Fluorescence spectroscopy and imaging of dynamics and microstructure of acrylic polymer emulsions
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Chapter 2

Detection of Co-solvents in Polymer Latices†

Abstract

In this chapter we report the determination of partitioning of coalescing agents (organic co-solvents) in water borne latex emulsions by means of a fluorescence method. An environment-sensitive fluorescent probe 1 was copolymerized via emulsion polymerization. The presence of organic co-solvents inside the polymer particles is revealed by the photophysical properties of the probe. In particular, the position of the fluorescence emission maximum of co-polymerized 1 can be used to measure the amount of coalescing agent present in the polymer particles. The spectral shifts are shown to be due to the softening of the matrix, rather than to solvation of the probe by the added co-solvent.

2.1 Introduction

From the points of view of environment and health, water based polymer emulsions (latex materials) provide an attractive alternative for coatings that are applied from an organic solvent. In order to obtain smooth and coherent films, it is, however, often still necessary to add a small amount of organic co-solvent to achieve optimal coalescence of the latex particles during film formation. Legislation requires reduction of the use of these so-called Volatile Organic Components (VOC’s), which makes it important to select the most effective coalescing agents. During film formation the co-solvent should not evaporate too fast, before the particles start to coalesce, or too slow, so that it adversely affects the mechanical properties of the final film.

It is of interest to be able to monitor the presence of co-solvent in the polymer particles by a non-invasive experimental method. Toussaint described a model for the prediction of the distribution of coalescing agents between polymer and water phase. The same author proposed a model for calculation of the lowering of $T_g$ and minimum film formation temperature (MFFT) of latex particles on the addition of a coalescing agent. te Nijenhuis investigated the role of coalescing agent in the film formation process of monodisperse acrylic latex by using photo correlation spectroscopy (PCS), atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM) etcetera. In further experiments they reported the influence of drying, aging and drying temperature on the latex material.

We will explore the use of fluorescence spectroscopy, which has emerged as a useful tool for the investigation of many phenomena in materials and biological sciences. Fluorescent probe molecules have been used to observe processes occurring at the molecular length scale in complex, heterogeneous environments with high sensitivity and selectivity. In the field of polymer physics and chemistry, fluorescent dyes have been used e.g. to investigate polymerization mechanisms, kinetics, crosslinking, coalescence, void closure and diffusion of polymers in film formation.

In the present study we use a solvatochromic probe that provides information about the polarity and mobility of its microenvironment. This probe was used to monitor the partitioning of five different coalescent agents in polymer emulsions, quantitatively. Styrene-co-2-ethylhexyl acrylate (S/EHA) copolymers were used as typical hydrophobic latices and methyl methacrylate-co-ethyl acrylate (MMA/EA) represented hydrophilic latices. By changing the ratios of monomers, low $T_g$ and high $T_g$ variations with similar hydrophilicity were made. The coalescing agents that were employed to formulate the latices were 2,2,4-trimethyl-1,3-pentanediol mono(2-methyl
Detection of Co-solvents in Polymer Latices

propanoate) (Texanol), di(propylene glycol) n-butyl ether (DPnB), ethylene glycol ethyl hexyl ether (EEH), di(propylene glycol) methyl ether (DPM) and ethylene glycol ethyl ether acetate (EEA). DPnB, Texanol and EEH being moderately polar and not well soluble in water were expected to partition towards the polymer phase of the latex. EEA and DPM, on the other hand, have 24% and 100% solubility in water, respectively, and were anticipated to partition to the aqueous phase of the polymer emulsion (for properties of co-solvents see section 2.5.4).

The fluorescent label used, compound 1, is composed of three functional units: an amino group, acting as electron donor, a cyanonaphthalene unit, that acts as electron acceptor, and a maleimide unit, which can be used for covalent coupling reactions to different substrates. Interestingly, the maleimide group acts as a quencher of fluorescence in 1, but after an addition reaction in which the maleimide double bond is removed, the charge-transfer fluorescence of the sigma-coupled donor-acceptor system is turned on. This is well known for its sharp sensitivity to the polarity and mobility of the medium.\textsuperscript{26, 33-38}

Compound 1 was covalently attached in the backbone of the co-polymer by co-feeding it in a small quantity together with the monomer mixture. Addition of n-butylamine to 1 provided compound 2, which was used as a low-molecular weight model of co-polymerized 1 (Scheme 1).

