Free volume changes in polyvinyl acetate measured by fluorescence spectroscopy

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Fluorescence probes dispersed randomly in polyvinylacetate (PVAc) were used to follow changes in the matrix free volume with temperature and during isothermal physical ageing in the glassy state. The emission intensity of Auramine O shows a change in temperature coefficient at the glass transition temperature of PVAc. During isothermal ageing, after a quench from the equilibrium melt, the emission intensity shows a time-dependent increase, interpreted as due to the relaxation of matrix free volume. The change in Auramine O fluorescence intensity with ageing time is compared with the increase in the characteristic time for momentary stress relaxation of PVAc. These properties are found to be qualitatively self-consistent using theoretical arguments based on free volume concepts.

(Keywords: physical ageing; free volume; stress relaxation)

INTRODUCTION

Physical ageing of an amorphous polymer refers to time-dependent changes in the material properties of the glassy state. This process occurs because of the non-equilibrium character of the glassy state[1]. The changes in the mechanical properties are generally interpreted as due to a decrease in the free volume fraction contained in the polymer[2]. Of particular interest in this regard is a statistical mechanical theory of the bulk polymeric state developed by Simha and Somcynsky[3] in which the free energy is expressed in terms of a free volume function, h. In the melt, $h(P, T)$ is determined by minimization of the free energy; in the glass, $h(P, T, t_a)$ is a function of formation history, expressed in terms of the ageing time, t_a, and is evaluated from the free energy function at finite chemical affinity. Thus, above T_g, $h(P, T)$ can be computed numerically from PVT data; below T_g, $h(P, T, t_a)$ can be computed from volume recovery data. Recently, Robertson, Curro and Simha[4–7] have concluded that it is possible to establish quantitative connections between volume recovery data in polymer glasses and the change in viscoelastic shift parameter for stress relaxation during physical ageing via the Simha–Somcynsky theory.

Several spectroscopic techniques have been shown to be sensitive to changes in free volume of polymers. The rotational mobility of probe molecules dispersed in the polymer matrix, and monitored by electron spin resonance (e.s.r.) linewidth[8–11] or fluorescence anisotropy measurements[12], shows a temperature dependence which can be correlated with variations of the matrix free volume as described, for example, by the Williams–Landel–Ferry (WLF) parameters. Also, the emission intensity of certain fluorophores, dispersed in viscous media, decreases as the matrix viscosity decreases[13,14]. This effect is traced to an increase in non-radiative decay of excited singlets due to the enhanced mobility of the probe and the matrix as the temperature rises[13–16]. Finally, the lifetime of positrons, trapped in polymer matrices in the form of orthopositronium, shows a change in temperature coefficient in the glass transition region[17–19]. A quantitative correlation has been found between the positron lifetime spectrum and the Simha–Somcynsky free volume parameter for polyvinyl acetate[20]. An important point is that the mobility of chemical probes is a strong function of the size of the probe. Large probes tend to be less sensitive to free volume changes.

Comparatively few spectroscopic studies of changes in free volume during physical ageing of polymers have been reported. Sung and co-workers have used photo-isomerizable probes[21,22] to investigate changes in free volume of polymeric matrices. The percentage *cis* to *trans* conversion is found to be sensitive to the free volume level and shows a significant decrease during isothermal physical ageing in the glass, after a quench from the equilibrium melt. By covalently attaching isomerizable labels to chain ends and chain centres, it was further demonstrated that the free volume at chain ends is greater than at the centres, and thus it is evident that a distribution of free volume elements must be considered, as used in the Robertson–Curro–Simha theory[6,7].

Changes in positron lifetime spectral parameters in polymers during long-term physical ageing have been reported[20,23,24]. A recent study[20,23] suggests that it is possible to determine the Simha–Somcynsky free volume function of polymers during long-term isothermal physical ageing from the positron lifetime spectrum. Finally, changes in the e.s.r. spectrum of nitroxide spin probes dispersed in polymers during physical ageing have been described[25,26]. Numerical connections between the

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decrease in rotational correlation time and the ageing free volume function of Simha–Somcynsky have been identified[25,26].

