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Citation: *The Journal of Chemical Physics* **131**, 171104 (2009); doi: 10.1063/1.3261730

View online: <http://dx.doi.org/10.1063/1.3261730>

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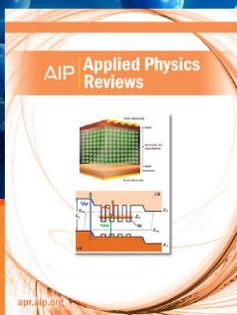
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Molecular rotor dynamics influenced by the elastic modulus of polyethylene nanocomposites

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(Received 7 August 2009; accepted 17 October 2009; published online 5 November 2009)

We observed that the excited-state twisting motion of 3,3'-diethyloxycarbocyanine in polymer nanocomposites (PNCs) depends strongly on the elastic modulus of medium. PNCs consist of low density polyethylene dispersed with surface-functionalized nanodiamonds with various alkyl groups. The mechanical properties of the PNCs were measured by a nanoindentation method, and the photoisomerization processes of the cyanine dye doped in the composites were investigated by time-resolved fluorescence spectroscopy. It was found that the molecular rotor dynamics in rigid media should be quantitatively describable by the elastic modulus of polymer. © 2009 American Institute of Physics. [doi:10.1063/1.3261730]

The mechanical properties of polymer nanocomposite (PNC) are influenced by polymer itself, nanofiller characteristics, and interfacial interactions between them.^{1,2} In this work, we used low density polyethylene (LDPE) as a matrix and the alkyl-functionalized nanodiamonds as a filler. Polyethylene (PE) is a simple and popular polymer that contains only carbon and hydrogen atoms connected by single C–C and C–H covalent bonds.³ Therefore, alkyl-functionalized nanodiamonds (NDs) are expected to enhance the mechanical properties of the PNC by their favorable van der Waals interaction with PE matrices. As depicted in Fig. 1, the mechanical properties of PNC such as hardness and elastic modulus can be controlled by the degree of filler content and the alkyl chain length of the functional group. The mechanical properties of polymer can be obtained by atomic force microscopy (AFM) nanoindentation.^{4,5}

The isomerization process of electronically excited molecules in rigid media has been known for a long time. A few examples are stilbene and its analogs,^{6,7} azobenzene and its derivatives,^{8,9} cyanovinyljulolidines,^{10–13} rigidochromic coordination complexes,¹⁴ and protein.¹⁵ The concept of free volume theory¹⁶ has been used to describe how a small molecule can rotate in a rigid environment of polymer. 3,3'-diethyloxycarbocyanine (DOC) iodide is one of polymethine dyes, which has been widely used as a microenvironment probe because its fluorescence quantum yield depends on medium viscosity or rigidity.^{16–19} DOC undergoes a *trans-cis*-photoisomerization in the electronically excited state. The increase in environmental rigidity slows down the isomerization process of DOC, resulting in the increase in the fluorescence quantum yield or lifetime. We measured the elastic modulus of LDPE composites by AFM nanoindentation and the fluorescence lifetime of DOC doped in the composites. We observed that the fluorescence lifetime of DOC depends strongly on the elastic modulus of the matrix.

Pristine NDs with 99% purity and average size of ca. 5 nm were obtained from JSC Diamond Center, Russia. LDPE

(MW: ~35 000) and DOC iodide were purchased from Aldrich. ND powders were oxidized in the 3:1 mixture of H₂SO₄ (98%) and HNO₃ (70%) under sonication for a few hours. Alkylated NDs were prepared by the esterification of carboxylated NDs under an acidic condition: ND-COOH + ROH (excess) → ND-COOR (R=methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, and 2-ethylhexyl). One mM of DOC stock solution was prepared in ethanol. 1 mg of LDPE was dissolved in 1 ml of tetrahydrofuran (THF). A 2 μl of DOC aliquot was added to LDPE solution for the fluorescence lifetime measurement. In order to make dye-doped nanocomposites, ND-alkyl was added to the LDPE solution and sonicated for 1 h. The weight percentage of ND to LDPE was varied from 1% to 11%. The solution was cast on a cover glass, spin coated, and dried in an oven at 80 °C for 24 h. The sample thickness appeared to be ca. 1 μm. The fluorescence lifetime was measured by time-correlated single photon counting (TCSPC) method. The laser source is a picosecond neodymium-doped yttrium aluminum garnet laser operating at a wavelength of 467 nm at 20 MHz. The detector used was a microchannel plate photomultiplier tube (PMT) (Hamamatsu 3809-07). A fast TCSPC board (Becker-Hickl SPC-830) was used for data collection and processing. To avoid local photobleaching of the dye in the polymer, the sample was continuously scanned at a rate of 1 Hz per line in the area of 100 × 100 μm². The fluorescence lifetime was extracted from the measured decay curve by a nonlinear least squares fit with deconvoluting the instrument response func-

