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Apparent reversal of physical aging by electron beam irradiation — further investigations

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An investigation into the irradiation of physically aged glassy polymers has lead to further refinements of a previous study. Polymers used in this investigation were: polycarbonate, polystyrene, and poly(ethylene terephthalate). In this work we have followed up an earlier study in which it was observed that the characteristic DSC enthalpy relaxation peak associated with physical aging was reduced when the sample was irradiated with an electron beam accelerator below T_g. This reduction was proportional to the dose the sample received. In this work we have investigated the volumetric changes that occur in these samples as well as further enthalpic relaxation studies. It was found through the use of the classical Charlesby–Pinner analysis that there exists a strong correlation between the scission G value, $G(s)$, and little if any for the cross-linking G value, $G(x)$ with the enthalpic relaxation behavior. This leads us to modify our earlier hypothesis and conclude that the phenomenon is primarily caused by internal energy changes manifested in endgroup creation through main chain scission during irradiation and not accompanied by the typical density changes associated with physical aging. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

When an amorphous material is cooled rapidly below its glass transition temperature, it typically leads to nonequilibrium behavior due to the presence of quenched in excess free volume. If local motion can occur within the glassy state, the system will 'relax' and densify with time, often showing near logarithmic behavior[1]. The rate of this decrease depends on the aging temperature relative to the glass transition temperature of the polymer. The glass transition temperature is generally defined as the temperature where the volume–temperature curve changes slope, which in turn is cooling or heating rate-dependent[1–3]. Free volume reduction is one manifestation of physical aging and occurs at temperatures below the glass transition temperature (T_g) in the amorphous phase of polymers. It is closely interrelated with the glass transition in polymers, and theories that describe and predict physical aging have often been closely tied to these glass transition theories. As discussed by McKenna[4], theories of the glass transition can be separated into thermodynamic[5–7] and kinetic/free volume theories[8–13]. Unfortunately, at this time there is not a universally accepted theory of the glass transition in polymers or other materials. Because of the lack of an accepted theory of the glass transition, physical aging is also not completely understood. Further work is required to enable us to understand the role the various molecular variables play in physical aging.

From a practical standpoint, physical property changes are well known to occur over time in many amorphous polymers and reflect the reduced free volume and molecular mobility that occur with physical aging. Time-dependent changes in the mechanical properties and permeation of

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gases in glassy polymers are common and are often a resultant of aging[14,15]. It is, therefore, important for those utilizing amorphous materials below T_g to have some understanding of these potential time-dependent changes in product design and manufacturing. In addition, exposure of polymers to high energy ionizing radiation in some working environments is possible in selected applications, and it is especially important to account for any additional changes that may occur in these materials as a result[16–18].

Physical aging is also associated with enthalpy relaxation and is, therefore, observable by differential scanning calorimetry (DSC) by the well known excess endothermic relaxation peak that often occurs at or near T_g. the amount of physical aging is generally taken to be roughly proportional to the area associated with this peak[19]. Therefore, one can typically measure the extent of physical aging by subtracting the second (quenched) DSC scan from the first scan and measuring the area under the resultant peak. Another common method of measuring physical aging is through the changes in density (volumetric changes) in materials by direct density measurement or through relative changes by dilatometry. An important thermodynamic equation that relates these two variables comes from the definition of enthalpy. At constant pressure:

$$\Delta H_p = \Delta U + P\Delta V \qquad (1)$$

where H = enthalpy, U = internal energy, P = pressure, and V = volume. As mentioned above, physical aging can be measured both by volumetric and enthalpic changes. Volumetric changes and enthalpic changes typically follow similar trends with aging, though data often cannot be easily directly translated from one to the other. This can be partially attributed to the internal energy changes. In this work, we will show that this typical trend does not occur; i.e.

volumetric and enthalpic changes do not scale with one another; the reasons for which will be discussed later.