These studies suggest that it should be possible to establish quantitative comparisons between free volume parameters as measured by spectroscopic probes and time and temperature dependences of other material properties of amorphous polymers. A major problem in comparing properties of glassy polymers, sensitive to free volume, is the requirement of establishing identical thermal histories. It is thus advantageous to use the same polymer sample, hence avoiding the possibility of specimen-dependent variations in glass transition temperature.

In this paper, we describe comparisons between the time evolution of the fluorescence intensity of Auramine O in polyvinylacetate during isothermal annealing below T_g and the corresponding variation in the viscoelastic shift parameters which characterize ageing of the shear stress relaxation of the same polymer sample. To study changes in the matrix free volume elements during relaxation towards the equilibrium state, fluorescent probes are randomly dispersed into the polymer at small concentrations. The probes are then excited to a singlet state by irradiating them with photons of appropriate wavelength. The excited probes return to their ground state either by fluorescing or by dissipating the excess energy by friction or momentum transfer to the matrix, a process termed internal conversion. If the probe is free to rotate or vibrate it is more likely to return to its ground state by internal conversion. If, on the other hand, those motions are severely hindered, the probe is more likely to emit a photon, i.e. fluoresce. Thus, the mobility of a probe is directly related to the free volume around it. Loutfy[16] has suggested an expression describing the fluorescence intensity:

$$F = F_0 \exp(V_m / bV_f) \qquad (1)$$

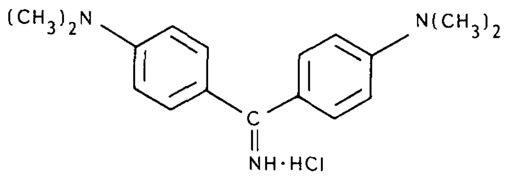
Here V_m is a critical volume necessary for motion of the spectroscopically active group in the probe molecule, V_f is the free volume of the polymer, F is the fluorescence intensity, F_0 is the fluorescence intensity of unhindered probes and b is a system-dependent constant. Equation (1) is qualitatively consistent with experimental observation that the fluorescence quantum yield of larger probes in polymeric matrices is larger than that of smaller probes and is inversely proportional to the matrix free volume.

EXPERIMENTAL

Fluorescence spectroscopy

Fluorescence measurements were performed using an Aminco–Bowman spectro-fluorimeter, with the capability of generating corrected spectra via the ratio method using a reference photomultiplier tube (PMT). A digital microvoltmeter was used to monitor the output of the PMTs, and a thermocouple inserted directly into the sample was used to monitor the sample temperature. To avoid photodegradation of the probe during experiments over extended periods of time, a mechanical shutter was installed to enable intermittent illumination of the sample. Using a custom-made sample cell holder, temperature regulation to ±0.1°C was achieved.

Polyvinylacetate (PVAc) samples were supplied by DSM. The glass transition temperature of the received sample was 29°C, measured by differential scanning calorimetry (d.s.c.) analysis at a heating rate of $10°C\,min^{-1}$. The fluorescent probe Auramine O was obtained from Molecular Probes Inc. (Junction City, OR 97448, USA):



Polyvinylacetate samples doped with Auramine O at a concentration $<10^{-5}$ M were prepared by dissolving probe and polymer in spectral grade acetone. The mixture was heated and stirred to ensure random distribution of the probe. Optically clear cylindrical samples, suitable for fluorescence analysis, were prepared using a custom-made vacuum mould, following a design of Plazek[27]. It is pertinent to note that the d.s.c. glass transition temperature of the doped sample increased slightly ($T_g = 32°C$) over the untreated material, presumably because of loss of low molecular weight components. The samples were initially annealed in an oven at 60°C, removed, and quickly placed in the spectrometer. The sample temperature reached the final quench temperature in approximately 2 min. The probe was excited at $\lambda_{exc} = 380$ nm; fluorescence emission was monitored at $\lambda_{em} = 480$ nm.

