

Dynamics of α -Tetralone at Elevated Pressure and in Mixture with Oligostyrene

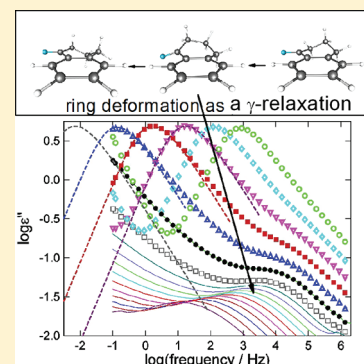
Stella Hensel-Bielowka,^{*,†} Patryk Włodarczyk,^{*,‡} Michal Mierzwa,[‡] Marian Paluch,[‡] and Kia L. Ngai[§]

[†]Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland,

[‡]Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland, and

[§]CNR-IPCF, Dipartimento di Fisica, Università di Pisa, Largo Bruno Pontecorvo 3, I-56127, Pisa, Italy

ABSTRACT: By using the dielectric relaxation method, we studied molecular dynamics of α -tetralone. Our purpose was to reveal the molecular origin of secondary processes observed for this very simple-structured molecule. To this end, we carried out dielectric measurements at both ambient and elevated pressure of neat α -tetralone and in mixture with oligostyrene. By means of both experimental observations and theoretical calculations, we proved that one of the secondary relaxations has the intramolecular origin, while the other is undoubtedly the intermolecular process called Johari–Goldstein relaxation characteristic of the glassy state.



INTRODUCTION

One of the currently active research areas in the research field of glass transition is the search and discovery of the supposedly universal Johari–Goldstein (JG) β -relaxation in various kinds of glassformers.^{1–17} The JG β -relaxation is a restricted kind of secondary relaxation having dynamic and thermodynamic properties mimicking that of the primary α -relaxation,^{18–23} and hence it is important to be included in constructing a fundamental and complete theory of glass transition. This claim is futile unless the JG β -relaxation is identified and found in any glassformer.²⁴ Although JG β -relaxation has been found in different kinds of glassformers, any study of the dynamics of a new glassformer poses another challenge. The burden for experimental verification is particularly heavy in some glassformers where the JG β -relaxation either is not readily resolved from the dominant α -relaxation or is overshadowed by the presence of a non-JG secondary relaxation. Fortunately, various changes imposed on the glassformer have helped to uncover the JG β -relaxation in many different circumstances so far. Examples include physical aging,²⁵ elevating pressure,^{9–13,26–28} and mixing with another glassformer.^{16,17,19,29,30}

In this paper, we present a dielectric relaxation study of the dynamics of a low molecular glassformer, α -tetralone (1,2,3,4-tetrahydro-1-naphthalenone; 1-tetralone) with the molecular formula $C_{10}H_{10}O$, which presents another challenge to discover the JG β -relaxation. The circumstances making it difficult to find the JG β -relaxation in α -tetralone will become clear when the data are presented later. Before that, perhaps the chemical structure of α -tetralone depicted in Figure 1 can presage the predicament. One part of α -tetralone is effectively a rigid phenyl

ring, and if alone (or with small substituents like the methyl group) it is expected to produce a genuine JG β -relaxation because there is no intramolecular degree of freedom; i.e., it has one stable conformation in its ground state. However, the other part of α -tetralone is the flexible cyclohexyl ring, well-known to have several conformations. The molecule can easily switch between some of these conformations, giving rise to secondary relaxation intramolecular in nature, and is not the JG β -relaxation (similar to decahydroisoquinoline³¹). The oxygen double bonded to the cyclohexane ring endows it with a significant dipole moment, resulting in the secondary relaxation from conformation change to have sizable dielectric strength and the possibility of overshadowing the JG β -relaxation of α -tetralone. Moreover, attaching the flexible cyclohexane ring to the benzene-like part of α -tetralone can have the effect like internal plasticization of the latter by the former and thereby reduction of intermolecular coupling in α -tetralone as compared to toluene (benzene with a methyl group attached). For neat glassformers, a measure of the degree of intermolecular coupling is the width of the frequency dispersion of the α -relaxation or the parameter n appearing in the Kohlrausch stretched exponential correlation function

$$\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}] \quad (1)$$

used to fit the data after Fourier transformation from time to frequency. Hence, by performing isothermal dielectric relaxation

