Structural relaxation patterns of an optically labelled polymer at cryogenic temperatures

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A specific conformational microstate of a doped polymer (poly(methacrylic acid)) is optically labelled by burning a narrow spectral hole into the absorption of the dopand molecule. The hole is then used in thermal cycling experiments as a highly sensitive probe for thermally induced structural relaxation processes. The temperature range investigated covers more than two orders of magnitude, namely from 520 mK to 60 K. Even at extremely low temperatures the polymer undergoes thermally activated relaxation processes as detected via the recovery and broadening of the hole. The relaxation pattern as a function of temperature can be modelled in a quantitative fashion. It is shown that the probability distribution of the conformational barriers is $\sim 1/\sqrt{V}$. It seems that there is no lower cut-off barrier and that the distribution diverges for $V \rightarrow 0$.

(Keywords: relaxation patterns; hole burning; cryogenic temperatures)

INTRODUCTION

Many features of the physics of polymers are an outcome of their non-ergodicity. Upon solidification from the melt, the polymer is trapped in a special conformational state from which it cannot easily escape on short timescales[1,2]. Since this conformational state is, as a rule, not a global minimum of the free energy, but rather a local one, relaxation processes are going on, and the polymer starts to explore the phase space around the special conformational state in which it has been trapped, as time goes on or as temperature or some other parameters are changed. Usually these relaxation processes have a rather local character in the sense that it is only a rather small number of atoms which change their places. Owing to the local character and because the free energy varies markedly for amorphous solids, we expect a broad distribution of structural relaxation rates similar to that in small-molecule organic glasses. This distribution may extend over almost 20 orders of magnitude, reaching from microseconds to thousands of years[3]. The structural relaxation rates, no matter whether they are due to tunnelling or activated relaxation processes, are mainly determined by the height of the barrier that separates the interacting conformational substrates in phase space. Information on the distribution of relaxation rates is a prerequisite to understanding ageing processes of polymers. To understand ageing of polymers is technologically very important with respect to many aspects of polymer application. Just one example in this context is the optical data storage for which polymers seem to be of increasing importance[4].

Spectral hole burning offers an excellent technique to measure structural relaxation processes as a function of either time or temperature. The method is highly accurate owing to the sharpness of spectral holes at low temperature[5]. It has been shown that relaxation as a function of time occurs in a logarithmic fashion. The bounds of the rate distribution could be determined for many glassy solids and could be shown to cover many orders of magnitude[3,6]. Very recently we succeeded in modelling thermally irreversible features of the recovery of optical holes due to structural relaxation processes[7,8]. This was possible by introducing a freezing (or melting) condition for the locally relaxing group into the dynamic models for hole relaxation[9].

EXPERIMENTAL

The technique of spectral hole burning has been described in a series of papers (for example see ref. 5). Briefly, narrow-bandwidth laser light is irradiated into the broadband absorption of a photoreactive dye molecule doped into an amorphous matrix frozen to cryogenic temperatures. Light absorption leads to a frequency-selective bleaching of the excited dye molecules and, hence, a hole appears in the spectrum. At low temperatures the hole may be extremely narrow, i.e. several orders of magnitude narrower than the broad inhomogeneous width. The contours of the hole are roughly determined by the homogeneous lineshape function. In order to use the hole as a probe for structural relaxation, temperature cycling experiments are most straightforward. In such an experiment[10], the principle of which is sketched in *Figure 1*, a hole is burnt at the lowest accessible temperature. We call this temperature the burning temperature T_b. In our case T_b was 520 mK and 4 K. After burning, the temperature of the sample is raised to some value T, which we call the excursion temperature, and is immediately cycled back to T_b again. Here, the

