portant quantity, $\Delta H_{\infty}(T_a)$. This extrapolation assumes that the heat capacity of most linear polymers in the liquid state at temperatures not too far above the glass transition region (e.g., PVME, $T_g + 15 \le T \le T_g + 55$ K) can be represented by a linear function of temperature. This assumption may not be strictly correct. Moreover, in the derivation of ΔH_{∞} ($=Q_E$) which Petrie and Marshall give in ref 2, the glassy and liquid heat capacities are both assumed to be temperature independent. Thus, it can be concluded that the reliable estimation of $\Delta H_{\infty}(T_a)$ in terms of the PM model is not yet assured. Another shortcoming of this model is the lack of a distribution of relaxation times.

Several additional long time aging experiments in the DSC, with t_a = 6–7 days at an aging temperature of 240 K, were performed on a PVME sample with a view to resolving the question of which model (PM or CF) best describes enthalpic aging processes in PVME. However, no conclusive results could be obtained from these experiments because of practical difficulties which were encountered in maintaining thermal equilibrium inside our Perkin-Elmer DSC II under subambient conditions for extended periods of time. Once this problem has been dealt with, it is hoped that more definitive answers to some of the above questions will be found.

While only two models for describing enthalpic aging effects in polymer glasses were considered in this work, it should be noted that there are other ways of analyzing enthalpic aging data, e.g., the theoretical models of Hodge[5] and Kovacs[13] and the peak-shifting technique of Hutchinson.[14] These models mainly deal with the shape and position of the peak(s) in the $C_p(T)$ curve and not directly with enthalpy differences which are our main concern.[10]

However, it can be shown that the isothermal single relaxation time KAHR model[13] can be directly related to the Petrie/Marshall model. The results for PVME can be stated in terms of this model (with a reference temperature $T_r = T_{g(\text{midpt})} = 254.1$ K) as follows: $\theta = E_H/RT_r^2 = 0.76$, the structure parameter $x = 1 - C\Delta C_p/\theta = 0.20$, and $\ln(\tau_r) = E_H/RT_r - \ln(A) = 0.54$ (i.e., $\tau_r = 1.72$ min). These values are not unreasonable and fall within the limits of those anticipated for polymer glasses.[13]

The analysis of the shapes of our PVME C_p curves in terms of the phenomenological model of Hodge will be the subject of a separate publication.[6]

Conclusions

Enthalpic aging data for poly(vinyl methyl ether) covering several aging temperatures have been subjected to analysis by two different models of physical aging in polymer glasses, and the temperature dependence of the parameters of the Cowie/Ferguson model have been established. Additional work will seek to both (a) establish what is the most realistic model physically for enthalpy relaxation and (b) investigate enthalpy relaxation/physical aging effects in miscible polymer blends.

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Physical Aging Studies in Polymer Blends. 2. Enthalpy Relaxation as a Function of Aging Temperature in a Poly(vinyl methyl ether)/Polystyrene Blend

John M. G. Cowie[*,†] **and Roderick Ferguson**[†]

Department of Chemistry, University of Stirling, Stirling, Scotland FK9 4LA.

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ABSTRACT: A series of enthalpy relaxation experiments at different aging temperatures was conducted on a poly(vinyl methyl ether)/polystyrene blend using a differential scanning calorimeter (DSC). The enthalpic aging data were analyzed in terms of two models for describing physical aging in polymer systems. Comparisons were also made between blend and homopolymer aging data. It has been found that the PVME component in the blend appears to age independently of the PS component and is responsible for essentially all of the aging effects measured. The PS component will, however, retard the physical aging processes of PVME in the blend.

Introduction

The long-term stability of polymers and their property retention are influenced by two possible processes. The first process is chemical degradation which involves chemical bond modification and/or rupture, and the second process is physical aging. While physical aging is less obvious than the former process, it is nevertheless quite important as it may lead to noticeable changes in polymer properties over long periods of time such as embrittlement.

[†] Present address: Department of Chemistry, Heriot-Watt University, Riccarten, Edinburgh, Scotland EH14 4AS.

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By physical aging one means the time dependence of changes in the behavior of an amorphous polymer held at temperatures below the glass transition; such changes are normally the result of continuous slow relaxation of the glass from its initial nonequilibrium state toward its final thermodynamic equilibrium state. Volume and enthaply relaxations are then features of aging and the time dependence of small strain mechanical properties can also be used to follow this process.