Scheme 1. Chemical structures of 1 and its n-butyl amine adduct 2. Copolymerization of the maleimide unit and Michael addition of the amine remove the double bond, turning on the fluorescence of the “Fluorotrope” unit.\textsuperscript{39-40}

In the present chapter we show how the fluorescence of the labeled polymer emulsions responds to the presence of co-solvents. In particular, the shift of the emission maximum can be quantitatively related to the amount of co-solvent present in the polymer phase. In subsequent Chapters we shall apply the newly developed detection method to the dynamics of co-solvents in mixtures of latices, and in the process of film formation.
2.2 Results and Discussion

2.2.1 Fluorescence of Model Compound 2

Model compound 2 contains a donor-bridge-acceptor chromophore whose emission strongly depends on the polarity and polarizability of the medium. Fluorescence spectra and quantum yields of 2 were measured in solvents of various polarities ranging from non-polar to highly polar. Spectra are shown in Figure 1. The fluorescence characteristics of 2 in organic solvents as well as industrial solvents (coalescing agents) are listed in Table 1.

![Figure 1. Steady-state fluorescence spectra of model compound 2 in A) organic solvents, B) in industrial solvents (coalescing agents).](image)

Compounds 1 and 2 are members of a large family of Charge-Transfer emitters originating from a parent compound nicknamed Fluoroprobe, which show exceptionally large solvatochromic spectral shifts in emission. Replacement of the piperidine in the original Fluoroprobe by a tropane unit increased its weak charge transfer (CT) absorption. The attachment of a maleimido unit at the donor aniline group allowed to make a covalent bond between the fluorescent probe and many reactive systems. Interestingly, the maleimide group quenches the charge-transfer fluorescence, which can be restored after removal of double bond by an addition reaction. The relevance of this behaviour is that unpolymerized probe molecules will not affect the fluorescence measurements.

Excitation of these compounds at 315 nm results in population of a locally excited (LE) state, which undergoes very rapid relaxation to the charge transfer (CT) state. In tropane derivatives such as 2, however, direct excitation to the CT state is possible at wavelengths beyond the red edge of the LE absorption band.
Table 1. Fluorescence properties of model compound 2 in various solvents.

<table>
<thead>
<tr>
<th>Organic solvent</th>
<th>$\lambda_{\text{max}}^{a}$ (nm)</th>
<th>$\nu_{\text{r}}^{b}$ (cm$^{-1}$)</th>
<th>$\phi^{c}$</th>
<th>$\tau^{d}$ (ns)</th>
<th>$\Delta f^{e}$</th>
<th>Width (nm)</th>
<th>Skewness</th>
<th>$k_{\text{r}}^{f}$ = $\phi/\tau$</th>
<th>$k_{\text{nr}}^{g}$ = $1/\tau - k_{\text{r}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>418</td>
<td>23600</td>
<td>0.61</td>
<td>4.2</td>
<td>0.10</td>
<td>62</td>
<td>0.47</td>
<td>0.145</td>
<td>0.09</td>
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<tr>
<td>Toluene</td>
<td>468</td>
<td>21000</td>
<td>0.52</td>
<td>8.5</td>
<td>0.13</td>
<td>90</td>
<td>0.38</td>
<td>0.061</td>
<td>0.06</td>
</tr>
<tr>
<td>Dibutylether</td>
<td>466</td>
<td>21000</td>
<td>0.56</td>
<td>8.1</td>
<td>0.19</td>
<td>92</td>
<td>0.38</td>
<td>0.069</td>
<td>0.05</td>
</tr>
<tr>
<td>Chloroform</td>
<td>511</td>
<td>19200</td>
<td>0.49</td>
<td>11</td>
<td>0.25</td>
<td>114</td>
<td>0.30</td>
<td>0.045</td>
<td>0.05</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>553</td>
<td>17700</td>
<td>0.1</td>
<td>4.1</td>
<td>0.29</td>
<td>123</td>
<td>0.36</td>
<td>0.024</td>
<td>0.22</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>557</td>
<td>17600</td>
<td>0.17</td>
<td>4.0</td>
<td>0.31</td>
<td>125</td>
<td>0.37</td>
<td>0.043</td>
<td>0.21</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>557</td>
<td>17600</td>
<td>0.16</td>
<td>6.2</td>
<td>0.32</td>
<td>125</td>
<td>0.23</td>
<td>0.026</td>
<td>0.14</td>
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<tr>
<td>Acetone</td>
<td>606</td>
<td>16200</td>
<td>0.004</td>
<td>0.78</td>
<td>0.37</td>
<td>144</td>
<td>0.26</td>
<td>0.005</td>
<td>1.28</td>
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<tr>
<td>Acetonitrile</td>
<td>629</td>
<td>15600</td>
<td>0.0034</td>
<td>0.11</td>
<td>0.39</td>
<td>154</td>
<td>0.21</td>
<td>0.031</td>
<td>9.06</td>
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<tr>
<td>Texanol</td>
<td>555</td>
<td>17700</td>
<td>0.063</td>
<td>1.9</td>
<td>0.31</td>
<td>138</td>
<td>0.11</td>
<td>0.033</td>
<td>0.49</td>
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<tr>
<td>DPNB</td>
<td>562</td>
<td>17600</td>
<td>0.11</td>
<td>2.3</td>
<td>0.31</td>
<td>130</td>
<td>0.11</td>
<td>0.048</td>
<td>0.39</td>
</tr>
<tr>
<td>EEA</td>
<td>563</td>
<td>17500</td>
<td>0.083</td>
<td>3.8</td>
<td>0.31</td>
<td>126</td>
<td>0.22</td>
<td>0.022</td>
<td>0.24</td>
</tr>
<tr>
<td>DPM</td>
<td>570</td>
<td>17300</td>
<td>0.02</td>
<td>1.7</td>
<td>0.33</td>
<td>143</td>
<td>0.08</td>
<td>0.012</td>
<td>0.58</td>
</tr>
</tbody>
</table>