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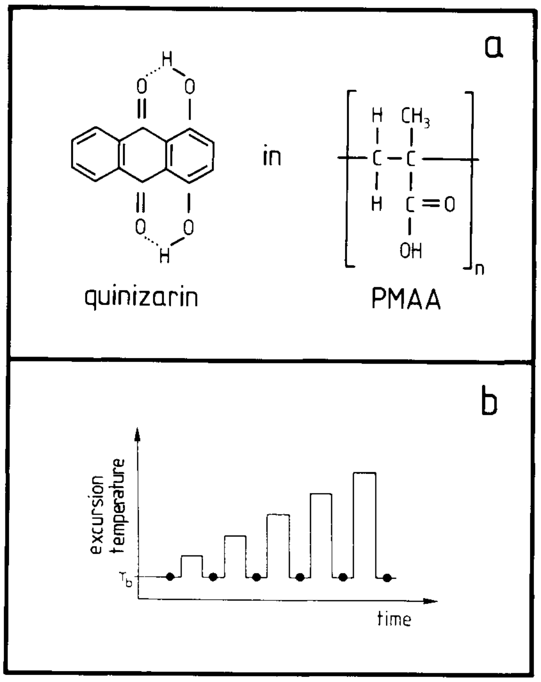

Figure 1 (a) The system investigated: quinizarin-doped poly(methacrylic acid) (PMAA). (b) Sketch of the basic idea of a temperature cycling hole burning experiment. The hole is burnt at T_b, usually the lowest accessible temperature. Then the area and the width of the hole as a function of excursion temperature are measured. The filled circles represent the system whose properties are always measured at the same temperature, namely T_b

changes that the hole suffered through the cycle by the structural relaxation processes being induced are measured. There are three interesting quantities. These are the shape, the area and the width of the hole. The shape usually does not change; it remains Lorentzian when it was Lorentzian before the cycle[9]. However, the area and the width do change[7,8]. Note that it is only the cycling temperature that is varied. The hole is always measured at the same temperature, namely T_b. For temperatures below 4 K we used a ^{3}He-type cryostat. For higher temperatures a ^{4}He-flow-type cryostat was used. The data sets obtained from two experiments with different cryostats were joined in the proper way, so that the whole data set refers to a burning temperature of 520 mK. The accuracy of the temperature was ± 0.01 K below 4 K and ± 0.1 K above. The time τ needed for a cycle was between a few minutes and an hour. The results did not depend in a measurable way on this time. Hole burning was performed with a pulsed dye laser. Power levels and burning times at 4 K were of the order of 400 μJ cm^{-2} per pulse, 30 Hz and 5 min, respectively. We stress that burning at 520 mK is very critical as far as the power level is concerned. Minimal heating due to light absorption may lead to erroneous results. We reduced the power level to 40 μW cm^{-2} by using a continuous-wave (CW) Ar$^+$ laser and extended the burning times to 60 min. The holes were measured with a high-resolution spectrometer (0.25 cm^{-1}). We note that the holes are, to a certain amount, saturated, and hence do not reflect the homogeneous line[11]. This is, however, of no concern, since we are only interested in the change due to temperature cycles. The holes were fitted to a Lorentzian. From that fit the change in area and width was determined. A Lorentzian was in any case a rather good fit despite the saturation broadening.

As a model system of dye-doped amorphous matrix, we took poly(methacrylic acid) (PMAA) doped with quinizarin (*Figure 1a*). Samples were prepared in a similar way as has been described in ref. 11. Concentration and thickness were 10^{-3} mol/kg polymer and 0.5 mm, respectively.

RESULTS

The temperature range investigated covers more than two orders of magnitude, namely from 520 mK to 60 K. *Figure 2* shows the recovery of the hole (i.e. the relative area) as a function of excursion temperature. In the whole range the data can be fitted to a temperature law of the form[7]:

$$A/A_0 = 1 - \sqrt{(T/T^*)}$$

with T^* being of the order of 100 K. Note that the hole recovers even at temperatures as low as 520 mK. The absorption of the sample is shown in the inset. The arrow marks the position where hole burning was done (5145 Å).

In *Figure 3*, the change in hole width ($\Delta\omega_{ir}$) as a function of excursion temperature is shown. The data can,