Received: July 25, 2011

Revised: November 16, 2011

Published: November 28, 2011

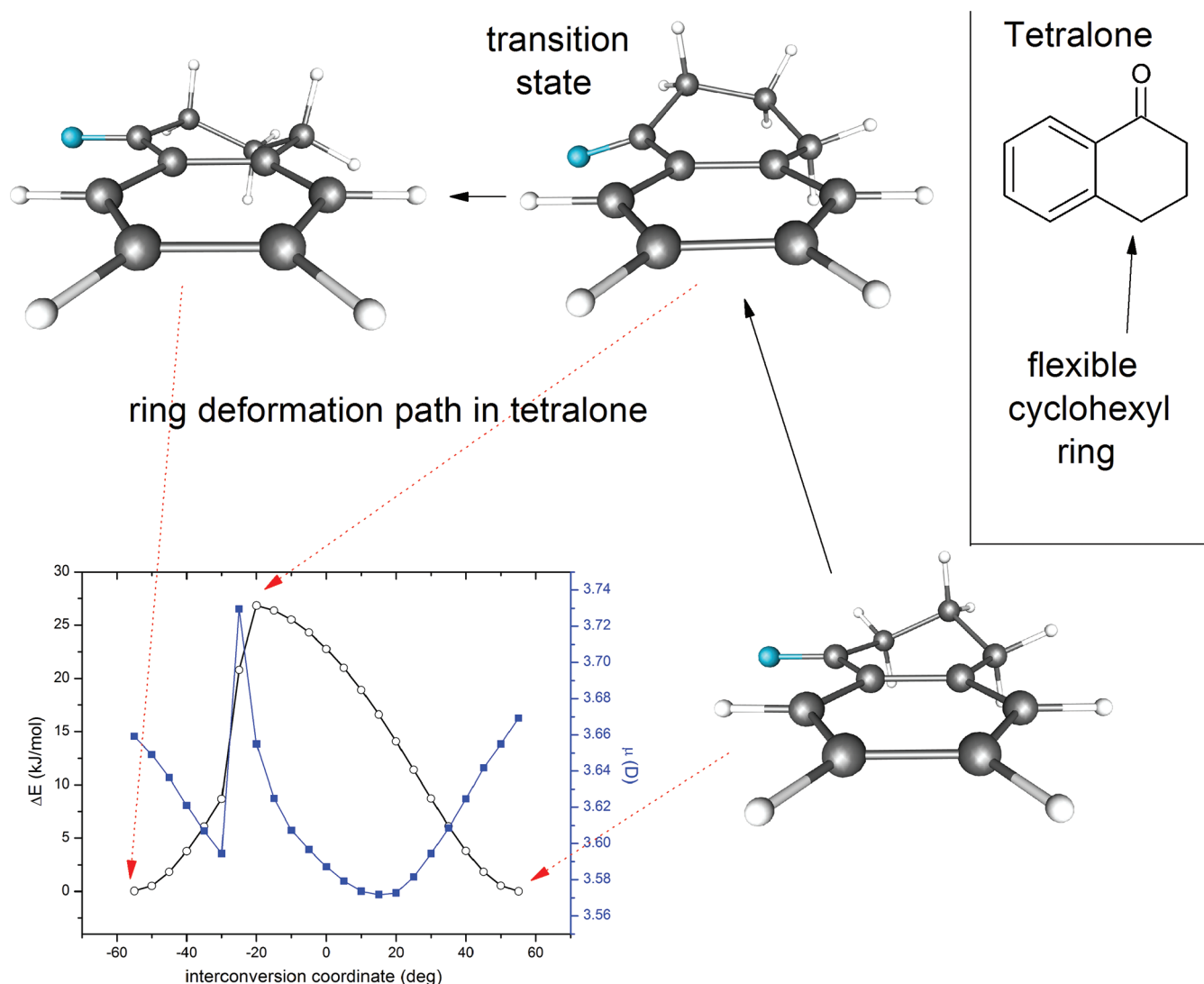


Figure 1. Visualization of the conformational interconversion in α -tetralone. This is the probable origin of γ -relaxation observed in the dielectric spectra. In the inset, one can find the behavior of potential energy and the dipole moment value during the interconversion.

measurements on α -tetralone and comparing them with the published data on toluene, we can expect a reduction of the full-width at half-maximum (fwhm) of the α -loss peak or the parameter n . Well established before is the correlation between either the fwhm or n with the ratio τ_α/τ_β at any fixed τ_ω ,^{26,32–35} where τ_β is the JG β -relaxation time. Combining the statements in the above, we can expect the JG β -relaxation to be closer to the α -relaxation in α -tetralone than in toluene,³⁶ hence making the former more difficult to be resolved from the latter.

Relating molecular structure to dynamics is a worthwhile undertaking. On the basis of the molecular structure of α -tetralone, we have anticipated what its dynamic properties would be like before experimental study and measurements were made. The results reported in the following sections will show how well the anticipated dynamic properties conform to reality.

EXPERIMENTAL AND COMPUTATIONAL

Isothermal dielectric measurements were carried out using a Novo-Control GMBH Alpha dielectric spectrometer. The

temperature was controlled by the Quatro system, employing a nitrogen gas cryostat. Temperature stability of the sample was achieved better than 0.2 K/s.

The high-pressure measurements were carried out using the setup produced by the PAS Institute of High Pressure Physics "Unipress". The setup consisted of a U11 gas compressor and GC10/12 high-pressure chamber using helium gas as a pressure transducing media. The setup allows us to carry out the measurements under the pressure up to 1.5 GPa in the temperature range from -75°C to $+100^\circ\text{C}$. The sample was placed in the stainless steel capacitor with a diameter of 10 mm and a gap of 100 μm using the Teflon (PTFE) spacers. The capacitor was sealed using Teflon tape.

Oligostyrene for mixtures was used with molecular weight 820 and polydispersity index 1.01. The sample was bought from Sigma-Aldrich.

All the calculations were done with the use of the Orca quantum program.³⁷ The geometry of the tetralone molecule was optimized with the use of density functional theory (DFT), on the B3LYP/6-31+G* level of theory. Afterward, an energy

Table 1. All the Results Obtained by QM Calculations^a

method	ΔE (kJ/mol)	ΔZPE	E_a (kJ/mol)
ri-ccsd(t)/cc-pvdz	31.7	0.5	32.2
b3lyp/6-311++g**	26.0	0.5	26.5
b3lyp/6-31+g*	26.9	0.5	27.4
expt			30.5

^a The energies ΔE were calculated in the methods presented in the table, while the geometry was optimized at the b3lyp/6-31+g* level. ΔZPE (zero point energy) presented in all rows was calculated with the b3lyp/6-31+g* method. Activation energy E_a is the sum of electronic energy barrier ΔE and ΔZPE energy difference.

scan was performed on the structure which was in the energetic minimum in the same functional and basis set. The scan was performed by changing the dihedral angle in the cyclohexyl unit of the tetralone molecule. The energy vs dihedral angle plot is presented in Figure 1. The transition state (TS) of conformational interconversion was found by the eigenvector following method. TS optimization was performed on the structure with the highest energy. The optimized TS was further verified by performing vibrational analysis if it could meet criteria for first-order saddle point (one imaginary frequency). To calculate ΔZPE we have also performed vibrational analysis of the structures in energetic minima. The energy of optimized structures was recalculated with the coupled cluster and DFT method in a higher level of basis set. The coupled cluster method was used with the refractive index (RI) approximation (approximation of certain integrals) as implemented in orca.