$^{a}$ wavelength, $^{b}$ frequency, $^{c}$ fluorescence quantum yield, $^{d}$ fluorescence lifetime, $^{e}$ see equation 4, $^{f}$ radiative rate constant, $^{g}$ nonradiative decay rate constant.

As shown in Table 1 and Figure 1, 2 exhibits a bathochromic shift of the fluorescence emission maximum of more than 200 nm upon transfer from non-polar cyclohexane ($\lambda_{\text{max}}$ 418 nm) to a strongly polar solvent such as acetonitrile ($\lambda_{\text{max}}$ 629 nm). The emission quantum yield gradually decreases with increasing polarity due to the decrease of the radiative rate constant and the increase of the non-radiative charge recombination.40, 46 Emission of Fluoroprobes in hydroxylic solvents tends to be quite strongly quenched.46 In the “industrial” solvents used in this study 2 showed fluorescence in the range of 550-570 nm. All of these have one hydroxyl group in their chemical structure, except EEA. In the hydroxylic solvents, the fluorescence lifetimes are a bit shorter, but the fluorescence quantum yields are still acceptable.

For the characterization of the spectral shapes the spectra $I(\lambda)$ were fitted (Igor Pro 6.0, Wavemetrics, Inc., Lake Oswego, OR 97035, USA) with a skewed Gaussian function (Equation 1).

$$I(\lambda) = I_{0} + I_{\text{max}} \exp \left(-\ln 2 \left[ \ln(1 + 2s(\lambda - \lambda_{\text{max}})w) / s \right]^{2} \right)$$  \hspace{1cm} (1)

In this equation $I_{0}$ is a baseline parameter, $I_{\text{max}}$ the maximum intensity, occurring at $\lambda_{\text{max}}$. The width of the band is characterized by $w$, and the skewness by $s$.

The width of the emission spectra increased gradually with increasing polarity of the
solvent. In non-polar cyclohexane and polar acetonitrile it was 62 and 154 nm, respectively, according to the fit with Equation 1.

Fluorescence quantum yields $\Phi_f$ of 2 were determined by comparing the integrated emission spectrum $F_s$ of the sample with that ($F_R$) of reference compound quinine bisulphate in 1N H$_2$SO$_4$ ($\Phi_R = 0.56$) according to Equation 2,

$$\Phi_f = \frac{\phi_R F_s f_R n_s^2}{F_R f_R n_R^2}$$  \hspace{1cm} (2)

In Equation 2 $f_s$ and $f_R$ are the absorption factors ($f = 1 - 10^{-A}$, where $A$ is absorbance) and $n_s$ and $n_R$ are the refractive indices of the solvents for sample and reference, respectively.

