

Internal motion of an electronically excited molecule in viscoelastic media

Ah-Young Jee, Eunhye Bae, and Minyung Lee

Citation: *The Journal of Chemical Physics* **133**, 014507 (2010); doi: 10.1063/1.3454724

View online: <http://dx.doi.org/10.1063/1.3454724>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/133/1?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

Relative energies, structures, vibrational frequencies, and electronic spectra of pyrylium cation, an oxygen-containing carbocyclic ring isoelectronic with benzene, and its isomers

J. Chem. Phys. **139**, 174302 (2013); 10.1063/1.4826138

On the internal rotations in *p*-cresol in its ground and first electronically excited states

J. Chem. Phys. **127**, 024307 (2007); 10.1063/1.2752163

Calculation of the τ dependence of the vibration–internal rotation–overall rotation interactions in $\text{C}_2\text{H}_5\text{OH}$ from molecular structure and molecular dynamics

J. Chem. Phys. **122**, 204306 (2005); 10.1063/1.1898220

A combined nuclear dynamics and electronic study of the coupling between the internal rotation of the methyl group and the intramolecular proton transfer in 5-methyltropolone

J. Chem. Phys. **117**, 7525 (2002); 10.1063/1.1503317

Internal dynamics in azetidine: A microwave and *ab initio* study

J. Chem. Phys. **114**, 2237 (2001); 10.1063/1.1334876



NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP Applied Physics Reviews

Internal motion of an electronically excited molecule in viscoelastic media

Ah-Young Jee, Eunhye Bae, and Minyung Lee^{a)}

Department of Chemistry and Nanoscience, Ewha Womans University, Seoul 120-750, Republic of Korea

(Received 20 March 2010; accepted 26 May 2010; published online 7 July 2010)

The twisting motion of *trans*-4-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide (4-DASPI) in the excited state was investigated in solutions and various polymers in order to understand dependence of molecular rotor dynamics on viscoelasticity. It was observed that the internal motion of electronically excited 4-DASPI correlates strongly with dynamic viscosity and elastic modulus. Our results also showed that condensed phase dynamics of 4-DASPI are governed by the explicit mode coupling between the rotamerizing coordinate and mechanical properties of viscoelastic media. © 2010 American Institute of Physics. [doi:10.1063/1.3454724]

I. INTRODUCTION

Viscoelasticity is an important physical property of condensed matter. The mechanical property of a liquid is usually described by viscosity and that of a solid is expressed by elasticity. Molecular rotor dynamics influenced by such medium properties have been investigated in liquids^{1–5} and solids,^{6–10} but any congruent analysis encompassing both regimes together has not emerged yet due to lack of relevant data. Thus, it is desirable to study molecular motions in viscoelastic media with a well-characterized dye. For this purpose, we have chosen *trans*-4-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide (4-DASPI) as a molecular probe (Fig. 1) and investigated its excited-state dynamics in both liquids and solids. 4-DASPI has been widely used as an environment-probing dye and its spectroscopic characteristics are relatively well known.^{11–20} 4-DASPI is one of hemicyanine dyes in which the dimethyl amino group is an electron donor and the methylpyridinium group is an electron acceptor. Such an intramolecular charge transfer (ICT) character is responsible for the interesting dynamics of the electronically excited molecule.¹³

The fluorescence lifetime of 4-DASPI depends on both of polarity and viscosity (stiffness). The solvent polarity dependence of steady-state absorption and emission spectra of 4-DASPI was explained by the resonance structure between the benzenoid and quinoid forms.¹⁴ The fluorescence quantum yields of 4-DASPI are enhanced markedly by the increase of environmental rigidity which slows down the rotamerism process.^{15,16} There are four possible rotamerism processes in 4-DASPI: one double and three single bond rotations. Unlike stilbene and its derivatives which isomerize around a double bond in the excited state, the *trans*-*cis* isomerization yield of 4-DASPI around the bond is very low.¹² The torsional motion of the dimethylamino group is unlikely because the corresponding charge transfer state is much higher than the Franck–Condon (FC) state.¹³ A theoretical calculation done by Cao *et al.*¹⁴ showed that the barrier height for the rotation of methylpyridium ring is approxi-

mately 7.3 kJ/mol. A frequency upconversion experiment showed that the excited lifetime of 4-DASPI derivatives is approximately 30 ps, irrespective of the length of alkyl chains attached to the pyridinium ring.¹⁹ This indicates that the methylpyridium twisting is not a major source of the nonradiative relaxation. Therefore, the θ twisting around the single bond appears to be the major nonradiative decay channel of electronically excited 4-DASPI (Fig. 1).^{12–14,19}

This work concerns the θ rotamerism process of 4-DASPI. The fate of electronically excited 4-DASPI was depicted in Fig. 2. The initially prepared FC state is relaxed to the localized excited (LE) state or ICT state, which decays radiatively or undergoes an internal rotation to the twisted ICT (TICT) state. The rate process from LE (ICT) to TICT is much faster than the possible internal conversion from LE (ICT) to the ground state. Therefore, the internal conversion process was not included in the figure for simplicity. The TICT state is known to be nonfluorescent.^{12–14} We first examined the solvent viscosity dependence of the internal rotation of 4-DASPI in liquids (water-glycerol mixtures). Then, we measured the fluorescence lifetimes of 4-DASPI in various polymers covering low density polyethylene (LDPE), polyvinyl alcohol (PVA), high density polyethylene (HDPE), ultrahigh molecular weight polyethylene (UHMWPE), polyvinyl chloride (PVC), polycarbonate (PC), polycaprolactam (nylon 6), poly(methyl methacrylate) (PMMA), polystyrene (PS), and polyacrylic acid (PAA). We observed that the internal twisting processes of 4-DASPI correlated strongly with solvent viscosity and Young's modulus of polymers. Based on our results, we attempted to delineate the condensed phase dynamics of electronically excited 4-DASPI in terms of viscosity and modulus.

II. EXPERIMENTAL

4-DASPI and glycerol were purchased from Sigma-Aldrich. The molecular weight (MW) of the polymers specified by suppliers was given in the parenthesis: LDPE (35 000), HDPE (125 000), UHMWPE (4 500 000), PS (192 000), PVA (120 000), PC (64 000), PMMA (115 000), and PAA (240 000) were obtained from Sigma-Aldrich. Nylon 6 (18 000) was bought from Polyscience, Inc. Different

^{a)}Author to whom correspondence should be addressed. Electronic mail: mylee@ewha.ac.kr.

