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PAPER

Low-temperature dynamics in amorphous polymers and low-molecular-weight glasses—what is the difference?

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Numerous experiments have shown that the low-temperature dynamics of a wide variety of disordered solids is qualitatively universal. However, most of these results were obtained with ensemble-averaging techniques which hide the local parameters of the dynamic processes. We used single-molecule (SM) spectroscopy for direct observation of the dynamic processes in disordered solids with different internal structure and chemical composition. The surprising result is that the dynamics of low-molecular-weight glasses and short-chain polymers does not follow, on a microscopic level, the current concept of low-temperature glass dynamics. An extra contribution to the dynamics was detected causing irreproducible jumps and drifts of the SM spectra on timescales between milliseconds and minutes. In most matrices consisting of small molecules and oligomers, the spectral dynamics was so fast that SM spectra could hardly or not at all be recorded and only irregular fluorescence flares were observed. These results provide new mechanistic insight into the behavior of glasses in general: At low temperatures, the local dynamics of disordered solids is not universal but depends on the structure and chemical composition of the material.

1. Introduction

A wide variety of non-crystalline solids ranging from polymers and glasses to biological materials and nano-objects are characterized by complex internal structures which may be strongly different on a microscopic level. The local disorder and heterogeneities of these materials lead to fundamentally different properties as compared to crystals. One of the striking and mysterious peculiarities of disordered solids is the pronounced universality of their properties at low temperatures. As numerous experiments have shown, the dynamic behavior of almost all non-crystalline dielectric solids at low temperatures is very similar and does not depend qualitatively on their physical structure and chemical composition. Common features include anomalies in the thermodynamic properties, relaxation and noise behavior, nonlinear acoustic properties, *etc.* A striking and well-known example of such universal properties is the Boson peak, an anomalous excess vibrational density of states over that predicted by the Debye model. The universality of the dynamic properties is one of the reasons why different kinds of disordered dielectric solids are very often simply referred to as “glasses”.

The question as to why the properties of materials, which are completely different on a microscopic level, show such a universal behavior has not yet found a clear answer and is the subject of debates.

The universal properties of low-temperature glasses are described in the framework of the widely accepted standard tunnelling (ST) model,^{1,2} which reproduces most of the experimental data at $T < 1\text{--}2\text{ K}$ quite well. In a set of recent theoretical studies, the problem of the universality of glasses was considered in more detail. For example, the soft-potential (SP) model, which can be considered as a generalization of the ST model, is able to explain the universal properties in a broader temperature interval.³ Both the ST and SP model have been developed on a purely phenomenological basis. They do not consider the microscopic nature of a material or its excitation modes. The authors of another theoretical study^{4,5} put forward the hypothesis that the r^{-3} law describing the distance dependence of the interaction between defect centers in disordered solids, can be responsible for the universality of glasses. However, the question regarding the microscopic origin of these defects remained open. The systematic analysis of the low-temperature properties of glasses in ref. 6, based on a microscopic description, explains the universality as a consequence of the collective dynamics of several adjacent molecules or atoms, which, in a first approximation, reduces any dependencies on the microscopic structure. The phenomenological model developed in ref. 7, which is based

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on the concept of the double-well centers, attributes the observed dynamic universality of low-temperature glasses to a many-body interaction of centers with an internal degree of freedom. The authors of another theoretical study have introduced the microscopic translationally invariant glass model.⁸ It ascribes the universality of low-temperature glasses to the collective origin of their potential energy landscape.

On the other hand, most phenomena related to the internal dynamics at higher temperatures close to the glass transition—fragility, viscosity, relaxations—depend strongly on the special structure and chemical composition of the disordered solid.^{9,10} This circumstance is clearly revealed by the fact that the dynamic glass parameters depend on the molecular weight (M_w) of the glass-forming molecules. In particular, a large variety of important results about the M_w dependence of glass dynamics were obtained in polymers and oligomers.^{9–20} Moreover, in a set of experiments it was found that also the low-temperature dynamic behavior of some disordered systems, for example proteins,²¹ and even of some systems with a simpler structure (e.g., some polymers), differs from that which is usually observed in glasses and predicted by the ST or SP model. Hence, not all disordered systems exhibit low-temperature dynamic properties which follow the above-mentioned universality.