RESULTS AND DISCUSSION

Internal Conformations of α -Tetralone and Conformation Change. Because the pseudo cyclohexane ring in α -tetralone is attached to the phenyl part, it is not pristine cyclohexane. Its exact conformations and the kinetics of conformation changes cannot be taken from that of cyclohexane and have to be determined by ourselves. To accomplish this task, we use mainly density functional theory (DFT) for calculations. We have used this method in our earlier works to determine the microscopic origin of secondary relaxation modes in decahydroisoquinoline,³⁸ carbohydrates,^{39–41} and vitamin A acetate.⁴² The α -tetralone molecule has a very rigid structure. Two carbons which connect the aromatic ring with the nonaromatic one, as well as the carbon from the carbonyl group, have sp^2 hybridization. Therefore, the molecule is much more rigid than the single cyclohexyl ring. Only the three sp^3 carbons in the nonaromatic tetralone ring are flexible. We have found only two energetically stable conformations of α -tetralone. In both conformations, only one sp^3 terminal carbon is deviated from the plane of the entire molecule by 27° . These conformations are different due to the direction of the deviated carbon atom (see Figure 1 for details). The transition state, i.e., the structure which has maximum energy on the conversion path between two minima, has the oxygen atom in out of plane position. The angle between the oxygen and the aromatic ring plane in the transition state is equal to 25° . Deflection of the oxygen from the plane of the molecule by 25° causes the sudden change of dipole moment (up to 0.2 D). Consequently, one can observe such a motion by broadband dielectric spectroscopy. To compare the experimentally observed secondary mode to the conformational conversion occurring in α -tetralone, we have calculated the activation energy of such

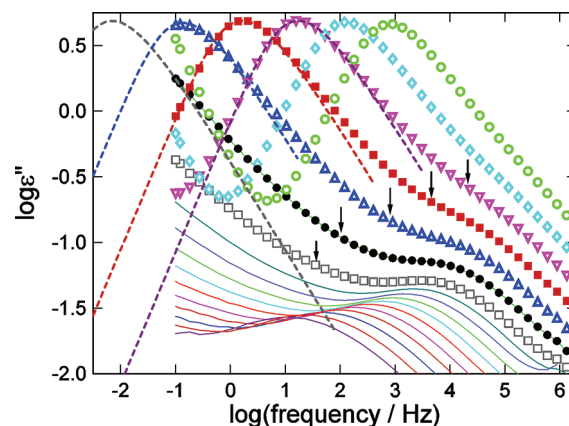


Figure 2. Dielectric spectra of α -tetralone in the temperature range 138–206 K below and above $T_g = 179.5$ K at ambient pressure. The dashed lines are the fits by Fourier transform of the Kohlrausch–Williams–Watts function in eq 1 with $n = 0.32$. The arrows indicate the primitive relaxation frequencies calculated from eq 3 for five temperatures above T_g .

conversion. The geometry of molecules was optimized at the B3LYP/6-31+g* level of theory; however, activation energies were further recalculated in the higher basis set as well as in the ab initio coupled cluster method. The coupled cluster method was used with the so-called RI approximation in combination with the double- ζ cc-pvdz basis set. Results are presented in Table 1. In the first column of the table, there is an electronic energy barrier for interconversion, while in the second one there is a ZPE (zero point energy) vibrational correction. Activation energy is the sum of the electronic energy barrier and the vibrational correction. Vibrational correction was calculated on the B3LYP/6-31+g* level of theory in all cases. As one can see, the energy calculated by use of DFT and the B3LYP hybrid functional is underestimated by 3–4 kJ/mol. The energy calculated in the CC method is very close to the experimental value (only 1.7 kJ/mol difference). While CC calculations are far more demanding, we have used only the double- ζ basis set. Application of the triple- ζ basis set could give even more accurate results. In summary we have found the conformational interconversion which corresponds to the experimentally observed γ -process. On an atomic level, this change of conformation is in fact deformation of the part of the cyclohexyl ring. The calculated activation energy equal to 32.2 kJ/mol is in great agreement with the activation energy of γ -relaxation in the dielectric spectra (30.5 kJ/mol). It has been shown that calculations for isolated molecules stay in satisfactory agreement with experimental values of activation energies for relaxation modes which are insensitive to pressure.³⁸ Thus, it can be concluded in such cases that the surroundings of molecules in a real system have a minor influence on the energy barrier. Therefore, the activation energy for conformational interconversion in isolated molecules can be directly compared to the energy barrier of the local secondary relaxation mode (γ).

Dynamics at Ambient Pressure. Isothermal dielectric loss data of α -tetralone at ambient pressure are shown in Figure 2 at many temperatures above and below the glass transition temperature T_g without the presence of crystallization. The spectra reveal a resolved secondary relaxation on the high-frequency side of the dominant α -loss peak. The guides to the dynamics from the structure given in the Introduction can now be compared with the experimental data. First, we examine whether the fwhm

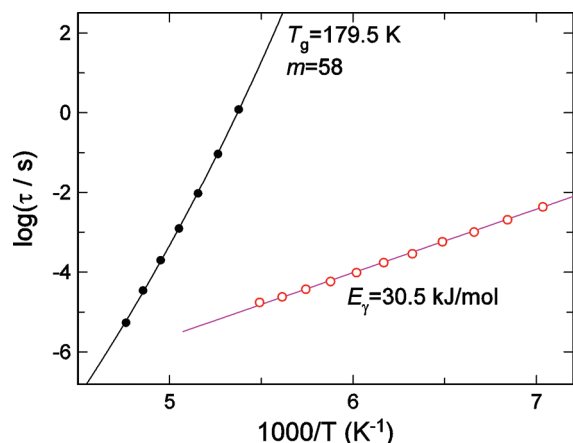


Figure 3. Relaxation map of the α - and γ -relaxation times for the α -tetralone obtained at ambient pressure. The parameters of the VFT law used to fit α -relaxation are $\log(\tau_{\infty\alpha}) = -24.8$, $D_T = 22.8$, and $T_0 = 97$ K. From the VFT fit, we determine $T_g = 179.5$ K and $m = 58$. The parameters of the Arrhenius law fitting the γ -relaxation are $\log(\tau_{\infty\gamma}) = -13.57$ and $E_\gamma = 30.5$ kJ/mol.

