J. Phys. Chem. A **1998,** *102,* 5451−5455

Solvent Dependence of the Hydrodynamical Volume of Dendrimers with a Rubicene Core

S. De Backer,[†] Y. Prinzie,[†] W. Verheijen,[†] M. Smet,[‡] K. Desmedt,[‡] W. Dehaen,[‡] and F. C. De Schryver*,[†]

Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200 F, 3001 Leuven (Heverlee), Belgium

Received: October 23, 1997; In Final Form: January 7, 1998

Four generations of a dendrimer with a fluorescent core consisting of a rubicene moiety are synthesized. The biexponential nature of fluorescence decay in toluene indicates the presence of two emitting conformations. Molecular modeling suggests that a conformation where the dendrons interact with the core is not improbable. The relative weight of the two decay times indicates that the contribution of that conformation in toluene increases as the dendrimer generation increases. In acetone and acetonitrile however the fluorescence decay is, except for the fourth generation, monoexponential. The hydrodynamical volume of the dendrimer is determined in toluene, a good solvent, acetone, a medium quality solvent, and acetonitrile, a poor solvent, with the time-resolved fluorescence depolarization technique. No change of the hydrodynamical volume is found in toluene in a temperature range between 20 and 94 °C. This suggests that the dendrimers of all the generations are fully expanded in this solvent. In acetonitrile however the hydrodynamical volume of the dendrimers is substantially smaller than in toluene and acetone. This effect is most clear for the fourth-generation dendrimer. For this compound the hydrodynamical volume is only a few percentages larger than the excluded volume.

1. Introduction

Dendrimers[1−5] are highly branched, monodisperse macromolecules formed by reiterative reaction sequences. The number of branching points between the periphery and the central core corresponds with the generation number of the dendrimer. To engineer the desired properties of such a macromolecule, it is crucial to know fundamental properties such as dimensions, the internal density profile, and the influence of temperature and solvent quality on these parameters. The first attempt to understand this relation theoretically dates from 1983,[6] resulting in a rather simple picture of a dendrimer where the monomers of the consecutive generations lie in concentric layers around the core. In 1990 Lescanec and Muthukumar[7] proposed a quite different picture with the possibility of backfolding of the dendrons. Despite an important number of recent studies[8−11] published, the controversy is still not completely solved.

To the best of our knowledge no experimental data concerning the influence of the solvent on the hydrodynamical volume of dendrimers are available in the literature. By means of the intrinsic viscosity the dimensions of the dendrimers can be estimated.[13] Inherent to this technique, this can only be done in good solvents. As a consequence of the high sensitivity of fluorescence techniques, fluorescence depolarization or fluorescence anisotropy is a good alternative for the determination of the hydrodynamical volume in solvents in which the dendrimers poorly dissolve. The study of the anisotropy decay of the fluorophore allows measuring the rotational dynamics, i.e. the rotational correlation time, ϕ, of the dendrimer. From this rotational correlation time the hydrodynamical volume (V_h) can be calculated using the Stokes−Einstein−Debye relation (SED).

$$\phi = \frac{V_h \eta}{kT} \tag{1}$$

with η the viscosity of the solvent, k the Boltzmann constant, and T the absolute temperature. Small and neutral solutes tend to rotate faster than predicted by eq 1.[14,31] The effect is explained on the basis of kinetic models[15,16] or by models taking into account the molecularity[17,18] of the solvent. This failure of eq 1 is most pronounced when the volume of the molecules of the solvent and the solute are of the same magnitude. Since the excluded volume of even the smallest generations of the dendrimers is at least 10−100 times larger than the volume of the solvent, a good correlation with continuum-based models assuming sticking boundary conditions is expected.[19] The shape of the rotor is only of importance in the case of very flat or elongated solutes.[20]

Dendrimers are often seen as unimolecular micelles.[21] In analogy, in most of the photophysical studies published up to now, a fluorophore is added to electrostatically,[22−24] hydrophobically,[25] or sterically[26] interact with the dendrimer. Another approach is to bind the dendrons covalently and symmetrically to a single fluorophore. In this particular report a rubicene derivative as a core is covalently linked to the dendrons (Figure 1).

2. Materials and Methods

Materials. 5,12-Dihydroxyrubicene was synthesized starting from 1,5-dichloroanthraquinone and 4-methoxyphenyllithium, following a general procedure for disubstituted rubicenes that was recently found in our group.[27] The Fréchet benzyl bromides of the second and third generation were prepared following either the usual method[28] or our improved procedure[29] for a

---

* To whom correspondence should be addressed.