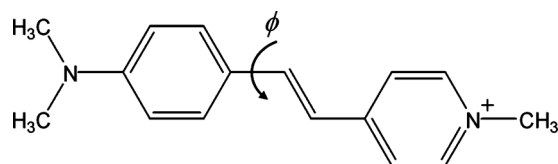


FIG. 1. The molecular structure of 4-DASPI. The angle θ depicts the internal twisting motion.

solvents were used to prepare polymer solutions: tetrahydrofuran for LDPE, PVC, PMMA, and PC; decalin for HDPE and UHMWPE; 6:1 mixture of dimethyl sulfoxide and water for PVA; cyclohexane for PS; water for PAA; and 2,2,2-trifluoroethanol for nylon 6. All films were prepared by spin coating and drying in an oven at 70 °C for 24 h. The drying procedure is primarily necessary to eliminate remnant solvents in polymer. Moreover, the high temperature annealing over a prolonged time structurally equilibrates the polymer film which exists in a nonequilibrium state upon spin coating. The thickness of polymer films is about 1.2 μm , and each of the polymer films contains approximately 5 μM of 4-DASPI.

A Brookfield rheometer (LVDV-IIIU) was used to determine solvent viscosity at 24 °C: The viscosity values of pure water and glycerol were measured as 0.93 and 910.3 cP, respectively. The vol/vol mixture ratios of water:glycerol and their viscosity values were 4:1 (2.6 cP), 2:1 (4.4 cP), 1:1 (8.9 cP), 1:2 (28.4 cP), 1:4 (82.7 cP), 1:8 (208.4 cP), 1:16 (351.9 cP), and 1:64 (691.6 cP). The absorption and emission spectra were measured by a spectrophotometer (UV-2450, Shimadzu) and spectrofluorometer (F-4500, Hitachi), respectively. The excitation wavelength was 440 nm and the fluorescence was collected from 450 to 800 nm. The fluorescence quantum yield of the sample was determined according to the procedure,^{21,22}

$$\Phi = \Phi_{\text{ref}} \frac{(1 - 10^{-A_{\text{ref}}})n^2 S}{(1 - 10^{-A})n_{\text{ref}}^2 S_{\text{ref}}}, \quad (1)$$

where n is the refractive index, A the absorbance, and S the integrated emission intensity. Rhodamine 123 (R123) in ethanol was used as a reference standard ($\Phi_{\text{ref}}=0.9$).²³

The fluorescence lifetime of 4-DASPI in polymer was measured by time-correlated single photon counting (TCSPC). The light source was a picosecond diode laser operating at a wavelength of 467 nm (Picoquant). The average laser power is about 300 μW at 40 MHz. By following the company's specification, the laser power was lowered by a factor of 3 to improve the instrument response function (IRF). The repetition rate was reduced to 10 MHz to cover the broad range of the emission decay curve. An inverted confocal microscope (TE2000-S, Nikon) with an oil immersion objective lens (NA 1.4, x60) was used as a platform for sample excitation and fluorescence detection. A single mode fiber was used to introduce the laser beam into the microscope. It is not a polarization maintaining fiber, and thus the light polarization is randomized at the sample excitation. A 488 nm long pass filter (Semrock) was used to collect all the sample emission above the cutoff wavelength. The fluorescence signal was detected by a microchannel plate photomul-

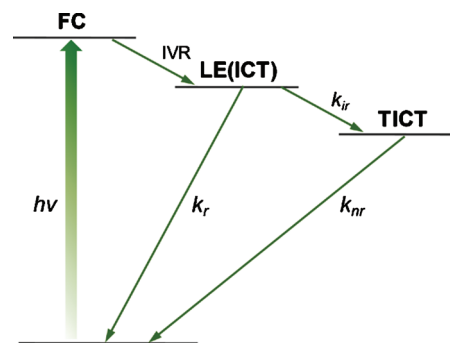


FIG. 2. The excited-state level kinetics of 4-DASPI.

tipplier tube (R3809U-07, Hamamatsu Photonics). To avoid possible photochemical bleaching and glass softening effects,²⁴ the sample on top of the microscope was continuously scanned by a atomic force microscopy (AFM) controller (XE-100, Park Systems) in the area of $100 \times 100 \mu\text{m}^2$ at 1 Hz. A fast TCSPC board (SPC-830, Becker-Hickl) was used to obtain the fluorescence signal, and the fluorescence decay curve was analyzed by a software (Fluofit, Picoquant). The IRF of the TCSPC system is about 150 ps. The fluorescence lifetimes were extracted from the measured decay curves by a nonlinear least squares fit with deconvolution of IRF.

III. RESULTS AND DISCUSSION

A. Twisting dynamics in viscous media

The fluorescence quantum yield of a fluorophore is given by

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

where k_r is the radiative rate constant and Σk_{nr} is sum of the nonradiative rate constants, consisting of the internal conversion, intersystem crossing, and any reactive channels such as internal rotation or isomerization. It has been reported that 4-DASPI has very low yields of internal conversion and intersystem crossing.^{13,14} If the internal rotation is much faster than other nonradiative decay processes, then Σk_{nr} is approximately given as k_{ir} , the rate constant for internal rotation. The k_r depends on the refractive index of medium.²⁵ For example, the radiative decay rate constant of 4-DASPI is $1.28 \times 10^8 \text{ s}^{-1}$ in water and $1.56 \times 10^8 \text{ s}^{-1}$ in glycerol. Figure 3 shows the fluorescence emission spectra of 4-DASPI in water-glycerol mixtures. The fluorescence quantum yield increases when the solvent viscosity increases as a result of slowing down the large amplitude motion of the molecular rotor in the excited state. Traditionally, dependence of the fluorescence quantum yield on solvent viscosity has been described by the Förster-Hoffman equation,²⁶

$$\log \Phi = C + x \log \frac{\eta}{T}, \quad (3)$$

where the slope x is obtained by a log-log plot at constant temperature. It should be mentioned that Eq. (3) is an approximation, and valid when $k_r \ll k_{ir}$. If the internal rotation

