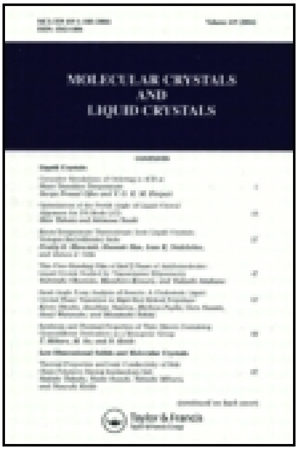

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Fast Dephasing in Glasses Induced by Tunneling States and Local Modes

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To cite this article: Stephan J. Zilker, Dietrich Haarer, Yuri G. Vainer, Andrei V. Deev, Michail A. Kol'chenkq & Roman I. Personov (1998): Fast Dephasing in Glasses Induced by Tunneling States and Local Modes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 314:1, 143-148

To link to this article: http://dx.doi.org/10.1080/10587259808042470

Mol. Cryst. Liq. Cryst., 1998, Vol. 314, pp. 143–148
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FAST DEPHASING IN GLASSES INDUCED BY TUNNELING STATES AND LOCAL MODES

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We present a comprehensive investigation of fast line broadening processes in two amorphous polymers, polymethylmethacrylate and polyisobutylene. Using a combination of two-pulse and incoherent photon echo spectroscopy, we have studied the homogeneous linewidth of embedded impurity molecules in a wide temperature range, namely 0.4–22 K. Thus, we are able to separate clearly between the two active dephasing mechanisms, two-level systems and low-frequency modes.

Keywords: photon echo, amorphous solids, optical dephasing

INTRODUCTION

Numerous photon echo studies have aimed at the investigation of low-temperature dephasing processes of chromophores embedded in amorphous solids [1,2,3,4,5,6]. The homogeneous linewidth (being in glasses per definition the linewidth measured by a two-pulse photon echo experiment [1]) essentially provides information about two dephasing mechanisms which are present in glasses: relaxations caused by two-level systems (TLS) and by local low-frequency modes (LFM). Two-level systems and LFM give rise to the well-known low-temperature anomalies of amorphous solids [7]. By measuring the temperature dependence of the homogeneous linewidth, spectroscopic techniques can obtain information about the distribution of the energy splitting E between the two levels of the involved TLS. The standard TLS model [8], which assumes a flat distribution of E, e.g. $P(E)$=const., gives rise to a linear dependence of the homogeneous linewidth of chromophores embedded in amorphous solids. A more precise calculation, which takes the temperature dependence of the TLS relaxation rate into account, yields a slightly nonlinear temperature dependence. In the region 0.1–1 K the latter can be approximated by a $T^{1.1}$ power law [9].

The second active dephasing mechanism, low-frequency modes (LFM), is also a peculiarity of glasses. LFM contribute to the homogeneous linewidth by an amount Γ_{LFM} which depends exponentially on the temperature [10]:

$$\Gamma_{\mathrm{LFM}}(T) = b\,\frac{\exp(-\Delta E/kT)}{[1-\exp(-\Delta E/kT)]^2}\,. \tag{1}$$

ΔE is the activation energy of the low-frequency mode, which is typically in the range between 5 and 30 cm^{-1} [1,6]; b is the coupling constant of the mode. Thus, low-frequency modes can already contribute to the homogeneous linewidth at temperatures as low as 1.5 K [6].

As a consequence, one has to be quite careful when analyzing the temperature dependence obtained by a line-narrowing experiment: The two individual contributions have to be separated with high accuracy in order to determine the temperature dependence of the TLS dephasing. Already at 4 K the latter can be dominated by the broadening caused by LFM.