The solvent dependence of the emission energies of 2 can be quantified using the Lippert-Mataga equation (3).

$$\nu_{CT} = \nu_{CT} (0) - \frac{2\mu_{CT}^2}{\hbar c \rho^3} \Delta f$$  \hspace{1cm} (3)

$$\Delta f = \frac{(\varepsilon_s - 1)}{(2\varepsilon_s + 1)} - \frac{(n^2 - 1)}{(4n^2 + 2)}$$  \hspace{1cm} (4)

In this equation, the solvent dependence of the charge transfer emission wavenumber $\nu_{CT}$ is correlated to the solvent polarity parameter $\Delta f$, where $\nu_{CT} (0)$ is the emission maximum in the gas phase, $\mu_{CT}$ (in Debye) is the dipole moment of the charge transfer state, $\hbar$ is Planck’s constant, $c$ is the velocity of light, $\rho$ (Å) is the effective radius of the solvent cavity occupied by the molecule, $\varepsilon_s$ is the solvent dielectric constant and $n$ is the refractive index. Figure 2 shows the Lippert-Mataga plots of model compound 2. The slope of the plot according to Equation 3 is $27 \times 10^3$ cm$^{-1}$, in agreement with the values typically found for Fluoroprobes.43

![Figure 2](image)

Figure 2. A) Lippert-Mataga plot of model compound 2 in organic solvents B) radiative rate constants $k_r$ and non-radiative rate constants $k_d$ versus wavenumber.

Going from non-polar to polar solvents, the radiative rate constant $k_r$ of the charge-transfer emission decreases due to less efficient intensity borrowing from the
cyanonaphthalene transition, and the non-radiative decay rate $k_d$ increases as a result of the smaller energy gap.\textsuperscript{48}

When 2 is incorporated in a solid polymer film, it emits at relatively short wavelengths, namely 435 nm in polystyrene (PS), 445 nm in poly(methyl acrylate) (PMA) and 440 nm in poly(vinyl acetate) (PVAc) at 25 °C. In a solid film, reorientation of the polar side groups does not occur on the timescale of the excited state lifetimes (nanoseconds). Interestingly, when films of PMA and PVAc containing 2 were warmed to ~ 5 °C above their $T_g$ of 13 and 28 °C, respectively, fluorescence of the probe molecule was unchanged, showing that also under these conditions relaxation of dipolar groups is unimportant on the nanosecond timescale.\textsuperscript{49}

The emission wavelengths in the solid polymer films are longer than those in cyclohexane, probably because the somewhat polar ground state of 2 induces some polarization in the medium.

### 2.2.2 Properties of Latex Emulsions

Physical characteristics of the latices prepared are presented in Table 2. The glass transition temperatures determined experimentally were a bit higher than the anticipated values of 20 and 60 °C, but we will still use the calculated values to distinguish low and high $T_g$ materials in the text. Importantly, the addition of 1 did not cause a significant change in the physical and chemical properties of the latices.

Table 2. Fluorescence properties of model compound 2 in various solvents.

| Latex code\textsuperscript{a} | Compound 1 pH (ppm) | Viscosity mPa-s | Particle size nm | MFFT\textsuperscript{b} °C | $M_w$ kDa | Dry state $T_g$ °C | Free monomer (ppm) | S EHA MMA EA |
|-------------------------------|---------------------|-----------------|------------------|-----------------------------|------------|---------------------|-------------------|
| S/EHA20                       | 0                   | 2.3             | 25               | 113                         | 17         | 347                 | 22                | 10 60 |
| S/EHA60                       | 0                   | 2.2             | 27               | 111                         | 78         | 325                 | 69                | 3 7 |
| MMA/EA20                      | 0                   | 2.1             | 13               | 118                         | 13         | 689                 | 26                | 4 3 |
| MMA/EA60                      | 0                   | 2.1             | 13               | 127                         | 54         | 454                 | 68                | 7 3 |
| S/EHA20                       | 6                   | 2.3             | 30               | 108                         | 15         | 371                 | 26                | 15 215 |
| S/EHA60                       | 6                   | 2.2             | 25               | 109                         | 78         | 335                 | 70                | 11 6 |
| MMA/EA20                      | 6                   | 2.1             | 13               | 116                         | 12         | 707                 | 26                | 7 7 |
| MMA/EA60                      | 6                   | 2.1             | 13               | 123                         | 57         | 475                 | 68                | 90 17 |

\textsuperscript{a} The latices are coded as follows: first letters show the kind of co-polymer, numbers at the end refer to the (predicted) $T_g$ of the latex, for instance styrene-co-2-ethylhexylacrylate $T_g$ 20 °C is abbreviated as S/EHA20 and methyl methacrylate-co-ethylacrylate $T_g$ 20 °C as MMA/EA20 and so on.

\textsuperscript{b} MFFT stands for the minimum film formation temperature: it is the lowest temperature at which latex particles coalesce and from a transparent film.
2.2.3 Fluorescence Emission of Latex Emulsions

While 1 itself does not fluoresce, its covalent incorporation in the co-polymer turns on the fluorescence. The fluorescence of the latex thus shows the successful incorporation of the probe in the co-polymer.