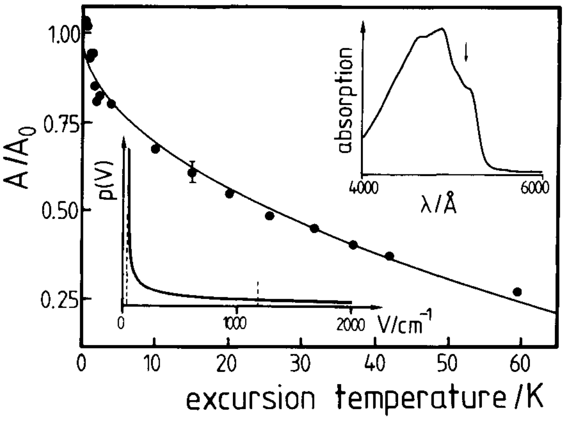

Figure 2 The relative hole area A/A_0 as a function of excursion temperature. A_0 is the extrapolated area to temperature zero. The two inserts show the absorption spectrum with the hole burning position marked, and the distribution function of barrier heights as obtained from the data. The latter follows a $1/\sqrt{V}$ law. Broken lines mark the limits of the experimentally probed range

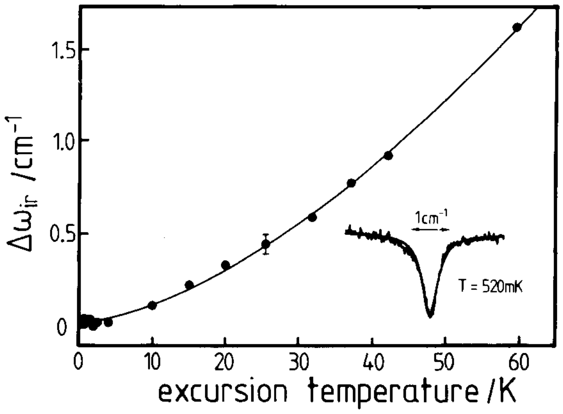

Figure 3 Thermally irreversible line broadening as a function of excursion temperature. The data are plotted with respect to a burning temperature of 520 mK. The shape of the hole at 520 mK is shown in the insert

in the whole range, be fitted to a temperature law of the form[9]:

$$\Delta\omega_{\mathrm{ir}} = aT^{3/2}$$

Note that, whereas the hole area decays rather rapidly in the temperature range from 520 mK to 2.5 K, the broadening is extremely slow. This behaviour reflects the fact that both processes are decoupled. The insert shows a trace of the hole at 520 mK before any temperature cycle was performed.

DISCUSSION

The two-level system (TLS) model for low-temperature polymers

In this section we give a brief outline on how we model structural relaxation processes of amorphous polymers as measured by a temperature cycling experiment. Our approach is based on the so-called TLS model developed to account for the anomalous thermal properties[12] of these materials and recently very often used to model also optical features[3,5]. *Figure 4a* shows a schematic view of a cut through the phase space of an amorphous polymer. The free energy along this cut is a random function. The simplest element of this random function which still allows for structural relaxation is a double well. In the physics of glasses such a double well is called a TLS (two-level system). It is a special feature of amorphous solids that the parameters of a TLS are widely distributed. These parameters are, for instance, the barrier V and the energy splitting E. Since amorphous solids are, as a rule, characterized by a sharply structured radial pair distribution function[1] on short length scales, for the moment we do not assume that d is distributed, too. Owing to the distribution of these parameters, the structural relaxation rates are distributed, too[13]. Since structural relaxation, no matter whether it is due to a tunnelling or an activated process, depends in an exponential fashion on V, the distribution of rates is incredibly broad, as mentioned above. Relaxation in a double well can be viewed as a structural rearrangement of a local group of atoms. Within the frame of the model we assume that these rearrangements are independent of each other. This is equivalent to a mean-field ansatz. A conformational microstate of the whole polymer is given by a definite occupation of the whole ensemble of TLS. There are several important features of the TLS model in its usual form: namely, that only the two lowest states in a double well are considered to be important (hence the name two-level system), that relaxation occurs only by tunnelling processes and that the relevant parameters E and λ are roughly uniformly distributed[12]. The parameter λ is called the tunnelling parameter and is a function of the barrier height V, the length d and the mass m of the tunnelling particle, according to:

$$\lambda = \left(\frac{mV}{2\hbar^2}d^2\right)^{1/2} \tag{1}$$

In the following we will modify this model in the sense that we allow for activated processes as well, and that the relevant distribution is the distribution of V instead of λ. The important difference is that a distribution in V can be directly measured[7] whereas a distribution in λ cannot.