One evident reason for the observed universality of glasses is related to the fact that all experimental techniques used so far to measure their dynamic parameters yield data which are averaged over a macroscopically large volume of the sample containing a large ensemble of low-energy excitations. In complex solids with pronounced internal disorder, however, the local dynamic parameters are expected to be subject to broad distributions. Averaging over these distributions leads to a partial, or even complete, loss of information about the microscopic details. Hence, the available experimental results are not expected to shed light on the internal dynamics of disordered solids on a microscopic level.

A powerful optical method which completely eliminates any kind of ensemble averaging is single-molecule spectroscopy (SMS).²² The individual fluorescence excitation spectra of single chromophore molecules (SMs) embedded in a transparent solid matrix as spectral probes yield information about the matrix dynamics in their local environment (see, e.g., ref. 45 and references therein).

The first SMS experiments on amorphous and semi-crystalline polymers at low temperatures were performed in the beginning of the 1990s.^{23–26} As compared to well-ordered crystals, the linewidths are usually distinctly broader and are subject to broad distributions, which is a consequence of the interaction with tunneling systems (TLSs) and quasi-localized low-frequency vibrational modes (LFMs). Both kinds of these low-energy excitations are inherent to the disordered solid state. Also spontaneous frequency jumps and light-induced bleaching of the chromophores occur more frequently in disordered solids than in crystals,²⁶ which is probably related to the presence of voids of free volume. Nevertheless, at least part of the spectra are usually stable enough to be recorded with laser scans of a few seconds duration. Splitting of SM lines into several components and frequency jumps caused by strong coupling to fast- and slow-flipping TLSs, respectively, are

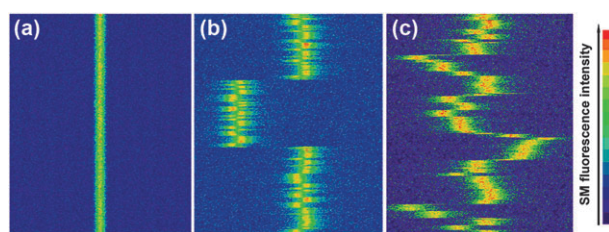


Fig. 1 Spectral trails of single chromophore molecules in different matrices: (a) typical behavior in (poly-)crystalline solids (*ortho*-dichlorobenzene²⁹): single stable line; (b) typical behavior in a polymer with high molecular weight (polyisobutylene; $M_w = 420\,000\text{ g mol}^{-1}$): splitting into 2^N line components (here $N = 2$) in agreement with the standard tunneling model; (c) low-molecular-weight organic glass (frozen toluene): rich and complex dynamics.^{30,31} All the spectral trails were recorded at $T = 7\text{ K}$. The experiments have shown, however, that the different slow single-molecule spectral behavior in (poly)crystalline, polymer and glassy systems is independent of temperature below a few kelvin.

detected and identified by repeated recording of fluorescence excitation spectra in a selected fixed spectral interval. The detected fluorescence excitation spectra of single molecules are represented in two-dimensional (2D) plots^{27,28} (Fig. 1), in which the horizontal axis corresponds to the laser excitation frequency, the vertical axis to the number (or time) of the scan, and the fluorescence intensity is encoded by the color (or gray) level. These 2D-plots reveal the temporal behavior of the individual SM spectra (spectral histories, trails, or trajectories).

The number of spectral components of a SM spectrum is usually 2^N , indicating the coupling to N nearby TLSs ($N = 2$ in the example of Fig. 1b). On the time scale of several tens of minutes, N is usually in the range 1–3.

In the past, most SMS studies on amorphous solids at low temperatures were performed on doped polymers with a high molecular weight (tens of thousands of monomer units). It was found that, with rare exceptions, these materials exhibit slow dynamics at $T < 3\text{--}5\text{ K}$, in accordance with the ST model.³² This result was confirmed^{33–35} by a detailed statistical analysis of the spectral moments and cumulants. It was demonstrated that the distributions of the first two cumulants of SM spectra in polyisobutylene (PIB) at $T = 2\text{ K}$ follow Lévy statistics as predicted by the main assumptions of the ST model (in particular the assumptions of a uniform spatial TLS density and dipole–dipole character of the SM-TLS interaction).