[†] Laboratory for Molecular Dynamics and Spectroscopy.

[‡] Laboratory for Organic Synthesis.

S1089-5639(97)03433-6 CCC: $15.00

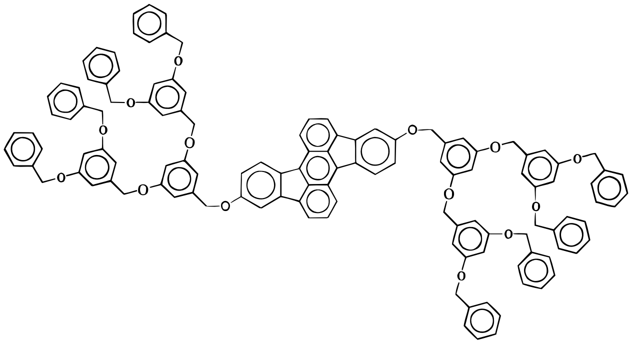


Figure 1. Molecular structure of a dendrimer of the second generation with a rubicene in the core, Rb_2.

fourth-generation dendron. Connection of these dendrons to the core reagent was done in the usual way, affording the dendrimers in good yield (50% for Rb_1 to 20% for Rb_4). Although the core reagent is insoluble in all organic solvents, the reaction proceeds smoothly and the resulting products are well-soluble in solvents such as dichloromethane and chloroform. The compounds were purified by column chromatography over silica gel with dichloromethane as the eluent. The dendrimers were fully characterized by ^1H and ^{13}C NMR spectroscopies. The spectra were relatively simple because of the symmetry of the compounds. No impurities or defective dendrimers could be detected in the NMR spectra, and the integration of the rubicene and dendron signals (^1H NMR) gives exactly the expected ratio. An upfield shift of 0.3 ppm is observed for the protons on the rubicene core as the generation increases from the first to the fourth.

Instrumentation. The absorption spectra are measured at 20 ± 1 °C with a Perkin-Elmer Lambda 6 UV−visible spectrophotometer. Steady-state fluorescence spectra are measured with an SLM-8000C spectrofluorimeter in L-format. The polarized emission decays are obtained by the single-photon-timing technique. The compounds are excited at 550 nm using the output of a pyrromethene (Exciton) dye laser, pumped by a beam-locked argon ion laser at 514 nm. Erythrosine in methanol ($\tau = 0.5$ ns) and in butanol ($\tau = 0.8$ ns) is used as reference compound. The repetition frequency of the excitation pulses is 800 KHz. All the decay traces are collected in 511 channels. The number of counts in the peak channel is around 10^4. The fluorescence photons are detected by a microchannel-plate (Hamamatsu R2809U). The full width at half-maximum of the instrument response function is typically around 50 ps. The solubility is estimated by the absorbance of a saturated solution or of an eventually diluted solution to an absorbance around 0.1. Solutions were filtered (pore size 0.2 μm) to avoid interference of nondissolved particles.

Data Analysis. The fluorescence intensity decays, $i(\theta,t)$ are collected at three different orientations, θ, of the emission polarizer (0°, 54.7°, 90°) and at two time increments (20 and 40 ps/channel). These decays are simultaneously analyzed using a global analysis fitting program[30] according to

$$i(\theta,t) = [\kappa(\theta)/3]\alpha \exp(-t/\tau)[1 + (3\cos^2\theta - 1)\sum_{j=1}^{m}\beta_j \exp(-t/\phi_j)] \qquad (2)$$

where τ represents the fluorescence decay time and ϕ_j the rotational correlation times of the fluorophore. $k(\theta)$ is a matching factor. In a previous report[31] we described the possible linking schemes that can be used.

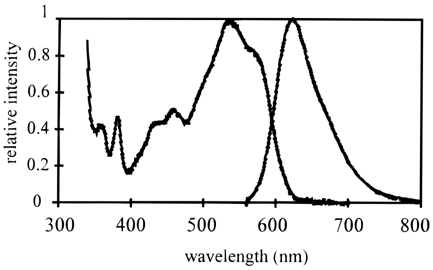


Figure 2. Absorption and emission spectrum of Rb_1 in toluene at room temperature. Excitation is at 550 nm.