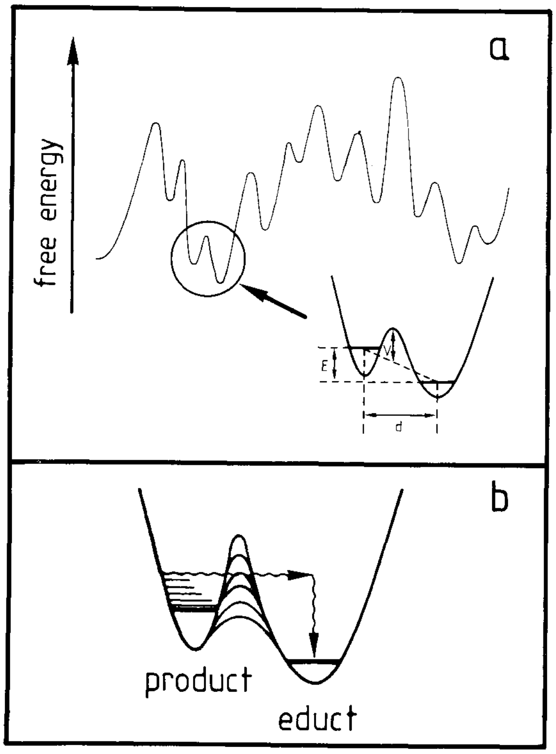

Figure 4 (a) Schematic view of the free energy for a random system cut along an imaginary coordinate. The simplest element of a random potential which allows for structural relaxation is a double well, a TLS. (b) Modelling of hole recovery: schematic representation of an 'extrinsic TLS', consisting of the photoproduct and the educt state. The barrier is distributed over a fairly large range

The recovery of the hole and the distribution of barrier heights

Very recently we have tackled the problem of hole recovery for a series of glasses[7]. The recovery of the hole as a function of excursion temperature is due to the fact that molecules return from the photoproduct state to their educt state. When there is a well defined barrier which separates the two states, one would expect a step-like behaviour. A situation like this occurs for some glasses and polymers doped with phthalocyanine. In this case the reaction barrier is determined by intramolecular interactions and hence has a pretty well defined value. Whenever the reaction barrier is determined by the local disorder of the amorphous host, the barrier is distributed, and one has a situation very much like the TLS model sketched above. As a matter of fact, product and educt states form a special kind of TLS, which we call extrinsic, in order to stress the fact that it is related to the dopand molecule[14]. Disorder-dominated barriers in such an extrinsic TLS are found, for example, in photophysical hole burning reactions or in photochemical hole burning reactions which involve the next-nearest solvent molecules. An example of the first type is tetracene in alcohol glass, where the reaction is due just to a rotation of the guest molecule in the solvent cage[14]. An example of the second type is quinizarin in alcohol glass[5,15]. Here, the reaction is due to light-induced formation of a hydrogen bond between probe molecule and solvent. We do not know exactly the reaction mechanism for quinizarin in PMAA, but from the experiments it is clear that there is no step-like recovery and hence we conclude that there is a distribution of barrier heights rather than a definite value. The situation is schematically depicted in *Figure 4b*.

In principle, the recovery of the hole could occur via tunnelling as well as via activated processes. In the case of tunnelling processes, the recovery would depend on cycling temperature only in a logarithmic fashion. Since this is not the case, we conclude that activated barrier crossing prevails. The rate for such a process is, in its simplest form, given by:

$$R = R_0 \exp(-V/kT) \qquad (2)$$

with R_0 being an attempt frequency of the order of $10^{12}\,\mathrm{s}^{-1}$. Since we have a wide distribution $p_v(V)$ of barrier heights, an interesting situation occurs: for a given excursion temperature T there exists a marginal barrier V_T which separates those centres that can relax within the experimental timescale τ from those that cannot relax. The first category of centres is characterized by barriers:

$$V \lesssim V_T \qquad (3)$$

whereas the second category has:

$$V \gtrsim V_T \qquad (4)$$

The marginal barrier is determined by the condition that the relaxation rate associated with V_T is roughly given by the experimental time τ (ref. 7). From this condition one has:

$$V_T = kT \ln(R_0 \tau) \qquad (5)$$

The area of the hole for a given excursion temperature T is made up by those educt–product pairs which have barriers higher than V_T. Hence, the hole area, which is the measured quantity, is given by:

$$A/A_0 = \int_{V_T}^{V_{\max}} p_v(V)\,\mathrm{d}V \qquad (6)$$

with $V_{\max}$ being an upper cut-off (a maximum barrier) for the distribution $p_v(V)$. The distribution $p_v(V)$ can be directly determined from the experiment by taking the derivative of the above expression. We stress that this experimental procedure is a very direct method for measuring $p_v(V)$. Of course, there are other experimental approaches in the literature[16,17] mostly based on kinetic experiments, from which $p_v(V)$ can be obtained by an incomplete inverse Laplace transformation. This method, however, suffers from low resolution. In a series of cases these experiments yielded an asymmetric distribution with an increasing probability density for low barriers. Our experiments show the same trend; however, the distribution is extremely asymmetric and has, for instance, nothing in common with an asymmetric Gaussian distribution. For low barriers it seems to diverge.

What kind of distribution do we expect? We stressed above that the product–educt pairs are very similar to the TLS of a random potential and therefore it is straightforward to apply TLS statistics. For a uniform distribution of λ (equation (1)) we get a distribution $p_v(V)$ of the form[7,14]:

$$p_v(V) \sim 1/\sqrt{V} \qquad (7)$$

assuming m and d to be sharp. Inserting equation (7) into equation (6) and using equation (5) we can directly calculate the recovery behaviour of the burnt hole as a function of excursion temperature. The result is:

$$A/A_0 = 1 - \sqrt{(T/T^*)} \qquad (8)$$

with T^* given by:

$$T^* = V_{\max}/k \ln(R_0 \tau) \qquad (9)$$

As stated above, equation (8) is an excellent fit to the observed recovery behaviour. Therefore, we conclude that equation (7) is an appropriate representation of the distribution of barrier heights in amorphous solids, including polymers. It is worthwhile to stress that equation (7) could be verified for all the amorphous systems that we have investigated so far[7,8]. The only exception found was a protein[18], but even in this case the distribution (7) is a very good description, if some discrete features superimposed on the glass-like distribution are taken into account.

Equations (8) and (9) show some noteworthy facts. First, the measured quantity A/A_0 (equation (8)) depends on the experimental time τ. However, since this dependence is logarithmic, and hence extremely weak, it does not play any role. As a matter of fact, this weak dependence ensures that the barriers can be measured with a high accuracy. Also, the log dependence warrants that the guess which we made for the parameter R_0 is not crucial. Even if our guess were wrong by several orders of magnitude, the consequence on the experimental results is not striking. The factor $\ln(R_0\tau)$ can be considered as rather well defined and is of the order of 30. Secondly, these lines of reasoning leave $V_{\max}$ as the only fitting parameter, which can be determined from the experiment. We found for quinizarin in PMAA a value of $2000\,\mathrm{cm}^{-1}$. A similar value was found for quinizarin in poly(methyl methacrylate) (PMMA).

Thermal relaxation in the vicinity of $T=0$

It is a most interesting result of our experiments that hole recovery occurs at temperatures as low as 520 mK and hence we conclude that there are thermally activated processes at temperatures as low as that. Equation (8) was obtained under the assumption:

$$V_{\min}/\ln(R_0\tau) < kT < V_{\max}/\ln(R_0\tau) \qquad (10)$$

with $V_{\min}$ being a lower cut-off in the distribution of barrier heights. If $kT < V_{\min}/\ln(R_0\tau)$, we will expect that the A/A_0 curve would bend over and run into a constant regime. Nothing like this occurs down to 520 mK which corresponds to a thermal energy of $0.35\,\mathrm{cm}^{-1}$. Hence, we conclude that:

$$V_{\min} < 10\,\mathrm{cm}^{-1}$$

We note that similar low barriers have been found recently in the photophysical hole burning system tetracene in alcohol glass[19]. The above observation imposes several restrictions on the reaction mechanism. There are many experiments which support the idea of a light-induced proton-transfer reaction as a possible hole burning mechanism for quinizarin-doped glasses[5]. The low-temperature data do not support such a mechanism. A proton could not be trapped in such a shallow minimum. It would immediately tunnel back to its original position. Hence, we conclude that the hole burning mechanism is rather based on a local conformational change in which the masses involved are much heavier than a proton so that trapping in extremely shallow minima is possible.