At higher temperatures ($T > 5\text{--}7\text{ K}$) the spectral dynamics of SMs is mainly determined by dephasing due to LFMs. The analysis of the temperature broadening of different SM spectra demonstrated that the LFM frequencies are subject to a broad distribution, which confirms the (quasi-)localized nature of these excitations.^{36,37} Moreover, the LFM energy spectrum turned out to agree with the so-called “Boson peak”, an excess vibrational density of states in addition to the Debye spectrum, which is common to disordered solids.^{31,38} Hence, the excess density of the Boson peak and the optical dephasing of chromophores seem to be caused by the same low-energy vibrational excitations. The coupling to LFMs gives rise to additional homogeneous broadening and spectral shifts of SM lines but does not affect the slow spectral dynamics due to TLSs.³⁹ It is supposed that at $T > 20\text{--}30\text{ K}$ thermally induced

relaxation processes in double-well potentials begin contribute to the observed dynamics of glasses.⁶

In contrast to polymers, SMS experiments on low-molecular-weight glasses have not been reported until recently. To our knowledge, the first data were published for toluene and perdeuterated toluene doped with tetra-*tert*-butylterylene (TBT).^{30,40} The surprising result was that the tunneling dynamics is much more complicated than in PIB, a typical amorphous polymer. In toluene, irregular jumps of the SM lines between several frequency positions and continuous random drifts were observed, which is completely different from the behavior in polymers (Fig. 1c). Hence, the ST model, which was originally developed to interpret the data of the dynamics in low-molecular-weight glasses, does not seem to describe their behavior on the nanometre scale. The energy spectra of the LFMs, on the other hand, agree with the respective Boson peak data of toluene.^{31,38}

Thus, the questions “What is the microscopic basis of the observed universality of glasses?” and “To which degree are the dynamic processes and their microscopic details really identical for all disordered solids and can be described in the framework of a unified theory?” are still open. They address the basics of our understanding of the elementary dynamic processes and their origins in solids and, hence, are of fundamental importance for the physics of the solid state on a microscopic level. Progress in this field can only be achieved with a technique which avoids ensemble averaging.

In this paper we present the results of a SMS study of the local spectral dynamics in low-molecular-weight organic glasses and amorphous oligomers and polymers with different molecular weight (M_w). Experiments were performed on toluene doped with tetra-*tert*-butylterylene, cumene, and propylene carbonate matrices doped with terylene and on oligo- and polyisobutylene with $M_w = 390, 2500, 33\,800$, and $420\,000\text{ g mol}^{-1}$ doped with tetra-*tert*-butylterylene.

The main goal of the study is to shed light on the fundamental problem of glass dynamics: Does the local dynamic behavior of low-temperature glasses depend on their internal structure?

2. Experimental

The polymer materials were purchased from Aldrich Inc. ($M_w = 420\,000\text{ g mol}^{-1}$) and Fluka (lower M_w values); terylene was obtained from the PAH Research Institute (Prof. W. Schmidt, Greifenberg, Germany). PIB doped with TBT was kindly provided by Prof. Th. Basché, University of Mainz. All chemicals were used as received without further purification.

Tiny amounts of chromophore molecules were dissolved in toluene, cumene, and propylene carbonate, which are liquids at room temperature. Then the solutions were highly diluted to concentrations of about $10^{-10}\text{ mol l}^{-1}$. Tiny droplets were placed between two microscope slides and quickly inserted into the sample chamber of the pre-cooled cryostat. Under these conditions toluene, cumene, and propylene carbonate form glasses of high optical quality. The oligo- and polyisobutylenes were dissolved in toluene and mixed with a low-concentrated solution of TBT in the same solvent. The resulting solutions were spin-coated onto microscope slides.

Detailed descriptions of the experimental apparatus were published previously.^{31,40} Briefly, the samples were cooled to temperatures of a few kelvin in a temperature-regulated He-4 cryostat (Cryovac) with an accuracy of the temperature control of $\pm 0.05\text{ K}$; temperatures between 4 and 7 K were maintained by placing them in a stream of cold helium gas. The fluorescence of the chromophores was excited with a frequency-stabilized tunable single-mode dye laser (Coherent 599-21) in the spectral range between 575 and 582 nm. The sample was wide-field illuminated from the back side by weakly focusing the laser radiation to a spot size of about $100\text{ }\mu\text{m}$ diameter. The fluorescence of SMs in this spot was collected with a microscope objective (Microthek, NA 0.9) inside the cryostat and imaged onto a sensitive Peltier-cooled CCD camera (PCO Sensicam QE). Residual laser light was blocked by the combination of an interference band-pass filter and a Schott glass filter RG610.