PREVIOUS WORK

In previous work from our laboratory[20], it was shown that aged samples of polystyrene (PS), poly(methyl methacrylate) (PMMA), and polycarbonate (PC) will all show, upon aging, the typical physical aging endotherm, as expected. However, when exposed to electron-beam generated radiation, it was shown that the enthalpic relaxation peak could be reduced and the amount of reduction of this peak was proportional to the dose the sample received. We believe this was the first known observation of a reduction in enthalpic relaxation without heating above T_g or mechanically straining the sample.

In addition, it was observed that PS took a much higher dose to completely eliminate the endotherm than for either PMMA or PC (see *Figure 1*). It was also assumed, based on the knowledge of radiation chemistry of polymers, that PS was predominantly cross-linking as a result of being irradiated while PC and PMMA predominantely were undergoing scission. Therefore, this apparent reversal of physical aging occurred in aged, glassy samples of very different radiation chemistry.

The issue of the sample being heated above T_g during irradiation (transfer of beam energy) was also addressed in this previous work and was shown not to be an issue.

A tentative explanation to account for the observed behavior was proposed at the time of the earlier report. Specifically, it was conjectured that the polymers were being impregnated with gas, which was produced as a result of the radiation chemistry events. Either a main chain scission or a cross-link can produce gas, although typically, cross-linking produces H_2 through hydrogen abstraction, and scission produces larger molecules such as CO_2. Evidence in support of this hypothesis was found in the polymers G_{gas} values[20]. A 'G' value is generally defined as the number of events per 100 eV of absorbed radiation. These events can refer to cross-linking, scission, radical yields or gas generation, for example, and various methods exist for calculating each specific G value. PS had a much lower G_{gas} formation value than PMMA and PS took a much higher dose to 'deage'; therefore, gas generation could be responsible.

Volumetric changes were not verified in order to help confirm the gas generation hypothesis; however, it was proposed that the density of these polymers should decrease and that this decrease should be proportional to the dose that the polymer received. It was desired to further clarify this earlier work by first quantifying what, if any, volumetric changes could be observed and then to follow up with any additional experiments to support or disprove the gas generation hypothesis. This report presents the results of this newer work.

EXPERIMENTAL

Materials and sample preparation

It was desired to reproduce some of the earlier work; hence, samples of PC (Macralon 2608, dispersity ratio = 2, $M_n = 16\,000$) and PS (dispersity ratio = 2, $M_w = 200\,000$) were acquired. It was decided to perform experiments on an additional polymer with different radiation chemistry so samples of PET ($M_n = 21\,500$) were acquired.
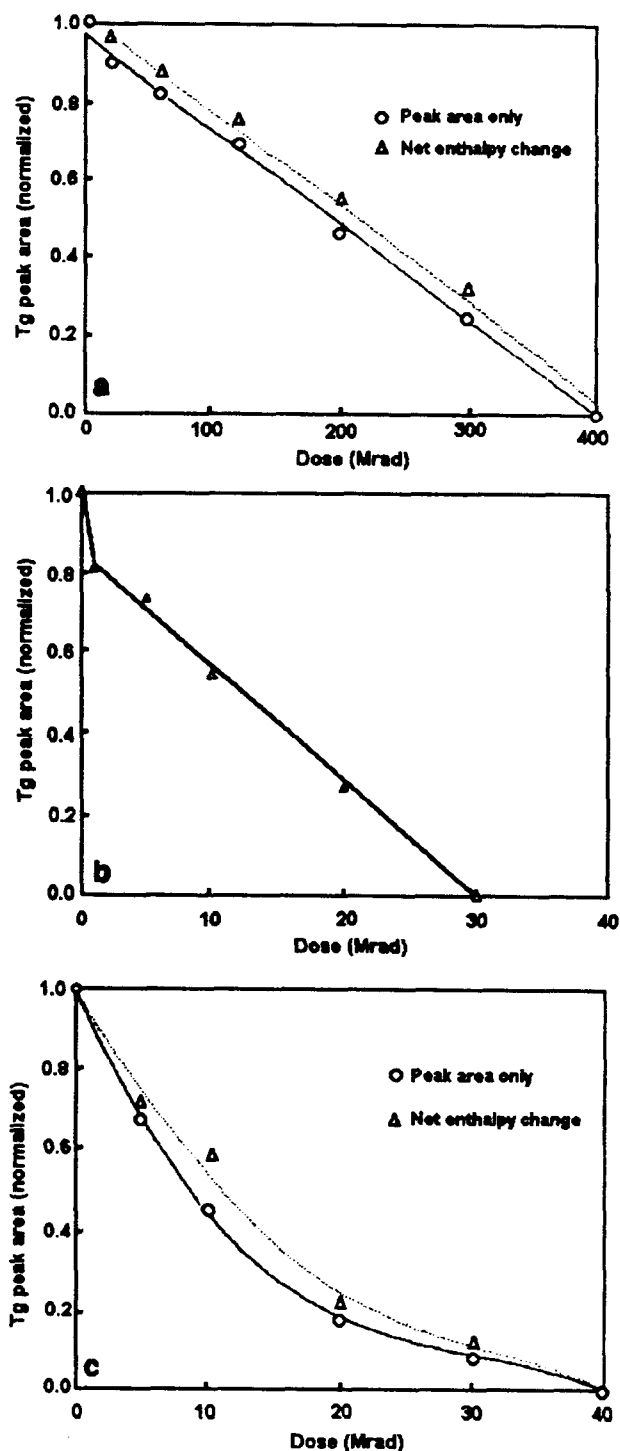

