

## Single-Molecule Conformations Probe Free Volume in Polymers

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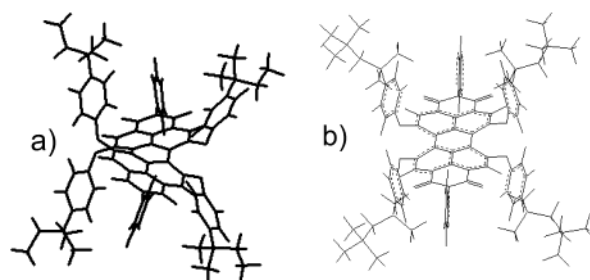
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The free volume is an intuitive theoretical concept<sup>1–12</sup> that has been proposed to explain the molecular properties and physical behavior of liquid and glassy states. Free volume is an open space that is freely moving in a medium.<sup>3–8</sup> It is constituted of sub nanometer-sized holes that appear in the medium due to structural disorder.<sup>9,10</sup> Due to thermal fluctuations, the free volume varies both in time and space.<sup>11,12</sup> At the early stages of its theoretical development, the free volume could only be deduced indirectly from specific volume experiments.<sup>13</sup> Small-angle X-ray and neutron diffractions have subsequently been used to determine density fluctuations and deduce free volume size distributions.<sup>14,15</sup> Finally, measurements of the photoisomerization rates of fluorescent probes<sup>16</sup> and positron annihilation lifetime spectroscopy (PALS) have led to a direct determination of the mean size of sub nanometer holes in polymeric materials.<sup>17,18</sup>

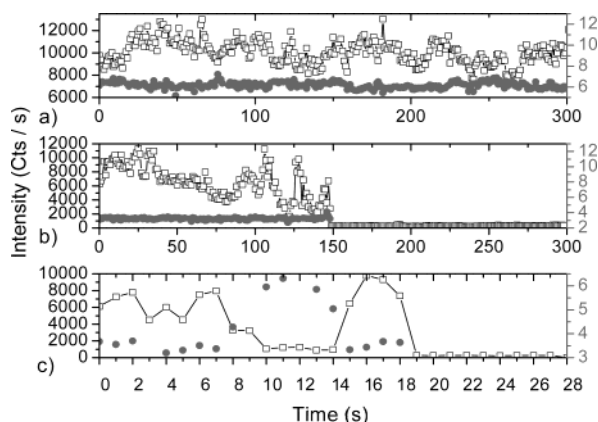
Single molecule spectroscopy (SMS) proved to be a powerful tool to study the local dynamics in polymers, both above and below the glass transition temperature  $T_g$ . In contrast to the previously cited ensemble methods, single molecule fluorescence experiments provide information on distributions and time trajectories of observables that would otherwise be hidden.<sup>19,20</sup> Recent studies of rotational and translational diffusion of a dye molecule embedded in a polymer matrix near the glass transition confirmed the spatially heterogeneous dynamics in this region.<sup>21</sup> In the glassy state, triplet lifetimes and intersystem crossing yields<sup>22,23</sup> and fluorescence lifetimes<sup>24</sup> of individual molecules embedded in a polymer host were shown to vary in time. In the latter case, the fluorescence lifetime fluctuations were shown to reveal segmental dynamics in polymers because of a relation with the Simha–Somcynsky<sup>9</sup> free volume theory.

In this communication, we show that the conformational dynamics of a single molecule in a polymer matrix allows a *direct* visualization of the *local* free volume. Specifically, the tetraphenoxy–perylene-tetracarboxy diimide (TPDI) dye molecule is known to present a twisted (Figure 1a) or a «flat» (Figure 1b) conformation of the core, with corresponding fluorescence lifetimes of 6.2 and 3.2 ns, when embedded in a poly(norbornene) (Zeonex) matrix.<sup>25</sup> The calculated van der Waals (VdW) volumes are 1.121 nm<sup>3</sup> for the twisted conformation and 1.322 nm<sup>3</sup> for the «flat» conformation of the molecule. This results in a 0.201 nm<sup>3</sup> volume difference between the two conformations.

In a polymer film, nonpolar side groups hinder an effective packing of the chains, causing a high mobility of the main chain and a lowering of the glass transition temperature. In two polymers of the same family, namely poly(methyl methacrylate) (PMMA,  $PI = 1.03$ ,  $T_g = 378$  K, Polymer Standards Service) or poly(*n*-butyl methacrylate) (*Pn*BMA,  $PI = 1.03$ ,  $T_g = 295$  K, Polymer Standards Service), this results in a mean hole volume, which is



**Figure 1.** Molecular structures of the two conformations of the dye molecule: (a) twisted core, (b) «flat» core.



**Figure 2.** Fluorescence lifetime (●) and intensity (□) time traces of TPDI molecules embedded in a *Pn*BMA matrix.

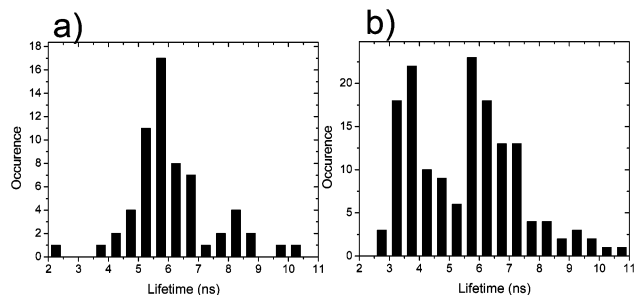
significantly lower in PMMA (0.105 nm<sup>3</sup>),<sup>14</sup> than in *Pn*BMA (0.132 nm<sup>3</sup>).<sup>18</sup> Notice that the latter value being determined by PALS may underestimate the “real” free volume, as PALS studies report generally smaller mean hole volumes than those reported by photochromic probe studies.<sup>16,28,29</sup> By spin coating a solution of a nanomolar concentration of the TPDI dye in PMMA or *Pn*BMA on a glass substrate, we expect and indeed show that the two conformations of the dye may distribute differently in the two matrixes and thus *directly* probe *local* free volume.

