7730 *Macromolecules* **2007,** *40,* 7730−7732

Application of Molecular Rotors to the Determination of the Molecular Weight Dependence of Viscosity in Polymer Melts

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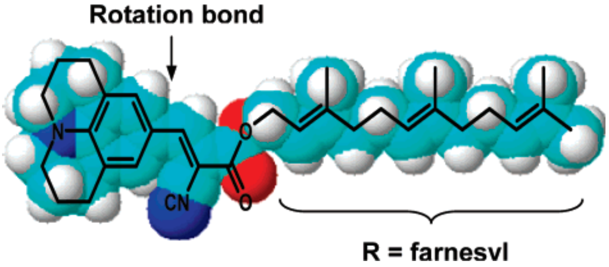
Received January 26, 2007
Revised Manuscript Received May 19, 2007

The molecular dynamics of polymers have been studied through measurements of such properties as (tracer) diffusivity (D) and (zero-shear) viscosity (η) in relation to the number-average molecular weight (M) of the polymer. These measurements can be compared with established theories, for example, the Rouse or reptation model for the cases involving polymer melts. Although numerous techniques are available for direct molecular-level measurements of the diffusivities in polymers, the viscosities of polymers have been measured exclusively using bulk measurements techniques with the most common method being the use of a conventional viscometer or rheometer. In this report, we demonstrate for the first time that fluorescent molecular rotors, farnesyl-(2-carboxy-2-cyanovinyl)-julolidine (FCVJ), can be used as an active probe for precise determination of the M dependence of η and the entanglement molecular weight of a polymer by using a molecular weight series of poly(propylene oxide) (PPOX) as model polymers. Our results are consistent with previous measurements and also with theories. There are a couple of key distinguishing features of using the fluorescent molecular rotor to probe the M-dependent η behavior for a polymer-based fluid. First, the quantum yield (i.e., the ratio of the number emitted photons to that of absorbed photons) of FCVJ is dependent strongly on the local free volume of the medium; therefore, this technique allows measurement of the microviscosity of the medium surrounding the rotor probe. Also, unlike the conventional method of measuring η using a viscometer or rheometer, the FCVJ-based η measurement does not require any external mechanical perturbation.

Scheme 1. Chemical Structure of Farnesyl-(2-carboxy-2-cyanovinyl)-julolidine (FCVJ)[a]



[a] The arrow indicates the julolidine−carboxy bond around which the nonradiative energy relaxation occurs via torsional rotation.

The term "molecular rotor" has been frequently referred to a group of intramolecular charge-transfer complexes that undergo nonradiative relaxation from the fluorescent excited state through intramolecular rotation.[1] In the excited singlet state of the molecule, the energy can be released either by fluorescence emission or by intramolecular rotation around a specific unit, which relaxes the molecule back to its ground state. For example, in FCVJ, this rotation occurs around the bond between the carboxy and cyanovinyl groups (as shown with an arrow in Scheme 1). With the two feasible mechanisms for energy relaxation, the quantum yield (Φ) can be given in terms of the intrinsic radiative rate (k_f) and the nonradiative (rotational) rate (k_{nr}) as $\Phi = k_f/(k_f + k_{nr})$; in general, k_{nr} is much greater than k_f,[1] and therefore $\Phi \approx k_f/k_{nr}$. For molecular rotors, k_{nr} is dominated by a torsional motion. Therefore, in a highly viscous medium, the relatively small free volume (V_f) in the matrix will restrict the intramolecular rotation, and the rotor will have a small k_{nr} and a large Φ. The relationship between k_{nr} and V_f can be typically expressed as $k_{nr} = k_{nr}^0 \exp[-x(V_0/V_f)]$, where k_{nr}^0 is the intrinsic rate in the zero-V_0 limit,[2] V_0 denotes the van der Waals volume of the solvent molecule, and x is a parameter that depends on the rotor chemistry.[3] Substituting the this relationship into the above equation for Φ yields $\Phi = (k_f/k_{nr}^0) \exp[-x(V_0/V_f)]$. Using the relation $\eta = \eta_0 \exp(V_0/V_f)$, the equation for Φ can be further simplified into an expression known as the Förster−Hoffmann expression[4]

$$\log \Phi = C + x \log \eta \tag{1}$$

where C is a system-dependent constant. Note here that log Φ is linearly proportional to log η.

