Macromol. Symp. **2005**, 230, 11–19 DOI: 10.1002/masy.200551136

Novel Color-Shifting Mobility Sensitive Fluorescent Probes for Polymer Characterization

Wolter F. Jager,[*1] *Otto van den Berg,*[1] *Stephen J. Picken*[2]

Summary: 1-Methyl-7-dimethylamino quinolinium tetrafluoroborate, a highly stable, highly fluorescent color-shifting mobility sensitive fluorescent probe was employed for detecting the glass transition and phase transitions, notably crystallization, in polymers and polymer blends. Glass transitions in amorphous and semi-crystalline polymers were detected by a change in gradient in emission wavelength λ_{max} versus T plots. Crystallization resulted in discrete blue shifts in λ_{max} versus T plots. Selective probing of PMMA in a PS/PMMA blend, down to a PMMA content of 1%, was demonstrated. Dielectric relaxation spectroscopy has established a clear link between the mobility of dipoles in PMMA and the emission wavelength of the fluorescent probe.

Keywords: blends; crystallization; fluorescence; glass transition; phase behavior

Introduction

Molecular probes are extremely useful tools for investigating specific properties of the medium in which they are incorporated. In order to obtain reliable information several requirements must be fulfilled. First of all, the medium should not be affected by the presence of the probe. This is quite a fundamental intrinsic problem that may, from a practical point, be solved by using low probe concentrations. In that case the bulk properties of the medium will not change and, in the absence of specific probe-medium interactions, the microenvironment of the probe, the part of the medium being sampled, will be unaffected as well. The information the probe is providing along with the underlying mechanism, is another relevant issue. Understanding the mechanism by which the medium is probed is crucial, since this will to a large extend define the scope and limitations of the method. The final issue, which is relevant for inhomogeneous complex systems i.e most practical application, is the location of the probe in the medium, since this part of the medium is probed exclusively. Controlling the location of the probe, which is facilitated by chemical modification in a straightforward manner, enables one to probe specific parts of complex media.

Various types of molecular probes are available, depending on the spectroscopic technique that is used. Well-known are UV-VIS, ESR, NMR, dielectric[1] and luminescent probes[2]. In all cases a high sensitivity and the absence of a background signal from the medium are required to keep probe concentrations as low as possible. In addition the probe signal should be affected by the medium in such a way that specific medium properties are monitored.

Our research is focused on the use of mobility sensitive color-shifting fluorescent probes, i.e. probes that detect changes in medium mobility by the shifts in the wavelength of their emission. Mobility sensitive fluorescent probes have been abundantly used in the field of polymer sciences for various applications such as monitoring polymerization reactions[3–5] and the diffusion of solvents into polymer layers,[6]

---

[1] Delft University of Technology, Faculty of Applied Sciences, Department of Polymer Materials and Engineering, Julianalaan 136, 2628 BL Delft, The Netherlands

[2] The Dutch Polymer Institute, PO Box 902, 5600 AX Eindhoven, The Netherlands

detecting phase transitions[7] and glass transition temperatures,[8,9] and monitoring physical ageing.[10] General advantages of fluorescence spectroscopy[2] are the high sensitivity, up to the molecular level,[11] the non-contact nature, allowing for remote sensing, and fast data acquisition, which allows for real-time measurements.[12] Information from the emission of probe molecules is commonly obtained from fluorescence depolarization, fluorescence intensity ($I_{\max}$), fluorescence lifetime (τ_F), and fluorescence wavelength ($\lambda_{\max}$) measurements. We prefer fluorescence wavelength measurements, because emission wavelengths are virtually unaffected by sample composition and geometry, so that light scattering and opaque samples are accessible. Therefore spatial resolution and imaging experiments can be performed with a large variety of samples that may be inhomogeneous and have the probe located at specific locations. In addition, determining the emission wavelength of a probe is a robust reliable and highly accurate procedure based on standard steady state fluorescence measurements.