The preparation of an initial nonequilibrium state in the polymer glass is usually carried out by quenching the polymer rapidly at a given cooling rate starting from an equilibrium state, which is 50–60 K above the glass transition temperature, T_g, down to the aging temperature, T_a, which is at least 5 K lower than T_g. A given cooling rate and aging temperature will produce a corresponding initial departure in enthalpy or volume from the thermodynamic equilibrium value. As physical aging proceeds, this departure from equilibrium will tend toward zero.

Physical aging experiments can be carried out on the same sample only if the effects of any previous thermal treatment have been erased by annealing the polymer at a temperature which is at least 40 K greater than T_g. Annealing times of 10–15 min have been found to be more than adequate for this purpose.[1]

Currently, only a few physical aging studies in polymer blends have been reported in the literature;[2,3] these have been mainly concerned with changes in mechanical properties with aging time and temperature. To our present knowledge, enthalpic aging in miscible polymer blends has not yet received much attention.

Conditionally miscible blends of polystyrene and poly(vinyl methyl ether), PVME, have been the subject of extensive examination,[4,5] but no aging studies have yet appeared. The results of a study of enthalpic aging effects in a poly(vinyl methyl ether) sample as a function of both aging time and aging temperature have recently been reported,[6] and we now wish to report the outcome of a similar study on a 50/50 wt% conditionally miscible blend of poly(vinyl methyl ether) and polystyrene, which was prepared by solvent casting from toluene.

Experimental Section

Heat capacity (C_p) measurements were made by using a computer-controlled Perkin-Elmer DSC2 as described previously.[1,6] All C_p measurements were taken by using the subambient mode of the DSC with dry ice/methanol as coolant, oxygen-free nitrogen as purge gas, and sapphire as the C_p standard. The scan starting and finishing temperatures were 220 and 360 K, respectively, but only C_p data in the range $231 \leq T \leq 360$ K were used in the final enthalpy determinations. A heating rate of 20 K min^{-1} and a cooling rate of 40 K min^{-1} were used throughout this work.

The sample of PVME was the same material which was fractionated as described previously,[1,6] and the polystyrene was a secondary standard. The number-average molecular weight, M_n, of the PVME was 44000 (as determined by membrane osmometry at 306 K in methyl ethyl ketone), and the polystyrene had M_n = 267000.

An approximately 50/50 wt % blend of PVME/PS was prepared by mixing two toluene solutions of the components and then casting the solution onto a PTFE plate. Final traces of solvent were removed by drying in a vacuum oven for 48 h at 333 K.

The four-stage thermal history which was used is this work was identical with that given previously for PVME and the excess enthalpy lost during aging, $\Delta H(t_a,T_a)$ determined as before.[1,6]

In order to erase the thermal history of the blend, the sample was annealed at 360 K for at least 10 min. This proved to be adequate because no changes were observed when the unaged C_p curve was compared with those obtained previously. It was found that there was no advantage in annealing the sample at higher temperatures; one must also be conscious of the fact that there is an LCST region above 380 K for this blend system.

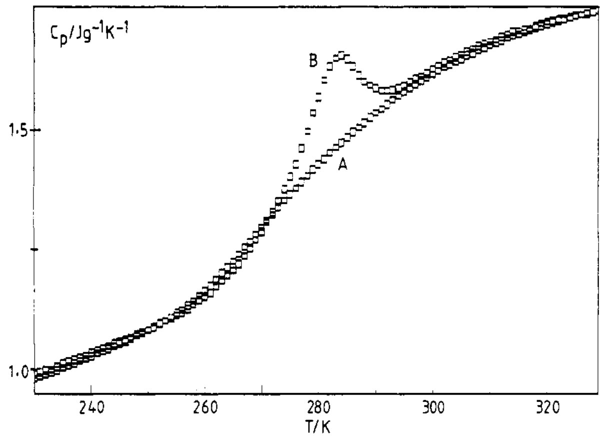

Figure 1. C_p data for the 50 wt % PVME/PS blend as a function of temperature and aging time. Curve A is C_p data obtained from an unaged sample, and curve B is C_p data which is typical of a long aging time experiment.