Figure 1 Plots of endothermic peak area vs dose for (a) PS, (b) PMMA and (c) PC[20]

Thin amorphous films (*ca* 1 ml) of PC were solvent cast from methylene chloride on Teflon and dried above the boiling point of the solvent in vacuum for 72 h. Samples of PS and PET were compression molded to 4 ml on smooth metal plates and quenched in ice water. Amorphous PET samples were scanned by DSC to ensure that no crystallization had occurred during molding. DSC experiments were performed on the 'as received' samples in comparison to the solvent cast samples to verify that the solvent had been removed. The observed T_g values for each material (10°C heating rate) were 150°C for PC, and 85°C for PET. Once formed, each film was physically aged for approximately 1 week at a temperature 30°C less than the T_g of the material.

Radiation exposure

All films were irradiated using an Energy Sciences (ESI) CB150 Electrocurtain as the radiation source under a nitrogen blanket of 200 ppm oxygen and a beam voltage of 175 keV. Samples were irradiated at no more than 2–10 Mrad per pass to avoid excessive sample heating. Samples were exposed to air between passes if a total dose of greater than 10 Mrad was required.

Thermal analysis

Enthalpy relaxation measurements for PET and PC were performed in a Perkin–Elmer DSC 7 system using heating rates of 10°C/min and cooling rates of 30°C/min. A baseline scan was performed using an empty pan and lid in the reference cell and another pan and lid in the sample cell. The pan and lid in the sample cell were used for the run after the baseline scan was completed. Samples were placed in the DSC within 10 min of irradiation. For all samples, the second heating was subtracted from the first heating and the resultant peak area measured from a reference baseline. Three to eight runs for each sample were repeated for consistency.

Density determination

A density gradient column was set up utilizing a NaBr/water mixture with a column range from $\rho = 1/130$ to 1.300 g/cc. A Gaertner Scientific Corporation cathatometer was used to note the position of the calibration beands ($\rho = 1.1660, \rho = 1.2000$ and $\rho = 1.2300$) as well as film samples.

Sol/gel analysis

Soluble portions of irradiated films were extracted using a fritted glass cylinder and THF solvent. Vials were removed periodically, dried and the weights recorded. Care was taken so that the solvent did not reach the top of the vial, but the film was below the level of the solvent. This procedure was repeated until a constant weight of the vial was achieved.