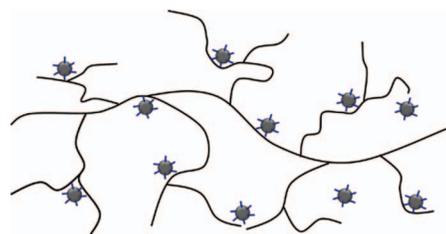


FIG. 1. Illustration of PE polymer dispersed with surface-functionalized nanodiamonds.

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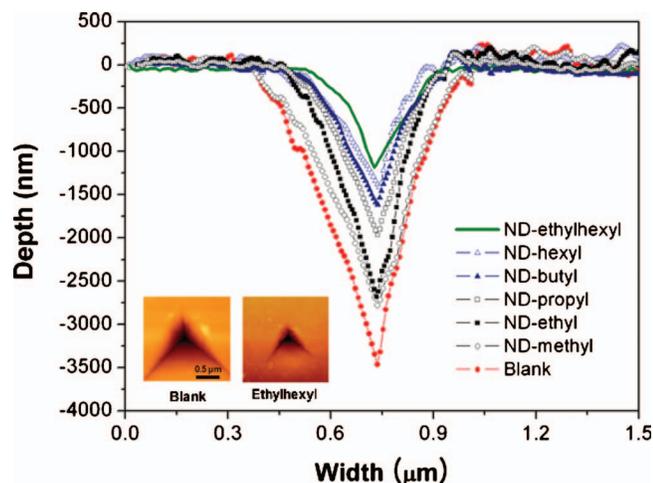


FIG. 2. The indentation-depth profile of ND-alkyl/LDPE nanocomposites with different alkyl groups at the 3 wt % ND. The inset shows the indentation images of neat and ND-ethylhexyl dispersed LDPE.

tion. The sample for nanoindentation was prepared as follows. PNCs of ND-alkyl/LDPE were prepared by molding. LDPE powders were mixed with ND-alkyl thoroughly at a predefined weight ratio and introduced into a round type mold. The container was heated to 120 °C and cooled down to room temperature. The prepared sample was a disk having the thickness of 1.2 mm and the diameter of 6 mm with a flat surface. AFM nanoindentation was carried out in an acoustic box with a Berkovich indenter that has a resonance frequency of 45.9 kHz and a spring constant of 145 N/m. The tip geometry consisted of a sharp three-sided pyramid with a half angle of 30°. We calculated the hardness and Young's modulus of a sample directly from the measured indentation image.

Figure 2 shows the typical indentation-depth profile of the nanocomposites at 3 wt % ND. The curves are obtained by sweeping the indentation image parallel to the baseline of the triangle that crosses the deepest point. The width is fairly symmetric and the depth covers from 3.5 μM for neat LDPE and 1.1 μM for ND-ethylhexyl/LDPE composite. As seen in the inset, the contact area of ND-ethylhexyl/LDPE is much smaller than that of neat polymer. Any sink-in or pile-up effects were not visibly seen in the data. In the indentation-depth profile, the indentation area and depth give information on hardness (H) and elastic modulus (E), respectively. That is, $H=F/A$, where F is the applied force and A is the contact area. The Young's modulus can be calculated by applying a Hertzian mechanics model,²⁰

$$E = \frac{4(1-\nu^2)F}{3 \tan \alpha h^2}, \quad (1)$$

where E is the elastic modulus, α is the tip half angle, ν is the Poisson ratio of matrix, and h is the maximum indentation depth. Hertz model states that Young's modulus is inversely proportional to the square of indentation depth at a given force. The hardness and Young's modulus of neat polymer and 36 nanocomposites were individually measured by the AFM nanoindentation. It was found that the functionalized ND with a longer alkyl chain increases the mechanical