Results and Discussion

Glass Transition. A single broad glass transition is observable by DSC, with $T_{g(en)}$ = 281.8 K (en = enthalpic), where $T_{g(en)}$ is defined by the intersection of the glassy state and liquid enthalpy curves. It can be shown that this definition of T_g (due to Richardson and Saville[7]) is identical with the "frozen in fictive temperature" or T_f as defined by Moynihan and co-workers.[8] This definition of T_g will be used throughout this work; however, for the sake of completeness, the other more commonly used values of T_g are $T_{g(onset)}$ = 258.5 K and $T_{g(midpt)}$ = 277.4 K. The glassy and liquid state heat capacities are both linear functions of temperature over the following temperature ranges:

$$C_p(\text{glass}) = 0.984 + 4.983 \times 10^{-3}(T - 232), \quad 232 \leq T \leq 250 \text{ K}$$

$$C_p(\text{liquid}) = 1.481 + 2.669 \times 10^{-3}(T - 232), \quad 335 \leq T \leq 355 \text{ K}$$

A value of ΔC_p = 0.391 J g^{-1} K^{-1} was obtained for the glass-to-liquid transition.

The breadth of the glass transition, ΔT, is 38.0 K, for the blend whereas the homopolymers PVME and PS have ΔTs of 3.4 and 6.7 K respectively. Thus this particular blend is miscible at least down to the polysegmental level.

For the enthalpy relaxation experiments, five aging temperatures (from $T_a = T_g - 30$ K to $T_a = T_g - 10$ K) and a wide range of aging times (from several minutes to a thousand minutes) were used.

Inspection of the resulting C_p versus T scans, particularly for the long aging time experiments, showed that the position of the C_p overshoot associated with enthalpic aging was not close to the end of the transition region, as is usually the case with most homopolymers, but was located near the middle of the transition region. Moreover, the shape of the overshoot was not as narrow as in the homopolymer case. Figure 1 shows C_p as a function of temperature for both an unaged sample (curve A) and an aged sample (curve B) of the PVME/PS blend.

The above observations prompted us to consider whether the physical aging processes occurring in the blend were mainly due to the poly(vinyl methyl ether) component, with little or no influence from the polystyrene component, at the aging temperatures studied. For the 50/50 wt % blend, these temperatures are nearly all above the T_g for pure PVME but very much lower than the T_g for pure PS.