The emission of the co-polymerized 1 has its maxima in the non-polar latex materials between 445 and 450 nm. This is at shorter wavelength than the emission of structurally similar model compound 2 in toluene (468 nm, Table 1). Despite the structural resemblance of the non-polar copolymer with toluene, the emission exhibited a blue shift of ~20 nm in the latex. For non-formulated polar and hydrophilic latex emission maxima were observed in the range of 470 - 476 nm. Although one might expect the emission bands to be broadened due to the inhomogeneity of the local environments of the fluorescent probe groups, the widths of the emission bands are similar to those of 2 in toluene.

The latices were “formulated” with the five different coalescing agents in 3, 6 and 9% w/w. Steady-state fluorescence spectra of the formulations were fitted with the skewed Gaussian function (Equation 1) to get accurate values of emission maxima and intensities, and to further characterize the band shape.

2.2.4 Hydrophobic S/EHA Latices

Addition of 3, 6 and 9% w/w coalescing agent resulted in bathochromic shifts of the emission, both for low and high \( T_g \) latices of S/EHA. Figure 3A presents the fluorescence spectra of low \( T_g \) S/EHA latex formulated with 0, 3, 6 and 9% w/w DPnB. Non-formulated latex (0 % DPnB) exhibited an emission maximum at 449 nm which shifted to 467 nm with 9% w/w DPnB. This large shift of 18 nm provides a means for the quantitative monitoring of partitioning of the co-solvent. For the high \( T_g \) latex of similar polarity (Figure 3B) the emission of the probe is slightly blue-shifted, with a maximum at 447 nm and it shifts by 13 nm to longer wavelength upon addition of 9 % DPnB.

The shapes of the emission spectrum changed as a function of co-solvent. They display an increase in width (from 81 to 98 nm), decrease in emission intensity and skewness (from 0.4 to 0.35). This effect was similar for all four coalescing agents except DPM, which hardly affected the shape of the emission spectra.

Figure 4A presents the effect of the five co-solvents on the emission of the low \( T_g \) S/EHA latex. Addition of up to 9 % of these coalescing agents brought about a smooth bathochromic shift with a decrease in the emission intensity. This shift was ~20 nm for EEH, Texanol, DPnB and EEA. The latex formulated with DPM showed a small shift of 2 nm. Although most of this fully water-soluble coalescing agent remained in
the aqueous phase, a small quantity of DPM apparently entered the latex particle.

Figure 3. Fluorescence emission of 1 co-polymerized in hydrophobic S/EHA latex formulated with DPnB, A) low $T_g$, B) high $T_g$.

Figure 4B shows the effect of coalescing agents EEH, Texanol, DPnB, EEA and DPM on high $T_g$ S/EHA latex. The emission maximum shifted 13 - 15 nm for EEH, Texanol, DPnB and EEA, but only 2 nm in the case of DPM (emission maximum values of co-polymerized 1 in co-solvents are reported in the Section 2.5.6).

Figure 4. Effect of %w/w of coalescing agents on the fluorescence emission maxima of hydrophobic S/EHA, A) low $T_g$, B) high $T_g$; hydrophilic MMA/EA, C) low $T_g$, D) high $T_g$. 
2.2.5 Hydrophilic MMA/EA Latices

Figure 5A shows fluorescence spectra of MMA/EA \( T_g \) 20 °C formulated with 0, 3, 6 and 9% w/w Texanol, showing a smooth red shift and intensity decrease with increasing amount of coalescing agent. For the corresponding high \( T_g \) latex (Figure 5B) the shift in emission maximum is seen to be much smaller, and the intensity decrease is also less. Figure 4C shows the emission maxima vs. coalescing agent percentage for the low \( T_g \) MMA/EA latices formulated with EEH, Texanol, DPnB and EEA. The red shift of the emission maximum amounts to 18 - 23 nm. For the high \( T_g \) latex (Figure 4D) the shift of emission maximum was in the range of 11 - 18 nm. The DPM formulated MMA/EA latices showed a bathochromic shift of 4 and 2 nm for low and high \( T_g \), respectively. Although these latices are much more hydrophilic than the S/EHA materials, DPM apparently prefers to stay mainly in the water phase.

Comparison of the four latex systems shows that the effect of the coalescing agents depends in particular on the \( T_g \) of the materials. In low \( T_g \) hydrophobic and hydrophilic acrylic emulsions addition of coalescing agent resulted in larger red shifts and intensity decreases than in the corresponding high \( T_g \) latices.