The program uses reference convolution, and the reference lifetime, τ_{ref}, is in all cases freely adjustable. The fitting parameters are determined by minimizing the global reduced χ_g^2,

$$\chi_g^2 = \sum_k^q \sum_i w_{ki}(I_{ki}^o - I_{ki}^c)^2/\nu \qquad (3)$$

where the index k sums over q experiments, the index i sums over the appropriate channel limits for each individual experiment, and w_{ki} are the weighting factors. I_{ki}^o and I_{ki}^c denote respectively the observed and calculated values corresponding to the ith channel of the kth experiment. ν represents the number of degrees of freedom for the entire multidimensional fluorescence decay surface. Using $Z_{\chi_g^2}$, the goodness of fits of analyses with different ν can be readily compared:

$$Z_{\chi_g^2} = \sqrt{\frac{\nu}{2}}(\chi_g^2 - 1) \qquad (4)$$

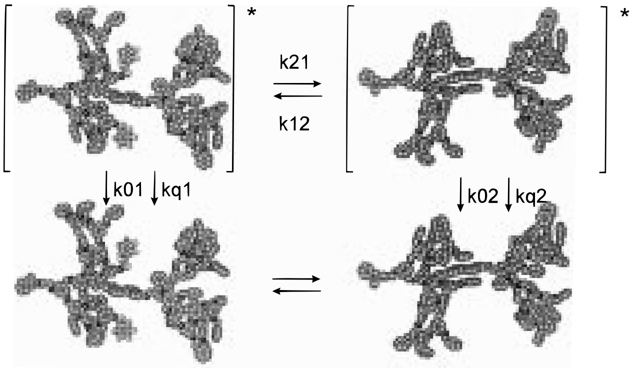
Global fits are considered as good when the values for the local $Z\chi_g^2$ are lower than 3 and the value for the global χ_g^2 is lower than 1.2. Details and performance of the global analysis program were reported previously.[30] All global analyses are performed on an IBM RISC 6150-125 computer.

3. Results and Discussion

Excited-State Properties. The absorption and emission spectra in toluene, shown in Figure 2, are independent of the size of the dendrons. The emission spectra at room temperature are independent of the excitation wavelength.

The quantum yield of fluorescence is 0.14 ± 0.02 at room temperature for all compounds. Photoacoustic measurements indicate that 85% of the energy is dissipated via a thermal path. Single-curve analysis might suggest that a monoexponential model is valid for the fluorescence decay. Global analysis of six experiments (three decays at different angles of the emission polarizer at time increments of 20 and 40 ps) however showed that a biexponential model is more appropriate for the measurements at room temperature in toluene. Fluorescence decays at room temperature in other solvents in which the dendrimers are quite soluble such as chloroform and THF also have to be analyzed according to a biexponential model. However at higher temperature the fluorescence decays in toluene can be fitted to a monoexponential model and the decay times tend to the same value for all generations. The data are shown in Table 1.

A two-conformation model resulting in two different decay times could explain the biexponential model of the fluorescence decay at room temperature. Recently Devadoss[32] et al. found evidence for an increasing amount of charge transfer between



Suggested three-dimensional structures of Rb_4 using a MM+ and an AMBER force field.

Figure 3. Bicompartmental scheme of the two conformations of Rb_4.

TABLE 1: Decay Times and Contributions of the Respective Decay Times (in Parentheses) of Rb_n at Different Temperatures in Toluene $\lambda_{exc} = 550$ nm, $\lambda_{em} = 620$ nm

	Rb_1		Rb_2		Rb_3		Rb_4	
T (°C)	$\tau 1$ (ns)	$\tau 2$ (ns)	$\tau 1$ (ns)	$\tau 2$ (ns)	$\tau 1$ (ns)	$\tau 2$ (ns)	$\tau 1$ (ns)	$\tau 2$ (ns)
21	3.1 (0.86)	1.5 (0.14)	3.1 (0.89)	1.2 (0.11)	3.3 (0.83)	1.7 (0.17)	2.3 (0.58)	4.1 (0.42)
50	2.89		2.91		2.96		2.0 (0.72)	3.3 (0.28)
75	2.87		2.89		2.88			
94	2.77		2.77		2.79		2.83	