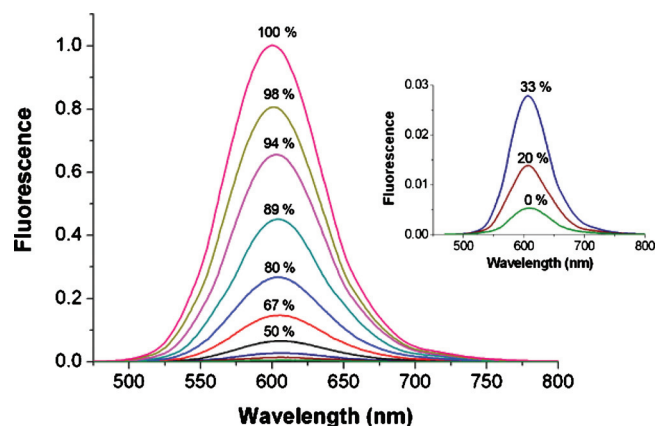


FIG. 3. The emission spectra of 4-DASPI in water-glycerol mixtures.

is a dominating rate process among other nonradiative decays, then the k_{ir} is given as

$$k_{ir} = k_r \left(\frac{1 - \Phi}{\Phi} \right). \quad (4)$$

The rate process for the internal rotation is viscosity and temperature dependent,²⁷

$$k_{ir} = F(\eta) \exp(-E_0/RT), \quad (5)$$

where η is the viscosity and E_0 is the barrier height. At intermediate friction, $F(\eta)$ is given by one-dimensional Kramers model,²⁸

$$F(\eta) = \frac{A\eta}{B} \left\{ \left[1 + \left(\frac{B}{\eta} \right)^2 \right]^{1/2} - 1 \right\}, \quad (6)$$

where A and B are parameters related to the well and barrier frequencies, respectively. At the high friction limit, the Kramers model approaches to the Smoluchowski approximation: $F(\eta) = C\eta^{-1}$. There are many cases where the Kramers model does not work properly and the excited-state dynamics exhibit fractional viscosity dependence.^{3,29–33} For the sake of simplicity, dependence of the internal rotation on solvent viscosity is expressed as a power-law function,

$$k_{ir} = \alpha \eta^{-\beta} \quad (0 < \beta < 1), \quad (7)$$

where α and β are empirical parameters. Figure 4 shows the

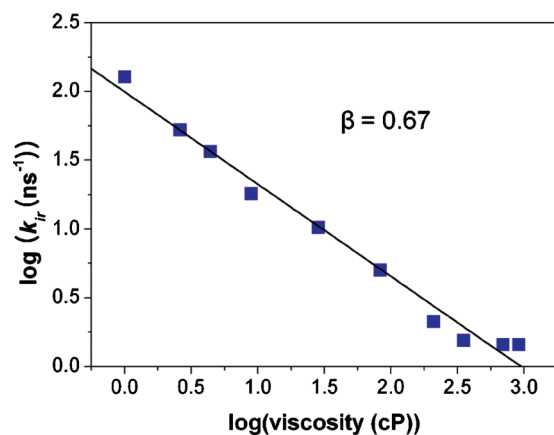


FIG. 4. The internal twisting rate constant of 4-DASPI as a function of viscosity.

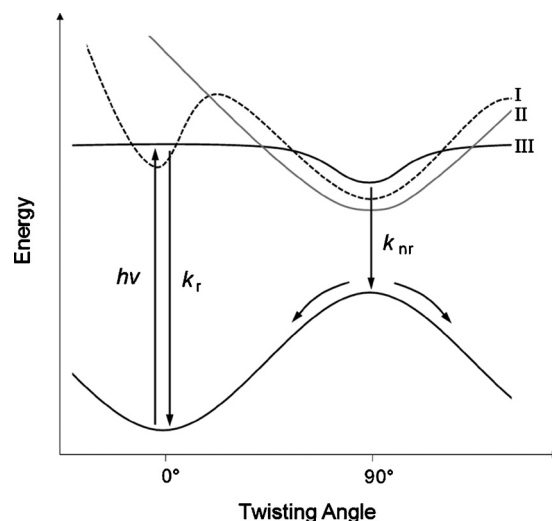


FIG. 5. The possible potential energy surfaces of a molecular rotor.

log-log plot of 4-DASPI data, and a fit to Eq. (7) gives the β value of 0.67. The decay dynamics of 4-DASPI in a narrow viscosity range of water-glycerol mixtures were recently measured by Rei *et al.*,³⁴ reporting the β value of 0.45. Previously, the β value of 0.55 was reported for the molecule in methanol-glycerol mixtures.¹⁷ The fractional viscosity dependence of isomerization reactions has been studied using the mode coupling theory, which finds a β value in the range of 0.5–0.8.³⁵ Our obtained value is in a close agreement with the theoretical prediction.

The fractional dependence has several origins such as the breakdown of Stokes law, multidimensionality, and the effect of time-dependent friction. There may be other factors such as the use of cosolvents³⁶ and existence of specific solute-solvent interactions.³⁷ The breakdown of the Stokes law happens when the solvent size is comparable or even larger than the solute.^{38–40} Multidimensionality means the reaction coordinate is not simply one dimensional, but other modes are involved in the reaction.⁴¹ Time-dependent friction, a non-Markovian dynamics, arises from the fact that the solute-solvent coupling through friction depends on the relative time scale.^{42–45} By applying the mode coupling theory, the time scale can be separated into the short (fast) and long (slow) components. In accordance, the viscosity is decomposed into two parts,⁴⁶

$$\eta(t) = \eta_{\text{short}}(t) + \eta_{\text{long}}(t). \quad (8)$$

The bulk viscosity is largely determined by the second term, but the ultrafast motion is coupled to the first term. The idea of frequency (or time) dependent friction is that a fast motion of a solute does not feel fully the mechanical friction contributed by the slow solvent motion. Thus, the effective friction acting on the solute motion becomes less than the bulk value, the static (zero-frequency) friction.

The rate processes in the excited state are governed by the potential surface. As depicted in Fig. 5, there are three possible cases: the activated, inverse, and flat potentials. The TICT state resides on the so-called sink region in the adiabatic, excited-state potential surface. The activated rate process depicted as I is relevant to the Kramers model [Eq. (6)].