The laser frequency was scanned in discrete steps over a defined interval (usually 500–2000 steps in a range of 5–30 GHz), and the fluorescence image was stored after each step. The fluorescence excitation spectra of individual molecules were extracted from this huge data base by locating the positions of bright spots on the camera chip and listing the summed signals in the corresponding pixel area together with the laser frequency values, as was described in detail in ref. 31 and 40. The dye concentration in our samples was adjusted to such a level that a few hundred chromophore spectra were recorded with the CCD chip within the full laser scan range. In contrast to a confocal scheme using a single-channel detector, the camera technique has the advantage that many SM spectra can be recorded in parallel.⁴⁴ Even more important, in cases of very fast matrix dynamics, when the complete spectral profile of a SM cannot be recorded and only short fluorescence flares appear, detecting these flares with a confocal set-up would hardly be possible, since the lack of stable signals prevents the adjustment of the focal spot. The fluorescence excitation spectra of a number of SMs were detected repeatedly in a series of consecutive laser scans. The spectral history (spectral trail) of each SM was represented in the form of a 2D-plot as shown in Fig. 1.^{27,28}

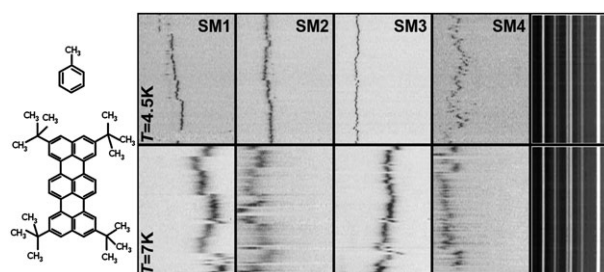


Fig. 2 Examples of the spectral trails of four selected TBT molecules in frozen toluene at 4.5 K (top panels) and 7 K (bottom panels). Each panel shows 100 consecutive scans over a spectral range of 30 GHz with 1000 frequency points and 20 ms integration time per point. The rightmost panels contain the absorption spectra of an iodine gas cell recorded in parallel with the SM spectra to control the stability of the laser. The structure formulae of toluene and TBT are presented on the far left.

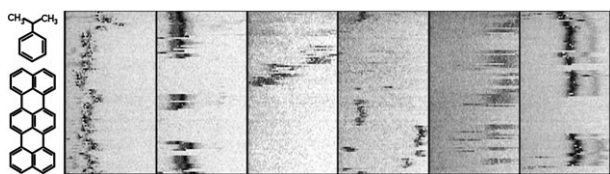


Fig. 3 Same as Fig. 2 for terrylene in cumene. $T = 4.5$ K; scan width 30 GHz; 1000 frequency points; integration time per point 20 ms; 100 scans.

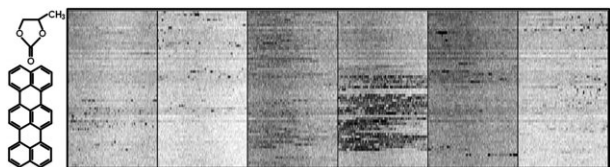


Fig. 4 Same as Fig. 2 for terrylene in propylene carbonate. $T = 4.5$ K; scan width 30 GHz; 1000 frequency points; integration time per point 30 ms; 100 scans.

3. Small matrix molecules

The spectral trails of SMs recorded in quickly frozen samples of the low-molecular-weight matrices toluene, cumene, and propylene carbonate are presented in Fig. 2–4, respectively. Fig. 2 shows typical data of single TBT molecules in toluene at $T = 4.5$ K (top panels) and 7 K (bottom panels). Here the dynamics is distinctly more complex than in amorphous polymers of high molecular weight (Fig. 1). It comprises irregular transitions between several frequency positions and continuous spectral creeping, as was reported before.³⁰ Fig. 2 demonstrates also how the trails of selected SMs change between 4.5 and 7 K. With increasing temperature the spectra broaden and their dynamics becomes even more complicated.

The slow dynamics (on the time scale of a few minutes) in frozen toluene cannot easily be reconciled with the standard tunneling TLS model at temperatures of a few kelvin. This is in striking contrast to amorphous polymers with high M_w . Comparative measurements with protonated and perdeuterated toluene^{30,31,40} revealed that at $T < 2$ –3 K the linewidths of SM spectra are mainly determined by tunneling processes, whereas at $T > 7$ K vibrational excitations yield the main contribution. Furthermore, the analysis of long-term spectral histories (up to a few hours) of single TBT molecules in frozen toluene and PIB ($420\,000\text{ g mol}^{-1}$)³¹ demonstrated that, in both matrices, the homogeneous spectral broadening does not change significantly during the whole time of the measurement (up to 5 h). This indicates that the local environment of the selected SMs is stable in both systems and does not undergo noticeable structural rearrangements at low temperatures.