Most mobility sensitive probes contain a chromophore in which the charge distribution in the ground state and the (light emitting) excited state is significantly different. Examples of such molecules are internal charge transfer (ICT) probes of the D-π-A[4] or D-σ-A type[3] or charge resonance (CR) probes,[5] organic salts of the D-π-A^+ X^- type. The Jablonski diagram in Figure 1 illustrates a simplified representation of the photo physics of an ICT probe. From Figure 1 it is clear to see that the change in charge distribution, from an apolar ground state to a strongly dipolar excited state, forces the solvent molecules to respond. This solvent rearrangement takes place during the excited state lifetime of the probe, and the extent of excited state stabilization will determine the emission wavelength of the probe. Since both the polarity and the mobility of the medium

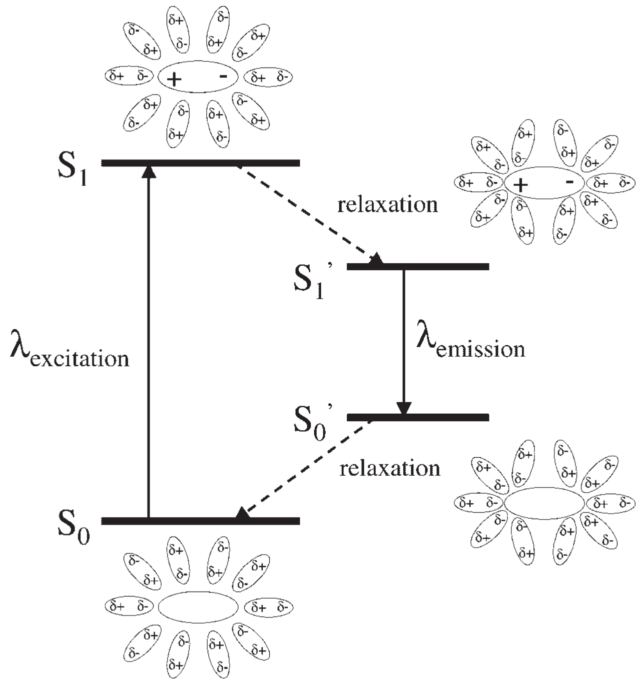
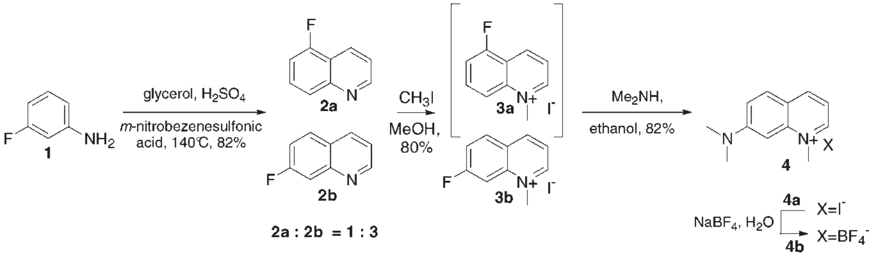


Figure 1.
Jablonski diagram representing the emission of a charge transfer probe in a polar medium.



Scheme 1.
Synthesis of compound **4b**.

determine the emission wavelength, ICT probes are *solvatochromic* and *rigidochromic*. In highly viscous media, charge resonance probes act by a similar mechanism.

Many ICT and CR molecules meet the requirements for applications in which the thermal and photochemical stability of the probe are not critical. For example, for monitoring polymerization reactions or solvent diffusion into films a large number of ICT and CR probes are available.[4] For determining glass transitions, (meso)phase transitions and measuring physical ageing, in particular at elevated temperatures, probe stability is of paramount importance. Not only should the probe survive these conditions without producing intervening degradation products, but also thermal rearrangements of the probe's excited state should not influence its emission. Therefore we developed a new class of charge resonance probes, the 1-alkyl-7-dialkylamino quinolinium salts. These molecules are extremely simple and rigid CR molecules, which are extremely stable and cannot undergo conformational changes in the excited state, so that the mobility of the *medium* is monitored exclusively.

In this paper we will introduce 1-methyl-7-dimethylamino quinolinium tetrafluoroborate (**4b**) and demonstrate the application of this molecule in detecting glass transition temperatures and phase transitions in polymers. The mechanism by which the color of the probe emission is influenced by the medium mobility is investigated. In addition the importance of the positioning of the probe in the medium will be demonstrated.