or n of α -tetralone is smaller than toluene as expected from the reduction of intermolecular coupling by the flexible cyclohexane ring attached. This is verified by the smaller $n = 0.32$ for α -tetralone obtained from the fit by the Fourier transform of the Kohlrausch function (eq 1) shown in Figure 2 compared with $n = 0.47$ for toluene (see Figure 5 in ref 36) at the same loss peak frequency ~ 0.1 Hz. The temperature dependence of the α -relaxation times τ_α shown in Figure 3 has been fitted by the Vogel–Fulcher–Tammann–Hesse law, from which T_g was determined by the temperature at which $\tau_\alpha = 100$ s is 179.5 K. The steepness or fragility index m defined by

$$m = \left[\frac{d \log(\tau_\alpha)}{d \left(\frac{T_g}{T} \right)} \right]_{T=T_g} \quad (2)$$

has the value of 58 smaller than $m = 105$ for toluene.⁴³ This is consistent with the correlation between n and m found for glassformers of the same class as in the present case of α -tetralone and toluene. Second, since there is only one resolved secondary relaxation, the question is whether it is the JG β -relaxation or the non-JG secondary relaxation coming from the change of conformation shown in Figure 1. The separation between the α -loss peak at ~ 0.1 Hz and the most probable frequency of the resolved secondary relaxation is about the same as toluene.³⁶ Thus, the resolved secondary relaxation is unlikely the JG β -relaxation because otherwise the correlation between the fwhm or n with the ratio τ_α/τ_β at a fixed τ_α would be violated.^{18,44,45} This conclusion is reinforced by calculating the primitive relaxation time τ_0 from τ_α and $n = 0.32$ for α -tetralone by the Coupling Model relation⁴⁶

$$\tau_\alpha = [t_c^{-n} \tau_0]^{1/(1-n)} \quad (3)$$

with $t_c = 2$ ps. The JG β -relaxation time should be approximately the same as τ_0 , but this is not the case for the resolved secondary relaxation of α -tetralone. As indicated by the arrows in Figure 2, the primitive frequency, $\nu_0 \equiv 1/(2\pi\tau_0)$, can be as much as 2 orders of magnitude lower than the most probable peak

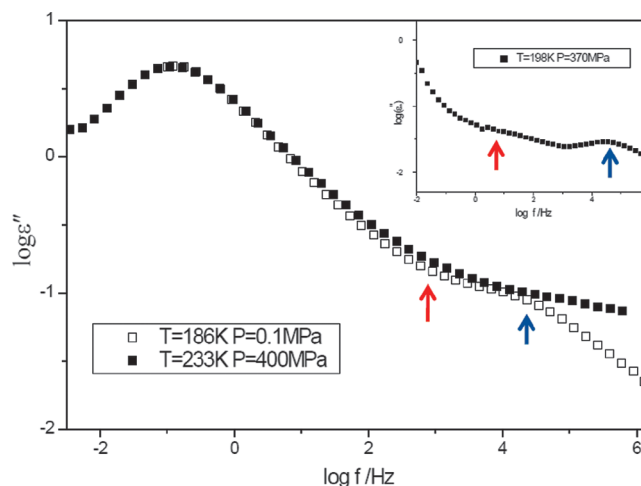


Figure 4. Comparison of the loss spectra with the same α -relaxation time obtained for the α -tetralone at ambient and elevated pressure. It can be seen that the γ -relaxation resolved at ambient pressure (indicated by the blue arrow) is no longer there at the elevated pressure. On the other hand, the ambient and elevated pressure data of the slower processes including the α -relaxation and the unresolved JG β -relaxation (location suggested by the primitive relaxation frequency indicated by the red arrow) superpose well. The slight difference of the loss of the unresolved JG β -relaxation at ambient and elevated pressure is due to a difference in change of dielectric strength of the α - and the unresolved JG β -relaxation to applied pressure. The inset shows the spectrum at elevated pressure of 370 MPa and below T_g from which it can be clearly seen that α -tetralone has another secondary (β) relaxation slower than the γ -relaxation.

frequency of the resolved secondary relaxation. Finally, the activation energy of the resolved secondary relaxation determined in Figure 3 has the value of 30.5 kJ/mol, in approximate agreement with the value of 32.2 kJ/mol for the energy barrier opposing conformation transition that we obtained by calculation (see Figure 1). Considering all the facts based on isothermal dielectric spectra at ambient pressure given above, we conclude that the resolved secondary relaxation originates from conformation transition of the flexible cyclohexane ring of α -tetralone and is not the JG β -relaxation. The JG β -relaxation is not resolved.

Dynamics at Elevated Pressure. The introduction of elevated pressure P in conjunction with changing temperature has been beneficial in bringing out some remarkable properties of the dynamics of all relaxation processes in glassformers. For the α -relaxation, the frequency dispersion is invariant to changing the combinations of P and T as long as τ_α is maintained constant.^{47,48} For the JG β -relaxation, not only is its relaxation time τ_β pressure dependent but also, more importantly, at a fixed τ_α the ratio τ_α/τ_β is invariant to variations in the combinations of P and T .²² These generally observed effects are remarkable because in these experiments changes in P made over 4 orders of magnitude from 0.1 MPa to 2 GPa can significantly modify specific volume and entropy of the sample even though there are changes of T to maintain τ_α constant. In contrast, the relaxation time τ_γ of non-JG secondary relaxation involving internal degrees of freedom of the molecule either is insensitive or increases little with increasing pressure. Due to the very different sensitivity of τ_β and τ_γ to pressure, the two secondary relaxations can be separated further apart by elevating pressure with the advantage of being able to resolve one from the other. Figure 4 shows some of these features

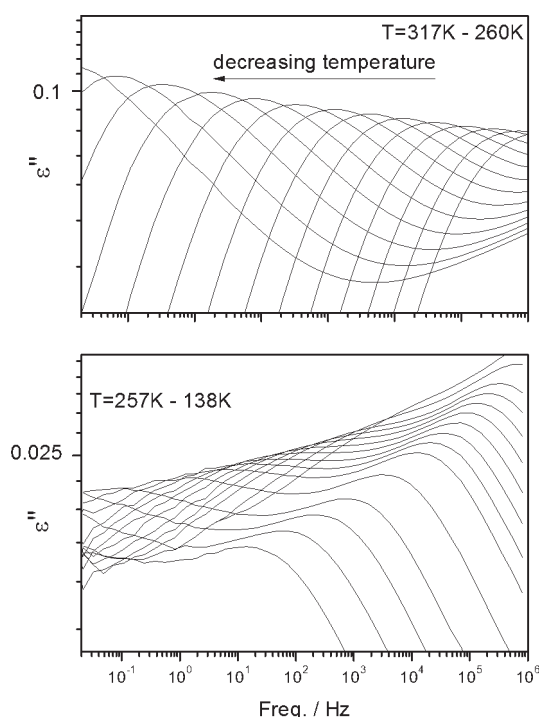


Figure 5. Spectra of the dielectric losses of the mixture of 10% of α -tetralone and oligostyrene obtained at ambient pressure in the temperature range (upper panel) above and (bottom panel) below T_g . The arrow indicates the direction of temperature changes during experiment. Appearing in the bottom panel are two resolved secondary relaxations. In the upper panel, the two secondary relaxations appear at higher frequencies than 10^6 Hz and cannot be seen above T_g .