A surprise comes from the data recorded in matrices of frozen cumene (Fig. 3) and propylene carbonate (Fig. 4). In cumene, a few SM spectra can still be recorded, but they are unstable and often interrupted by periods in which the line is at a remote frequency position outside the scan range. Other signals show such a fast dynamics that it is hardly possible to recognize them as fluorescence excitation spectra of SMs at all. The situation is even more extreme in the case of propylene carbonate. The CCD camera definitely detects short flares of

fluorescence, but the dynamics is so fast and covers such a broad frequency range that spectra cannot be recorded. The two latter examples show one probable explanation for the fact that SMS in low-molecular-weight glasses has not been reported earlier. Many of these glass formers may have a similarly fast dynamics as cumene and propylene carbonate, so it is difficult or impossible to record SM spectra, in particular with set-ups using a single-channel detector.

Qualitatively one can suggest at least a few reasons for the observed behavior. (i) “Weak” structural relaxations in the glassy matrix may lead to the continuous spectral drifts. These relaxations could be related to lower energy barriers in the potential energy landscape of frozen liquids as compared to long-chain polymers. The glass transition temperatures of toluene ($T_g = 117$ K), cumene ($T_g = 126$ K), and propylene carbonate ($T_g = 158$ K) are substantially lower than those of typical polymers (e.g., $T_g = 201$ K for PIB with $M_w = 420\,000\text{ g mol}^{-1}$), which indicates that there must be a marked difference in the barrier heights of the energy landscapes of low-molecular glasses and polymers. (ii) The potential energy landscape in frozen liquids may possess specific features not present in the case of polymers. Small molecules might form some more complicated amorphous state, consisting of nano-cells with short-range order and/or grains with a complicated disordered network of boundaries in between. In this case an energy surface could be present which cannot simply be reduced to a number of non-interacting TLSs and LFMs. One can expect that these microscopic peculiarities are not easy to detect in macroscopic (i.e., ensemble) experiments, although SMS is able to reveal them. (iii) The dynamics of the chromophore molecules themselves may have an influence on the observed glass dynamics, since their size significantly exceeds that of the matrix molecules. As a consequence, the probe molecules may prevent close packing of the matrix in their environment. (iv) In glasses consisting of small molecules or oligomers, there may be specific distributions of the TLS and/or LFM parameters and their relations, giving change to observed SM spectral dynamics which depends on the experimental time scale, temperature, as well as on the spectral resolution and scan width. These relations may be markedly different for different amorphous systems and appear as various slow SM spectral dynamics.

4. Oligomers and polymers of PIB

The striking differences between the spectral behavior of SM lines in low-molecular-weight glasses and long-chain polymers

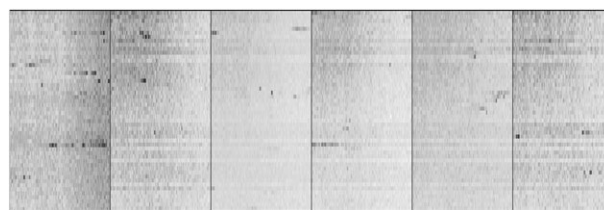


Fig. 5 Same as Fig. 2 for TBT in PIB with $M_w = 390\text{ g mol}^{-1}$. $T = 4.5$ K; scan width 30 GHz; 500 frequency points; integration time per point 80 ms; 50 scans.

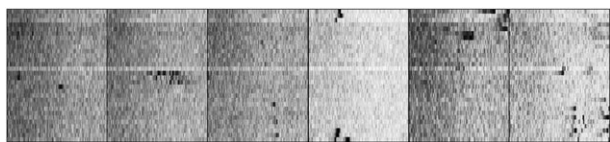


Fig. 6 Same as Fig. 2 for TBT in PIB with $M_w = 2500 \text{ g mol}^{-1}$. $T = 4.5 \text{ K}$; scan width 30 GHz; 500 frequency points; integration time per point 90 ms; 30 scans.