Synthesis and Characterization of the Probe

The synthesis of 1-methyl-7-dimethylamino quinolinium tetrafluoroborate (**4b**) is outlined in Scheme 1. From 3-fluoroanniline (**1**), a mixture of 7-fluoroquinoline (**2b**) and 5-fluoroquinoline (**2a**) is synthesized by a Skraup reaction.[13] After alkylation, pure 7-fluoro-N-methyl quinolinium iodide (**3b**) was isolated by crystallization. Finally 1-methyl-7-dimethylamino quinolinium tetrafluoroborate (**4b**) was obtained by a nucleophilic aromatic substitution with dimethylamine, followed by ion exchange. The reaction scheme described above, shows a highly flexible and efficient route towards 1-alkyl-7-dialkylamino quinolinium salts, because all the methyl substituents in **4b** are easily replaced by other groups. Exchanging the iodide by various anions is another option to obtain a large variety of probe molecules. We chose the tetrafluoroborate ion since it forms highly stable salts.

The absorption and emission spectra of **4b** in dichloromethane are shown in Figure 2. The absorption spectrum shows a strong CT band at 442 nm ($\varepsilon = 13000$) and strong fluorescence at 505 nm with an extremely high quantum yield ($\Phi_F = 0.7$). The thermal and photochemical stability of **4b** in PMMA films were investigated and compared to those of other fluorescent probe molecules, as illustrated in Figure 3. It was concluded that **4b** has a superior stability compared to other CR and ICT probes. Based on the large Stokes shift, between 60–105 nm in organic solvents, the

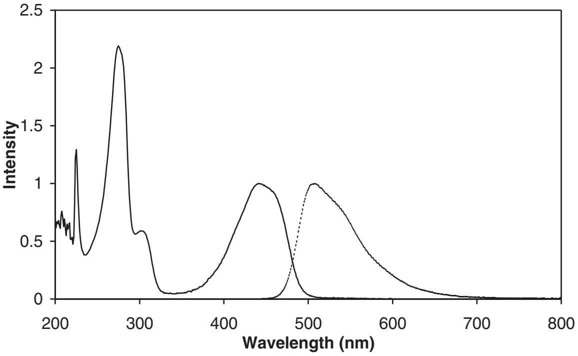


Figure 2.
Absorption (solid line) and emission (dotted line) of **4b** in dichloromethane.

high fluorescence quantum yield and the superior thermal *and* photochemical stability, it is anticipated that **4b** is a mobility sensitive color-shifting fluorescent probe that is suitable for demanding applications at elevated temperatures.

Detecting Glass Transition Temperatures in Amorphous Polymers, Semi-crystalline Polymers and Polymer Blends

Glass transition temperatures of a number of amorphous polymers were determined by temperature dependent measurements of the emission wavelength λ_{max} of **4b** in polymer films.[14] Figure 4 shows the results obtained for PMMA. Upon cooling λ_{max} decreases linearly, and around the glass transition a clear change in gradient is observed. Similar plots were obtained in PEMA, amorphous PC, and PET, and in all cases the temperature at which the change in gradient occurs, coincides with the T_g determined by DSC.[15] The correlation between results obtained by DSC and fluorescence, is convincingly demonstrated in a series of PMMA/PEMA copolymers shown in Figure 5.

Since the emission wavelength of **4b** can be accurately determined in opaque and scattering samples, T_g determination in semi-crystalline polymers and polymer

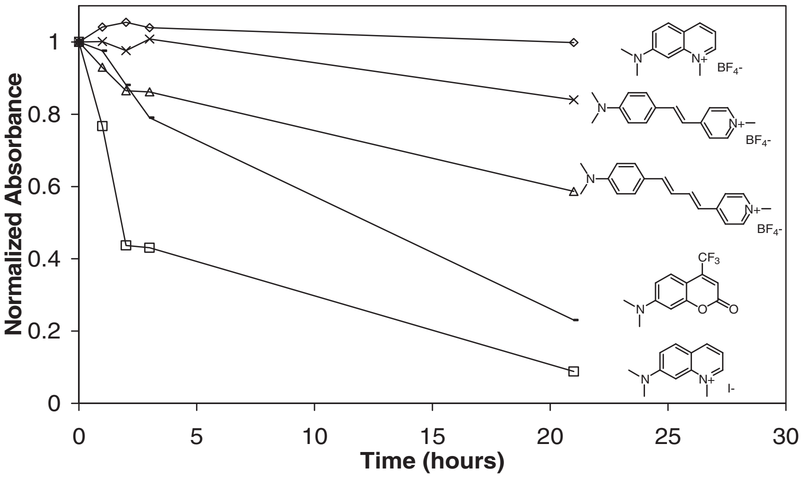


Figure 3.
Thermal degradation of various ICT and CR probes at 150 °C in PMMA films.

