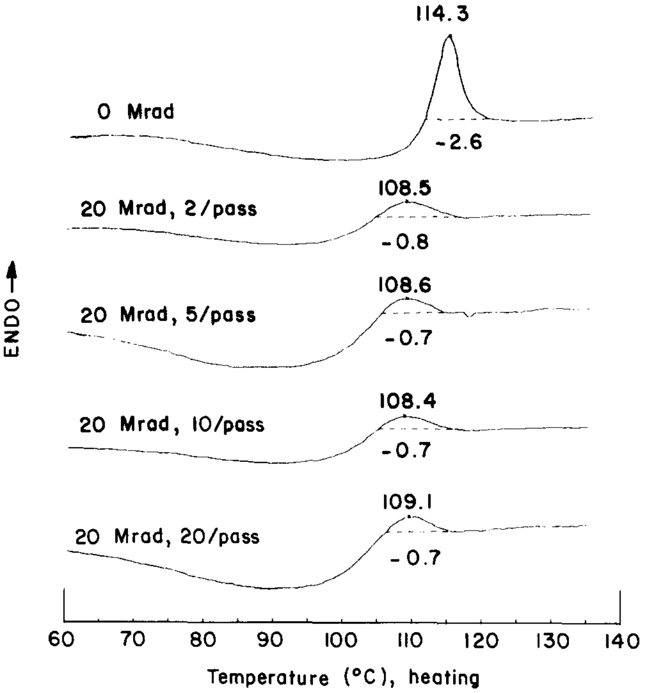

Figure 7 Effect of dose rate on the d.s.c. scan of aged PMMA after exposure to the indicated dose/dose rate (as *Figure 2*)

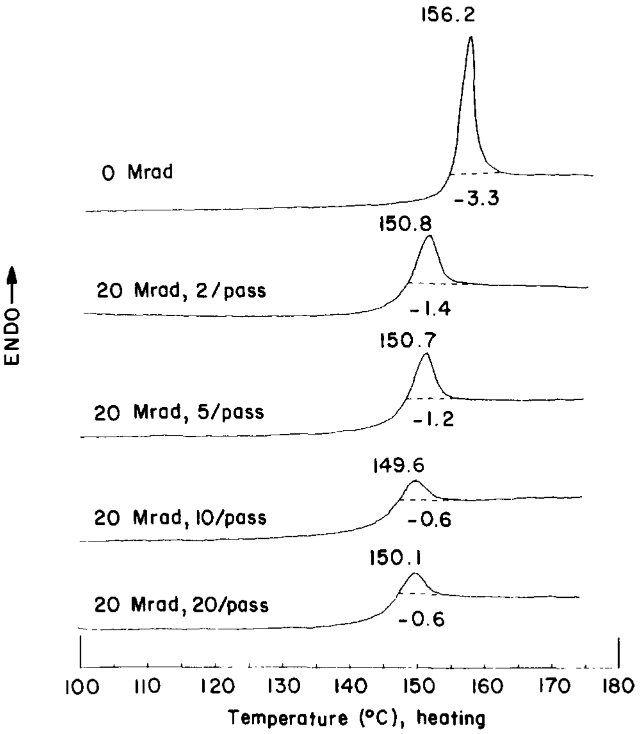

Figure 8 Effect of dose rate on the d.s.c. scan of aged PC after exposure to the indicated dose (as *Figure 2*)

the 'deageing' mechanism becomes more efficient as the dose rate increases from 2 to 10 Mrad/pass. This behaviour can be explained by the following hypothesis, which is consistent with the postulated 'deageing' mechanism.

Since PC is fairly permeable (especially compared to PMMA), some of the gaseous by-products may be diffusing out of the thin glassy films between passes at the low dose rates. Hence, the lost gas would have to be replaced by fresh gas before any further increase in free volume could take place. At a relatively high dose rate, the total gas production is almost instantaneous, so there is dramatically less time available for gaseous diffusion out of the film and the free-volume increase would be much more efficient.

This consideration may not equally apply to PMMA since it is much less permeable than PC (see *Table 1*), so there may not be a significant amount of gaseous diffusion out of the film in the timeframe of the radiation exposure. In addition, this may not apply to PS either, even though the permeability of PS is approximately the same as PC. Recall that PS has a much lower *G*(gas) value than PC, so there will be much less gaseous products building up in the film with each pass. This would result in a much smaller driving force for diffusion of gas out of the film.