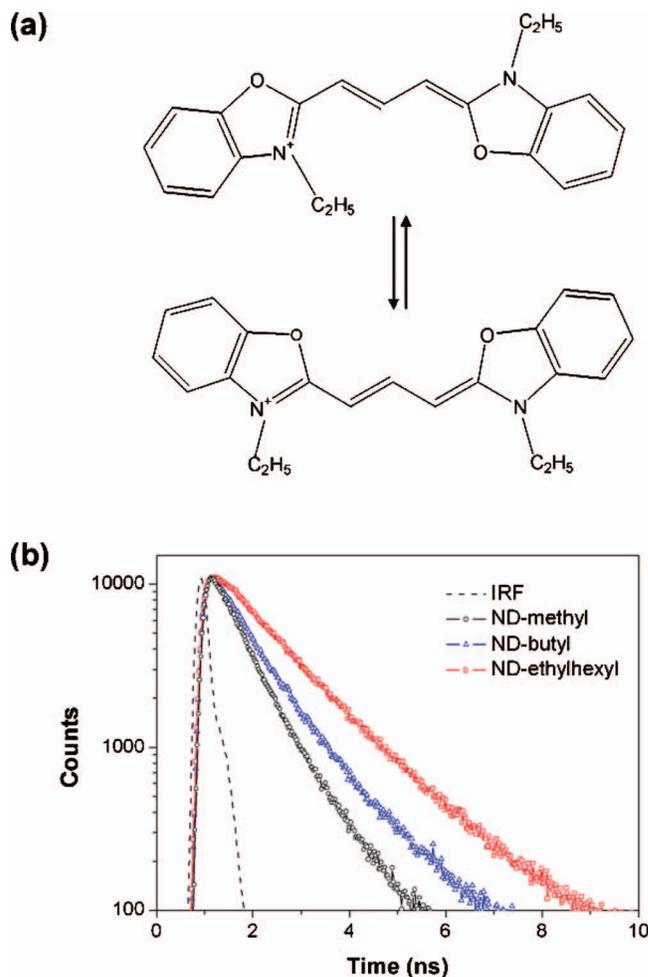


FIG. 3. The *trans-cis*-isomerization process of DOC (a) and its typical decay curves (b) in LDPE nanocomposites.

properties of the nanocomposites. The interfacial interaction between the polymer matrix and filler functional group is a key factor for the enhancement of the mechanical properties.²⁰

Figure 3(a) shows the *trans* \rightarrow *cis* photoisomerization process of DOC along the twisting coordinate. The nonradiative relaxation from the excited state to the ground state occurs at the perpendicular geometry where the excited state potential is minimum and the ground state is maximum.²¹ The fluorescence decay curves of DOC in ND-alkyl/LDPE at different ND content all show multiple exponential. Some of typical decay curves are shown in Fig. 3(b). We did not carry out any lifetime distribution analysis because all decay curves were well fit to double exponential. Then, the average lifetime (τ), defined as $a_1\tau_1 + a_2\tau_2$ ($a_1 + a_2 = 1$), was obtained and used as a characteristic time constant that represents the excited state dynamics of DOC in the polymer composite. The fluorescence lifetime is associated with the rate constant of the twisting motion by

$$\tau_F = \frac{1}{k_r + \Sigma k_{nr}}, \quad (2)$$

where k_r is the radiative rate constant and Σk_{nr} is the sum of the nonradiative rate constants including the twisting rate

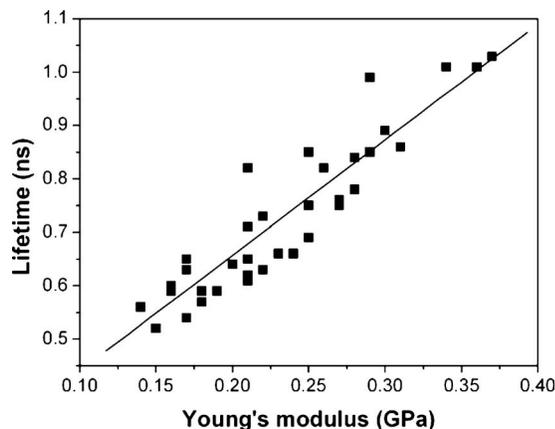


FIG. 4. The fluorescence lifetime of DOC as a function of Young's modulus.

constant.²² The torsional motion is affected by the potential barrier which largely determines the fluorescence lifetime. If the torsional motion is the major nonradiative decay channel, then its rate constant can be calculated from Eq. (2).