RESULTS AND DISCUSSION

Enthalpy relaxation changes

Enthalpy relaxation changes in PC and PET were observed after aging and exposure to radiation. All of the previous experiments performed on polycarbonate were reproduced. The first set of experiments were the dose vs endotherm reduction experiments. These experiments were reproduced several times with excellent repeatability. Sample DSC traces are shown in *Figure 2*. *Figure 3* summarizes all aged, irradiated PC data. Results are similar to those observed previously in this laboratory[20].

Hot pressed samples and quenched samples of amorphous PET were aged for 93 h at 60°C and then irradiated. As shown in *Figure 4*, the T_g for PET appears to drop at higher doses, clearly indicating that significant scission was occurring in this polymer. The endotherm reduction behavior is similar to the other polymers observed in this and the previous study (see *Figure 5*).

Volumetric changes

To gain additional information from the enthalpic observations and to see if enthalpic trends and density trends followed one another as is the usual case, volumetric studies were conducted. As stated in the introduction, it was a primary goal of this study to determine what, if any, volumetric changes were occurring in order to support the
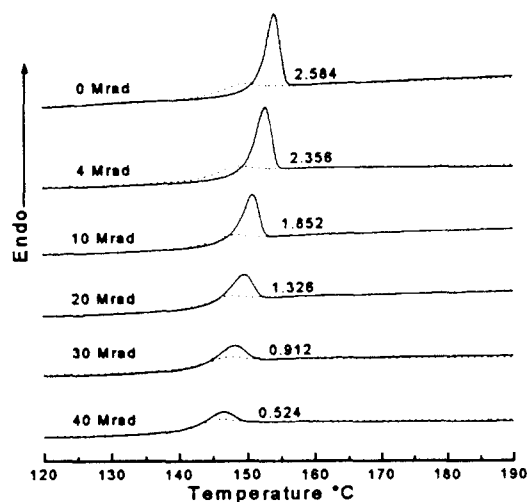

Figure 2 DSC scans of physically aged polycarbonate irradiated to the doses indicated. Numbers indicate the value of peak area in J/g
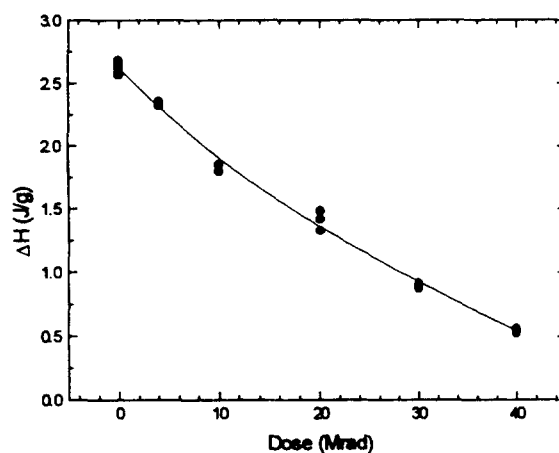

Figure 3 Plot of the excess enthalpy for all PC samples vs dose
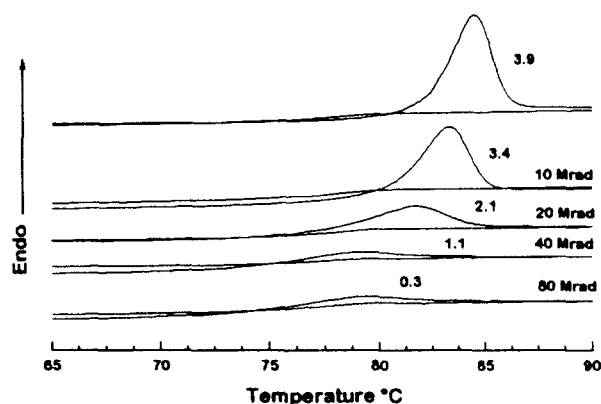