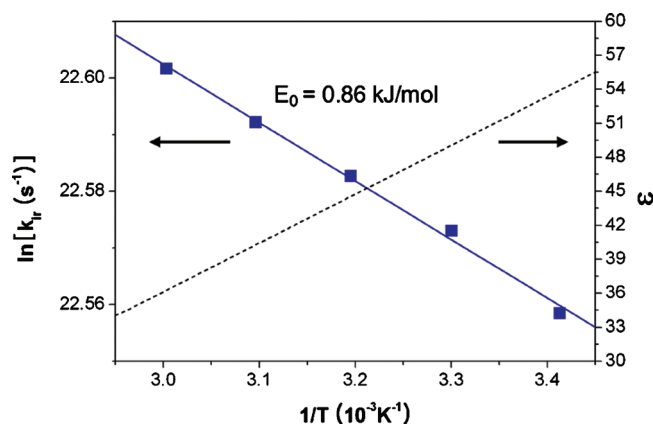


FIG. 6. The isoviscosity plot of 4-DASPI in water-glycerol mixtures. The temperature was varied from 20 to 60 °C, and the viscosity was fixed at 50 cP.

The other extreme is the repulsive potential (II) in which the viscosity dependence of the internal rotation showed an interesting behavior.^{47,48} The flat potential surface (III) is the case in which a simple diffusion equation can be applied due to the absence of the potential barrier (E_0). The shape of potentials can be estimated in part by the Arrhenius plot, but it is often complicated due to the viscous and polar effects. The total activation energy is given by

$$E_a = E_0 + aE_\eta + bE_\epsilon, \quad (9)$$

where E_η and E_ϵ are the activation energies associated with viscosity and polarity, respectively. The empirical parameters, a and b , account for the solvent-dependent strengths of viscosity and polarity. It is based on the decomposition of total friction into mechanical and dielectric parts,^{49,50}

$$\zeta_{\text{tot}} = \zeta_{\text{HD}} + \zeta_{\text{DF}}, \quad (10)$$

where ζ_{HD} and ζ_{DF} are hydrodynamic (mechanical) and dielectric frictions, respectively. Although there has been an issue on the separability of total friction,⁵¹ Eq. (10) is still in wide use.^{52,53} The friction is related to the viscosity by the Stokes law. As shown in Fig. 6, the barrier height has been often obtained by employing the isoviscosity plot in which the temperature is varied with maintaining the same viscosity.^{54,55} However, the isoviscosity plot eliminates only the viscosity activation energy and the polarity activation energy still remains. Figure 6 shows temperature dependence of the dielectric constant of water-glycerol mixtures (the dotted line) obtained from the Lorentz-Lorenz formula for dielectric constant,⁵⁶

$$\frac{\epsilon - 1}{\epsilon + 2} = \varphi_1 \left(\frac{\epsilon_1 - 1}{\epsilon_1 + 2} \right) + \varphi_2 \left(\frac{\epsilon_2 - 1}{\epsilon_2 + 2} \right) \quad (\varphi_1 + \varphi_2 = 1), \quad (11)$$

where ϵ is the dielectric constant and φ is the volume fraction. The increase of dielectric constant with the inverse of temperature, which acts oppositely against the rate constant, may be an indication that the dielectric friction is in operation for the internal motion of 4-DASPI in the water-glycerol mixtures. The isoviscosity plot gives the slope of 0.86 kJ/mol. This value is sum of the barrier height and polarity activation energy ($E_0 + bE_\epsilon$), which is three times less than

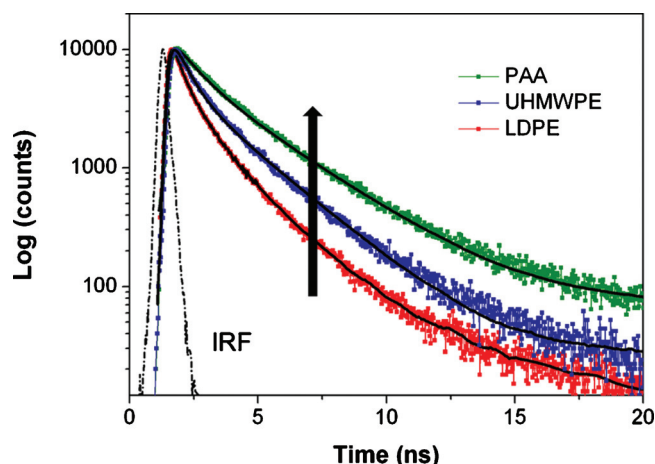


FIG. 7. The fluorescence decay curves of 4-DASPI in several polymers. The convoluted curves were shown in the solid lines, and the fit was performed on the judgment of weighted residuals and the reduced χ^2 .

the thermal energy at ambient temperature (~ 2.5 kJ/mol). The small value of 0.86 kJ/mol is attributable to the polarity activation energy, confirming the result of previous quantum chemical calculations.¹⁴ In general, the activation energy fluctuates along the polarity of solvent mixtures.⁵⁷ However, the rate process of 4-DASPI in the excited-state experiences a flat potential because the barrier height is much lower than the thermal energy.

B. Twisting dynamics in elastic media

Figure 7 shows the typical fluorescence decay curves of 4-DASPI in polymers. All the decays do not exhibit a single exponential behavior and the nonexponentiality arises from medium heterogeneity. In this case, the fluorescence decay is expressed as a sum of multiple exponentials,

$$I(t) = \sum_{i=1}^N \alpha_i \exp[-t/\tau_i], \quad (12)$$

where α is the amplitude and τ is the decay time constant. Then, the average lifetime is defined as

$$\langle \tau \rangle = \frac{\sum_{i=1}^N \alpha_i \tau_i}{\sum_{i=1}^N \alpha_i}. \quad (13)$$

A fitting program usually includes a few exponential terms with deconvolution capability. The true decay curve is obtained by optimizing the parameters (amplitudes and time constants). All the decay curves were satisfactorily fit to the biexponential function with acceptable residuals and adding more fitting parameters did not improve the quality of the fit. Therefore, the fit was limited to the double-exponential form for all the decay curves and the average fluorescence lifetimes were obtained through Eq. (13). This process does not mean that the excited level kinetics involves two different states or the probe resides in two different environments. The procedure is needed to obtain the average lifetime as a characteristic quantity that represents the excited-state dynamics of 4-DASPI. All the fitting parameters with the average lifetimes were tabulated in Table I.

TABLE I. The fluorescence lifetime of 4-DASPI in various polymers at room temperature (24 °C).