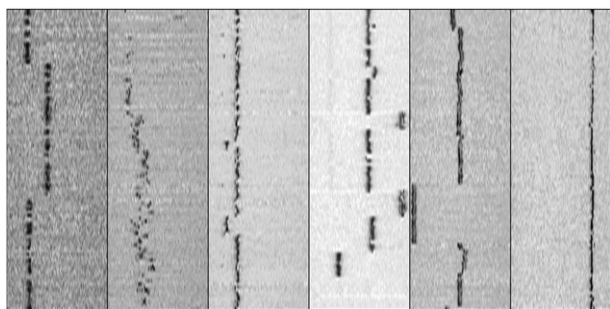


Fig. 7 Same as Fig. 2 for TBT in PIB with $M_w = 33\,800 \text{ g mol}^{-1}$. $T = 4.5 \text{ K}$; scan width 30 GHz; 1000 frequency points; integration time per point 25 ms; 100 scans.

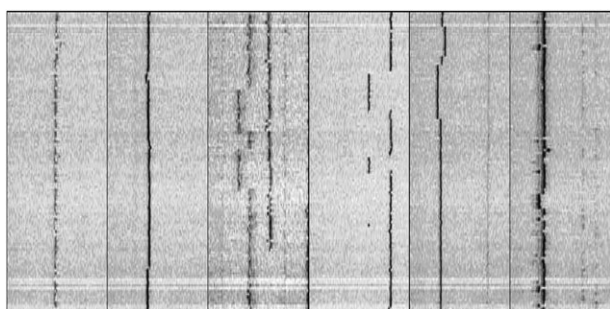


Fig. 8 Same as Fig. 2 for TBT in PIB with $M_w = 420\,000 \text{ g mol}^{-1}$. $T = 4.5 \text{ K}$; scan width 30 GHz; 1000 frequency points; integration time per point 40 ms; 100 scans.

lead to the question, at which chain length the qualitative transition occurs. Hence, we investigated the fluorescence signals of single TBT molecules in different oligo- and polyisobutylenes. The results for PIB with $M_w = 390$, 2500, 33 800, and 420 000 g mol^{-1} (corresponding to chain lengths of 7, 45, 605, and 7500 monomer units) are presented in Fig. 5–8, respectively.

In the matrices with the two shortest chain lengths, the chromophores behave in a similar way as in propylene carbonate: Spectral lines cannot be recorded; only short fluorescence flares appear (Fig. 5 and 6).

The situation changes fundamentally in the matrix of molecular weight 33 800 g mol^{-1} (Fig. 7). SM spectra can be recorded, and most of them have stable frequencies during periods of at least several minutes. They perform jumps between a small number of spectral positions, although this number appears not to be a power of two in all cases. In PIB with the highest molecular weight 420 000 g mol^{-1} , the dynamics is somewhat slower, and the SM lines show the typical behavior known in amorphous polymers (Fig. 8). The transition from “monomer-like” to “polymer-like”

behavior clearly occurs between chain lengths of 45 and 605 units. Hence, polymer chains must at least consist of about a hundred or a few hundred monomer units so the connectivity is sufficient to suppress the fast and rich dynamics of low-molecular-weight glasses to a large degree.

The above result shows surprising similarities to other properties of oligomers and polymers measured at higher temperatures. For example, the authors of ref. 16 studied the relaxation behavior of 1,4-polybutadienes of different chain lengths with NMR field cycling relaxometry in the temperature range between 203 and 389 K and found that the transition to typical polymer-like data occurred at chain lengths on the order of a hundred or a few hundred repeat units. Neutron scattering studies of the Boson peak in PIB with different M_w at $T = 100 \text{ K}$ ⁴¹ demonstrated that additional low-frequency scattering below the Boson peak occurs in samples with low molecular weights, decreases strongly for $M_w > 4040 \text{ g mol}^{-1}$, and then remains unchanged up to $M_w = 73\,000 \text{ g mol}^{-1}$. The authors attributed this transition to the faster motions of atoms near the chain ends. The thermal diffusion coefficient of mixtures of polystyrene with toluene⁴² and a number of other solvents⁴³ as measured at room temperature converged to constant values for polystyrene chains consisting of about 100 monomer units. The glass transition temperature and the diffusion behavior in the melt were investigated for polydimethylsiloxane and polystyrene, and also for these parameters a convergence toward the asymptotic polymer values was found at chain lengths on the order of a few hundred units.⁹ According to ref. 9, the segmental motion of a polymer chain in the melt slows down with increasing chain connectivity, causing the transition from small-molecule behavior to Rouse dynamics. The Rouse model is based upon the assumption of unentangled chains with Gaussian statistics. Our SMS data indicate that the chain connectivity seems to determine the tunneling dynamics at low temperatures in a similar way as the diffusion behavior at much higher temperatures.