Thermally irreversible line broadening

We stated above that the irreversible broadening of the hole and its recovery are two independent processes. This has been definitely shown for a variety of systems and is also reflected by the present data[20]. At very low temperatures recovery occurs much faster than broadening. Whereas the recovery is confined to the dynamics of the product–educt TLS (external), the broadening of the hole is a consequence of the relaxation processes occurring in the bulk TLS (internal), i.e. the broadening of the line directly probes the polymer.

What causes an optical hole to be irreversibly broadened by a temperature cycle? At any temperature (and, hence, also at the burning temperature T_b), we can subdivide the ensemble of bulk TLS into those which are in fast equilibrium because their relevant conformational barriers are low enough, and those which are permanently frozen because their barriers are sufficiently high. The latter ensemble is in a well defined microstate and does not contribute to the width of a hole burnt into the sample at the temperature considered. The demarcation line between the two categories of TLS may depend on time but is, for reasons discussed below, quite sharp. Hole burning can be considered as an optical label for the special microstate of the frozen TLS. Suppose the temperature is raised to some value T (the excursion temperature). Then TLS centres will cross the demarcation line from the frozen to the equilibrated regime. They melt. When the temperature is cycled back the reverse process happens. TLS will fall out of equilibrium, and get frozen again. But when a certain TLS freezes again, there is a finite probability that it will change its original position. For a special TLS characterized by a well defined relaxation time $T_1(E,\lambda,T)$ this will occur at a temperature T_f, which we call the freezing temperature and is determined by the condition:

$$T_1(E,\lambda,T_f)=\tau \qquad (11)$$

with τ being the experimental time. When the cycle is closed and the system is again at the burn temperature, those TLS which were frozen in a definite microstate before, will be frozen again, but the actual microstate will be different from the original one. For this new microstate the frequencies of the optically labelled molecules no longer coincide and hence the hole has broadened. This type of broadening is called spectral diffusion. Note that the big advantage of a temperature cycling experiment is the fact that it measures exclusively spectral diffusion processes whereas the normal hole burning experiments measure, in addition, the contribution from phonon scattering processes. It was shown by Black and Halperin[21] that the width due to spectral diffusion is determined by the number n_f of TLS which have changed their state during the time τ. During this time τ the system runs through a cycle, and hence we have to calculate the number of TLS having flipped an odd number of times because of cycling the temperature. We start with the Black and Halperin expression[21]:

$$\Delta\omega_{ir}=C\langle|\Delta/E|n_f\rangle_{E,\lambda}$$

$$=\tfrac{1}{2}C\bar{P}\int_{E_{min}}^{E_{max}} dE\,\mathrm{sech}^2(E/2kT)\int_{\lambda_{min}}^{\lambda_{max}} d\lambda\,(1-e^{-t/T_1}) \qquad (12)$$

Here C is a coupling constant, E the energy splitting, $\bar{P}$ the density of TLS states, E_{max}, E_{min} and λ_{max}, λ_{min} cut-off parameters in the relevant distribution functions, and Δ the energy asymmetry parameter. In the case when both TLS states are only weakly coupled, $\Delta/E=1$ holds.

In the above expression we have to introduce thermal irreversibility to account for our experiments[9]. We do it by making use of the freezing condition (equation (11)). To this end we consider again a special class of TLS, with a well defined freezing temperature $T_f(\lambda)$. For $T>T_f$, this class is in fast thermal equilibrium, and hence T_1 is very short compared to the experimental time and we can neglect the exponential in equation (12). The contribution $d(\Delta\omega_{ir})$ of this special class of TLS to the irreversible width of the hole is then given by:

$$d(\Delta\omega_{ir})=\tfrac{1}{2}C\bar{P}\,\mathrm{sech}^2(E/2kT)\,dE\,d\lambda \qquad (13)$$

This expression has to be integrated over the whole temperature range of the cycle, i.e. from T_b to T, under the constraint that for a given temperature T' only those TLS are taken into account for which their freezing temperature coincides with T':

$$\Delta\omega_{ir}=\tfrac{1}{2}C\bar{P}\int_{T_b}^{T} dT'\int_{E_{min}}^{E_{max}} dE\,\mathrm{sech}^2(E/2kT')\int_{\lambda_{min}}^{\lambda_{max}} d\lambda\,\delta(T'-T_f(\lambda)) \qquad (14)$$