If gaseous diffusion is indeed the origin of the PC deageing dependence on dose rate, then variations in elapsed time between radiation exposures (i.e. conveyor passes) should also influence the extent of deageing for a given dose. If the time between successive passes is increased, then there will be more time for gases to diffuse out of the film, which should result in a lower extent of deageing for a given dose, assuming that the proposed mechanism is valid. To determine if this is indeed the case, a time delay experiment was performed. Physically aged PC films with thicknesses less than 1 mil ($\sim 25\,\mu$m) were irradiated to 10 Mrad at 2 Mrad/pass, while the time between each pass was varied from 30 s to 5 min. Thin films with thicknesses less than 1 mil ($\sim 25\,\mu$m) were used because the diffusion time of the gases out of the film will be shorter as compared to the 3–4 mil ($\sim$76–102 μm) films used elsewhere in this work. Based on the proposed hypothesis, this should enhance the effects of the time delay between passes. The results of this experiment are shown in *Figure 9*. As shown, increasing the time between passes drastically reduces the extent of deageing that occurs as a result of exposure to

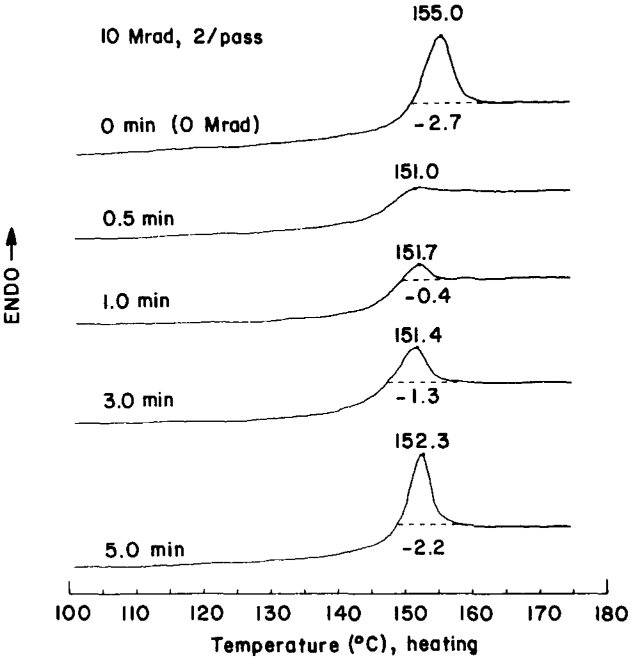

Figure 9 Series of d.s.c. scans of physically aged, solvent-cast PC films that have been irradiated to 10 Mrad at 2 Mrad/pass. The times indicated represent the elapsed time between successive exposures to the electron beam (as *Figure 2*)

10 Mrad at 2 Mrad/pass. This gives rather convincing evidence that gaseous diffusion is responsible for the dose-rate effects in PC and that this deageing phenomenon is the result of radiation-induced gas evolution.

It should also be noted that the dose-rate effects evident in PC would not explain the curvature in the peak area–dose plot of this polymer (see *Figure 5c*). Since lower dose rates decrease the extent of peak area loss, one would expect a lower rate of peak area loss at low doses compared with higher doses. However, the converse is displayed in *Figure 5c*, so dose-rate effects would not be a valid consideration. The effects of dose rate that have been illustrated also indicate that this radiation-induced 'deageing' is not the result of thermal heating. Although it has been reported[6] that partial deageing can occur by subsequent heating above the previous ageing temperature, this is not the case here. If thermal mechanisms were operative here, there would be a strong influence of dose rate, since this parameter determines the temperature rise during irradiation. It should be noted that there are tremendous differences in the temperature rise during processing in the dose-rate range of 2 Mrad/pass (up to 10°C/pass) to 20 Mrad/pass (up to 100°C/pass). However, there was very little effect of dose rate on PMMA and PS, and one would expect these glasses to be more sensitive than PC to heating effects (i.e. going above T_g), since they have a much lower glass transition temperature. Furthermore, even though dose-rate effects do exist for PC, thermal heating to temperatures above 120°C (ageing temperature of PC) are not theoretically possible at dose rates less than 20 Mrad/pass.

Effects on mechanical properties

Since it has been established that irradiation of aged polymeric glasses results in deageing as determined by d.s.c., it would be worth while to establish the occurrence of deageing by another technique. Since it is well known that mechanical properties are influenced by physical ageing, the effects of ageing and irradiation on the stress–strain behaviour of PC have been determined. In fact, mechanical property measurements may give a better indication of physical ageing than d.s.c., since the mechanical response of a system is directly dependent on its spectrum of relaxation times. The yield stress is a very sensitive parameter to physical ageing that can be obtained from stress–strain measurements, so an analysis of the effects of ageing and irradiation on this variable has been made. *Figures 10* and *11* illustrate the stress–strain response of quenched and aged PC (respectively) both before and after exposure to 60 Mrad. The thermal behaviour of the aged PC is shown in *Figure 4*. As shown earlier in *Figure 4*, a 60 Mrad dose is sufficient to completely erase the physical ageing of PC as determined by the d.s.c. *Figure 10* illustrates that exposure of the quenched PC film to 60 Mrad results in a significant decrease in the strain at break and a very slight *increase* in the yield stress. These alterations of mechanical response are due to the radiation exposure and corresponding changes in molecular weight that result. As shown in *Figure 11*, irradiation of the aged PC film results in a significant *decrease* in the yield stress and very little (if any) change in the strain at break—the latter parameter of course may be influenced by molecular weight. The radiation-induced decrease in the yield stress of only the aged glass indicates that deageing of the glass has indeed occurred. In fact, the stress–strain behaviour