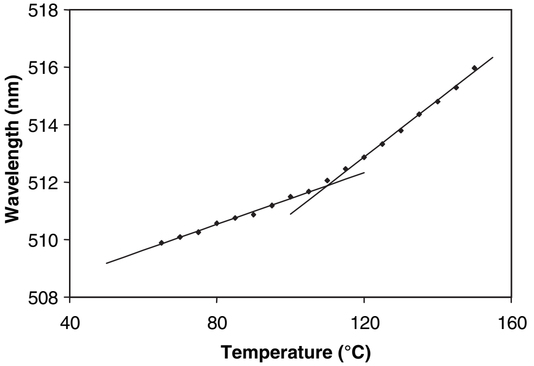


Figure 4.
Emission wavelength versus temperature plot from a PMMA film containing 0.05% of **4b** obtained upon cooling.

blends is achieved without experimental difficulty. Both systems are inhomogeneous, containing two distinct "phases", and therefore the location of the probe determines which "phase" is probed.

Incorporation of **4b** in PS/PMMA blends[14] resulted in films with a matrix droplet morphology in which the probe was dissolved in the PMMA droplets exclusively.[16] Figure 6 shows the temperature dependent emission wavelength of these films, from which the glass transition temperature of the PMMA droplets is determined even for films containing only 1% of PMMA. This approach will allow for a systematic study of the glass transition temperature of one specific component as a function of the morphology and dimensions of a blend.[9]

In semi-crystalline polymers the probe is expected to be located in the amorphous fraction exclusively and therefore the probe should be able to detect T_g. Results obtained in amorphous PC and semi-crystalline PC,[17] displayed in Figure 7, are almost indistinguishable, and this demonstrated that the presence of crystalline regions does not interfere with the measurements. For both polymers the same glass transition temperature was measured by fluorescence (and DSC), and no significant loss of sensitivity due to the presence of

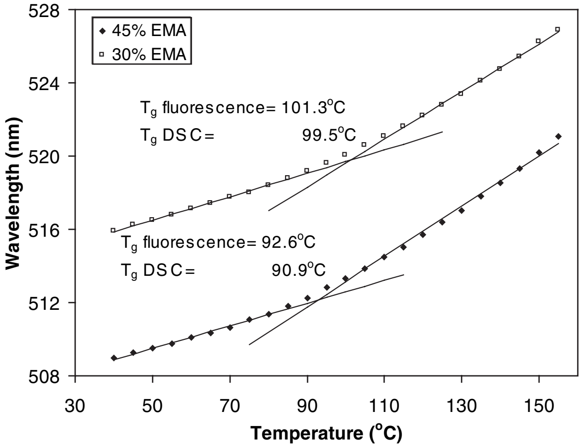


Figure 5.
Emission wavelength versus temperature plots from PMMA-co-PEMA films containing 0.05% of **4b** obtained upon cooling.

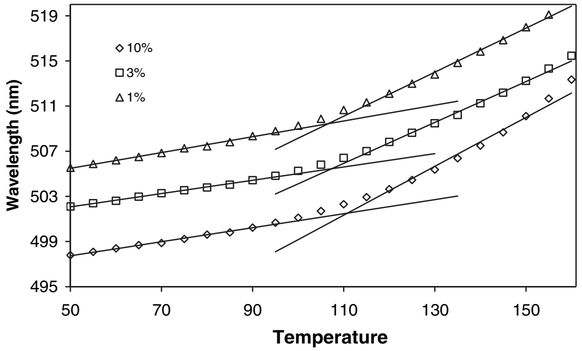


Figure 6.
Emission wavelength versus temperature plot from PS/PMMA blends containing 0.05% of **4b** in the PMMA fraction obtained upon cooling. The 1% data are shifted 5nm upwards, for clarity.