Figure 4 DSC scans for aged then irradiated (at 10 Mrad/pass) PET films

earlier gas generation hypothesis. It was hoped that an aged, then irradiated polymer would show a density similar to that of a freshly quenched sample, since they had similar endothermic responses. It was also assumed that an aged polymer sample should have a density significantly greater than either of them. The reason for this expectation can be found by referring back to equation (1), which shows that at constant pressure, enthalpic changes are manifested in a combination of internal energy changes and volumetric
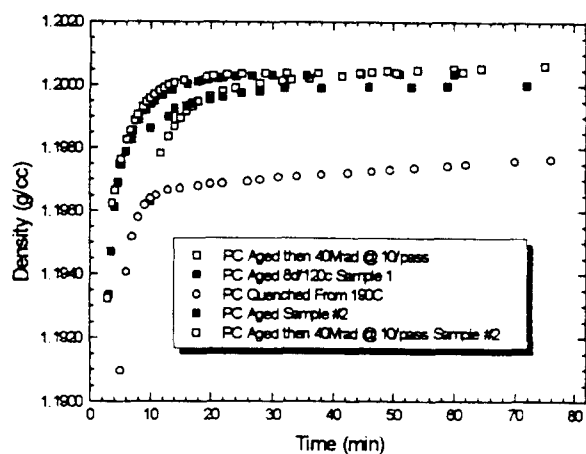
Figure 5 Apparent density as a function of time for different PC samples. ■ = aged samples. ○ = quenched sample. □ = aged then irradiated samples
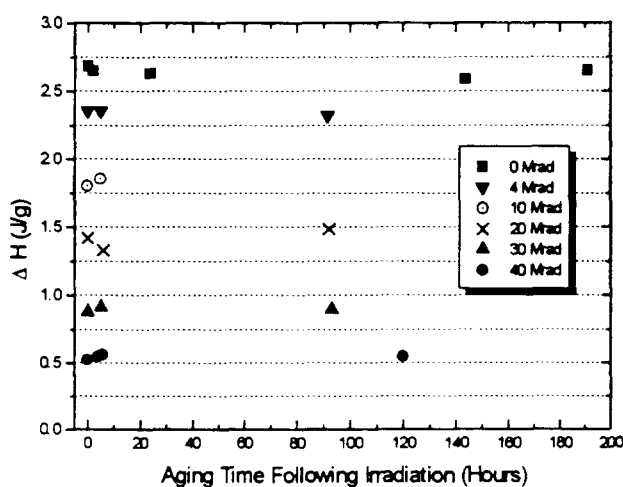
Figure 6 Summary of delayed DSC runs after irradiation showing that no significant changes in enthalpy relaxation behavior of irradiated films occurs as a function of time after irradiation exposure

changes. Since it is well known that aged and quenched amorphous polycarbonate have significantly different densities (and enthalpic behavior), it was surmised that this same trend would carry over to the irradiated samples (since the enthalpic behavior is similar). Therefore, density gradient column experiments were performed to establish whether or not volumetric changes scale with the observed internal energy changes.

Expected changes in density after aging are typically on the order of 0.0001–0.001 g/cc, depending on the polymer and the degree of volumetric relaxation. As expected, there is a significant observable difference between the quenched PC sample and the aged PC sample of 0.003 g/cc; however, there is no observable difference between the aged, then irradiated samples and the aged samples. As discussed previously, one would initially expect that PC samples that have similar enthalpy relaxation behavior would show similar densities. Indeed, samples with identical aging history did show identical densities when experiments were repeated. However, irradiated samples did not show densities similar to that of quenched samples, even though their enthalpy relaxation behavior was similar. The density column experiments therefore strongly indicate the enthalpy relaxation changes in irradiated aged polycarbonate results from internal energy changes, not volumetric changes as the earlier proposed gas generation hypothesis assumed.