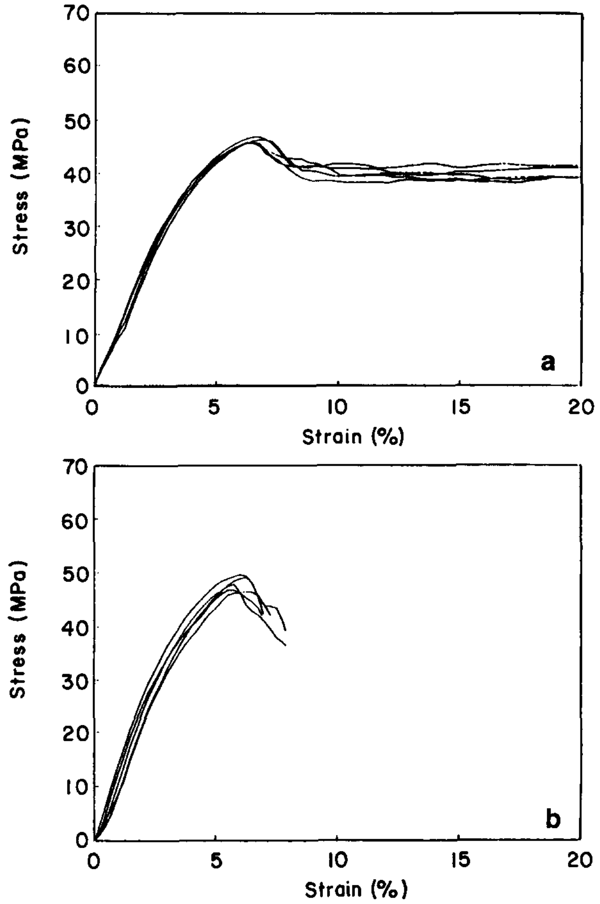

Figure 10 Stress–strain curves of quenched PC (a) before and (b) after exposure to 60 Mrad

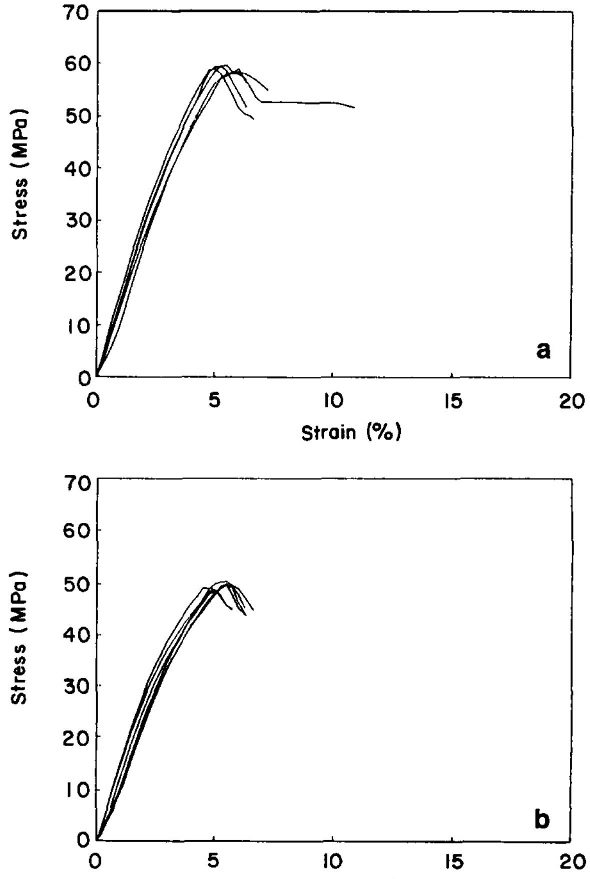

Figure 11 Stress–strain curves of aged PC (a) before and (b) after exposure to 60 Mrad

of the quenched and aged PC films that have been irradiated are indistinguishable, which is consistent with the results obtained by d.s.c.