Stress relaxation analysis

Torsional stress relaxation measurements were performed on Auramine O-doped PVAc samples using equipment developed at DSM Central Laboratory[28]. Physical ageing experiments were done at 20.3, 22.5 and 25°C to facilitate comparison with the fluorescence measurements. The PVAc sample was annealed in a vacuum oven at 45°C for one week and then press moulded at 100°C to form a test specimen of dimensions $3.65 \times 0.8 \times 0.204\,cm^3$. Stress relaxation studies during physical ageing of a doped sample were performed after well specified cooling histories into the glass.

RESULTS

Fluorescence measurements

The fluorescence intensity of Auramine O dispersed in PVAc shows a well defined change of the temperature dependence in the glass transition region as seen in *Figure 1*. In this experiment, performed under slow cooling, the emission intensity at $T > T_g$ corresponds to equilibrium conditions, whereas, for $T < T_g$, the data reflect the non-equilibrium properties of the glass. Evidently, from *Figure 1*, the glass transition region as measured by the Auramine O probe lies in the temperature range 25–34°C, with a fluorescence fictive temperature, T_f, defined by the intersection of the two straight lines at $T_f = 28°C$.

Several ageing experiments were done on Auramine O-doped samples in which the thermal histories were chosen to be comparable to those applied in the stress relaxation experiments. *Figures 2* and *3* show the time dependence of fluorescence intensity during isothermal annealing of the doped PVAc samples following fast

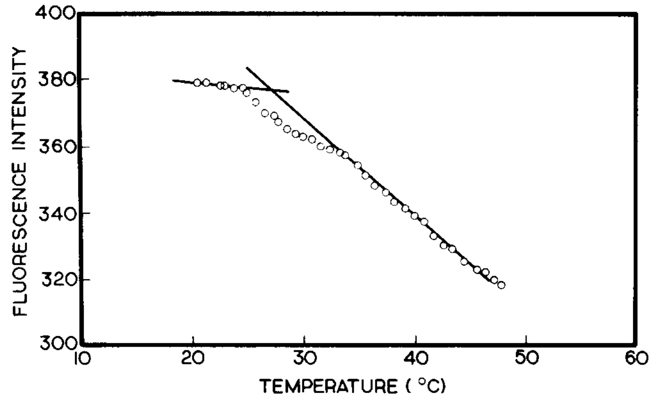


Figure 1 Fluorescence intensity of Auramine O in polyvinylacetate *versus* temperature. The sample was annealed at 50°C for 1 h and then cooled at a rate of 1°C $\min^{-1}$. Intersection of lines fit to the data above and below the glass transition region indicates a fictive temperature $T_f = 28$°C. For comparison, T_g of this sample, determined by d.s.c. at a heating rate of 10°C $\min^{-1}$, is 32°C

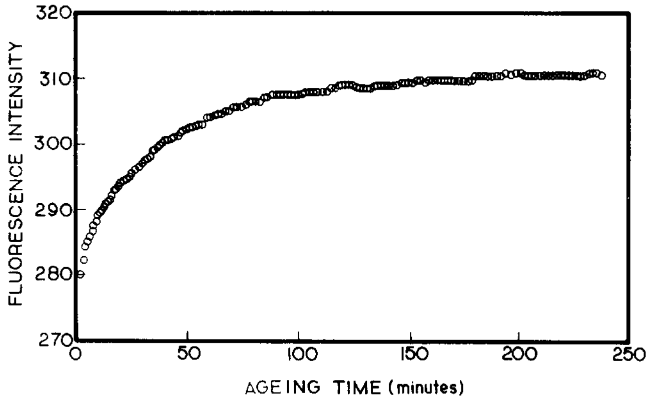


Figure 2 Fluorescence intensity of Auramine O in PVAc *versus* annealing time, t_a, at $T = 20.3$°C after a quench from equilibrium at $T = 60$°C