2.2.6 Formulation With Toluene

The coalescing agents employed in this study were highly polar compounds. In order to test whether the observed red shifts are related to co-solvent polarity, the low \( T_g \) hydrophobic S/EHA latex was formulated with toluene. Figure 6 shows the results. Formulation with toluene resulted in a bathochromic shift of up to 18 nm, with a decrease in fluorescence intensity and broadening of the spectra. The effect is similar to that of the polar coalescing agents.
2.2.7 Temperature Effect

Emission spectra and maxima of high $T_g$ MMA/EA latex containing 9% DPnB at temperatures between 15 and 35 °C are shown in Figure 7. Increased temperature resulted in a shift of the emission maximum by 12 nm to longer wavelength, with a gradual decrease in emission intensity.

2.2.8 Time-Resolved Fluorescence Decay of Latex Emulsion

The fluorescence decay profiles of co-polymerized 1 in the S/EHA and MMA/EA revealed that both latices exhibit two lifetimes, a component of $\sim$ 6 - 10 ns and a component of $\sim$ 1 - 2.5 ns. In some cases an additional component was observed at shorter wavelengths, which is attributable to a minor impurity in the polymer. A similar lifetime component was observed in the fluorescence decay profiles of neat...
non-labeled latex measured under the same conditions. Details are given in the Section 2.5.8. Figure 8 shows as a representative example a set of decay curves of S/EHA low $T_g$ latex obtained at various emission wavelengths. It is very clear from Figure 8 that a fast decay predominates at shorter wavelength while the emission at longer wavelengths is longer-lived.

Figure 8. Fluorescence decays at the indicated wavelengths of hydrophobic S/EHA $T_g$ 20 °C formulated with 9% Texanol. $\lambda_{exc}$ 380 nm. IRF = instrument response function.

Fluorescence decay curves measured for all the latex samples in this study resemble those shown in Figure 8. It proved impossible to fit the decay curves at different wavelengths in a global analysis with only two time constants. This is not unexpected, because the sample is likely to be heterogeneous at the molecular level, having fluorescent probe groups in various chemical environments. If the spectra would be subject to dynamical Stokes shifts, a fast decay at short wavelength should be accompanied by a rise at longer wavelengths. The rapid decay component which dominates at short wavelength might be due to the dynamic Stokes shift, but unfortunately, the signals at the red tail of the emission band were weak, and unambiguous observation of such a rise was not possible in most cases.

2.2.9 Differential Scanning Calorimetry (DSC) of Dry Latex

Differential Scanning Calorimetry was carried out to determine the $T_g$ of films cast from the latices with different amounts of coalescing agents after two weeks of drying. Unfortunately, attempts to determine the glass transition temperatures in the wet state were unsuccessful, probably because they were well below room temperature, so that freezing of the water phase complicated matters. Data obtained from dry state DSC measurements, however, showed smooth trends, and the effect of coalescing agent on the $T_g$ of the film was quite clear. Figure 9 shows the plots of $T_g$ versus % w/w coalescing agent. These measurements were carried out on the two weeks old dry films, but a clear decrease in $T_g$ with an increase in the amount of coalescing agent was observed. There was
not much difference in the $T_g$ of same latex formulated with three different kinds of coalescing agents. Although the fluorescence experiments clearly indicated that the water-miscible DPM hardly enters the latex particles in the wet state, it still decreased the $T_g$ of the partly dried film.

![Figure 9. $T_g$ versus % w/w coalescing agents of two weeks old films A) hydrophobic high $T_g$ (60 °C) S/EHA latex, B) hydrophilic high $T_g$ (60 °C) MMA/EA latex.](image)

### 2.3 Discussion

Detection of coalescing agents and determination of its partitioning between water and polymer phases by utilizing a solvatochromic fluorescent probe was found to be an effective tool during this research work. The emission of 1, co-polymerized in latex emulsions, showed a clear response to the presence of co-solvents: the fluorescence spectra broaden, their maxima shift to longer wavelengths, and the intensity decreases upon increasing co-solvent incorporation.

The fluorescence of co-polymerized 1 can be compared to that of model compound 2 (scheme 1). The emission of these donor-bridge-acceptor (D-$\pi$-A) fluorescent probes stems from a charge transfer state with a large dipole moment. Measurement of fluorescence emission of model compound 2 in a range of solvents, as expected, revealed extremely large solvatochromism. The fluorescence quantum yield of 2 gradually decreases with increasing polarity due to the decrease of the radiative rate constant and the increase of the non-radiative charge recombination. All coalescing agents used in this study contained at least one hydroxyl group, except EEA. Emission of 2 and other members of this class of probes tend to be quenched in hydroxylic solvents, but this effect was not a problem with the coalescing agents. The non-radiative decay rates were only slightly higher than in non-hydroxylic solvents with similar emission energies, and the quantum yields were still reasonable.