5. Conclusions

A single-molecule spectroscopy study was performed on several glass formers of low molecular weight and on oligomers and polymers of isobutylene with different chain lengths at temperatures of 4.5 and 7 K. Part of the low-molecular matrices show such a fast and rich dynamics that it is difficult or impossible to observe complete spectra of single chromophores. Only short and irregular fragments or fluorescence flares are recorded. The same is true in polyisobutylenes with chain lengths of 7 and 45 monomer units. The transition from monomer-like to polymer-like behavior occurs between 45 and 605 monomer units. In the latter case, many single-molecule lines are stable over periods of at least a few minutes and perform jumps between a small number of frequency positions. Between 605 and 7500 monomer units, the dynamics slows down somewhat more, but no fundamental change of the spectral behavior occurs. The crossover from small-molecule-like to polymer-like behavior occurs at similar chain lengths as fundamental changes of other parameters measured at much higher temperatures. These

include the glass transition temperature, relaxation and diffusion behavior, and the thermal diffusion coefficient. It can be concluded that the connectivity of the polymer chains determines macroscopic quantities and the local tunneling dynamics at low temperatures in a similar way.

The important outcome of this study is that the low-temperature dynamics of amorphous solids on microscopic length scales is not universal but depends qualitatively on the structure and chemical composition of the material. At least at $T > 2$ K, the spectral dynamics in low-molecular-weight glasses and short-chain polymers on a microscopic scale cannot be described within the standard tunneling model of low-temperature glasses, unlike the single-molecule spectral dynamics in long-chain polymers.