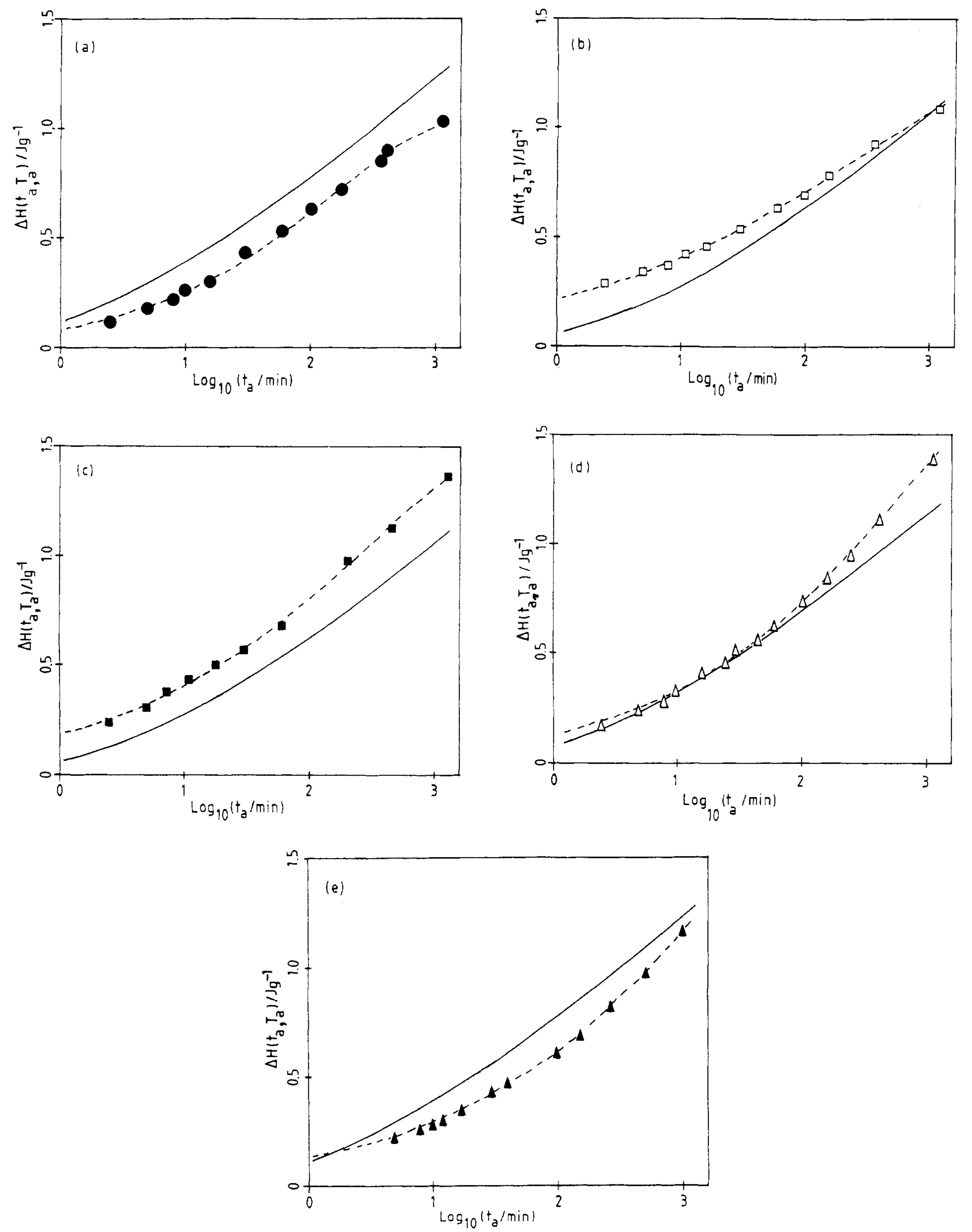

Figure 2. PVME/PS blend, $\Delta H(t_a,T_a)$ versus log (t_a) plots for five aging temperatures. Dashed lines are the fits to the Cowie/Ferguson model, and the full lines are the predicted time dependences of $\Delta H(t_a,T_a)$ according to the Petrie/Marshall model. The plots are labeled (a) T_a = 270 (●), (b) T_a = 265 (□), (c) T_a = 260 (■), (d) T_a = 255 (△), and (e) T_a = 250 K (▲).

Enthalpy Relaxation/Physical Aging. The enthalpic aging data were analyzed by using both the Cowie/Ferguson model (eq 1) and the Petrie/Marshall model (eq 3).

(a) The Cowie/Ferguson Model (CF).

$$\Delta H(t_a,T_a) = \Delta H_\infty(T_a)\ [1 - \Phi(t_a)] \qquad (1)$$

where

$$\Phi(t) = \exp[-(t/t_c)^\beta]$$

The three parameters $\Delta H_\infty(T_a)$, t_c, and β were determined by using a nonlinear least-squares curve-fitting algorithm as before.[6,9] $\Delta H_\infty(T_a)$ corresponds to the initial departure from equilibrium, t_c is a characteristic time, and β is related to the width of the underlying relaxation time spectrum for the enthalpic aging process. The function $\Phi(t)$ describes the kinetics of the approach of the system to the equilibrium state.

Figure 2 shows a plot of $\Delta H(t_a,T_a)$ versus log (t_a) for five

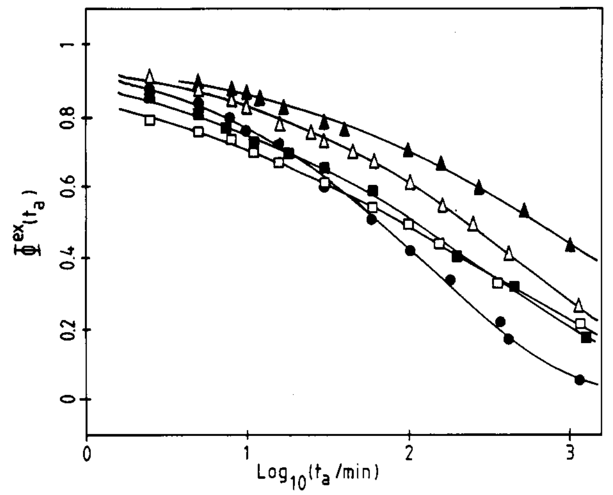

Figure 3. $\Phi^{ex}(t_a)$ versus log (t_a) plot for five aging temperatures as given in Figure 2.