The synthesis and purification of the TPDI dye molecule used in this study is described elsewhere.<sup>26</sup> The dye molecules were excited by 1.2 ps pulses at a wavelength of 543 nm and a repetition rate of 8.18 MHz (Spectra Physics, Tsunami, OPO, pulse picker, frequency doubler) in an inverted confocal microscope (Olympus, 100×). The excitation power *P* was set to 0.8 μW. The lifetime was measured by use of an avalanche photodiode (SPCM-AQ-14, EG & G Electro Optics) equipped with a time-correlated single photon counting card (Becker & Hickl GmbH, SPC 630) used in FIFO mode.<sup>27</sup>

Figure 2 shows typical fluorescence lifetime time trajectories of TPDI dye molecules embedded in a *Pn*BMA matrix. Of the 92

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**Figure 3.** Fluorescence lifetime distributions of TPDI molecules embedded in a PMMA (a) or in a PnBMA (b) matrix.

molecules investigated in this matrix, 70% show a continuous trace with a mean lifetime around 6.2 ns (Figure 2a). These molecules possess the most stable conformation with a twisted core and a minimum VdW volume. Similarly, almost all (59) molecules<sup>30</sup> embedded in a PMMA matrix show an analogous trace, with an analogous fluorescence lifetime (Figure 3a). For PMMA, because the mean free volume is 0.105 nm<sup>3</sup>, much lower than the volume difference (0.201 nm<sup>3</sup>) between the twisted and «flat» conformations of the dye molecule, the static structural disorder of the matrix does not provide space for the voluminous «flat» conformation. Since a similar situation arises in PnBMA for 70% of the molecules, we can conclude that, for these 66 positions in the matrix, the *local* free volume is much lower than 0.201 nm<sup>3</sup>.

On the contrary, 30% of the molecules embedded in PnBMA show a trace with a mean lifetime around 3.2 ns (Figure 2b). These 26 molecules correspond to a «flat» conformation of the core, which requires more volume to settle in the matrix than the twisted molecule. In this case, the static structural disorder of the matrix provides the free volume necessary for these molecules to settle. In 30% of the probed positions of the PnBMA matrix, the free volume is thus of the order of 0.201 nm<sup>3</sup>.

Finally, five molecules show a trace where the fluorescence lifetime jumps from a low to a high lifetime and reversibly for two of them. For example, Figure 2c shows the trace of a molecule that has first a mean lifetime of 3.5 ns for a period of 10 s, then jumps to a lifetime of 5.9 ns during 5 s, and then jumps back to a lifetime of 3.5 ns during 5 s, prior to bleach. At all times, the intensity trace is anticorrelated to the lifetime trace, excluding the occurrence of quenching effects. The observed behavior corresponds merely to a switching of the molecule between the «flat» and the twisted conformation, followed by the reverse process, due to the dynamic structural disorder of the matrix.

It is worthwhile to notice here that the first switch always occurs from the «flat» conformation to the twisted conformation, which is the most stable conformation. The reverse switch does not always occur. Figure 3 shows the fluorescence lifetime distribution of 59 TPDI molecules embedded in PMMA (a) and 92 molecules embedded in PnBMA (b). The bimodal distribution of lifetimes that appear in PnBMA clearly reflects the difference between the free volume distribution present in this matrix and in PMMA. In this respect, it is interesting to note that current experiments are performed at room temperature (292 K) for both polymer matrixes. While this temperature corresponds to a few degrees below the glass transition temperature in PnBMA, it is more than 80 K below the glass transition temperature in PMMA. The difference between the distributions observed in PMMA and PnBMA thus results from a combination of a different free volume distribution and a

difference in cohesion energy in each matrix at the working temperature. The intensity fluctuations observed in the traces of Figure 2 are probably due to the enhanced mobility of the side chains in the PnBMA matrix as compared to that in the PMMA matrix.

In conclusion, it is shown in this communication that single-molecule conformational changes can *directly* probe the *local* free volume in amorphous polymers. The spatial (free volume distribution) and temporal (dynamics of free volume) information obtained by monitoring the fluorescence lifetime fluctuations of single molecules situated at different locations of the matrix would have been hidden in ensemble experiments, due to the intrinsic process of averaging involved in these measurements. It is important to notice here that the bimodal form of the fluorescence lifetime distribution shown in Figure 3 does not imply that there are only two sizes of free volume within the PnBMA matrix, but is merely a consequence of the fact that the two stable conformations of the probe molecule only allow us to distinguish between free volume sizes larger or smaller than 0.201 nm<sup>3</sup>.

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