The emission maxima of co-polymerized 1 appeared at 445 – 450 nm in non-polar hydrophobic and at 470 – 476 nm in polar hydrophilic latices, respectively. This can be
compared to emission maxima of 2 in cyclohexane (418 nm), spin-coated polymer films (435 – 445 nm), toluene (468 nm) and chloroform (511 nm). Solvatochromic shifts in emission are largest when complete relaxation of the dipolar groups around the fluorophore can occur during the excited state lifetime. In solid films such relaxation does not occur, but emission was still found to be at somewhat longer wavelengths than in cyclohexane. This may be due to the higher refractive index, causing electronic polarization to stabilize the excited state, or to some extent of ground state polarization by the dipolar groups of the probe molecule. Even in the absence of co-solvents emission of co-polymerized 1 in the latices occurred at longer wavelengths than in solid films. In the polar hydrophilic latices fluorescence was at a longer wavelength than in the non-polar hydrophobic ones. These observations imply that some medium relaxation during the excited state lifetime can occur in the wet latices. In particular for the hydrophilic materials hydroplasticization may play a role. In this case the emission is at significantly longer wavelengths in the low $T_g$ latex than in the high $T_g$ material.

Broadening of spectral bands of 1-co-polymerized in latex was observed with an increase of the amount of coalescing agent. The broadening observed, however, resembles that in the case of 2 upon increase of the solvent polarity. Among the coalescing agents, EEH, Texanol and DPnB are less polar and almost not water miscible, EEA is moderately polar and partly water miscible whereas DPM is highly polar and completely miscible with water. Low $T_g$ hydrophobic (S/EHA20) and hydrophilic (MMA/EA20) latices exhibited large shifts of $\lambda_{\text{max}}$ of about 20 nm for EEH, Texanol, DPnB and EEA coalescing agents. For high $T_g$ latices the shift was a bit less pronounced (13 – 15 nm for S/EHA60 and 11 – 18 nm for MMA/EA60). The coalescing agents which are less water miscible (EEH, Texanol, DPnB, EEA) are expected to be in the co-polymer phase where they are efficiently sensed by the fluorescent dye 1. DPM, which is completely water miscible, was expected to be mainly in the water phase of the latex and indeed caused only very small spectral shifts. Interestingly, DPM appeared just as effective as the other coalescing agents in lowering the $T_g$ of films made from these latices. Water-miscible coalescing agents are therefore not necessarily useless! After application of the latex on a substrate most of the water evaporates within an hour, but the co-solvents stay in the polymer for weeks (Figure 9).

The bathochromic shift of $\lambda_{\text{max}}$ upon addition of co-solvents may be due to specific solvation of the probe molecules by the co-solvent, or to the general softening of the matrix. The experiment in which toluene was added as a co-solvent clearly proves that the latter is more important: toluene caused a similar red shift and change of intensity
and of the spectral shape as the much more polar co-solvents. The shift of $\lambda_{\text{max}}$ to longer wavelength with increase in temperature is also in agreement with this explanation. If solvent polarity would be dominant, a shift to shorter wavelength would be expected because the dielectric constant and the refractive index decrease with increasing temperature. The mobility of the medium, however, will increase with increasing temperature.

The emission maxima of co-polymerized 1 in the latices occur at shorter wavelengths than those of the reference compound 2 in liquid media with similar polarity. This indicates that complete relaxation of the medium around the probe in its charge transfer excited state does not occur. On the other hand, we do observe a dependence of the spectra on the chemical structure and on the presence of co-solvents. This suggests that time-resolved Stokes shifts should be detectable. In time-resolved experiments complicated multieponential decays were observed in all samples. The decay at each wavelength could be fitted with two or three lifetime components. The values of the time constants, however, varied with wavelength, and simple global fits with two or three lifetimes proved impossible. The longer lifetimes were similar to those of 2 with similar emission energies (5 – 10 ns), whereas the other component had a shorter lifetime. It is likely that this component, which is dominant at short wavelength, is due to the time-resolved Stokes shift. Unfortunately, the associated rise of the spectrum on the red edge could be observed only in a few cases. The time-resolved experiments are complicated by the presence of a weakly fluorescent impurity in latices at the short wavelength side of the band of co-polymerized 1 and by scattering of excitation light. More conclusive results might be obtainable, but are beyond the scope of the present study.