crystalline regions was observed. T_g measurements in nylons and polyethylene glycols were also successful and in the latter case an increase in T_g due to the addition of $LiClO_4$ was observed, in accordance with findings reported in the literature.[18] In PET the results obtained in PETg (amorphous) and PETc (semi-crystalline) were clearly different, as illustrated by Figure 8. PETg exhibits a clear glass transition at 80 °C, whereas the behavior of PETc is more complex.[19] Figure 8 suggests a "broad glass transition", between 80 °C and 120 °C, in accordance with recent literature reports.[20]

The previous experiments have convincingly demonstrated that the T_g of polar amorphous and semi-crystalline polymers is determined from the fluorescence of **4b**. In order to investigate the mechanism by which the probe detects T_g, we undertook a number of experiments in PMMA films doped with **4b**. Temperature dependent absorption revealed that the absorption of **4b** in PMMA is temperature independent. This implies that stabilization of the excited state during the lifetime of the probe ($S1 \rightarrow S1'$ in Figure 1) is the only factor responsible for the change in emission wavelength. Subsequently we have determined the fluorescence lifetime τ_F as a function of temperature. The results, displayed in Figure 8, show that τ_F decreases as the temperature increases with a distinct change in gradient around T_g. This result implies that *-everything else being equal-* blue shifts in emission should appear upon increasing the temperature, since a decreased lifetime should result in less stabilization of the excited state. Therefore

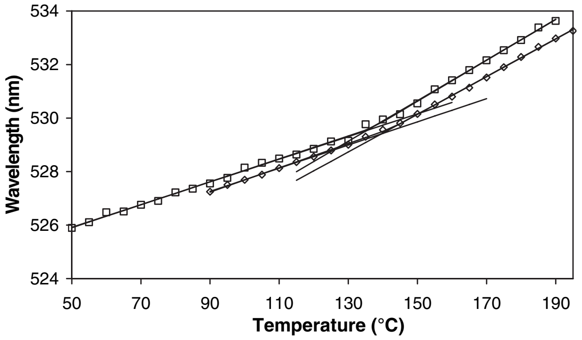


Figure 7.
Emission wavelength versus temperature plot from an amorphous PC film (squares) and a semi-crystalline PC film (diamonds) containing 0.05% of **4b** obtained upon cooling.

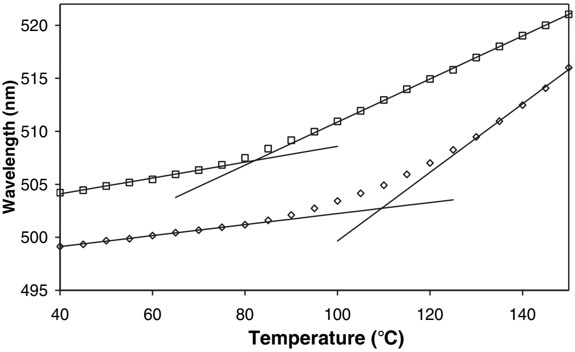


Figure 8.
Emission wavelength versus temperature plot from an amorphous PET film and a semi-crystalline PET film containing 0.05% of **4b** obtained upon cooling.

the red shift observed upon increasing the temperature, must result from an increased medium mobility, notably the mobility of dipoles in the medium.

We were able to proof this point by temperature dependent dielectric relaxation spectroscopy. In Figure 10a the dielectric loss ε'', corresponding to the fast components of the β-transition in PMMA,[21] is plotted as a function of temperature. Figure 10a shows that ε'' at 10^7 Hz, the frequency corresponding to a 10 ns lifetime, increases with increasing temperature. Since ε'' is connected to the heat generated by fluctuating dipoles, this implies a strong increase in dipole mobility. In Figure 10b a clear change in gradient in the log ε'' versus temperature plot is observed at the glass transition temperature. The striking similarity between Figures 10b and 4, demonstrates that the probe response is governed by the mobility of dipoles in the PMMA matrix, and this result confirms our hypothesis.