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References

- 1 P. W. Anderson, B. I. Halperin and C. M. Varma, *Philos. Mag.*, 1972, **25**, 1.
- 2 W. A. Philips, *J. Low Temp. Phys.*, 1972, **7**, 351.
- 3 V. G. Karpov, M. I. Klinger and F. N. Ignatiev, *Zhurnal Eksperimentalnoi Teor. Fiz.*, 1983, **84**, 760–775.
- 4 C. C. Yu, *Phys. Rev. Lett.*, 1989, **63**, 1160–1163.
- 5 A. J. Leggett, *Phys. B*, 1991, **169**, 322–327.
- 6 A. Heuer and R. J. Silbey, *Phys. Rev. B: Condens. Matter*, 1996, **53**, 609–619.
- 7 A. L. Burin and Yu. Kagan, *Phys. Lett. A*, 1996, **215**, 191–196.
- 8 R. Kuhn, *Europhys. Lett.*, 2003, **62**, 313–319.
- 9 Y. F. Ding, V. N. Novikov, A. P. Sokolov, A. Cailliaux, C. Dalle-Ferrier, C. Alba-Simionesco and B. Frick, *Macromolecules*, 2004, **37**, 9264–9272.
- 10 K. Kunal, M. Paluch, C. M. Roland, J. E. Puskas, Y. Chen and A. P. Sokolov, *J. Polym. Sci., Part B: Polym. Phys.*, 2008, **46**, 1390–1399.
- 11 T. G. Fox and P. J. Flory, *J. Polym. Sci.*, 1954, **14**, 315–319.
- 12 J. M. G. Cowie, *Eur. Polym. J.*, 1975, **11**, 79–300.
- 13 G. M. Bartenev and S. Y. Frenkel, *Polymer Physics*, St. Petersburg, 1990.
- 14 P. Jacobsson, L. Borjesson and L. M. Torell, *J. Non-Cryst. Solids*, 1991, **131–133**, 104–108.
- 15 Y. F. Ding, A. Kisliuk and A. P. Sokolov, *Macromolecules*, 2004, **37**, 161–166.
- 16 S. Kariyo, C. Gainaru, H. Schick, A. Brodin, V. N. Novikov and E. A. Rössler, *Phys. Rev. Lett.*, 2006, **97**, 207803.
- 17 S. Kariyo, A. Brodin, C. Gainaru, A. Herrmann, J. Hintermeyer, H. Schick, V. N. Novikov and E. A. Rössler, *Macromolecules*, 2008, **41**, 5322–5332.
- 18 J. Hintermeyer, A. Herrmann, R. Kahlau, C. Goiceanu and E. A. Rössler, *Macromolecules*, 2008, **41**, 9335–9344.
- 19 A. L. Agapov and A. P. Sokolov, *Macromolecules*, 2009, **42**, 2877–2878.
- 20 A. Abou Elfadl, A. Herrmann, J. Hintermeyer, N. Petzold, V. N. Novikov and E. A. Rössler, *Macromolecules*, 2009, **42**, 6816–6817.
- 21 D. T. Leeson, D. A. Wiersma, K. Fritsch and J. Friedrich, *J. Phys. Chem. B*, 1997, **101**, 6331–6340.
- 22 W. E. Moerner and M. Orrit, *Science*, 1999, **283**, 1670.
- 23 M. Orrit, J. Bernard, A. Zumbusch and R. I. Personov, *Chem. Phys. Lett.*, 1992, **196**, 595–600.
- 24 T. Basché, W. P. Ambrose and W. E. Moerner, *J. Opt. Soc. Am. B*, 1992, **9**, 829–836.
- 25 P. Tchénio, A. B. Myers and W. E. Moerner, *Chem. Phys. Lett.*, 1993, **213**, 325–332.
- 26 B. Kozankiewicz, J. Bernard and M. Orrit, *J. Chem. Phys.*, 1994, **101**, 9377–9383.
- 27 W. P. Ambrose and W. E. Moerner, *Nature*, 1991, **349**, 225–227.
- 28 W. P. Ambrose, T. Basché and W. E. Moerner, *J. Chem. Phys.*, 1991, **95**, 7150–7163.
- 29 A. A. Gorshelev, A. V. Naumov, I. Y. Eremchev, Y. G. Vainer, L. Kador and J. Köhler, *ChemPhysChem*, 2010, **11**, 182–187.
- 30 A. V. Naumov, Yu. G. Vainer and L. Kador, *Phys. Rev. Lett.*, 2007, **98**, 145501.
- 31 Yu. G. Vainer, A. V. Naumov and L. Kador, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **77**, 224202.
- 32 A. M. Boiron, P. Tamarat, B. Lounis, R. Brown and M. Orrit, *Chem. Phys.*, 1999, **247**, 119–132.
- 33 E. Barkai, R. Silbey and G. Zumofen, *Phys. Rev. Lett.*, 2000, **84**, 5339–5342.
- 34 A. V. Naumov, Yu. G. Vainer, M. Bauer, S. Zilker and L. Kador, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **63**, 212302.
- 35 E. Barkai, A. V. Naumov, Yu. G. Vainer, M. Bauer and L. Kador, *Phys. Rev. Lett.*, 2003, **91**, 075502.
- 36 A. V. Naumov, Yu. G. Vainer, M. Bauer and L. Kador, *Phys. Status Solidi B*, 2004, **241**, 3487–3492.
- 37 Yu. G. Vainer, A. V. Naumov, M. Bauer and L. Kador, *J. Chem. Phys.*, 2005, **122**, 244705.
- 38 Yu. G. Vainer, A. V. Naumov, M. Bauer and L. Kador, *Phys. Rev. Lett.*, 2006, **97**, 185501.
- 39 A. V. Naumov, Yu. G. Vainer, M. Bauer and L. Kador, *J. Chem. Phys.*, 2003, **119**, 6296–6301.
- 40 Yu. G. Vainer, A. V. Naumov, M. Bauer and L. Kador, *J. Lumin.*, 2007, **127**, 213–217.
- 41 B. Frick, G. Dosseh, A. Cailliaux and C. Alba-Simionesco, *Chem. Phys.*, 2003, **292**, 311–323.
- 42 J. Rauch and W. Köhler, *Macromolecules*, 2005, **38**, 3571–3573.
- 43 D. Stadelmaier and W. Köhler, *Macromolecules*, 2008, **41**, 6205–6209.
- 44 A. V. Naumov, A. A. Gorshelev, Yu. G. Vainer, L. Kador and J. Köhler, *Phys. Chem. Chem. Phys.*, 2011, DOI: 10.1039/C0CP01689F, this issue.
- 45 A. V. Naumov and Yu. G. Vainer, *Physics-Uspekhi*, 2009, **52**, 298–304.