Time-dependent enthalpy relaxation changes

Further DSC studies on PC resulted in additional evidence against the gas generation hypothesis. If indeed gas generation was responsible for the reduction in the endotherm at T_g, then as this gas diffused out of the film, the endotherm should change in the direction of an aged film.

For this series of experiments, samples of PC were irradiated as before and immediately tested. However, additional DSC experiments were performed on samples periodically up to 120 h after being irradiated. *Figure 6* summarizes these experiments by showing the resultant peak area as a function of time after film exposure to radiation. There is simply no change in the endotherm as a function of time beyond what one would expect in normal room temperature aging. Whatever gas was generated seems to have had a very small effect on the film volume and diffused out without changing the enthalpy relaxation behavior of the film.

Whatever the case, it appeared that gas generation is clearly not the probable cause of the observed enthalpy relaxation changes. No observable density changes were observed to help explain the deaging phenomena. There are, however, unquestionable enthalpic changes after irradiation. The analysis of the results so far presented therefore indicate that external energy changes are the source of the enthalpic relaxation. Work at this point focused on what origins of internal changes could cause the resultant enthalpic changes [refer to equation (1)]. The two principal events that occur during irradiation—scission reactions and cross-linking. The remainder of this work is focused on clarifying which event (or both) could result in significant internal energy changes.

At this point, work focused on the possibility that endgroup creation could be causing these internal energy changes which manifest themselves in the observed deaging phenomena. For this to occur, polystyrene would have to be scissioning during irradiation in the electron beam accelerator. Recall that PS is generally considered to have a radiation chemistry of a 'predominate cross-linker'. One method used to precisely quantify the amount of scission or cross-linking that occurs in a sample is to utilize the method outlined by Charlesby and Pinner in their classic work[21,22].

G value determination

The definition of $G(x)$ is the number of cross-links per 100 eV of absorbed radiation. As shown by Charlesby and Pinner (derivation not shown), $G(x)$ can be written:

$$G(x) = \frac{100 * N_A}{Dg * M_w}\left(\frac{2}{4 - \lambda}\right) \qquad (2)$$

where:

D_g = dose at which the gel first forms
M_w = initial weight average molecular weight
N_A = Avagadro's Number
λ = the ratio of G scission [$G(s)$] to $G(x)$

To accurately determine D_g and λ, the well known Charlesby–Pinner plot can be utilized. *Figure 7* illustrates the application of the data to their equation which is expressed in reduced form for simultaneous cross-linking and scission:

$$S + S^{1/2} = \frac{1}{2}\lambda + \left(2 - \frac{1}{2}\lambda\right)\frac{D_g}{r} \qquad (3)$$
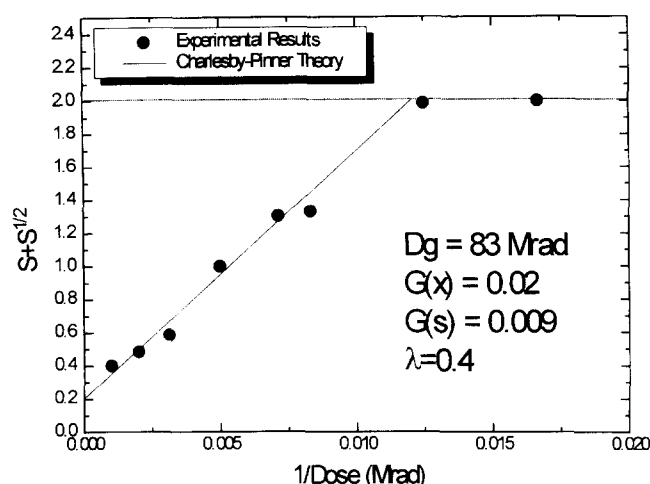
Figure 7 Charlesby–Pinner plot for PS. ● = experimental data. The Charlesby-Pinner equation with the derived values of D_g, $G(x)$ and $G(s)$ is shown
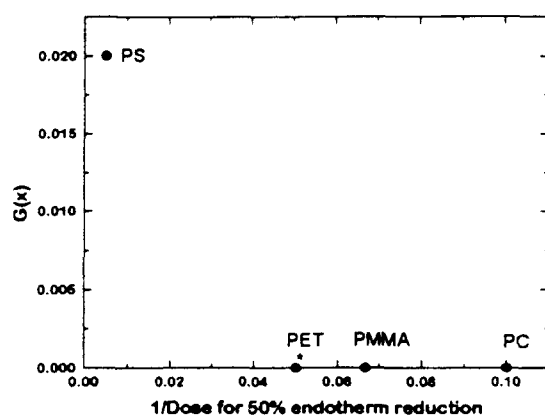
Figure 8 Physical aging endotherm correlation with $G(x)$. Dose in Mrad^{-1}