In the literature, there is an ongoing discussion whether the energy distribution of the TLS is indeed flat, or whether it has a slight curvature, e.g. $P(E) \sim E^{\mu}$, with μ=0.2–0.7. This would yield a superlinear temperature dependence of the TLS contribution Γ_{TLS} to the homogeneous linewidth

$$\Gamma_{\mathrm{TLS}}(T) = aT^{\alpha}, \tag{2}$$

where $\alpha = 1 + \mu$. The above ansatz for $P(E)$ is mostly empirical. It arises from many studies which observed superlinear power laws. However, these investigations were often limited to small temperature intervals [1,2,4,5], and did not reach temperatures below 1 K, where low-frequency modes can not anymore contribute to Γ_{h}. This leads to difficulties when trying to separate TLS- and LFM-dephasing. Already 14 years ago, Jackson and Silbey [11] pointed out that a sum of a linear TLS term and of an exponentially activated LFM term will look like a superlinear power law, if the experimental temperature window is limited to a small region.

Zilker and Haarer [6] performed the first subkelvin echo study on an organic glass, polymethylmethacrylate (PMMA) which showed a linear temperature dependence below 1 K. A fit to their data in a limited temperature interval, namely 1.2–2.1 K, however, yielded the $T^{1.3}$-behavior often observed in the literature; a low-frequency mode already influenced the linewidth at these temperatures. A similar behavior, namely a $T^{1.1}$-dependence was later obtained for another amorphous polymer, polyisobutylene, doped with tetra-tert-butylterrylene over the region 0.4–1.2 K [12].

The study described here was motivated by the still unknown form of the energy distribution of the TLS. In order to be able to accurately separate between TLS- and LFM-dephasing, we have investigated two polymer glasses, polyisobutylene (PIB) and polymethylmethacrylate (PMMA) doped with tetra-tert-butylterrylene (TBT) as chromophore over a wide temperature range. First results for TBT/PIB in a narrower temperature interval (0.4–4 K) have been published previously [12].

EXPERIMENTAL

Data below 4 K were obtained in a picosecond two-pulse echo apparatus which has been described previously [13]. For the experiments, energies of less than 10^{-4} J/cm^2 per pulse at a wavelength of 573 nm were used. Temperatures down to 0.4 K can be reached using a commercial ^{3}He bath cryostat (Janis Research Inc.). Above 4 K, the linewidth was determined by an incoherent photon echo experiment providing a time resolution of 25–30 fs [14]. The sample was mounted in a ^{4}He cryostat, the pulse energy was less than $2 \cdot 10^{-3}$ J/cm^2 per pulse.

Tetra-tert-butylterrylene (TBT) is a chromophore which has been previously used in single-molecule spectroscopy [15]. A TBT/PMMA sample (concentration $7 \cdot 10^{-5}$ M, 1 mm thickness) was prepared by copolymerization. Details of the sample preparation for TBT/PIB (concentration: 10^{-4} M with a thickness of 300 μm) can be found in [13].

RESULTS AND DISCUSSION

Fig. 1 shows the inverse of the pure dephasing time T_2^* of TBT in PMMA (equivalent to the homogeneous linewidth with the lifetime-contribution subtracted). Its temperature dependence is given by

$$\frac{1}{\pi T_2^*} = \Gamma_{\mathrm{TLS}} + \Gamma_{\mathrm{LFM}} = aT^{\alpha} + b\,\frac{\exp(-\Delta E/kT)}{[1-\exp(-\Delta E/kT)]^2}\,. \qquad (3)$$

The plot contains at about 2 K a clear crossover between the two different functional forms represented by the first and the second term of Eq. (3). Below 2 K, a linear temperature dependence is obtained. Above 2 K, a strong contribution of a low-frequency mode can be observed. We determine an activation energy of about 10.8 cm^{-1} from a fit with Eq. (3) (solid