the tolan segments and a *p*-dimethoxybenzene moiety at the focal point of the dendrimer as the size of the dendrimer increases. Since the stationary absorption and emission spectra do not depend on the choice of the solvent, we have no evidence for a charge-transfer state. Molecular modeling, however, suggests that interactions between the rubicene-like core and the dendrons are possible (see Figure 3). Further evidence for this interaction can be found in the upfield shift of the H NMR signal of the protons on the rubicene core for the higher generations. To get more insight in some kinetic aspects of the photophysical behavior of the two conformers, fluorescence decays of Rb_4 in acetone at four emission wavelengths and four quencher concentrations are globally analyzed according to a bicompartmental scheme[33] (see Figure 3). The fluorescence decays are recorded at 600, 620, 640, and 660 nm and at quencher concentrations of 0, 0.011, 0.0206, and 0.0301 M. The quencher is *p*-nitrobenzaldehyde. k_{ij} in Figure 3 indicates the rate constants from state j to state i. k_{q1} and k_{q2} correspond to the rate constant for quenching of conformers 1 and 2. To get a unique result k_{01} is kept constant during the analysis at 0.36 ns^{-1}, the reciprocal decay time of Rb_1 in acetone. The recovered values of the rate constants are $k_{21} = 0.042$ ns^{-1}, $k_{q1} = 5.3$ ns^{-1} M^{-1}, $k_{02} = 0.25$ ns^{-1}, $k_{12} = 0.010$ ns^{-1}, and $k_{q2} = 3.2$ ns^{-1} M^{-1}. The global χ^2 is 1.128, and the error on the parameters is less than 10%. The values for k_{12} and k_{21} suggest that the conversion from one conformation to the other is slow compared to the rate constant of fluorescence.

For the lowest generations the concentration of dendrons in the neighborhood of the core is rather small, and therefore the contribution of this interacting conformation is small. For the higher generations, however, the local concentration of dendrons increases and the contribution of interacting conformation increases. A temperature study in toluene showed that at 94 °C the decay can be described by a monoexponential function for all generations. The decay time is identical for all generations at high temperature, suggesting an identical photophysical behavior under these conditions. This suggests that at this temperature only the noninteracting conformation is present. However a fast equilibrium between conformers cannot be excluded.

Rotational Dynamics in Toluene. The anisotropy decays of all generations can be fitted to a single-exponential model, indicating that both conformations have the same rotational characteristics. The values for the calculated parameters do not depend upon the model used in the analysis of the fluorescence decay (mono- or biexponential model).

Table 2 suggests that the β-values decrease as the temperature increases and as the dendrimer grows. From theory[34] one finds that the values for the β-parameter are fully determined by the relative orientation of absorption and emission dipole. Consequently one expects for the same chromophore the same β-value. Deviations from this principle can be explained by very fast motions of the nuclei of the chromophore (librations[35]). These motions are faster at higher temperature, resulting in a decrease of β.

The rotational correlation times increase as the dendrimer becomes larger and decrease as the temperature increases. This is in agreement with what is expected on the basis of eq 1. With this equation the hydrodynamical volume can be calculated from the rotational correlation time assuming sticking boundary conditions. As mentioned in the Introduction, there is no evidence to doubt this assumption. Further arguments for the validity of this assumption are given in the section where the rotational dynamics in acetonitrile are discussed. The results, shown in Table 3, do not indicate a temperature dependence of V_h, indicating that the dendrimer is completely expanded in toluene at room temperature. The hydrodynamical volume for each generation is averaged over the temperature (V_{av}) and used in further calculations. The van der Waals volume is estimated from Edwards increments.[36]

Table 3 shows that V_{VDW} doubles roughly for each generation. The hydrodynamical volume, V_{av}, of the lower generations Rb1 and Rb2 follows this trend, while for the higher generations a saturation effect is observed. The effect is even more clearly observed when the free volume, V_{free} (the difference between V_{VDW} and V_{av}), is estimated.

Since the molecular weight increases faster than the hydrodynamical volume as the dendrimer grows, the density ($\rho = MW/V_hN_A$) of the dendrimer increases. Since the intrinsic viscosity is inversely proportional to the molar density, a similar although inverse plot is observed as reported by Mourey et al.[13] (see Figure 4). The negligible influence of temperature on the hydrodynamical volume indicates that already at room temperature the dendrimers are completely expanded.

Rotational Dynamics in Acetone. The solubility of the dendrimers in acetone is roughly 10−100 times smaller than in toluene. Time resolved data are collected in a similar way as in toluene. The results of global analysis of the data are shown in Table 4.