on elevating pressure in α -tetralone. The main figure presents an example of the spectra taken at two different combinations of P and T : (186 K, 0.1 MPa) and (233 K, 400 MPa). The invariance of the frequency dispersion of the α -relaxation is clear. The opposite is the case for the secondary relaxation resolved at ambient pressure, and the cause is precisely the insensitivity of its relaxation time to pressure. Consequently, while τ_α shifts to lower frequencies on increasing pressure from 0.1 to 400 MPa, the resolved secondary relaxation does not, and it is located at frequencies higher than 10^6 Hz, resulting in the disappearance of the secondary relaxation. The insensitivity to pressure of the resolved secondary relaxation at ambient pressure reaffirms that it originates from the conformation changes of the cyclohexane ring in α -tetralone. The inset of Figure 4 demonstrates the expected wider separation between τ_β and τ_γ at elevated pressure of 370 MPa and $T = 198$ K, causing the weaker and slower JG β -relaxation to be resolved and its existence in α -tetralone assured. This helps to support that the JG β -relaxation, although unresolved in the main figure, contributes to the loss between the α -relaxation and the γ -relaxation. This contribution being invariant to changes in a combination of P and T demonstrates the invariance of τ_α/τ_β in α -tetralone.

Dynamics in Solution with Oligostyrene. Elevated pressure helps to separate the JG β -relaxation further away from the γ -relaxation but not from the α -relaxation because the ratio, τ_α/τ_β , is invariant to variations in the combinations of P and T . Pressure does not enhance the relaxation strength of the JG β -relaxation either. Thus, although the JG β -relaxation of α -tetralone has finally been found by applying pressure, it was barely resolved

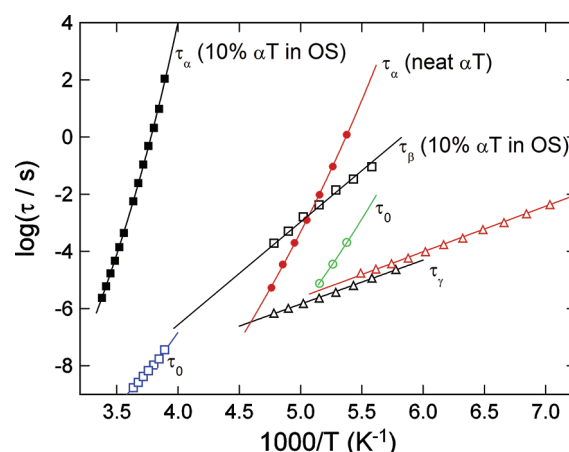


Figure 6. α -, β -, and γ -relaxation times of 10% α -tetralone (αT) in solution with oligostyrene (OS) obtained at ambient pressure (black symbols). The primitive relaxation times τ_0 calculated by the CM equation (eq 3) with $n = 0.68$ from τ_α of 10% αT in solution with OS are shown by blue squares and a blue line. The α - and γ -relaxation times of neat αT obtained at ambient pressure (red symbols). The primitive relaxation times τ_0 calculated by the CM equation (eq 3) with $n = 0.32$ from τ_α of neat αT are shown by green circles and a green line. The lines are VFTH fits to τ_α and Arrhenius fits to the τ_β and τ_γ .

near glass transition (see inset of Figure 4). Ultimately the adversity encountered in the search of the JG β -relaxation of α -tetralone can be traced to the weak intermolecular coupling/constraint originating from the presence of the flexible cyclohexane ring in its structure as anticipated by the discussion in the Introduction. Intermolecular coupling/constraint of α -tetralone can be enhanced by mixing it with another glassformer having higher T_g and less mobility, a method with proven success in the past.^{19,22} For dielectric relaxation measurements and the purpose of studying exclusively the polar component, α -tetralone in the present case, the choice of the other component is oligostyrene with the molecular weight 820 and polydispersity index equal to 1.01 because its $T_g = 282$ K is more than 80° higher than α -tetralone, plus the fact that it will not contribute to the observation due to the small dipole moment of its repeat units.

The isothermal spectra of 10 wt % of tetralone in oligostyrene at ambient pressure above and below T_g are presented in Figure 5. Compared with neat α -tetralone in Figure 2, there is an increase of the fwhm of the α -loss peak or equivalently the nonexponentiality parameter n , as expected from the enhancement of intermolecular coupling of α -tetralone by oligostyrene. The α -relaxation of α -tetralone in oligostyrene is much slower than neat α -tetralone, resulting in a higher $T_g = 257$ K. Accompanying these changes of the α -relaxation of α -tetralone when mixed with oligostyrene is the clear resolution of two secondary relaxations as opposed to only one in neat α -tetralone at ambient pressure. However, both secondary relaxations are much faster than α -relaxation and can only be captured within our frequency window $10^{-2} \leq \nu \leq 10^6$ Hz at temperatures below $T_g = 257$ K, defined by the temperature at which $\tau_\alpha = 100$ s. The change in relation between τ_α and the secondary relaxation times τ_β and τ_γ of α -tetralone on mixing with oligostyrene is best brought out by the relaxation map in Figure 6. For 10% α -tetralone (αT) in solution with oligostyrene (OS), the parameters of the VFTH fit of τ_α are given by $\log(\tau_{\infty\alpha}) = -23.5$, $D_T = 14.3$, and $T_0 = 164$ K. The steepness index m has the value of 71 evaluated at

$T_g = 257$ K. The slight increase of m from 58 to 71 on mixing with oligostyrene is in the right direction but much less than the increase in the fwhm of the loss peak or n as well as the increase in τ_α/τ_β . This mismatch originating from m is a more complex parameter than width of the α -dispersion. It is determined not only by intermolecular coupling but also by change of thermodynamic factors including volume and entropy with temperature.