Effects of ageing and irradiation

Up to this point, discussion has focused on establishing the existence of radiation-induced 'deageing' and some variables that may affect this behaviour. The effects of this 'deageing' on the subsequent *reageing* of these polymeric glasses will now be considered. In addition, possible effects of physical ageing on the radiation-induced changes in glassy polymers will also be briefly explored in this context.

A series of d.s.c. scans was made for various ageing times of PS with the following respective histories: (1) quenched; (2) quenched, then exposed to 400 Mrad; and (3) aged, then exposed to 400 Mrad. The only noticeable difference that was found among these specimens is the depressed T_g (by 4°C) and an increased initial ageing rate of sample (3). These differences are not large, but they are worth noting. The lower observed T_g of the aged and irradiated specimen (sample (3)) could be due to a greater concentration of low-molecular-weight products in the glass that were produced during radiation exposure. Since this glass was aged prior to exposure, the lower free volume may have hindered the diffusivity of the low-molecular-weight products. Furthermore, physical ageing has been shown to significantly increase the solubility of gases in glassy polymers[2]. Both of these possibilities would result in a higher concentration of low-molecular-weight products in PS, thereby plasticizing the polymer and lowering the T_g. It should be noted, however, that physical ageing does not seem to affect the extent of radiation crosslinking in PS. As shown in *Table 2*, the quenched and aged PS have the same gel fraction after exposure to 400 Mrad.

A similar series of d.s.c. scans was obtained for PMMA as was just described for PS. Again, the respective sample histories are: (1) quenched; (2) quenched and exposed to 60 Mrad; and (3) aged and exposed to 60 Mrad. It was found that the irradiated PMMA has a much faster ageing rate than the unirradiated PMMA and ages to a much greater extent (as characterized by d.s.c.). The T_g of the irradiated glasses was more than 10°C lower than that of the unirradiated glass, which explains the accelerated ageing behaviour. The depressed T_g of the irradiated glasses is due to the degradation in molecular weight resulting from radiation exposure (see *Table 2*). It should also be noted that there may be some small differences between the two irradiated glasses as well. It appears as though the quenched, irradiated PMMA ages slightly faster and has a slightly lower glass transition temperature than the aged, irradiated PMMA. The g.p.c. results are consistent with this behaviour as they indicate that the quenched PMMA has a somewhat lower molecular weight. It is also interesting to note that irradiation of this sample resulted in an increase in the polydispersity (M_w/M_n), while the polydispersity of the aged PMMA decreases (as compared to unirradiated PMMA). The reasons for this are not clear based on the data available, but a possible speculation is that the lower free volume of the aged sample may promote more recombination of the scissioned chains (i.e. enhanced 'cage effect'), which would result in a higher molecular weight. In any case, the effects of ageing on the extent of chain scission are not severe, but further experimentation is certainly warranted to make any firm conclusions and to obtain a better understanding of the role that physical ageing plays in the radiation-induced chain scission and/or crosslinking of PMMA or other glassy polymers.

Table 2 Effects of irradiation on the molecular weight of PMMA and the gel fraction of PS

Sample	M_n	M_w/M_n	Gel (%)
Quenched PMMA 0 Mrad	87000	2.0	–
Quenched PMMA 60 Mrad	run 1 15000	2.5	–
	run 2 20000	1.8	
Aged PMMA 60 Mrad	run 1 18500	2.0	–
	run 2 23000	1.6	
Quenched PS 400 Mrad	–	–	64±3
Aged PS 400 Mrad	–	–	67±3

CONCLUSIONS

This work has illustrated that an apparent physical 'deageing' of polymeric glasses can be facilitated by exposure of the glass to electron beam radiation as determined by d.s.c. and yield stress behaviour, although dilatometry would also be useful to confirm the results obtained. The extent of 'deageing' is controlled by the exposure dose. Although it has not been definitively proven, all the data reported clearly support the postulated 'deageing' mechanism that involves an increase in free volume of the aged glass by radiation-induced internal gas evolution. As has been illustrated, the relative rates of radiation-induced 'deageing' of PS, PC and PMMA follow the same trends as the radiation sensitivity (and likely G(gas)) of these polymers. It was also shown how the dose rate can affect the deageing behaviour. Furthermore, reageing of the deaged glasses was shown to be possible and this subsequent ageing behaviour was compared to the ageing behaviour of the unirradiated and irradiated *quenched* glasses. Some differences were found to exist among these various glasses, which illustrates that changes in molecular weight and structure (due to radiation exposure) can alter the ageing behaviour of glasses. In addition, the last section has primarily illustrated that the rate and extent of ageing can be significantly influenced by changes in molecular weight and structure. Furthermore, it has indicated that physical ageing may influence the radiation-induced changes in polymeric glasses, which to date has not been considered in the literature.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support of the 3M Corporation and the Amoco Corporation.

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