A monoexponential model is sufficient to describe the fluorescence decay of Rb_1 to Rb_3. For Rb_4 a biexponential model is necessary. The hydrodynamical volume and free volume are calculated in a similar way as in toluene. Despite the lower solubility in acetone compared to toluene, the hydrodynamical volume at room temperature is comparable with the hydrodynamical volume in toluene.

Rotational Dynamics in Acetonitrile (ACN). The solubility of the dendrimers in ACN is roughly 1000−10 000 times smaller than in toluene. Time-resolved data are collected in a similar way as in the other solvents. The results of global analysis of the data are shown in Table 5.

TABLE 2: β-Values and Rotational Correlation Times of Rb_n in Toluene at Different Temperatures

	$\beta_{21°C}$	$\beta_{50°C}$	$\beta_{75°C}$	$\beta_{94°C}$	$\phi_{21°C}$ (ns)	$\phi_{50°C}$ (ns)	$\phi_{75°C}$ (ns)	$\phi_{94°C}$ (ns)	solubility mol/L (21 °C)
η toluene (mPa s)[a]					0.60	0.42	0.33	0.28	
Rb_1	0.34	0.32	0.31	0.31	0.60	0.34	0.28	0.21	*b*
Rb_2	0.35	0.34	0.31	0.33	1.15	0.70	0.57	0.42	*b*
Rb_3	0.34	0.33	0.32	0.31	1.87	1.20	0.90	0.72	3×10^{-3}
Rb_4	0.31	0.30		0.29	2.81	1.80		1.19	5×10^{-3}

[a] Values from ref 37 or interpolated from the available data in that reference. [b] Due to lack of large amounts of product, the solubility of Rb_1 and Rb_2 could not be verified. A solubility similar to Rb_3 and Rb_4 can be supposed.

TABLE 3: Van der Waals Volume (V_{VDW}), Hydrodynamical Volume of Rb_n in Toluene at Different Temperatures, the Averaged Hydrodynamical Volume (V_{av}), and Free Volume (V_{free})

	MW[a] (g/mol)	V_{VDW} (Å^3)	$V_{21°C}$ (Å^3)	$V_{50°C}$ (Å^3)	$V_{75°C}$ (Å^3)	$V_{94°C}$ (Å^3)	V_{av} (Å^3)	V_{free} (Å^3)
Rb_1	962	875	4030	3540	4070	3740	3850/250	2900
Rb_2	1810	1619	7710	7290	8300	7530	7700/400	6100
Rb_3	3506	3107	12 500	12 497	13 100	12 900	12 700/300	9600
Rb_4	6898	6083	18 800	18 850		21 100	19 600/1300	13 600

[a] Molecular weight.

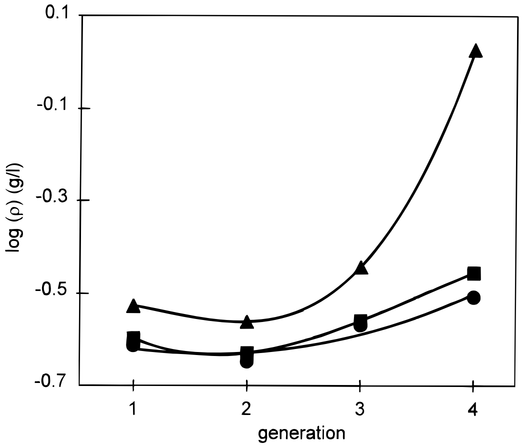


Figure 4. Logarithmic plot of the molecular density (ρ) as a function of generation in toluene (■), in acetone (●), and in ACN (▲).

TABLE 4: Fluorescence Decay Parameters, V_{hydr}, V_{free}, and Solubility of Rb_n in Acetone at Room Temperature

	τ (ns)	β	ϕ (ns)	χ^2	V_{hydr}[b] (Å^3)	V_{free} (Å^3)	solubility (mol/L)
Rb_1	2.82	0.33	0.30	1.11	3770	3000	2×10^{-5}
Rb_2	2.86	0.35	0.61	1.09	7700	6080	1×10^{-5}
Rb_3	2.97	0.33	0.98	1.13	12 400	9300	3×10^{-4}
Rb_4[a]	2.58 (0.59) 3.79 (0.41)	0.29	1.67	1.13	21 200	15 100	2×10^{-4}

[a] Biexponential model is necessary to satisfactorily describe the fluorescence decay; the relative contributions of both decay times are indicated in parentheses. [b] Assuming a viscosity of 0.32 mPa s as interpolated from ref 37.