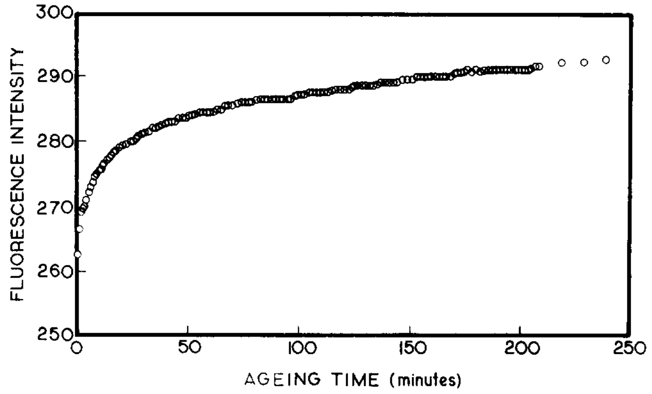


Figure 3 Fluorescence intensity of Auramine O in PVAc *versus* annealing time, t_a, at $T = 25$°C, after a quench from equilibrium at $T = 60$°C

cooling from thermal equilibrium at 60°C to, respectively, 20.3 and 25°C. Since thermal equilibrium is reached within 2 min, the increase in fluorescence intensity with ageing time seen in *Figures 2* and *3* is assumed to be due to a decrease in free volume.

Stress relaxation measurements

A sample of the Auramine O doped polymer was subjected to stress relaxation analysis. Before the measurements were started, the sample was first conditioned for 15 min at 40°C and then cooled within 1 or 2 min in a nitrogen gas stream to room temperature, and put into the oven of the stress relaxation equipment, which is pre-equilibrated at the required measuring temperature. The momentary stress relaxation curves were measured at 20.3 (±0.2), 22.5 (±0.3) and 25.0°C (±0.2°C). *Figure 4* shows the results at 25°C after ageing times of $\frac{1}{4}$, $\frac{1}{2}$, 1, 2, 5 and 70 h. The loading times for the stress relaxation curves were limited to <10% of the ageing times to minimize the effect of ageing during the stress relaxation experiments.

Using procedures described elsewhere[28], a master stress relaxation curve can be generated by horizontal and slight vertical shifts of the individual momentary curves. In agreement with previous observations the derived master curve is described excellently by the equation

$$G(t, t_a, T) = G_0(t/t_0)^c \exp - (t/t_0)^a \qquad (2)$$

with $a = 0.45$ and $c = -0.010$. Here G_0 is the initial modulus, and $t_0(t_a, T)$ is the ageing time and temperature-dependent characteristic relaxation time. In *Figure 5* the resulting master curve is represented, and in *Figure 6* the characteristic parameters t_0 at the three temperatures are plotted as functions of the ageing time t_a. The results of physical ageing experiments at three temperatures are reproduced in *Table 1* where we show values of the logarithm of the shift factor, t_0, at specified ageing times, t_a, as well as the corresponding initial

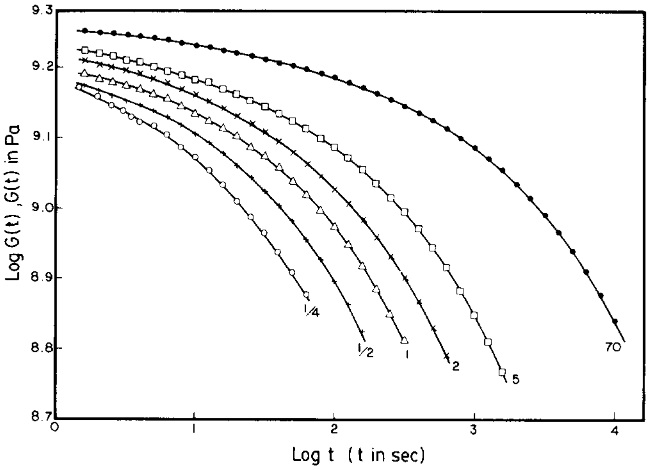


Figure 4 Momentary stress relaxation of PVAc, doped with Auramine O during annealing at $T = 25$°C after a quench from equilibrium at $T = 40$°C, for a series of ageing periods (in hours)