For τ_β and τ_γ of α -tetralone in the mixture with oligostyrene, the fits in Figure 6 to their Arrhenius T -dependences in the glassy state have parameters given by $\log(\tau_{\infty\beta}/s) = -20.7$ and $E_\beta = 68.7$ kJ/mol for the β -relaxation and $\log(\tau_{\infty\gamma}/s) = -13.54$ and $E_\gamma = 29.4$ kJ/mol for the γ -relaxation. The activation energy for β -relaxation is similar to the values of energies found by Crossley for the similar compounds in the polystyrene matrices.⁴⁹

We have also calculated the primitive relaxation time τ_0 of α -tetralone in the mixture with oligostyrene from τ_α and $n = 0.68$ by eq 3. The value of $n = 0.68$ used here is obtained from the fit of the

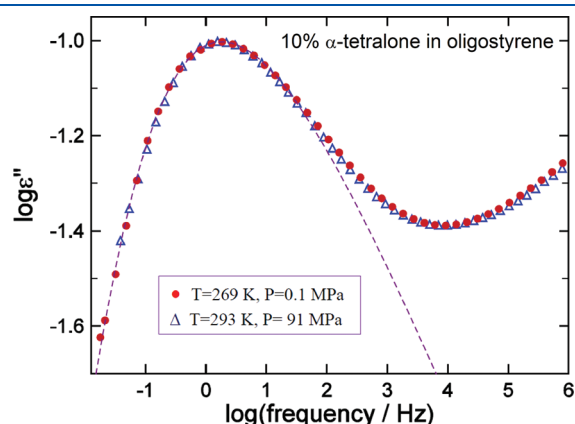


Figure 7. Comparison of the spectra with the same α -relaxation time obtained for the mixture of 10% α -tetralone with oligostyrene at ambient and elevated pressure. There is nearly perfect superposition of the two sets of data for the mixture over the whole frequency range.

α -loss peak by the Fourier transform of the Kohlrausch stretched exponential function. An example of the fit will be given by Figure 7 in the next subsection. While the calculated τ_0 are in the liquid state, the data of τ_β are available in the glassy state of the mixture. Nevertheless, there is rough agreement between τ_0 and τ_β when the Arrhenius temperature dependence of τ_β is extrapolated to approach T_g .

One can observe from the relaxation map in Figure 6 that there is hardly any difference of τ_γ whether it is for neat α -tetralone or for α -tetralone in a mixture with oligostyrene. This property is evidence that the γ -relaxation involves intramolecular degrees of freedom with kinetics insensitive to mixing with oligostyrene. The likely candidate is the conformational transition of the cyclohexane ring of α -tetralone.

Dynamics in Solution with Oligostyrene under Pressure.

The interesting and rich dynamics of α -tetralone in the mixture with oligostyrene are worth further study under pressure. First and foremost, we test the invariance of the frequency dispersion of the α -relaxation of α -tetralone to different combinations of P and T at constant τ_α . The result is presented in Figure 7 where it can be seen that there is nearly perfect superposition of the data taken at $T = 269$ K and $P = 0.1$ MPa with that at $T = 293$ K and $P = 91$ MPa for not only the α -loss peak but also over the entire frequency range. Although the entire β -relaxation cannot be captured within the frequency window, the good superposition of the low-frequency flank of its loss peak suggests it is also superposable, and the ratio τ_α/τ_β is invariant.

Both α -loss peaks are well fitted by the Fourier transform of the Kohlrausch function with $n = 0.68$, significantly larger than $n = 0.32$ of neat α -tetralone. This value of $n = 0.68$ was used to calculate τ_0 shown before in Figure 7.

For completeness, we have also measured the dynamics of α -tetralone in the mixture with oligostyrene at a constant temperature of 293 K by varying pressure in the range from 0.1 to 461 MPa. The spectra shown in Figure 8 reveal again the α -, β -, and γ -relaxations. Of particular interest is the significant pressure dependence of the β -relaxation even in the glassy state. This can

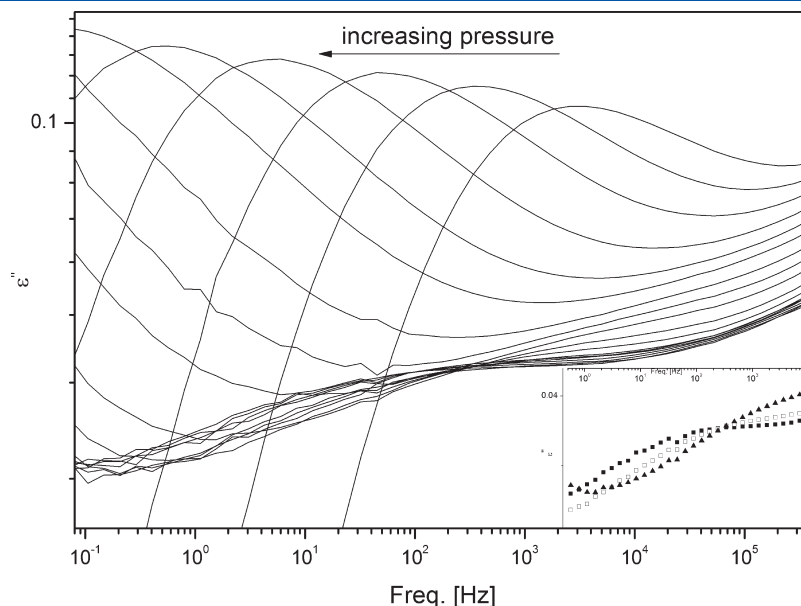


Figure 8. Examples of the dielectric loss spectra of the mixture of 10% α -tetralone and oligostyrene obtained at 293 K on varying pressure from 0.1 to 461 MPa. The arrow indicates the direction of pressure changes. In the inset, three chosen spectra obtained below T_g are presented to show clearly the pressure evolution of the β -relaxation.