The use of this equation as the basis for interpreting data from molecular rotor-based measurements has been demonstrated in the studies of actin polymerization,[5] tubulin assembly,[6] phospholipid microviscosity,[7] and polymerization reaction.[8] In this report, we for the first time demonstrate the utility of this approach in quantitatively evaluating the molecular weight dependence of viscosity in polymer melts. In the above-mentioned prior studies, the molecular rotor used was 9-(dicyanovinyl)-julolidine (DCVJ). In the present work, we use a more hydrophobic rotor, FCVJ, which contains a farnesyl segment that is covalently attached to the fluorescent DCVJ moiety and is therefore expected to be more compatible with the hydrophobic core of lipid bilayers[9] and with many hydrocarbon-based polymers. Prior studies indicate that FCVJ is more photostable and has a greater sensitivity for η measurements than other rotors.[9]

Previously, the relaxation behavior of FCVJ in mixtures of glycerol and ethylene glycol has been shown to be describable using the Förster−Hoffmann relation.[9] To demonstrate the feasibility of using FCVJ for studying a wider range of materials, we measured the fluorescent intensities for FCVJ in different alcohols ($CH_3(CH_2)_nOH$) ranging from methanol to pentanol and also a series of monodisperse PPOX with varying molecular weights; the number-average molecular weights (M_n) of the polymers are 425, 725, 1000, 2000, 2700, 3000, 3500, and 4000 g/mol (according to the supplier's information), and their polydispersity indices (PDI) are 1.07, 1.00, 1.01, 1.03, 1.04, 1.05, 1.08, and 1.17, respectively, to the molecular weight values, as determined by size exclusion chromatography (SEC). All alcohols and polymers were purchased from Sigma (Saint

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10.1021/ma0702288 CCC: $37.00

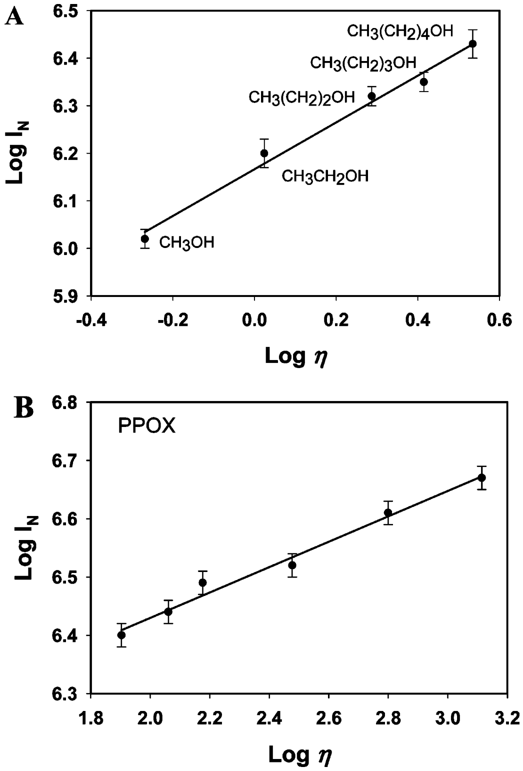

Figure 1. Plots of log I_N vs log η. Here, I_N denotes the normalized intensity of FCVJ dissolved in a matrix of (A) alcohols of varying alkyl chain length (from methanol to pentanol) and (B) poly(propylene oxide) (PPOX) with varying M_n's (425, 725, 1000, 2000, 2700, and 3500 g/mol). The η data shown in the plots (in units of cP) were provided from the vendors. In both cases, the log I_N vs log η plots are well described by the Förster−Hoffmann relation. Linear fitting gives log $I_N = 6.166 + 0.4910$ log η for FCVJ in alcohol and log $I_N = 5.994 + 0.2179$ log η for PPOX.