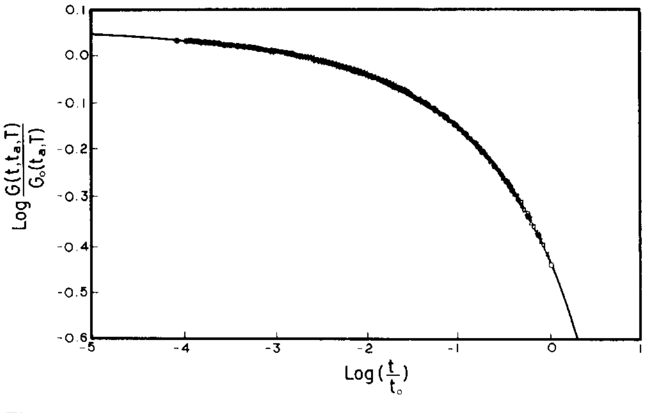


Figure 5 Master curve of the time dependence of the stress relaxation of PVAc, doped with Auramine O. Data representing annealing experiments at $T = 20.3$, 22.5, and 25°C were superposed.——, Equation (2)

moduli, G_0. The modulus G_0 remains virtually constant, independent of t_a and T. Consistent with free volume arguments used by Struik[1], these data follow relations of the form $d(\log t_0)/d(\log t_a) = \text{constant}$, namely

$$T = 20.3°\text{C}: \quad \log t_0 = 2.95 + 0.92 \log t_a \qquad (3a)$$

$$T = 22.5°\text{C}: \quad \log t_0 = 2.81 + 0.86 \log t_a \qquad (3b)$$

$$T = 25.0°\text{C}: \quad \log t_0 = 2.57 + 0.84 \log t_a \qquad (3c)$$

DISCUSSION

To facilitate comparisons of the stress relaxation data with the fluorescence results, it is useful to provide a description of how the total free volume and the volume of the probe may be expected to influence each experiment. Based on Loutfy's arguments, we express the fluorescence intensity, F, of Auramine O by equation (1). Accordingly the emission intensities corresponding to free volume states 1 and 2 are related by:

$$\ln(F_1/F_2) = \frac{V_m}{b}\left(\frac{1}{V_{fs1}} - \frac{1}{V_{fs2}}\right) \qquad (4)$$

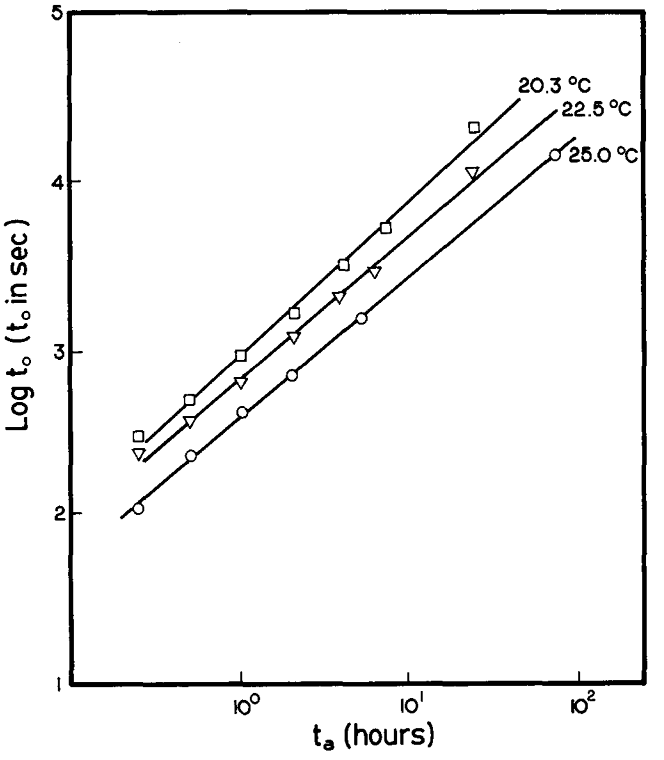


Figure 6 Mechanical relaxation time, t_0, against annealing time, t_a, for thermally quenched PVAc, doped with Auramine O, at $T = 20.3$, 22.5 and 25°C