In ACN the hydrodynamical volume at room temperature is lower than in toluene and acetone, and for Rb_4 it even decreases compared to Rb_3. This indicates that the dendrimers only collapse, as the quality of the solvent is very poor. Consequently the density increases as the solvent quality decreases (see Figure 4). Calculation of the free volume indicates that Rb_4 in ACN is completely collapsed. The rotation is still slightly slower than predicted on the basis of eq 1, with V_{VDW} as the actual volume of the solute. This rejects the possibility of slipping boundary conditions.

Deviations from eq 1 are found for small neutral molecules and for polar and charged molecules. Small neutral molecules tend to rotate faster than predicted on the basis of eq 1. The dendrimers in good solvents show the opposite behavior, suggesting that they cannot be seen as small molecules. Moreover, the molecular volume of toluene is twice the molecular volume of acetone; the rotational correlation times, corrected for viscosity effects, however are comparable. The molecular volumes of ACN and acetone, on the other hand, are of the same magnitude, and the rotational correlation times differ substantially. If it would be necessary to take into account the molecularity of the solvent, the opposite trend would be observed. Slower rotation than predicted on the basis of eq 1 is found for polar molecules in polar solvents and is explained as dielectric friction. Since the dendrimers in this study are neutral, this explanation can be rejected. These arguments demonstrate that the use of eq 1 is justified in this study.

TABLE 5: Fluorescence Decay Parameters, V_{hydr}, V_{free}, and Solubility of Rb_n in ACN at Room Temperature

	τ (ns)	β	ϕ (ns)	χ^2	V_{hydr}[b] (Å^3)	V_{free} (Å^3)	solubility (mol/L)
Rb_1	2.76	0.34	0.29	1.09	3230	2360	8×10^{-6}
Rb_2	2.81	0.35	0.60	1.12	6590	4970	5×10^{-6}
Rb_3	3.10	0.33	0.88	1.15	9730	6620	8×10^{-7}
Rb_4[a]	2.43 (0.69) 4.11 (0.31)	0.21	0.59	1.10	6490	407	8×10^{-7}

[a] Biexponential model is necessary to satisfactorily describe the fluorescence decay; the relative contributions of both decay times are indicated in parentheses. [b] Assuming a viscosity of 0.36 mPa s as interpolated from ref 37.

4. Conclusions

The fluorescence depolarization technique is proposed for determination of the hydrodynamical volume of fluorophore-labeled dendrimers. Due to the high sensitivity of fluorescence, this approach can be used up to very low concentrations of the dendrimer, in contrast to intrinsic viscosity measurements. The biexponential character of the fluorescence decay suggests the contribution of two conformations of the dendrimer.

Analysis of the anisotropy decay in toluene shows that the hydrodynamical volume increases strongly for the lowest generations, but at higher generations a saturation effect is observed. In a next step the hydrodynamical volumes are compared in three solvents: toluene (high solubility), acetone (medium solubility), and acetonitrile (low solubility). The hydrodynamical volume of the dendrimers in acetone and toluene does not change remarkably. In acetonitrile, however, the hydrodynamical volume decreases strongly compared to the hydrodynamical volume in acetone and toluene. The hydrodynamical volume of a fourth-generation dendrimer in ACN is close to the excluded volume, indicating a complete collapse. Calculation of the molar density confirms that the dendrimer becomes more and more dense as it increases in generation and when the quality of the solvent decreases.

Acknowledgment. S.D.B thanks the "Vlaams Instituut voor de bevordering van het Wetenschappelijk Technologisch onderzoek in de industrie" for a predoctoral fellowship. Prof. Dr. N. Boens and Prof. Dr. M. Ameloot are gratefully acknowledged for updating the global analysis software. The continuing support of the Ministry of Scientific Programming (DWTC) through Grant UIAP-IV-11 as well as the FWO is acknowledged.

References and Notes

(1) Zimmerman, S. C.; Zeng, F.; Reichert, D. E.; Kolotuchin, S. V. *Science* **1996**, *271*, 1095.

(2) Murat, M.; Grest, G. S. *Macromolecules* **1996**, *29*, 1278.