Louis, MO), except for two of the polymers (with $M_n = 3000$ and 4000 g/mol) which were purchased from Alfa Aesar (Ward Hill, MA). SEC measurements were performed on a Waters Breeze HPLC system equipped with two Phenogel columns of 0.4 and 0.05 μm pore sizes using tetrahydrofuran (THF) as solvent (1 mL/min, 30 °C), and the PDI values were calculated using a molecular weight calibration based on polystyrene standards. The peak fluorescence intensity (I_p) at emission wavelengths between 480 and 500 nm and the absorbance (I_{abs}) at 435−445 nm were measured from FCVJ dissolved at a concentration of 30 μg/mL in alcohol or PPOX using a spectrofluorometer (Spex Fluoromax-3, Jobin-Yvon, Stanmore, UK) and a spectrophotometer (Beckman DU520 UV/vis spectrophotometer, Fullerton, CA), respectively. The normalized intensity, I_N ($\propto\Phi$), was calculated as the ratio of I_p to I_{abs}, and this eliminates a possible error associated with variations in the FCVJ concentration among samples. The measured values of log I_N are linearly related to log η for FCVJ in alcohol or PPOX (Figure 1 A,B), as predicted by eq 1.

The Förster−Hoffmann relation can readily be converted into an equation for describing the relationship between I_N and M, using the established scaling laws for the M dependence of η in polymer melts. The single chain dynamics of polymers in melts is well understood within the framework of either the Rouse model or the reptation model.[10−13] In the Rouse picture which is most relevant to low molecular weight (i.e., unentangled) polymer melts,[14] the intrachain excluded volume interactions and the hydrodynamic coupling between monomers within the chain are effectively screened by the corresponding effects of interchain origin. The mathematical consequence is

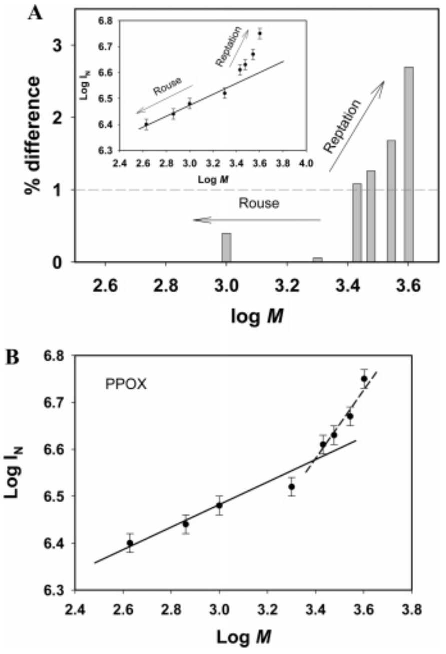

Figure 2. Determination of the critical molecular weight (M_c) for entanglement effect in η on the basis of the Förster−Hoffmann correlation. (A) The log I_N data points for the two lowest molecular weight PPOX (425 and 725 g/mol) were fit with eq 4 to obtain a straight line, and the resulting fit is compared with data points at other molecular weights (inset). Also shown is a plot of the percentage difference between the predicted values of log I_N by the straight line and the measured log I_N values, given as a function of log M. The data points which deviate by more than 1% from the straight line were considered to be in the entangled entangled regime. (B) A plot of log I_N vs log M. The measured log I_N vs log η profile was fit in two parts, i.e., M_n = 425−2000 g/mol (corresponding to the Rouse regime) and M_n = 2700−4000 g/mol (the entangled regime). The fit results are log $I_N = 5.778 + 0.2351$ log M and log $I_N = 3.855 + 0.7996$ log M for unentangled and entangled PPOX, respectively. The two lines cross each other at log $M = 3.406$.

that $\eta_{Rouse} \propto \langle R_G^2\rangle$, where $\langle R_G^2\rangle$ is the mean-square radius of gyration of the chain in the unperturbed (i.e., Gaussina) state.[15] Combining this result with the Gaussian scaling (i.e., $\langle R_G^2\rangle \propto M$)[16] yields

$$\eta_{Rouse} \propto M \tag{2}$$

For entangled (high molecular weight) polymers, the motion of a chain is further restricted by the presence of the topological constraints caused by chain entanglements, and the reptative motion becomes the dominant mode of relaxation. In a simplistic picture that ignores the dynamic nature of the entanglement constraint itself, the stress relaxation due to the curvilinear motion of a polymer along its contour is characterized by the scaling:[14]