No.	Polymer	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	⟨τ⟩ (ns)	χ ²
1	LDPE	0.73	0.42	0.27	1.88	0.81	1.17
2	PVA	0.72	0.51	0.28	2.15	0.97	1.28
3	HDPE	0.67	0.54	0.33	2.22	1.09	0.95
4	UHMWPE	0.63	0.54	0.37	2.43	1.24	1.07
5	PVC	0.62	0.68	0.38	2.41	1.34	1.01
6	PC	0.65	0.58	0.35	3.47	1.59	1.25
7	Nylon 6	0.64	0.60	0.36	3.72	1.72	1.21
8	PMMA	0.65	0.70	0.35	3.72	1.76	1.00
9	PS	0.49	0.83	0.51	2.72	1.79	1.07
10	PAA	0.46	0.85	0.54	2.89	1.95	1.10

The molecular volume of 4-DASPI is about 247 Å³. The internal rotation of 4-DASPI involves two moving groups: the *N,N*-dimethylaniline (A) and methylpyridylethylene (B) moieties. The molecular volumes of A and B are 122 and 125 Å³, respectively. As shown in Fig. 8, the twisting motions require different reaction volumes around the rotamerizing coordinate, although they are similar in size. The A group undergoes basically a cylindrical motion, which needs a minimal displacement of polymer chains. On the other hand, the B group requires a relatively large reaction volume for rotation. Therefore, the internal motion of A is more viable than that of B in a “polymer environment.” Our notion does not include the volume-conserving process that might occur in certain photoisomerization reactions in rigid media.⁵⁸

The polarity parameter has been scaled by many methods such as the Kosower *Z*-value,⁵⁹ Reichardt *E*_T(30),⁶⁰ and Kamlet–Taft triple parameters (α , β , and π^*).⁶¹ Without using any solvatochromic dyes, the polarity parameter (Δf), also known as orientation polarizability, can be obtained by⁶²

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}, \quad (14)$$

where ϵ is the dielectric constant and n is the refractive index of medium. The first part of the equation is the low frequency (or static) polarizability that takes the solvent orientation into account, and the second is the high frequency (optical) polarizability that measures the solvent electron re-orientation. Since the value of the refractive index does not vary much among polymers (the second term), it acts as a

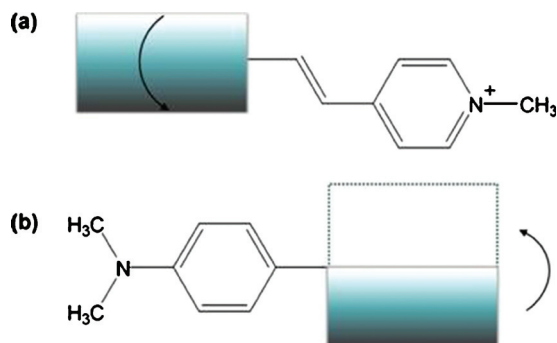


FIG. 8. The internal rotation of 4-DASPI; (a) is the motion of the *N,N*-dimethylaniline moiety and (b) is that of the methylpyridylethylene moiety.

scaling factor in Eq. (14). Therefore, Δf is mostly determined by the dielectric constant (the first term). Although the majority of work on medium polarity has been done in liquids, there has been growing interest in the polar character of polymers. Paley *et al.*⁶³ first carried out detailed studies on the polarity of polymers. They obtained *E*_T(30) and Kamlet–Taft parameters for many types of polymers. Since then several groups concerned the polar nature of polymers,^{64–66} and the research was further extended to the concept of micropolarity using single molecule spectroscopy.^{67,68} In Fig. 9(a), we have plotted the average fluorescence lifetime of 4-DASPI as a function of polarity parameter. The Δf values were calculated from the known polymer data.⁶⁹ It seems that the fluorescence lifetime of 4-DASPI does not correlate much with polymer’s Δf . Another model for molecular rotor dynamics in polymer is the free volume theory.^{70,71} Recent investigations by single molecule spectroscopy enriched our understanding on the role of free volumes for the molecular dynamics in rigid media.^{72,73} Polymer contains the interstitial and hole-free volume in the void space.⁷⁴ Positron annihilation lifetime spectroscopy (PALS) directly measures the free volume hole sizes of polymers. In Fig. 9(b), the fluorescence lifetime of 4-DASPI was plotted as a function of free volume hole size. PALS data for ten different polymers were obtained from the literature.^{75,76} The figure shows that the fluorescence lifetime does not correlate well with the average free volume hole size of the ten polymers chosen in this work. The results of another molecular rotor, 9-dicyanovinyljulolidine, have already shown that the free volume theory does not explain satisfactorily the internal twisting dynamics in polymer.⁷³ The results lead us to suggest the use of elastic modulus as an alternative to free volume. There are three types of elastic modulus, namely, Young’s, shear, and bulk modulus. They are interrelated each other, and thus one is calculated from the others if Poisson’s ratio of the material is known. Young’s moduli of the ten polymers were previously measured by AFM in the nanoindentation-depth mode.⁷⁷ In Fig. 9(c), the fluorescence lifetime of 4-DASPI was plotted as a function of Young’s modulus obtained from the AFM data. In comparison with the polarity parameter and free volume hole size, Young’s modulus is correlated with the fluorescence lifetime of 4-DASPI. Therefore, the measured average lifetime is related to the rate constant for the internal rotation through