Detection of Crystallization in Semi-crystalline Polymers

Crystallization of polymers were clearly observed by changes in the probe's emission wavelength, despite the fact that probes are expected to be located in the amorphous fraction of semi-crystalline polymers. Figure 11 shows the emission of **4b** in a PEG 8000 film upon cooling. Crystallization at 35 °C results in a distinct 5 nm blue shift in emission, while the glass transition at −43 °C is expressed by the familiar change in gradient. Most likely

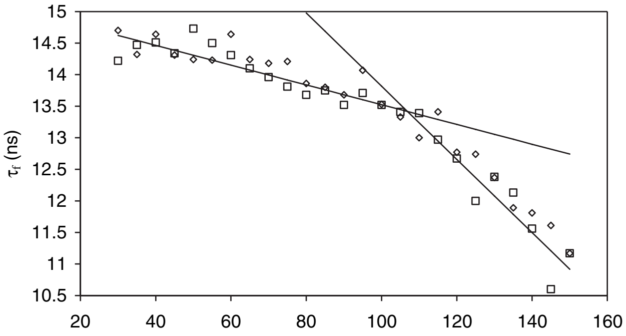


Figure 9.
Fluorescence lifetime τ_f of **4b** in PMMA films measured during cooling (squares) and heating (diamonds).

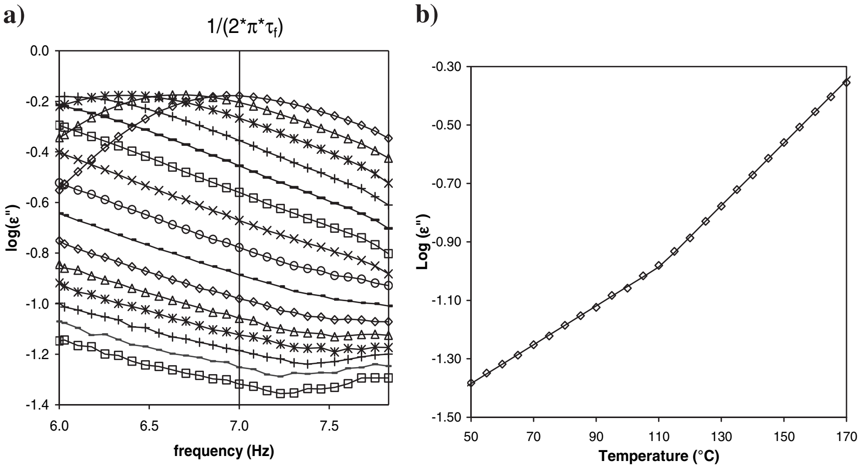


Figure 10.
a: Dielectric relaxation spectrum of PMMA taken at different temperatures; 50 °C bottom curve 170 °C upper curve(left) b: Plot of ε'' versus T derived from the DRS spectra (right).

probe molecules are expelled from the crystallizing regions and temporarily enriched in more rigid amorphous regions adjacent to the crystal edges. Figure 10 suggests that without this effect a change in gradient upon crystallization would be observed. Like in the blends the position of the probe in the polymer matrix has a pronounced influence on its performance.

Conclusions

We have synthesized and characterized **4b**, a highly stable, highly fluorescent molecule and demonstrated that this compound is an excellent color-shifting mobility sensitive fluorescent probe. It was demonstrated that his probe detects glass transitions and crystallization in polymers. Glass transitions were detected by a change in gradient in λ_{max} versus T plots, whereas crystallization results in discrete jumps in λ_{max} versus T plots. In more complex inhomogeneous media, basically everything but amorphous polymers, the position of the probe in the medium, is crucial. Selective probing of one polymer in a blend was demonstrated. Dielectric relaxation spectroscopy has established a clear link

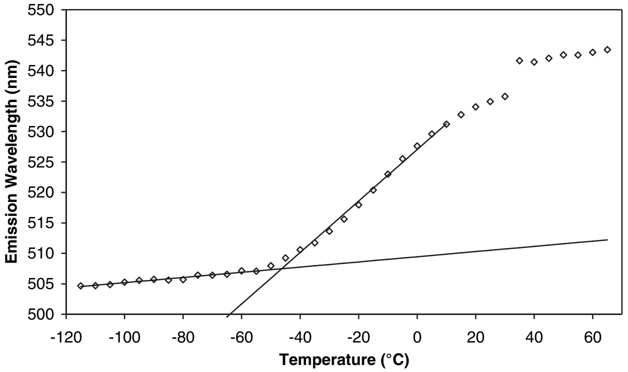


Figure 11.
Emission wavelength versus temperature plot from a PEG 8000 film containing 0.05% of **4b** obtained upon cooling.

between the mobility of dipoles in PMMA and the emission wavelength of the fluorescent probe, thus providing a general mechanism for detecting T_g in fairly polar polymers.