Table I
Parameters and Error Limits Obtained from the Levenberg/Marquardt Nonlinear Least-Squares Curve Fit of PVME/PS Blend Enthalpic Relaxation Data to Equation 1[a]

T_a, K	$\Delta H_\infty(T_a)$, J g^{-1}	log (t_c)[b]	β	$\Delta H_\infty(T_a)$,[c] J g^{-1}
270.0	1.08 ± 0.02	2.15 ± 0.03	0.499 ± 0.011	5.47
265.0	1.39 ± 0.07	2.46 ± 0.12	0.316 ± 0.011	7.13
260.0	1.65 ± 0.06	2.47 ± 0.08	0.373 ± 0.009	9.04
255.0	1.88 ± 0.08	2.74 ± 0.08	0.412 ± 0.009	11.14
250.0	2.09 ± 0.26	3.25 ± 0.22	0.364 ± 0.013	13.35

[a] See text for details. [b] t_c is the characteristic time in minutes. [c] Obtained from the Petrie/Marshall model, eq 4a.

different aging temperatures, viz., T_a = 250, 255, 260, 265, and 270 K, for the 50/50 wt % PVME/PS blend. This figure also includes theoretical curves which were obtained by using both the CF model and the Petrie/Marshall model. Figure 3 depicts the corresponding plot of $\Phi^{ex}(t)$ versus log (t_a), where $\Phi^{ex}(t) = 1 - \Delta H(t_a,T_a)/\Delta H_\infty(T_a)$ and $\Delta H_\infty(T_a)$ is obtained from the nonlinear least-squares curve fit using eq 1. The resulting values of $\Delta H_\infty(T_a)$, log (t_c), and β (together with error estimates) are listed in Table I.

For the PVME/PS blend, $\Delta H_\infty(T_a)$ depends linearly on the temperature difference between the glass transition and the aging temperature ($T_g - T_a$): viz.

$$\Delta H_\infty(T_a) = 0.529 + 0.050(T_g - T_a) \qquad (2)$$

where $\Delta H_\infty(T_a)$ is in J g^{-1}. The temperature dependence of $\Delta H_\infty(T_a)$ for both the blend and the PVME homopolymer in terms of $T_g - T_a$ is shown in Figure 4.

For 10 K ≤ $T_g - T_a$ ≤ 30 K, the ratio of ($\Delta H_\infty(T_a)$ blend)/($\Delta H_\infty(T_a)$ PVME homopolymer) is approximately 0.41, and the composition of the blend in terms of the PVME component is 0.50 by weight fraction. Recalling that ΔH_∞ is the initial departure from the final equilibrium state, this implies that most of the aging is dominated by the PVME component. If the blend was behaving like a true mixture, then one might expect that ΔH_∞(blend) would lie in between ΔH_∞(PVME) and ΔH_∞(PS). At $T_a = T_g - 10$ K, one finds that ΔH_∞(PS) = 3.20 J g^{-1} and ΔH_∞(PVME) = 2.83 J g^{-1} but ΔH_∞(blend) = 1.08 J g^{-1}, which is considerably lower than even the value for PVME.

We were interested to examine whether there was much difference in the aging behavior of the blend when aging temperatures were selected which were both above and below the T_g of the pure component PVME (which is 255.6 K[6]). It was found that over the aging temperature range studied, which encompasses the PVME T_g, ln (t_c) of the blend does not follow a pseudo-WLF equation in terms of $T_g - T_a$ as was observed for PVME.[6] Instead, for aging temperatures above that of the T_g of the pure PVME component, this parameter varies relatively slowly compared to that of pure PVME as seen in Figure 5; but when the aging temperatures were below the T_g of pure PVME, ln (t_c) appears to increase and eventually approach the slope of the curve obtained for the PVME homopolymer. However, the data are insufficient to allow any firm conclusions to be made on this point.

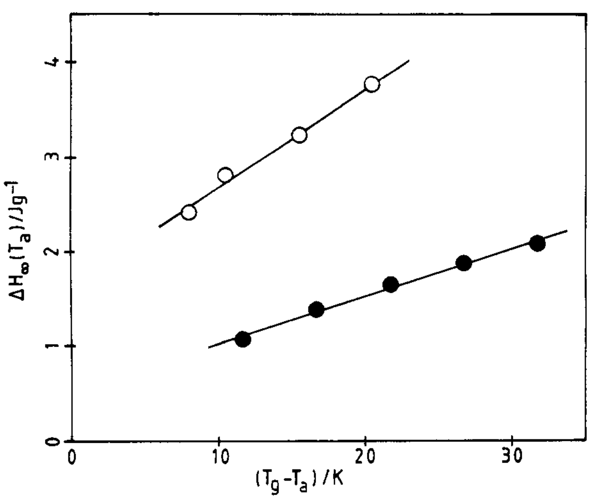

Figure 4. $\Delta H_\infty(T_a)$ versus $T_g - T_a$ plot for 50/50 wt % blend (●) and PVME homopolymer (○).