(3) Sheiko, S. S.; Eckert, G.; Ignat'eva, G.; Muzafarov, A. M.; Spickerman, J.; Räder, H. J.; Möller, M. *Macromol. Rapid Commun.* **1996**, *17*, 283.

(4) (a) Fréchet, J. M. J.; Gitsov, I. *Macromol. Symp.* **1995**, *98*, 441. (b) Voit, B. I. *Acta Polym.* **1995**, *46*, 87. (c) Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1995**, *132*, 875. (d) Service, R. F. *Science* **1995**, *267*, 458.

(5) Fréchet, J. M. J.; Hawker, C. J.; Gitsov, I.; Leon, J. W. *Pure Appl. Chem.* **1996**, *A33* (10), 1399.

(6) de Gennes, P.-G.; Hervet, H. *J. Phys. Lett. Fr.* **1983**, *44*, L351.

(7) Lescanec, R. L.; Muthukumar, M. *Macromolecules* **1990**, *23*, 2280.

(8) Murat, M.; Grest, G. *Macromolecules* **1996**, *29*, 1278.

(9) Boris, D.; Rubinstein, M. *Macromolecules* **1996**, *29*, 7251.

(10) Carl, W. *J. Chem. Soc., Faraday Trans.* **1996**, *92* (21), 4151.

(11) Chen, Z. Y.; Cui, S. *Macromolecules* **1996**, *29*, 7973.

(12) La Ferla, R. *J. Chem. Phys.* **1997**, *106*, 688.

(13) Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Fréchet, J. M. J.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **1992**, *25*, 2401.

(14) Williams, A. M.; Jiang, Y.; Ben-Amotz, D. *Chem. Phys.* **1994**, *180*, 119.

(15) Evans, G. T.; Evans, D. R. *J. Chem. Phys.* **1984**, *81*, 6039.

(16) Ravi, R.; Ben-Amotz, D. *Chem. Phys.* **1994**, *183*, 385.

(17) Gierer, A.; Wirtz, K. Z. *Z. Naturforsch. A* **1953**, *8*, 532.

(18) Dote, J. L.; Kivelson, D.; Schwartz, R. *J. Phys. Chem.* **1981**, *85*, 2169.

(19) Hartman, R. S.; Konitsky, W. M.; Waldeck, D. H.; Chang, Y. J.; Castner, E. W. *J. Chem. Phys.* **1997**, *106*, 7920.

(20) Fleming, G. R. *Chemical Applications of Ultrafast Spectroscopy*; Oxford University Press: New York, 1986; p 132.

(21) Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1287.

(22) Gopidas, K. R.; Leheny, A. R.; Caminati, G.; Turro, N. J.; Tomalia, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 7335.

(23) Turro, C.; Niu, S.; Bossmann, S. H.; Tomalia, D. A.; Turro, N. J. *J. Phys. Chem.* **1995**, *99*, 5512.

(24) Turro, N. J. *Pure Appl. Chem.* **1995**, *67* (1), 199.

(25) Caminati, G.; Turro, N. J.; Tomalia, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 8515.

(26) (a) Jansen, J. F.; Meijer, E. W. *J. Am. Chem. Soc.* **1995**, *117*, 4417. (b) Jansen, J. F.; de Brabander-van den Berg, E. M.; Meijer, E. W. *Science* **1994**, *266*, 1226.

(27) Smet, M.; Shukla, R.; Fülöp, L.; Dehaen, W. Manuscript in preparation.

(28) Hawker, C.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.

(29) L'abbé, G.; Forier, B.; Dehaen, W. *J. Chem. Soc., Chem. Commun.* **1996**, 2143.

(30) Crutzen, M.; Ameloot, M.; Boens, N.; Negri, R. M.; De Schryver, F. C. *J. Phys. Chem.* **1993**, *97*, 8133.

(31) De Backer, S.; Dutt, G. B.; Ameloot, M.; De Schryver F.; Müllen, K.; Holtrup, F. *J. Phys. Chem.* **1996**, *100*, 512.

(32) Devadoss, C.; Bharathi, P.; Moore, *J. Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1633.

(33) van Stam, J.; Van Dommelen, L.; Boens, N.; Zachariasse, K.; De Schryver, F. C. *J. Phys. Chem.* **1995**, *99*, 9386.

(34) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983; p 111.

(35) Zinsli, P. E. *Chem. Phys.* **1977**, *10*, 299.

(36) Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 261.

(37) Lide, D. R. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1992−1993.