This expression can be solved by introducing new variables, namely $x=E/2kT'$ and T_f:

$$\Delta\omega_{ir}=kC\bar{P}\int_{T_b}^{T} dT'\,T'\int_{0}^{\infty} dx\,\mathrm{sech}^2x\,|[\partial\lambda/\partial T_f]_x|_{T_f=T'} \qquad (15)$$

Here we have assumed that $E_{min}\ll kT_b$ and $E_{max}\gg kT$, with T being the excursion temperature. This condition may not always be fulfilled. As a matter of fact we found for PMMA that an upper cut-off around $E_{max}=16\ \mathrm{cm}^{-1}$ had to be assumed to account for the observed results[9,20]. Note that one power in T is lost in the case when this approximation breaks down.

Equations (15) and (11) are the basic relations to model thermally irreversible relaxation of a low-temperature polymer. Note that we have not yet considered a specific relaxation process. We stressed above that relaxation in a TLS can either occur via tunnelling or via activated processes. In many low-molecular-weight organic glasses we could indeed show that a superposition of both processes accounts perfectly for the measured relaxation pattern[20]. Let us for the moment assume that in the polymer considered, activated processes (equation (2)) prevail. Then, we use the freezing condition and calculate, with the aid of equation (1), $\lambda(T_f)$:

$$\lambda^2 = \frac{md^2}{2\hbar^2} kT_f \ln(R_0\tau) \qquad (16)$$

This is inserted into equation (15). We then find:

$$\Delta\omega_{ir}^{(th)} = \tfrac{1}{3} C\bar{P}k^{3/2} \left(\frac{md^2}{\hbar^2} \ln(R_0\tau) \right)^{1/2} (T^{3/2} - T_b^{3/2}) \int_0^\infty dx\, \mathrm{sech}^2 x \qquad (17)$$

where (th) stands for thermally activated. The results in *Figure 3* are fitted to this expression. We think the fit is extremely satisfactory.

We conclude that, in low-temperature PMAA, activated processes lead even at very low temperatures to structural rearrangements of the polymer matrix, which in turn shows up in an irreversibly broadened hole. Temperature cycling hole burning experiments are probably the most direct method to probe ageing of low-temperature polymers. The broadening of the hole follows a $T^{3/2}$ law. There is no indication for tunnelling relaxation, which would result in a linear temperature dependence. We believe that this behaviour results from the constraints imposed on the TLS by the covalent bonding in the backbone. The covalent bonding may result in the fact that the masses and length scales involved in structural relaxation of a TLS are rather large so that tunnelling is prohibited, a result that was also found in PMMA. Note that equation (17) depends on the experimental time via $\ln(R_0\tau)$. Again, it is this extremely weak logarithmic time dependence that warrants a sharply defined demarcation line between equilibrated and frozen TLS. Finally we stress that in PMAA unlike in PMMA there seems to be no upper cut-off E_{max} in the energy distribution of TLS in the temperature range investigated. We conclude that $E_{max} \gg 42\ \mathrm{cm}^{-1}$.

SUMMARY AND CONCLUSIONS

We demonstrated that thermal relaxation in non-ergodic systems can be investigated with high accuracy by hole burning temperature cycling experiments. We found that the conformational barrier heights follow a distribution of the form $p_V \sim 1/\sqrt{V}$. This distribution is a direct outcome of the so-called tunnelling model of glasses, in which the tunnel distance and the tunnelling mass are well defined. However, it is worth while to stress that even if these latter quantities are distributed the above distribution of barrier heights is compatible with the tunnelling model. We found that the phase space of a polymer can be well modelled within the framework of the tunnelling model, i.e. by assuming rather local structural relaxation processes which are independent of each other. The irreversible features of our experiment can be properly accounted for by introducing a freezing (or melting) condition for a local TLS. Via the freezing condition the experimental timescale appears in the expressions for the line broadening and hole recovery, a typical keymark for non-ergodicity. However, this time dependence is logarithmic and hence so weak that it is experimentally insignificant.

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