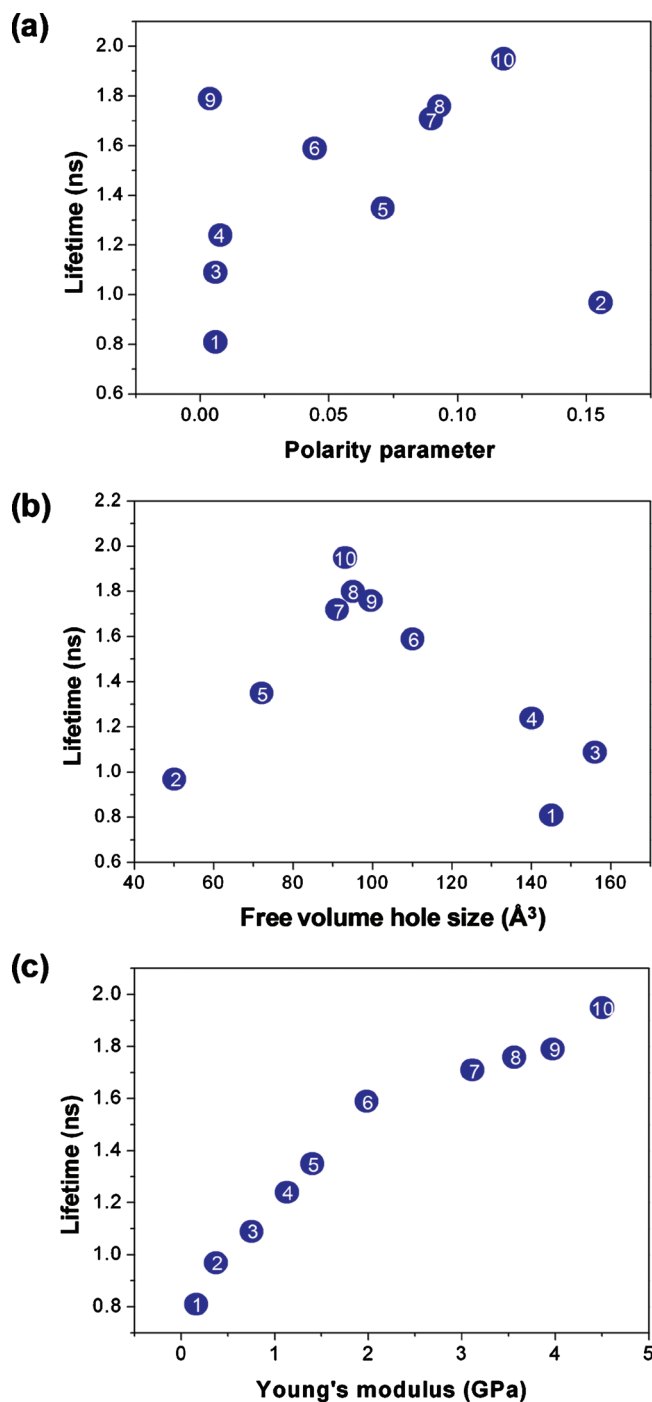


FIG. 9. The average lifetime of 4-DASPI as a function of the polarity parameter (a), free volume hole size (b), and Young's modulus (c). Ten polymers were numerically tagged in Table I.

$$\langle \tau \rangle = \frac{1}{k_r + k_{ir}}. \quad (15)$$

In analogy of viscosity, k_{ir} is related to Young's modulus (E),

$$k_{ir} = \alpha E^{-\beta}. \quad (16)$$

It implies that the molecular rotor can be used as a photomechanical sensor because Young's modulus of a material can be simply obtained by measuring the fluorescence lifetime. In Fig. 10, the k_{ir} was plotted as a function of E . The fit gives the α and β values of 0.66 (ns⁻¹) and 0.32, respectively.

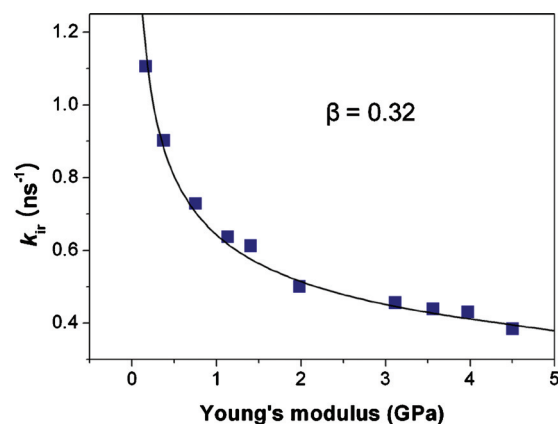


FIG. 10. Dependence of the internal rotation rate constant of 4-DASPI on Young's modulus of polymer.

Recently, the twisting motion of 4-DASPI in blends of PS and ultralow density polyethylene was investigated in our laboratory.⁷⁸ Strong dependence of 4-DASPI dynamics on the elastic modulus was observed with the α and β values of 0.56 (ns⁻¹) and 0.39, respectively. Although two experiments were carried out in different polymer environments, the α and β values were qualitatively similar.

C. Internal motion in viscoelastic media

Our work on the excited-state rotamerism processes of 4-DASPI were independently investigated in liquids and in solids. The water-glycerol mixtures and various polymers were used to provide liquid and solid media. The twisting dynamics were correlated with the viscosity in liquids and to the elastic modulus in solids. Viscosity is a quantitative measure of medium fluidity and Young's modulus is that of medium stiffness. One interesting observation is that the average lifetime of 4-DASPI in LDPE is shorter than in glycerol. The average lifetime of 4-DASPI was obtained as 1.05 ns in glycerol and 0.81 ns in LDPE. It is not understood well at this point, but may be due to the difference in the excited-state potential surfaces and associated dynamics. In our data, the heterogeneity parameter β in solids is much smaller than that in liquids, reflecting the higher inhomogeneous nature of polymer environments.

A particle motion in viscoelastic media is describable by the generalized Langevin equation.⁷⁹ For a viscoelastic polymer, the complex modulus accommodates both viscous and elastic properties, consisting of the energy storage and loss parts,

$$G^* = G' + iG'', \quad \text{with } |G^*| = \sqrt{(G')^2 + (G'')^2}, \quad (17)$$

where G' and G'' are elastic and viscous moduli, respectively. The loss tangent is given by $\tan \delta = G''/G'$, where δ is the phase angle. The complex viscosity is defined by

$$\begin{aligned} \eta^* &= G^*/i\omega = G'/i\omega + iG''/i\omega = (G''/\omega) - i(G'/\omega) \\ &= \eta' - i\eta'', \end{aligned} \quad (18)$$

in which the dynamic viscosity (η') is related to the loss modulus (G''), not to the storage modulus (G'). That is, the energy is dissipated through η' and G'' , while it is stored

through η' and G' . It means that, in the viscoelastic response, elastic modulus is not a mirror image of dynamic viscosity, and vice versa. In this work, the fluorescence lifetime was only related to the storage (elastic) modulus because it was experimentally measured quantity. However, the twisting motion is coupled to both of storage and loss moduli. Thus, the loss modulus may also be included to explain the explicit mode coupling between the isomerizing coordinate and medium deformation. The loss modulus governs liquid and starts to decrease as the phase becomes solid. On the other hand, the storage modulus governs solid and start to decrease as the phase becomes liquid. The gel point is the crossover region in the phase where the loss and storage moduli are the same. Future work around the crossover point should be interesting and will give an insight into molecular rotor dynamics in soft matter.

IV. CONCLUSION

As an endeavor to understand molecular rotor dynamics in viscoelastic media, the excited-state dynamics of 4-DASPI were investigated in water-glycerol mixtures and ten different polymers covering LDPE, PVA, HDPE, UHMWPE, PVC, PC, nylon 6, PMMA, PS, and PAA. It was observed that the internal twisting processes of 4-DASPI correlate strongly with the mechanical properties of viscoelastic media. Based on stochastic dynamics, we attempted to delineate the internal motion of electronically excited 4-DASPI in terms of complex viscosity and modulus.