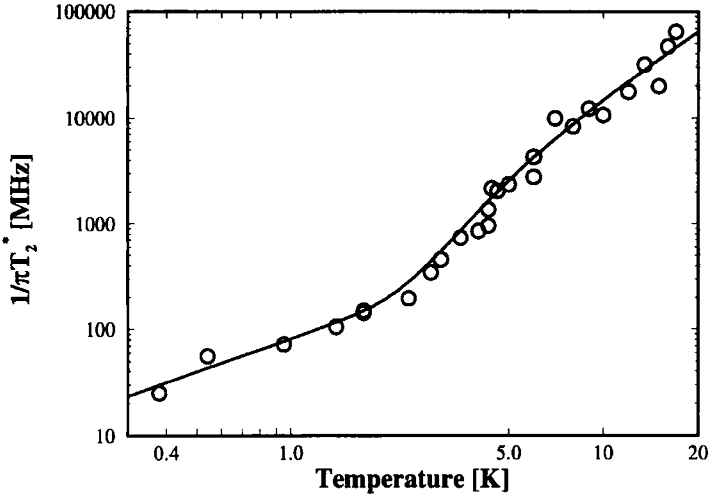

Figure 1: Pure dephasing contribution to the homogeneous linewidth of TBT in PMMA (circles) together with a fit with Eq. (3) (solid line).

line in Fig. 1), whose parameters are given in Table 1. This agrees with the linear dependence previously obtained in PMMA doped with zinc-meso-tetraphenylporphin (ZnTPP) [6]. Fig. 2 shows $1/\pi T_2^*$ for TBT/PIB. As in the case of PMMA, a crossover to an exponentially activated behavior is obtained at about 2 Kelvin. The activation energy of the low-frequency mode (ΔE = 13.4 cm^{-1}), however, is higher. Below 1.2 K, we obtain a slightly superlinear temperature dependence ($\alpha = 1.1$).

Thus, both systems studied show a nearly linear dependence of the homogeneous linewidth at low temperatures. This is in agreement with the assumption that the distribution of TLS energy splittings $P(E)$ is basi-

Table 1: Fit parameters for the homogeneous linewidth of TBT/PMMA and TBT/PIB according to Eq. (3).

	a [MHz/K$^\alpha$]	b [GHz]	α	ΔE [cm^{-1}]
PMMA	81	34.5	1.0	10.8
PIB	33.8	24.5	1.1	13.4

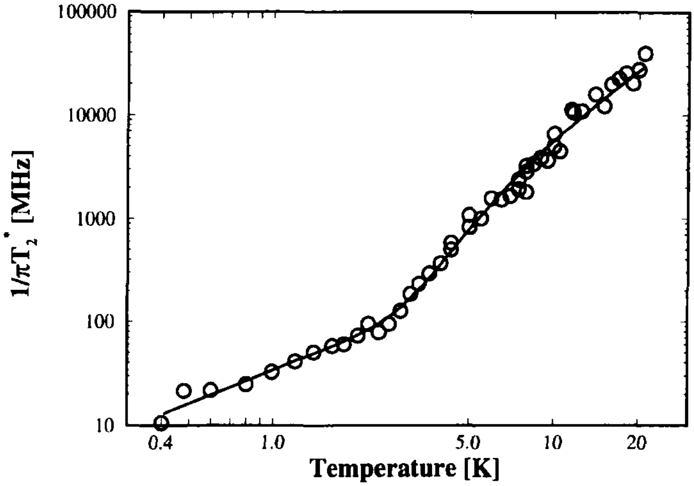

Figure 2: Pure dephasing contribution to the homogeneous linewidth of TBT in PIB (circles) together with a fit with Eq. (3) (solid line).

cally flat in these two specific glasses. A clear crossover between a linear TLS-contribution and an exponentially activated low-frequency mode term can be observed at 2 K. Consequently, it is impossible to fit the data over the whole temperature interval using only one power law. However, this conclusion is limited to the investigated systems, other glasses may behave differently.

CONCLUSIONS

In conclusion, we have shown that the temperature dependence of the homogeneous linewidth of TBT in two amorphous polymers, PMMA and PIB, is made by from two contributions, due to TLS- and LFM-dephasing. We were able to separate both with good accuracy, and to conclude about the distribution of the energy splittings of the TLS in both matrices. We deduce that data taken over a limited temperature interval are not able to accurately account for the true temperature dependence.

In future, it will be important to investigate more amorphous solids in comparable detail in order to find out, whether a flat energy distribution is a common feature of polymeric glasses.

ACKNOWLEDGMENTS

Part of this work was supported by the Volkswagen-Stiftung (AZ I/70 526) and by the Deutsche Forschungsgemeinschaft (SFB 279).

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