irradiated in the electron beam radiation source in a 200 ppm oxygen atmosphere.

G value correlation

We have distinctly shown that irradiation of aged polymers reduces the observed enthalpic relaxation peak. This reduction increases with increasing dose. It has also been shown that in higher G value polymers, this reduction occurs at lower doses than with low G value polymers (recall PS). Since there are only two possible final events that can occur, cross-linking or scissioning, then there may be a correlation with $G(x)$ or $G(s)$.

Possible correlations of $G(x)$ or $G(s)$ with radiation exposure would intuitively result in the following relationship. Since either G value (by definition) indicates the number of events per given unit of absorbed dose, more events (for correlation) would intuitively result in more thermodynamic changes. Therefore, for a polymer with a high G value, a low dose would be required for the enthalpy relaxation response. For a polymer with a low G value, a high dose would be required for the enthalpy relaxation response.

To summarize all our radiation chemistry and enthalpy relaxation data to this point for analysis and correlation, *Table 1* is provided.

In *Figure 8*, the $G(x)$ values are plotted as a function of dose required for reduction of 50% of the enthalpy relaxation endotherm. The 50% value was chosen arbitrarily but is representative of other values. Data representing PET are marked with an asterisk because it is uncertain whether they have a truly zero $G(x)$ value. However, since its T_g dropped when irradiated in a similar fashion to that of PC, it is thought that its $G(x)$ value is small or very close to zero. In *Figure 8*, there is no correlation between $G(x)$ and the dose required for endotherm reduction. What this indicates is that cross-linking does not appear to significantly change the enthalpic state of the polymer—at least not to the point where enthalpic relaxation changes are observable. It would

Table 1 Summary of radiation chemistry and enthalpy relaxation data for this study

Polymer	$G(x)$	$G(s)$	G value source	Dose for 50% endo reduction	Source for endotherm data
PC	0	~1	estimated from DSC	20 Mrad	This study
PMMA	0	1.6	*Polymer* handbook[23]	13 Mrad	McHerron *et al.*[20]
PS	0.02	0.009	This study	200 Mrad	McHerron *et al.* [20]
PET	~0	0.8	*Polymer* handbook[20]	25 Mrad	This study

where:

S = soluble portion of the polymer
r = dose

Utilization of the above analysis was required for accurate analysis of the radiation chemistry of polystyrene. Irradiated samples were extracted to constant weight and these final weights used to produce the Charlesby–Pinner plot for 300 k PS as shown in *Figure 7*. The Charlesby–Pinner plot shows a non-zero y intercept $= \lambda/2$, which indicates that some scission occurred in the irradiated samples. In this case, D_g was found to be 83 Mrad and extrapolation to infinite dose to derive the λ value resulted in $G(x) = 0.02$ and $G(s) = 0.09$. This means that roughly one main chain scission occurred for every 2.2 cross-links. Therefore, significant scission occurred when PS was

be desirable to have a 100% cross-linking polymer to prove this point definitively; however, the four data points shown do strongly indicate that there is no correlation with cross-linking.