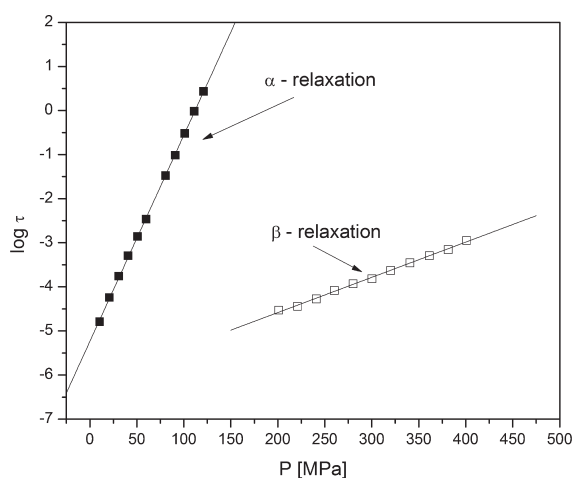


Figure 9. Pressure dependence of the relaxation times of α - and β -relaxations of the α -tetralone component in the mixture of 10% α -tetralone with oligostyrene.

be seen in the inset of Figure 8, where three chosen spectra obtained below T_g are used to show the β -relaxation is shifting to lower frequencies on increasing pressure. The complete pressure dependences of τ_α and τ_β are summarized in Figure 9. The significant pressure dependence of τ_β observed in the glassy state of the mixture is another indication that the β -relaxation is the JG β -relaxation.

SUMMARY AND CONCLUSIONS

In this paper, we studied the dynamics of neat α -tetralone and in mixture with oligostyrene. We chose this molecule as it has a very simple structure with only one substituent giving the dipole moment. During temperature-dependent experiment at ambient pressure in the neat sample, we observe structural and secondary relaxation. On the basis of the Coupling Model, we classified the secondary relaxation as non-JG. Thus, we called it γ -relaxation. With use of quantum-mechanical calculations we were able to detect the kind of motion which was responsible for this process. On the other hand, we were interested in whether the intermolecular secondary relaxation (JG β -process), which is supposed to be a universal phenomenon for glasses, can be found for this sample. For this purpose, we carried out the pressure-dependent experiments. Due to the high tendency of crystallization of the neat α -tetralone, we were not able to perform measurements in the whole range of relaxation times. However, we were able to observe that on the high-frequency flank of the α -relaxation another phenomenon appears. By mixing the α -tetralone with oligostyrene we were able to separate the α - and the JG β -processes and track the evolution the β -relaxation in the wide range of temperatures and pressures. On the basis of the observations we made for this process, we conclude that this is the requested JG β -process for the α -tetralone.

AUTHOR INFORMATION

Corresponding Author

*E-mail: stella.hensel-bielowka@us.edu.pl; pwlodarc@us.edu.pl.

ACKNOWLEDGMENT

The authors (P. Włodarczyk, M. Paluch) are deeply thankful for the financial support of their research within the framework of

the project entitled From Study of Molecular Dynamics in Amorphous Medicines at Ambient and Elevated Pressure to Novel Applications in Pharmacy, which is operated within the Foundation for Polish Science Team Programme cofinanced by the EU European Regional Development Fund.

REFERENCES

- (1) Johari, G. P.; Goldstein, M. *J. Phys. Chem.* **1970**, *74*, 2034.
- (2) Johari, G. P.; Goldstein, M. *J. Chem. Phys.* **1970**, *53*, 2372.
- (3) Johari, G. P.; Goldstein, M. *J. Chem. Phys.* **1971**, *55*, 4245.
- (4) Goldstein, M. *J. Non-Cryst. Solids* **2011**, 249.
- (5) Benkhof, S.; Kudlik, A.; Blochowicz, T.; Rössler, E. *J. Phys.: Condens. Matter* **1998**, *10*, 8155.
- (6) Blochowicz, T.; Kudlik, A.; Benkhof, S.; Senker, J.; Rössler, E. *J. Chem. Phys.* **1999**, *110*, 12011.
- (7) Kudlik, A.; Benkhof, S.; Blochowicz, T.; Tschirwitz, C.; Rössler, E. *J. Mol. Struct.* **1999**, *479*, 201.
- (8) Vogel, M.; Tschirwitz, C.; Schneider, G.; Koplin, C.; Medick, P.; Rössler, E. *J. Non-Cryst. Solids* **2002**, 307–310, 326.
- (9) Hensel-Bielowka, S.; Paluch, M. *Phys. Rev. Lett.* **2002**, *89*, 025704.
- (10) Hensel-Bielowka, S.; Paluch, M.; Ziolo, J.; Roland, C. M. *J. Phys. Chem. B* **2002**, *106*, 12459.
- (11) Paluch, M.; Pawlus, S.; Hensel-Bielowka, S.; Kaminska, E.; Prevosto, D.; Capaccioli, S.; Rolla, P.; Ngai, K. L. *J. Chem. Phys.* **2005**, *122*, 234506.
- (12) Roland, C. M.; Hensel-Bielowka, S.; Paluch, M.; Casalini, R. *Rep. Prog. Phys.* **2005**, *68*, 1405.
- (13) Kaminska, E.; Kaminski, K.; Hensel-Bielowka, S.; Paluch, M.; Ngai, K. L. *J. Non-Cryst. Solids* **2006**, *352*, 4672.
- (14) Schneider, U.; Brand, R.; Lunkenheimer, P.; Loidl, A. *Phys. Rev. Lett.* **2000**, *84*, 5560.
- (15) Lunkenheimer, P.; Wehn, R.; Riegger, T.; Loidl, A. *J. Non-Cryst. Solids* **2002**, 307–310, 336.
- (16) Kessairi, K.; Capaccioli, S.; Prevosto, D.; Sharifi, S.; Rolla, P. A. *J. Non-Cryst. Solids* **2007**, *353*, 4273.
- (17) Capaccioli, S.; Kessairi, K.; Shahin, T. M.; Prevosto, D.; Lucchesi, M. *J. Non-Cryst. Solids* **2011**, *357*, 251.
- (18) Ngai, K. L.; Paluch, M. *J. Chem. Phys.* **2004**, *120*, 857.
- (19) Mierzwa, M.; Pawlus, S.; Paluch, M.; Kaminska, E.; Ngai, K. L. *J. Chem. Phys.* **2008**, *128*, 044512.
- (20) Capaccioli, S.; Kessairi, K.; Prevosto, D.; Lucchesi, M.; Rolla, P. A. *J. Phys.: Condens. Matter* **2007**, *19*, 205133.
- (21) Capaccioli, S.; Prevosto, D.; Kessairi, K.; Lucchesi, M.; Rolla, P. A. *J. Non-Cryst. Solids* **2007**, *353*, 3984.
- (22) Kessairi, K.; Capaccioli, S.; Prevosto, D.; Lucchesi, M.; Sharifi, S.; Rolla, P. A. *J. Phys. Chem. B* **2008**, *112*, 4470.
- (23) Ngai, K. L. In *Relaxation and Diffusion in Complex Systems*; Lam, L., Ed.; Springer: New York, 2011.
- (24) Capaccioli, S.; Thayyil, M. S.; Ngai, K. L. *J. Phys. Chem. B* **2008**, *112*, 16035.
- (25) Casalini, R.; Roland, C. M. *Phys. Rev. Lett.* **2009**, *102*, 035701.
- (26) Kaminski, K.; Kaminska, E.; Paluch, M.; Ziolo, J.; Ngai, K. L. *J. Phys. Chem. B* **2006**, *110*, 25045.
- (27) Paluch, M.; Pawlus, S.; Hensel-Bielowka, S.; Kaminski, K.; Psurek, T.; Rzoska, S. J.; Ziolo, J.; Roland, C. M. *Phys. Rev. B* **2005**, *72*, 224205.
- (28) Kaminska, E.; Kaminski, K.; Paluch, M.; Ziolo, J.; Ngai, K. L. *J. Chem. Phys.* **2007**, *126*, 174501.
- (29) Blochowicz, T.; Rössler, E. A. *Phys. Rev. Lett.* **2004**, *92*, 225701.
- (30) Blochowicz, T.; Lusceac, S. A.; Gutfreund, P.; Stuhn, B. *J. Phys. Chem. B* **2011**, *115*, 1623.
- (31) Paluch, M.; Pawlus, S.; Hensel-Bielowka, S.; Kaminska, E.; Prevosto, D.; Capaccioli, S.; Rolla, P. A.; Ngai, K. L. *J. Chem. Phys.* **2005**, *122*, 234506.
- (32) Kaminski, K.; Kaminska, E.; Hensel-Bielowka, S.; Chelmecka, E.; Paluch, M.; Ziolo, J.; Włodarczyk, P.; Ngai, K. L. *J. Phys. Chem. B* **2008**, *112*, 7662.