ACKNOWLEDGMENTS

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Grant No. 2010-0541-1).

- ¹K. Dahl, R. Biswas, and M. Maroncelli, *J. Phys. Chem. B* **107**, 7838 (2003).
- ²B. D. Allen, A. C. Benniston, A. Harriman, S. A. Rostron, and C. Yu, *Phys. Chem. Chem. Phys.* **7**, 3035 (2005).
- ³C. J. Wohl and D. Kuciauskas, *J. Phys. Chem.* **109**, 21893 (2005).
- ⁴K. S. Mali, G. B. Dutt, and T. Mukherjee, *J. Chem. Phys.* **128**, 124515 (2008).
- ⁵M. K. Kuimova, G. Yahioglu, J. A. Levitt, and K. Suhling, *J. Am. Chem. Soc.* **130**, 6672 (2008).
- ⁶R. S. H. Liu and G. S. Hammond, *Proc. Natl. Acad. Sci. U.S.A.* **97**, 11153 (2000).
- ⁷C. J. Ellison and J. M. Torkelson, *J. Polym. Sci., Part B: Polym. Phys.* **40**, 2745 (2002).
- ⁸R. A. Evans, T. L. Hanley, M. A. Skidmore, T. P. Davis, G. K. Such, L. H. Yee, G. E. Ball, and D. A. Lewis, *Nature Mater.* **4**, 249 (2005).
- ⁹A. Y. Jee, S. Park, H. Kwon, and M. Lee, *Chem. Phys. Lett.* **477**, 112 (2009).
- ¹⁰A. Y. Jee, H. Kwon, and M. Lee, *J. Chem. Phys.* **131**, 171104 (2009).
- ¹¹H. Gormer and H. Gruen, *J. Photochem.* **28**, 328 (1985).
- ¹²P. Fromherz and A. Heilemann, *J. Phys. Chem.* **96**, 6864 (1992).
- ¹³B. Strehmel, H. Seifert, and W. Rettig, *J. Phys. Chem. B* **101**, 2232 (1997).
- ¹⁴X. Cao, R. W. Tolbert, J. L. McHale, and W. D. Edwards, *J. Phys. Chem. A* **102**, 2739 (1998).
- ¹⁵J. Kim and M. Lee, *J. Phys. Chem. A* **103**, 3378 (1999).
- ¹⁶J. Kim, M. Lee, J. H. Yang, and J. H. Choy, *J. Phys. Chem. A* **104**, 1388 (2000).
- ¹⁷Z. S. Pillai, P. K. Sudeep, and K. G. Thomas, *Res. Chem. Intermed.* **29**, 293 (2003).
- ¹⁸J. Kabatc, B. Osmialowski, and J. Paczkowski, *Spectrochim. Acta, Part A* **63**, 524 (2006).
- ¹⁹T. Shim, M. Lee, S. Kim, J. Sung, B. K. Rhee, D. Kim, H. Kim, and K. B. Yoon, *Mater. Sci. Eng., C* **24**, 83 (2004).
- ²⁰T. Shim, M. H. Lee, D. Kim, and Y. Ouchi, *J. Phys. Chem. B* **112**, 1906 (2008).
- ²¹M. Grabolle, M. Spieles, V. Lesnyak, N. Gaponik, A. Eychmuller, and U. Resch-Genger, *Anal. Chem.* **81**, 6285 (2009).
- ²²K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishi, and S. Tobita, *Phys. Chem. Chem. Phys.* **11**, 9850 (2009).
- ²³R. F. Kubin and A. N. Fletcher, *J. Lumin.* **27**, 455 (1983).
- ²⁴Y.-P. Zhao, L.-Y. Yang, C. J. Simmons, and R. S. H. Liu, *Chem. Asian J.* **4**, 754 (2009).
- ²⁵S. J. Strickler and R. A. Berg, *J. Chem. Phys.* **37**, 814 (1962).
- ²⁶T. Förster and G. Hoffmann, *Z. Phys. Chem.* **75**, 63 (1971).
- ²⁷See, for example, *New Trends in Kramers' Reaction Rate Theory*, edited by P. Talkner and P. Hanggi (Kluwer Academic, London, 1995).
- ²⁸H. A. Kramers, *Physica (Amsterdam)* **7**, 284 (1940).
- ²⁹G. Jas, W. A. Eaton, and J. Hofrichter, *J. Phys. Chem. B* **105**, 261 (2001).
- ³⁰K. L. Litvinenko, N. M. Webber, and S. R. Meech, *J. Phys. Chem. A* **107**, 2616 (2003).
- ³¹D. A. Harris, M. B. Orozco, and R. J. Sension, *J. Phys. Chem. A* **110**, 9325 (2006).
- ³²V. I. Stsiapura, A. A. Maskevich, V. A. Kuzmitsky, V. N. Uversky, I. M. Kuznetsova, and K. K. Turoverov, *J. Phys. Chem. B* **112**, 15893 (2008).
- ³³R. R. Cheng, T. Uzawa, K. W. Plaxco, and D. E. Makarov, *J. Phys. Chem. B* **113**, 14026 (2009).
- ³⁴A. Rei, G. Hungerford, and M. I. C. Ferreira, *J. Phys. Chem. B* **112**, 8832 (2008).
- ³⁵R. Biswas and B. Bagchi, *J. Chem. Phys.* **105**, 7543 (1996).
- ³⁶D. K. Klimov and D. Thirumalai, *Phys. Rev. Lett.* **79**, 317 (1997).
- ³⁷P. Zhou, P. Song, J. Liu, K. Han, and G. He, *Phys. Chem. Chem. Phys.* **11**, 9440 (2009).
- ³⁸P. S. Hubbard, *Phys. Rev.* **131**, 1155 (1963).
- ³⁹M. Lee, A. J. Bain, P. J. McCarthy, C. H. Han, J. N. Haseltine, A. B. Smith, and R. M. Hochstrasser, *J. Chem. Phys.* **85**, 4341 (1986).
- ⁴⁰K. L. Wiemers and J. F. Kauffman, *J. Phys. Chem. A* **105**, 823 (2001).
- ⁴¹S. Takeuchi, S. Ruhman, T. Tsuneda, M. Chiba, T. Taketsugu, and T. Tahara, *Science* **322**, 1073 (2008).
- ⁴²R. F. Grote and J. T. Hynes, *J. Chem. Phys.* **73**, 2715 (1980).
- ⁴³B. Bagchi and G. R. Fleming, *J. Phys. Chem.* **94**, 9 (1990).
- ⁴⁴R. A. Denny and B. Bagchi, *J. Phys. Chem. A* **103**, 9061 (1999).
- ⁴⁵T. Pradhan, H. A. R. Gazi, and R. Ramadass, *J. Chem. Phys.* **131**, 054507 (2009).
- ⁴⁶G. Srinivas, A. Mukherjee, and B. Bagchi, *J. Chem. Phys.* **114**, 6220 (2001).
- ⁴⁷B. Bagchi, G. R. Fleming, and D. W. Oxtoby, *J. Chem. Phys.* **78**, 7375 (1983).
- ⁴⁸J. L. Alvarez, A. Yartsev, U. Aberg, E. Akesson, and V. Sundstrom, *J. Phys. Chem. B* **102**, 7651 (1998).
- ⁴⁹R. S. Hartman and D. H. Waldeck, *J. Phys. Chem.* **98**, 1386 (1994).
- ⁵⁰M. L. Horng, J. A. Gardecki, and M. Maroncelli, *J. Phys. Chem. A* **101**, 1030 (1997).
- ⁵¹P. V. Kumar and M. Maroncelli, *J. Chem. Phys.* **112**, 5370 (2000).
- ⁵²G. B. Dutt and T. K. Ghanty, *J. Chem. Phys.* **116**, 6687 (2002).
- ⁵³B. R. Gayathri, J. R. Mannekutla, and S. R. Inamdar, *J. Fluoresc.* **18**, 943 (2008).
- ⁵⁴M. Lee, J. N. Haseltine, A. B. Smith III, and R. M. Hochstrasser, *J. Am. Chem. Soc.* **111**, 5044 (1989).
- ⁵⁵D. C. Todd and G. R. Fleming, *J. Chem. Phys.* **98**, 269 (1993).
- ⁵⁶W. Heller, *J. Phys. Chem.* **69**, 1123 (1965).
- ⁵⁷T. Pradhan, P. Ghoshal, and R. Ramadass, *J. Phys. Chem. A* **112**, 915 (2008).
- ⁵⁸R. S. H. Liu and G. S. Hammond, *Acc. Chem. Res.* **38**, 396 (2005).
- ⁵⁹E. M. Kosower, *J. Am. Chem. Soc.* **80**, 3253 (1958).
- ⁶⁰K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.* **661**, 1 (1963).
- ⁶¹M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.* **98**, 377 (1976).
- ⁶²J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 3rd ed. (Springer, New York, 2006).
- ⁶³M. S. Paley, R. A. McGill, S. C. Howard, S. E. Wallace, and J. M. Harris, *Macromolecules* **23**, 4557 (1990).
- ⁶⁴S. Spange, E. Vilsmeier, K. Fisher, R. S. Prause, Y. Zimmermann, and C.