In *Figure 9*, $G(s)$ values for each polymer are plotted vs 1/ Dose for 50% reduction in the enthalpy relaxation peak. PC is marked with an asterisk because its $G(s)$ value was not directly calculated. One can see the strong correlation shown on this plot thereby supporting the endgroup creation hypothesis. On a thermodynamic level, this indicates that the resultant observed enthalpic changes in these polymers manifest themselves through internal changes principally caused by the creation of these new endgroups. New endgroups would also increase the disorder (entropy) of the system, which would drive the system towards a higher internal energy state at constant volume.
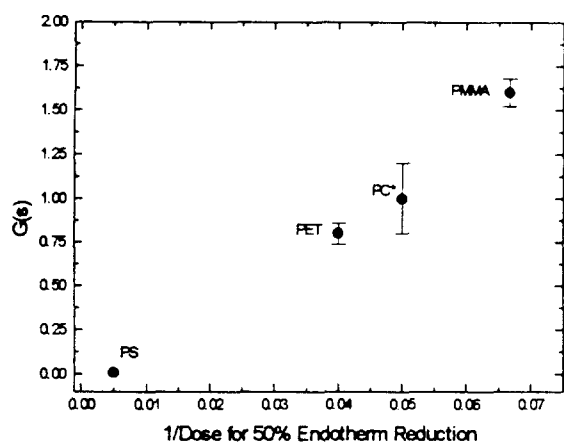
Figure 9 Physical aging endotherm correlation with $G(s)$. Dose in Mrad^{-1}. Error bars indicate the range of $G(s)$ values based on radiation chemistry data from the literature[23] and from this work

CONCLUSIONS

This work has served to further investigate and clarify previous work performed in the area of irradiating physical aged glassy polymers. A phenomenon was observed for aged amorphous polymers exposed to electron beam irradiation. An apparent reversal of physical aging through enthalpy relaxation was observed. This 'deaging' does not involve heating above the glass transition temperature of the polymer. It was found that there was not an expected reduction in density that accompanied this deaging phenomena. It was further observed that irradiated films did not regain their enthalpy relaxation aged status in the time scale that would normally be associated with any diffusion of gases out of the films. Indeed, it was found that this deaging phenomenon had a strong correlation with the radiation G values; i.e. low $G(s)$ and $G(x)$ value polymers such as polystyrene took a much higher dose to deage than PMMA or PC. It was concluded through experimental determination of G values associated with scission and cross-linking [$G(s)$ and $G(x)$], that there is a very strong correlation of this phenomena with $G(s)$ and little, if any, correlation with $G(x)$, indicating that the number of endgroups play an important role in entropy and therefore can play a principal role in the internal energy state of the glassy polymer.

The ramifications of this study to the mechanical behavior of amorphous polymers used in environments where they are exposed to radiation are of interest. Suppose a physically aged amorphous polymer is irradiated with no corresponding change in volume (as we have shown). Normally, one would expect an amorphous material that does not display an enthalpic aging peak to be more ductile than one that shows the peak. However, one would also expect an amorphous material with a higher density to behave in a more brittle fashion than the same material with a lower density (more free volume). How will such a system behave if it then undergoes deformation? DSC measurements would

predict more ductile behavior relative to the non-irradiated and aged sample but density measurements would predict a more brittle behavior. Predictions of such behavior based on enthalpic or volumetric data alone, however, are further complicated by the issue of main chain scission as reductions in molecular weight would also be expected to lead to more brittle behavior.

Finally, the most significant conclusion reached in this work is the important role internal energy can play in physical aging. It is typically observed in aging studies that enthalpic changes are at least proportional to volumetric changes due to small internal energy changes. In this work we have shown that this assumption is not always valid and that in this study, when chain scission occurs, internal energy changes can dominate the changes in the enthalpic state of polymers and are not accompanied by significant density changes.

ACKNOWLEDGEMENTS

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