- (33) Grzybowska, K.; Paluch, M.; Grzybowski, A.; Wojnarowska, Z.; Hawelek, L.; Kolodziejczyk, K.; Ngai, K. L. *J. Phys. Chem. B* **2010**, *114*, 12792.
- (34) Kaminski, K.; Kaminska, E.; Włodarczyk, P.; Paluch, M.; Ziolo, J.; Ngai, K. L. *J. Phys.: Condens. Matter* **2008**, *20*, 335104.
- (35) Wojnarowska, Z.; Hawelek, L.; Paluch, M.; Sawicki, W.; Ngai, K. L. *J. Chem. Phys.* **2011**, *134*, 044517.
- (36) Hensel-Bielowka, S.; Paluch, M.; Ngai, K. L. *J. Chem. Phys.* **2005**, *123*, 014502.
- (37) Neese, F. *Orca - an ab initio, Density Functional and Semiempirical program package*, Version 2.6; University of Bonn: Bonn, Germany, 2008.
- (38) Włodarczyk, P.; Czarnota, B.; Paluch, M.; Pawlus, S.; Ziolo, J. *J. Mol. Struct.* **2010**, *975*, 200.
- (39) Włodarczyk, P.; Kaminski, K.; Adrjanowicz, K.; Wojnarowska, Z.; Czarnota, B.; Paluch, M.; Ziolo, J.; Pilch, J. *J. Chem. Phys.* **2009**, *131*, 125103.
- (40) Kaminski, K.; Włodarczyk, P.; Adrjanowicz, K.; Kaminska, E.; Wojnarowska, Z.; Paluch, M. *J. Phys. Chem. B* **2010**, *114*, 11272.
- (41) Kaminski, K.; Włodarczyk, P.; Hawelek, L.; Adrjanowicz, K.; Wojnarowska, Z.; Paluch, M.; Kaminska, E. *Phys. Rev. E* **2011**, *83*, 061506.
- (42) Wojnarowska, Z.; Paluch, M.; Włodarczyk, P.; Hawelek, L.; Wrzalik, R.; Ziolo, J.; Wygledowska-Kania, M.; Bergler-Czop, B.; Brzezinska-Wcislo, L.; Bujak, P. *Phys. Rev. E* **2011**, *83*, 051502.
- (43) Döb, A.; Hinze, G.; Schiener, B.; Hemberger, J.; Böhmer, R. *J. Chem. Phys.* **1997**, *107*, 1740.
- (44) Capaccioli, S.; Prevosto, D.; Lucchesi, M.; Rolla, P. A.; Casalini, R.; Ngai, K. L. *J. Non-Cryst. Solids* **2005**, *351*, 2643.
- (45) Sekula, M.; Pawlus, S.; Hensel-Bielowka, S.; Ziolo, J.; Paluch, M.; Roland, C. M. *J. Phys. Chem. B* **2004**, *108*, 4997.
- (46) Ngai, K. L.; Yee, A. F. In *Relaxations in Complex Systems*; Ngai, K. L., Wright, G. B., Eds.; U. S. Government Printing Office: Washington, DC, 1985; p 145.
- (47) Ngai, K. L.; Casalini, R.; Capaccioli, S.; Paluch, M.; Roland, C. M. In *Fractals, Diffusion and Relaxation in Disordered Complex Systems, Advances in Chemical Physics*; Kalmykov, Y. P., Coffey, W. T., Rice, S. A., Eds.; John Wiley & Sons: New York, 2006; Vol. 133, pp 497.
- (48) Ngai, K. L.; Casalini, R.; Capaccioli, S.; Paluch, M.; Roland, C. M. *J. Phys. Chem. B* **2005**, *109*, 17356.
- (49) Crossley, J.; Mazid, M. A.; McLellan, C. K.; Mountain, P. F.; Walker, S. *Can. J. Chem.* **1978**, *56*, 567.