- Schmidt, *Macromol. Rapid Commun.* **21**, 643 (2000).
- ⁶⁵ Q. Shen, D. Mu, L. W. Yu, and L. Chen, *J. Colloid Interface Sci.* **275**, 30 (2004).
- ⁶⁶ B. Szczupak, A. G. Ryder, D. M. Denisio, Y. A. Rochev, A. V. Gorelov, and T. J. Glynn, *Appl. Spectrosc.* **63**, 442 (2009).
- ⁶⁷ Y. Hou, A. M. Bardo, C. Martinez, and D. A. Higgins, *J. Phys. Chem. B* **104**, 212 (2000).
- ⁶⁸ A. Hattori, H. Sato, and M. Vacha, *Chem. Phys. Lett.* **435**, 311 (2007).
- ⁶⁹ J. E. Mark, *Polymer Data Handbook*, 2nd ed. (Oxford University Press, London, 2009).
- ⁷⁰ M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.* **77**, 3701 (1955).
- ⁷¹ J. C. Jansen, M. Macchione, E. Tocci, L. Lorenzo, Y. P. Yampolskii, O. Sanfirova, V. P. Shantarovich, M. Heuchel, D. Hofmann, and E. Drioli, *Macromolecules* **42**, 7589 (2009).
- ⁷² D. Wöll, E. Braeken, A. Deres, F. C. De Schryver, H. Uji-i, and J. Hofkens, *Chem. Soc. Rev.* **38**, 313 (2009).
- ⁷³ C.-Y. J. Wei and D. A. Vanden Bout, *J. Phys. Chem. B* **113**, 2253 (2009).
- ⁷⁴ P. M. Budd, N. B. McKeown, and D. Fritsch, *J. Mater. Chem.* **15**, 1977 (2005).
- ⁷⁵ K. S. Vinodh, B. Ghadei, S. K. Chaudhuri, J. B. M. Krishna, D. Das, and A. Saha, *Radiat. Phys. Chem.* **77**, 751 (2008); C. M. Paranhos, B. G. Soares, J. C. Machado, D. Windmoller, and L. A. Pessan, *Eur. Polym. J.* **43**, 4882 (2007); G. Dlubek, J. Stejny, T. H. Lupke, D. Bamford, K. Petters, C. K. Hubner, M. A. Alam, and M. J. Hill, *J. Polym. Sci., Part B: Polym. Phys.* **40**, 65 (2002); M. A. Monge, J. A. Diaz, and R. Pareja, *Macromolecules* **37**, 7223 (2004); G. N. Kumaraswamy and C. Ranganathaiah, *Polym. Eng. Sci.* **46**, 1231 (2006); A. P. Richard, *Prog. Polym. Sci.* **22**, 1 (1997); R. Kumar and R. Prasad, *Nucl. Instrum. Methods Phys. Res. B* **256**, 238 (2007); C. M. Huang, E. W. Hellmuth, and Y. C. Jean, *J. Phys. Chem. B* **102**, 2474 (1998); E. Gomaa, *Physica B* **390**, 203 (2007).
- ⁷⁶ A. Y. Jee, E. Bae, and M. Lee, *J. Phys. Chem. B* **113**, 16508 (2009).
- ⁷⁷ A. Y. Jee and M. Lee, *Polym. Test.* **29**, 95 (2010).
- ⁷⁸ A.-Y. Jee and M. Lee, *ChemPhysChem* **11**, 793 (2010).
- ⁷⁹ T. G. Mason and D. A. Weitz, *Phys. Rev. Lett.* **74**, 1250 (1995).