We write that the free volume quantity detected by the probe is $V_{fs} = V - V_m$, where V_m is defined following equation (1). We obtain

$$\ln(F_1/F_2) = \frac{1}{b}\left(\frac{V}{V_{fs1}} - \frac{V}{V_{fs2}}\right) \qquad (5)$$

or

$$\ln(F_1/F_2) = \frac{1}{b}\left(\frac{1}{f_{s1}} - \frac{1}{f_{s2}}\right) \qquad (6)$$

where the f_{si} indicate fractional free volumes. Equations (5) and (6) are to be compared with an analogous Doolittle-type relation for the mechanical relaxation times:

$$\ln(t_{01}/t_{02}) = \left(\frac{V^*}{B}\right)\left(\frac{1}{V_{fm1}} - \frac{1}{V_{fm2}}\right)$$

where V^* is a critical volume required for mechanical relaxation, and $V_{fm} = V - V^*$ is the free volume pertinent for the process. Defining free volume functions again, one obtains

$$\ln(t_{01}/t_{02}) = \frac{1}{B}\left(\frac{1}{f_{m1}} - \frac{1}{f_{m2}}\right) \qquad (7)$$

Writing $\lambda = (V - V^*)/(V - V_m) = f_m/f_s$, and comparing equations (5) and (6), we deduce

$$\ln(t_{01}/t_{02}) = (b/\lambda B) \ln(F_1/F_2) \qquad (8)$$

Using the second free volume state as a reference state and the first as an ageing time-dependent state we can write:

$$\ln(t_0/t_{0,\text{ref}}) = (b/\lambda B) \ln(F_1/F_{2,\text{ref}}) \qquad (9)$$

This equation suggests plots of $\ln[t_0(t_a)/t_{0,\text{ref}}]$ *versus* $\ln[F(t_a)/F_{\text{ref}}]$, where $t_{0,\text{ref}}$ and F_{ref} correspond to some suitably chosen reference state. These are shown in *Figures 7* and *8* for data at quench temperatures of, respectively, 25 and 20.3°C. In each case the reference state was chosen to be at an ageing time of 15 min, thus corresponding to the earliest time at which t_0 was determined. Values of $\log[t_0(t_a)/t_{0,\text{ref}}]$ at intermediate times between those measured were interpolated from a smooth curve fit through the experimental points (*Figure 6*). The straight lines shown in *Figures 7* and *8* represent least squares fit to the data according to equation (9):

$$T = 25°\text{C}: \quad \log(t_0/t_{0,\text{ref}}) = 44.2 \log(F/F_{\text{ref}}) \qquad (10a)$$

$$T = 20.3°\text{C}: \quad \log(t_0/t_{0,\text{ref}}) = 33.5 \log(F/F_{\text{ref}}) \qquad (10b)$$

Table 1 Mechanical relaxation times, t_0, during physical ageing of PVAc

$T_a = 20.3°\text{C}$			$T_a = 22.5°\text{C}$			$T_a = 25.0°\text{C}$		
t_a (h)	$\log t_0$	$\log G_0$	t_a (h)	$\log t_0$	$\log G_0$	t_a (h)	$\log t_0$	$\log G_0$
$\frac{1}{4}$	2.45	9.198	$\frac{1}{4}$	2.34	9.202	$\frac{1}{4}$	2.03	9.210
$\frac{1}{2}$	2.67	9.217	$\frac{1}{2}$	2.54	9.206	$\frac{1}{2}$	2.34	9.200
1	2.93	9.214	1	2.77	9.209	1	2.60	9.201
2	3.20	9.219	2	3.06	9.215	2	2.82	9.208
4	3.48	9.217	3.7	3.30	9.214	5	3.17	9.208
7	3.70	9.217	6	3.44	9.218	70	4.12	9.216
23.5	4.28	9.236	22.5	4.02	9.223			