The average fluorescence lifetime of DOC in LDPE nanocomposites was plotted as a function of Young's modulus in Fig. 4. It shows that the fluorescence lifetime of DOC increases as the Young's modulus of the PNC increases. Although data are scattered ($R^2=0.912$), $\langle\tau\rangle$ seems to be linearly correlated with Young's modulus [$y(\text{ns})=2.05 \times (\text{GPa})+0.26$]. Since the existence of ND cannot increase the quantum efficiency of DOC, the lifetime increase should be due to the enhancement of the mechanical properties of the nanocomposite. Recently, it was observed that the excited-state twisting motion of Nile Red in various polymers depends on Young's modulus of polymer.²³ In this case, specific dye-matrix interaction can be varied from polymer to polymer because ten different polymers were used to cover a broad range of Young's modulus (0.14–4.15 GPa). The fluorescence lifetime of Nile Red was nonlinearly proportional to Young's modulus. In this work, Young's modulus was varied by adding nanoparticles in one polymer. Young's modulus is a macroscopic quantity, but the twisting motion of DOC occurs at the molecular level. Therefore, the effective modulus (micromodulus of elasticity) associated for the twisting motion should be different from the bulk modulus. As a medium rigidity sensor, DOC undergoes relatively a large amplitude motion in the excited state. We chose LDPE as a polymer matrix, owing to its relatively small Young's modulus (0.14 GPa) in comparison with other common polymers.

The internal motion of small molecules in rigid media has been qualitatively described by free volume, but we are the first to convert it to the elastic modulus in a quantitative manner. The free volume hole of LDPE measured by positron annihilation lifetime spectroscopy (PALS) is 145 \AA^3 ,⁸ and the calculated molecular volume of DOC is 303 \AA^3 .²⁴ The isomerization motion of DOC requires at least half of its molecular volume. This means that the free volume of LDPE is not sufficient for the reaction volume of the photoisomerization process of DOC. If there is not enough space for isomerization, then reorganization or expansion of local environments in the medium is required to create a reaction

volume. As an example, the volume expansion up to 17% was observed for an azobenzene polymer in the course of photoisomerization.²⁵ The isomerization process imposes a stress on the matrix, and the degree of deformation depends on the mechanical properties of the matrix. The molecular rotor dynamics of DOCI in LDPE nanocomposites can be describable by a stochastic Langevin equation of motion, which contains a complex modulus of matrix. The isomerizing reaction is coupled to both storage and loss moduli. In this work, the fluorescence lifetime was related to the storage (elastic) modulus because it was experimentally measured quantity. However, the loss modulus may also be included to explain the explicit mode coupling between the isomerizing coordinate and medium deformation. Finally, multidimensionality of the isomerization reaction should also be considered.²⁶ That is, the isomerizing motion may not be necessarily the out-of-plane motion, but in-plane torsion can be involved in a confined geometry. In any case, the elastic modulus of medium plays a key role in the built-in process of the reaction volume for molecular rotor dynamics.

In summary, we measured the fluorescence lifetimes of DOCI in LDPE nanocomposites by picosecond TCSPC. To cover a broad range of elastic modulus, detonation nanodiamonds were surface functionalized with various alkyl groups, and then they were dispersed into LDPE. Nanoindentation was carried out by AFM, and Young's modulus of PNCs was obtained from the indentation-depth profile. The results showed that longer alkyl chains in the functional group of ND interact strongly with LDPE, and thus give higher Young's modulus. The photoisomerization processes of the cyanine dye doped in the composites were investigated by time-resolved fluorescence spectroscopy. We found that the elastic modulus of medium rather than free volume is the determining factor for molecular rotor dynamics occurring in rigid media.

ACKNOWLEDGMENTS

This work was supported by a grant from the National Research Foundation.

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