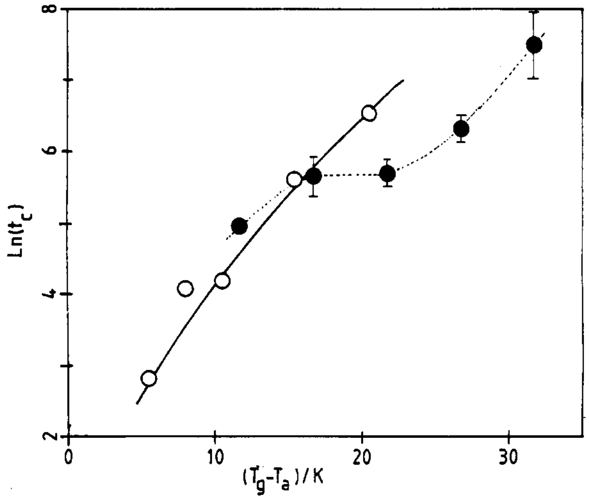

Figure 5. ln (t_c) versus $T_g - T_a$ plot for 50/50 wt % blend (●) and PVME homopolymer (○), with t_c in minutes. The dashed curve is an aid to guide the eye through the blend data, and the solid line is the WLF fit to the PVME homopolymer data.

The parameter β is approximately constant (0.393) for all five aging temperatures considered here. For the two component homopolymers, β(PVME) = 0.572 and β(PS) = 0.35.[11] In general, a smaller value of β implies both (a) a broader distribution of relaxation times for the elementary processes which give rise to physical aging phenomena and (b) a larger value for the time taken for the enthalpy to relax to within 99.9% of the equilibrium value.[6] The observation that β(blend) $\simeq$ β(PS) suggests that even though the polystyrene component does not seem to contribute directly to the magnitude of the enthalpic aging observed in the blend, it nevertheless influences the kinetics governing the approach to thermodynamic equilib-

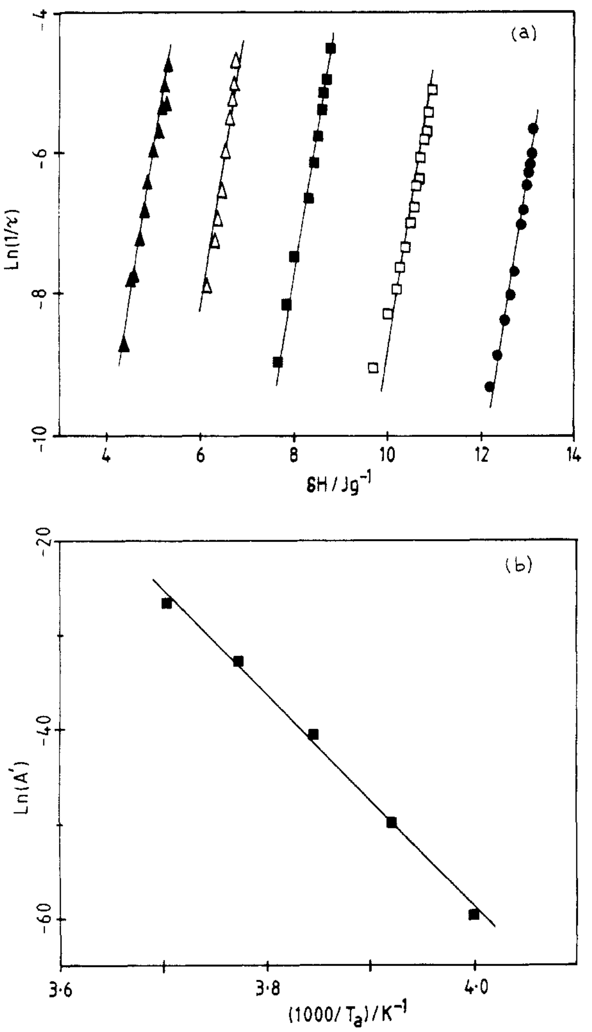

Figure 6. (a) Petrie/Marshall ln $(1/\tau)$ versus δH plot for five aging temperatures as given in Figure 2. (b) Petrie/Marshall Arrhenius plot of ln (A') versus $1000/T_a$ (see text for details).

rium.