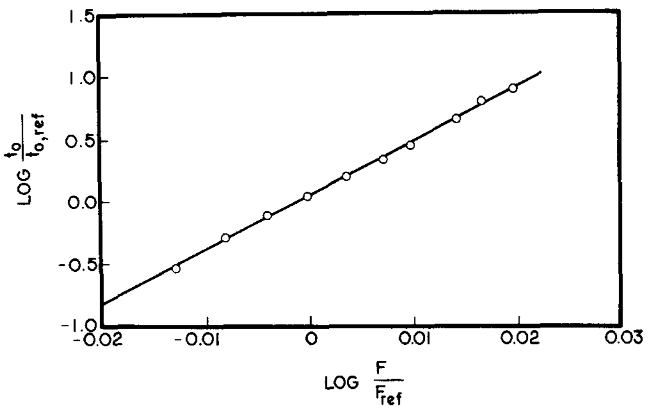


Figure 7 Fluorescence ageing shift parameter, log $[F(t_a/F(t_{a,ref})]$, *versus* mechanical ageing shift parameter, $\log[t_0(t_a)/t_0(t_{a,ref})]$, for Auramine O doped PVAc. Quench temperature $T_a=25°C$, reference state $t_{a,ref}=15$ min

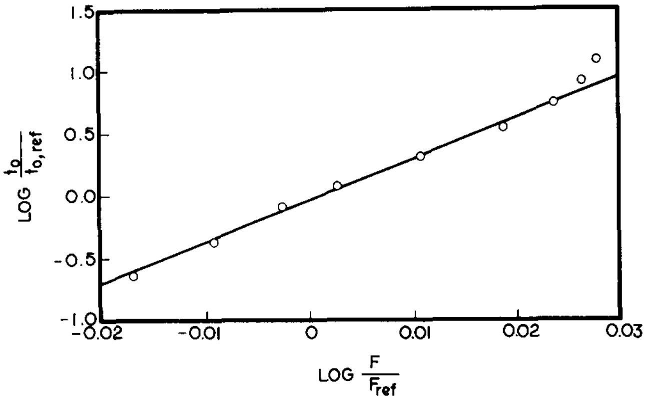


Figure 8 Log $[F(t_a)/F(t_{a,ref})]$ *versus* log $[t_0(t_a)/t_0(t_{a,ref})]$ for Auramine O doped PVAc. Quench temperature $T_a=20.3°C$, reference state $t_{a,ref}=15$ min

The difference in proportionality constant between $T=25°C$ and $T=20.3°C$ evidently reflects a temperature dependence of one or more of the parameters b, B and λ. Qualitatively, we suggest that an increase of V^* relative to V_m with increasing temperature may be the most important effect.

Figures 7 and *8* indicate that equation (10) accurately describes the relationship between fluorescence and mechanical data in the initial part of the ageing process, but small deviations occur during the latter stages of the experiment at 20.3°C. It appears that fluorescence is becoming insensitive to changes in the total free volume, while mechanical measurements continue to show effects due to free volume relaxation. However, additional data are required to confirm this observation.

CONCLUSIONS

In the initial stages of the ageing process of a polymer the fluorescence emission intensity of the probe Auramine O dispersed in the polymer matrix is proportional to the characteristic times for stress relaxation of the polymer. In the latter stages of ageing the fluorescence data seems to be less sensitive to the changes in the total free volume. Fluorescence measurements show promise as a spectroscopic probe for changes in free volume in amorphous polymers during physical ageing.

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