Acknowledgements: Drs. Michael Wübbenhorst, Harry Donker and Peter Verheijen are gratefully acknowledged for their contributions connected with DRS and fluorescence lifetime measurements and data analysis, respectively. The work of O. Van den Berg, W. F. Jager and S. J. Picken forms part of the research programme of the Dutch Polymer Institute, project number 151.

[1] O. v.d. Berg, W. G. F. Sengers, W. F. Jager, S. J. Picken, M. Wübbenhorst, *Macromolecules* **2004**, *37*, 2460.

[2] J. R. Lakowicz, "*Principles of Fluorescence Spectroscopy*", Kluwer Academic and Plenum Publishers, New York, 1999.

[3] H. J. Van Ramesdonk, M. Vos, J. W. Verhoeven, G. R. Möhlmann, N. A. Tissink, A. Meesen, *Polymer* **1987**, *28*, 951.

[4] W. F. Jager, A. A. Volkers, D. C. Neckers, *Macromolecules* **1995**, *28*, 8153.

[5] W. F. Jager, D. Kudasheva, D. C. Neckers, *Macromolecules* **1996**, *29*, 7351.

[6] K. J. Shea, D. Y. Sasaki, G. J. Stoddard, *Macromolecules* **1989**, *22*, 1722.

[7] L. W. Jenneskens, H. J. Verhey, H. J. van Ramesdonk, J. W. Verhoeven, K. F. van Malsen, H. Schenk, *Recl. Trav. Chim. Pays-Bas* **1992**, *111*, 507.

[8] R. O Loutfy, D. M. Teegarden, *Macromolecules* **1983**, *16*, 452.

[9] C. J. Elison, J. M. Torkelson, *Nat. Mater.* **2003**, *2*, 695.

[10] J. S. Royal, J. M. Torkelson, *Macromolecules* **1992**, *25*, 1705.

[11] R. A. L. Vallee, N. Tomczak, L. Kuipers, G. J. Vancso, N. F. van Hulst, *Phys. Rev. Lett.* **2003**, *91*, 038301.

[12] S. Hu, R. Popielarz, D. C. Neckers, *Macromolecules* **1998**, *31*, 4107.

[13] L. Bradford, T. J. Elliott, F. M. Rowe, *J. Chem. Soc.* **1947**, 437.

[14] All polymer films were prepared by casting films from dichloromethane solution, and annealed at $T = T_g + 50\,^\circ C$ for 10 minutes prior to fluorescence measurements.

[15] DSC heat flow curves of all samples were recorded with a Perkin Elmer DSC-7. Indium was used for temperature calibration. All samples were annealed for 10 minutes at $T = T_g + 50\,^\circ C$ and subsequently cooled at a rate of 10 K/min. Glass transition temperatures were determined from the C_p inflection point via differentiation.

[16] Probe **4b** does not dissolve in PS and no emission is obtained from PS films containing the probe. All emission characteristics are equal to those in PMMA, which excludes emission from probe molecules located at the interface.

[17] The degree of crystallinity in semi-crystalline PC was 25% based on the enthalpy of heating of 110 ± 2 J g^{-1} reported by: J. P. Mercier, R. Legras, *Polymer Letters* **1970**, *8*, 645.

[18] T. H. Joykumar Singh, S. V. Bhat, *Bull. Mat. Sci.* **2003**, *26*, 707.

[19] The degree of crystallinity in PETc was $30 \pm 4\%$ based on the enthalpy of heating of 140 ± 20 J g^{-1} reported by: A. Mehta, U. Gaur, B. Wunderlich, *J. Polym. Sci. Part B.: Phys.* **1978**, *16*, 289.

[20] For PETc the coexistence of an amorphous and a rigid amorphous "phase" is postulated, see: (a) M. Song, D. J. Hourston, *J. Therm. Anal.* **1998**, *54*, 651. (b) K. De Clerck, H. Rahier, B. Van Mele, P. Kiekens, *J. App. Pol. Sci.* **2003**, *89*, 3840.

[21] J. P. Runt, J. J. Fitzgerald, "*Dielectric Spectroscopy of Polymeric Materials: Fundamentals and Applications*", American Chemical Society, Washington DC, 1997.