(b) The Petrie/Marshall Model (PM).[6,10]

$$\Delta H(t_a,T_a) = \Delta H_\infty(T_a)[1 - \Phi(t_a)] \qquad (3)$$

where

$$\Phi(t_a) = \exp[-t_a/\tau]$$

and τ itself is a function of aging time, i.e., $\tau = \tau(t_a)$. Unlike the previous model, $\Delta H_\infty(T_a)$ is obtained by an extrapolation of the liquid enthalpy curve of the reference unaged sample via

$$\Delta H_\infty(T_a) = \int_{T_a}^{T^*} C_{p(\mathrm{liq})}(T) - C_p(T)\,\mathrm{d}T \qquad (4a)$$

Here T^*, the upper limit in this integral, is selected to be at least 30 K above T_g; $C_{p(\mathrm{liq})}(T)$ is obtained from a linear least-squares fit to the heat capacity of the unaged sample in the liquid state, and $C_p(T)$ is the experimentally determined heat capacity of the unaged sample. Column 5 of Table I lists the values of $\Delta H_\infty(T_a)$ which were obtained via this method.

The parameter $1/\tau$ appearing in eq 3 is a measure of the rate of relaxation of the system as it approaches thermodynamic equilibrium. Rearrangement of eq 3 yields

$$\frac{1}{\tau} = -\frac{1}{t}\ln(\Phi) = -\frac{1}{t}\ln\left[1 - \frac{\Delta H(t_a,T_a)}{\Delta H_\infty(T_a)}\right] \qquad (4b)$$

and Figure 6a shows a plot of log $(1/\tau)$ versus δH = $\Delta H_\infty(T_a) - \Delta H(t_a,T_a)$, the departure from equilibrium, for all five aging temperatures investigated during this study.

The dependence of ln $(1/\tau)$ upon both the aging temperature and the departure from equilibrium is given by

$$\ln(1/\tau) = \ln(A') + C\delta H \qquad (5a)$$

where

$$\ln(A') = \ln(A) - E_H/RT_a \qquad (5b)$$

Here, τ is in minutes, A is in min^{-1}, E_H is an apparent activation energy for enthaply relaxation in kJ mol^{-1}, and C is a constant. Values of the parameters ln (A), E_H, and C were determined by linear least-squares fits to the blend aging data in the same manner as previously described.[6] The set of parallel straight lines also shown in Figure 6a are drawn with a slope equal to C, and Figure 6b is the corresponding Arrhenius plot of ln (A') versus $1/T_a$.

The Petrie/Marshall parameters for the 50/50 wt % blend are ln (A) = 388.2, E_H = 929.0 kJ mol^{-1}, and C = 4.08 g J^{-1}. These parameters can be compared with the average of the homopolymer values[6,11] (viz., ln (A) = 237.6, E_H = 649.3 kJ mol^{-1}, and C = 1.93 g J^{-1}), and it is immediately apparent that the PM enthalpic aging parameters for the blend cannot be obtained by taking an average of the two sets of homopolymer parameters.

The (single) glass transition for this blend measured by DSC implies that there is miscibility for segment lengths of ca. 50 monomer units or greater, and this glass transition can be thought of as resulting from an average of the homopolymer properties. The fact that the enthalpic aging parameters of the blend are not obtained from a linear average of the homopolymer parameters implies that the size of the relaxing agents responsible for enthalpic aging might be considerably less than those responsible for the glass transition of the blend; i.e., enthalpic aging provides one with a much smaller dynamic probe than does conventional DSC measurements.

It is useful to examine the t_e values for this blend in terms of the two theoretical models, where t_e is the time taken for the excess enthalpy lost on aging to have come to within 99.9% of thermodynamic equilibrium. This quantity can be readily calculated from both models by using the appropriate equations. The values of t_e for the 50/50 wt % blend at $T_a \simeq T_g - 15$ (=265 K) are t_e = 3.92 × 10^4 min (Cowie/Ferguson) and t_e = 2.28 × 10^{15} min (Petrie/Marshall). In other words, t_e(PM) is ca. 10^{10} times as long as t_e(CF) for this blend. This raises additional questions as to the validity of extrapolating liquid enthalpy data down to below the glass transition in the case of blends.