$$\eta_{rep} \propto M^3 \tag{3}$$

Now combining eqs 1−3 gives

$$\log I_N \propto X' \log M \tag{4}$$

where the value of X' will depend on where the system is in the Rouse regime or in the reptation regime. To identify the molecular weight at which the entanglement transition occurs in PPOX, the log I_N vs log M plot was fit with a straight line. From this analysis, we estimated the Rouse regime to lie in the M range less than or equal to 2000 g/mol; this regime was characterized by a single optimal value of X' which gives an accurate fit of the corresponding set of data to within 1% precision (see the inset of Figure 2). Accordingly, the other regime of behavior observed in the M range between 2700 and 4000 g/mol is believed to correspond to that of reptation. In order to quantitatively determine the critical molecular weight for entanglement, M_c, the log I_N vs log M data in each regime were fit with eq 4 (the fitting results are shown in Figure 2B), and we obtained the linear relations $\log I_N = 5.778 + 0.2351 \log M$ for the low molecular weight PPOX melts and $\log I_N = 3.855 + 0.7996 \log M$ for the entangled regime. These two lines intersect at $\log M = 3.406$, which gives $M_c = 2547$ g/mol. It is known that viscometry gives an M_c value that is typically 2−3 times larger than the entanglement molecular weight (M_e) estimated from the rubbery plateau modulus; i.e., $M_c \approx (2-3)M_e$.[17] It is interesting to note that the resulting value of M_c (2547 g/mol) is much less than the previously reported value of $M_c \approx 6000-7000$ g/mol,[18,19] but it is instead in a much better agreement with the entanglement molecular weight of PPOX.[16] We suspect that this discrepancy reflects the fundamental difference between the molecular level and macroscopic measurements, the exact nature of which deserves further investigation.

As can be seen from eqs 1, 2, and 4, the ratio of the value of X' (estimated with Figure 2B) to the value of x (Figure 1B) is expected to be unity for unentangled PPOX melts whose behavior follows the Rouse scaling law. This ratio is indeed close to one (i.e., $X'/x = 1.08$), confirming the Rouse-like behavior of the PPOX melts in the low molar mass limit. Similarly, we find $X'/x = 3.40$ for the entangled PPOX melts, indicating the scaling relation $\eta \propto M^{3.40}$; this result is in excellent agreement with the known behavior $\eta \propto M^{3.4\pm0.2}$ universally observed from a wide range of polymers.[13,17,20,21]

In summary, our work demonstrates the feasibility of using a fluorescent molecular rotor, farnesyl-(2-carboxy-2-cyanovinyl)-julolidine (FCVJ), for the studies of polymer melt dynamics. Since this technique probes the local free volume of the medium surrounding the rotor molecule, we believe this method to be a useful adjunct to traditional bulk η measurement techniques for polymers. By way of example, FCVJ has been used to determine the molecular weight (M) dependence of the viscosity (η) in poly(propylene oxide) (PPOX) melts in a range of molecular weights covering the Rouse and entangled reptation regimes. On the low molecular weight side (i.e., $M_n = 425-2000$ g/mol), we found a scaling behavior consistent with the Rouse model (i.e., $\eta \propto M$). Higher molecular weight PPOX ($M_n = 2700-4000$ g/mol) exhibited the scaling behavior typical of entangled polymer liquids (i.e., $\eta \propto M^{3.4}$). The crossover between these two regimes occurred at a molecular weight of $M_c = 2547$ g/mol, which is significantly less than the reported value of $M_c = 6000-7000$ g/mol for the critical molecular weight for entanglement for PPOX determined by conventional viscometry but is instead in good agreement with the entanglement molecular weight of PPOX ($M_e = 2832$ g/mol) determined on the basis of rheometric plateau modulus measurements.

Acknowledgment. We thank Darcy J. Lichlyter for her help with the spectrofluorometer and spectrophotometer measurements. NIH as well as MU Bioprocessing & Biosensing Center supported this work. J.S.L. gratefully acknowledges the fellowship provided by the Korean Research Foundation of the Korean Government (MOEHRD) (KRF-2005-214-D00271).

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MA0702288