An additional point about comparing the curve fits obtained from the CF and PM models should be made here; namely, that while inspection of Figure 2 shows that for most of the aging temperatures investigated the CF model gives a visually superior fit to the aging data, it should be noted that this initial impression might be misleading. Furthermore, it might be argued that the PM model uses three adjustable parameters, whereas the CF model uses four parameters, thus automatically leading to an improved fit. However, calculations using a statistical "F test" on all of our curve fits showed that the CF model did indeed give a statistically significant improvement over the PM model.

Both models imply that the blend ages more slowly than PVME when aged at comparable temperatures below T_g. This supports the hypothesis that physical aging in this blend is determined mainly by the lower T_g component, while the higher T_g component merely serves to retard the aging of the lower T_g component.

One other striking difference between the enthalpic aging data for the blend and that for the homopolymer is that while the phenomenological model of Hodge and Berens[12a] can be applied successfully to the homopolymer C_p data, we have been unable to obtain reasonable curve fits to any of the C_p data for the blend. This is believed to be due to the breadth of the glass transition process(es) occurring in the blend ($\Delta T = 38$ K compared with $\Delta T \simeq 6$ K for a typical homopolymer). We are currently engaged in the (somewhat lengthy) process of analyzing our enthalpic aging data for this and several other polymer systems in terms of the Hodge/Berens phenomenological model and will report the results in a subsequent publication.

Conclusions

Enthalpic aging phenomena in a conditionally miscible blend of polystyrene and poly(vinyl methyl ether) have been analyzed in terms of two models of physical aging in polymer glasses. The results show that aging in the blend is slower than in the case of the lower T_g component. Furthermore, it is suggested that it is the more mobile lower T_g component which appears to be responsible for most of the aging effects measured. We realize, however, that the higher T_g component (polystyrene) must provide a minor contribution to the total aging, although at these temperatures the PS enthalpy relaxation processes should be much slower than those for PVME.

It is thought that enthalpic aging involves the motions of much smaller dynamic units than does the glass transition process. Hence, enthalpic aging could be another useful probe for studying miscibility and immiscibility in polymer blends.

Further work in this area could involve (a) studying the effects of composition on the enthalpic aging process in a blend and (b) the investigation of a more compatible system such as polystyrene/poly(α-methylstyrene) blends.

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Registry No. PVME, 9003-09-2; PS, 9003-53-6.

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Studies of the Antenna Effect in Polymer Molecules. 12. Photochemical Reactions of Several Polynuclear Aromatic Compounds Solubilized in Aqueous Solutions of Poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene)

M. Nowakowska,[†] B. White, and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1.
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ABSTRACT: The solubilization and photochemical reactions of several polynuclear aromatic compounds (PNA) in aqueous solutions of poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS-VN) have been studied. The solubilization of PNA compounds has been shown to be quite efficient in aqueous solutions of PSSS-VN. In the absence of oxygen, irradiation of the aqueous polymer solution containing anthracene led to the photosensitized dimerization reaction. In the presence of oxygen photooxidation of the PNA compounds involving singlet oxygen occurred.

Introduction

Various synthetic polyelectrolytes consisting of hydrophobic and hydrophilic groups have been found to form hydrophobic microdomains within the polymer coil in aqueous solution.[1-10] This conformation enables solubilization of both aliphatic and aromatic hydrocarbons. Moreover, many of the known synthetic polyampholytes exhibit this behavior at low degrees of ionization.

In the previous studies in this series it has been shown that the novel polyelectrolyte poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS-VN) efficiently solubilized large hydrophobic compounds.[9,10] Solubilization was found to be only slightly affected by a change in pH or ionic strength. It has also been shown that PSSS-VN exhibits very promising photocatalytic activity. The polymer sensitizes photochemical reactions of solubilized compounds by absorbing light in the UV-visible spectral region and transferring the excitation energy to the solubilized molecules. It is believed that this phenomenon has potential practical applications.

Many of the polynuclear aromatic compounds (PNA) are thought to be carcinogenic. Although such compounds are only sparingly soluble in water, they can be easily introduced into the human body. Thus the search for a

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[†] On leave from the Faculty of Chemistry, Jagiellonian University, Krakow, Poland.

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