2.4 Conclusion

Low and high $T_g$ hydrophobic S/EHA and hydrophilic MMA/EA co-polymer latices were prepared via emulsion polymerization and labeled with an organic solvatochromic fluorophore, co-polymerized into the polymer backbone. These latices were formulated with five coalescing agents, which caused systematic changes in the spectra of the fluorophore as a function of co-solvent concentration. With increasing amounts of coalescing agent there was an increasing red shift of emission maximum with a decrease in fluorescence emission and a broadening of the band. The spectral changes are attributed to increased mobility of the media rather than to solvation by the co-solvent.

Time-resolved fluorescence measurements of the labeled latices revealed complex decays. In addition to a decay time that resembles that of model fluorophore 2, there was a shorter lifetime, which is likely to be due to the dynamical Stokes shift that is relatively slow in these viscous media.
The smooth dependence of the spectral parameters on the amount of co-solvent present can be applied to investigate the dynamics of co-solvents in latex mixtures, and in film formation. This work is described in Chapters 3 and 4.

2.5 Experimental Details

2.5.1 Materials

The monomers styrene (Shell), 2-ethyl hexylacrylate (FPC), methyl methacrylate (Proquigel) and ethyl acrylate (FPC) were used as received. The coalescing agent 2,2,4-trimethyl-1,3-pentanediol mono(2-methyl propanoate) (Texanol) was obtained from Eastman. Di(propylene glycol) n-butyl ether (DPnB), ethylene glycol ethyl hexyl ether (EEH), di(propylene glycol) methyl ether (DPM) and ethylene glycol ethyl ether acetate (EEA) were obtained from Aldrich and were used as received. The fluorogenic probe molecule 1 was available from previous work in our laboratory. Column chromatography of the crude compound 1 was carried out using silica gel as stationary and diethylether as a mobile phase. The retention factor (Rf) of the compound 1 in diethylether was 0.71 and the recovery was 93 %.

2.5.2 Preparation of Latex Materials

Two types of polymer emulsions were prepared: (i) hydrophobic styrene-co-2-ethylhexyl acrylate co-polymers (S/EHA), and (ii) hydrophilic methyl methacrylate-co-ethyl acrylate co-polymers (MMA/EA). These latices were prepared in series of batches in low $T_g$ (~ 20 °C) and high $T_g$ (~ 60 °C) versions by varying the ratio of “hard” to “soft” monomers. $T_g$-values were calculated according to the Fox-equation (Equation 5).

$$\frac{1}{T_g} = \sum_n \frac{X_n}{T_{gn}}$$  \hspace{1cm} (5)

Where $x_n$ and $T_{gn}$ are the weight fractions and the glass transition temperatures (K) of the components in the corresponding homopolymers. In our latex 2 % acrylic acid (AA) was added during the emulsion polymerization and it was used as a third monomer for the calculation of dry state $T_g$ of the final latex. $T_g$s of the homopolymers poly styrene (PS), poly ethylhexyl acrylate (PEHA), poly methyl methacrylate (PMMA), poly ethyl acrylate (PEA) and poly acrylic acid (PAA) were 100 °C, -50 °C, 105 °C, -24 °C and 105 °C, respectively.

In the hydrophobic latex the molar ratio of styrene (“hard monomer”) and 2-ethyl hexylacrylate (“soft monomer”) was 2.5 : 1 and 8 : 1, for low and high $T_g$, respectively. Hydrophilic latex materials with low and high $T_g$ were prepared by using different ratios of methyl methacrylate (hard) and ethyl acrylate (soft) monomers, namely 0.75 : 1 and 2.75 :
Detection of Co-solvents in Polymer Latices

1 for low and high $T_g$ latices, respectively. Each latex was prepared in two batches, one without labeling and the other with labeling with co-polymerized-1.

Table 3. Emulsion polymerization recipe for the preparation of set of four non-labeled latices of low and high $T_g$ styrene-co-ethylhexylacrylate (S/EHA) and methyl methacrylate-co-ethyl acrylate (MMA/EA) latices.

<table>
<thead>
<tr>
<th>Component weight (g)</th>
<th>S/EHA20</th>
<th>S/EHA60</th>
<th>MMA/EA20</th>
<th>MMA/EA60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>885</td>
<td>885</td>
<td>885</td>
<td>885</td>
</tr>
<tr>
<td>Sodium laurylsulphate (SLS)</td>
<td>19.7</td>
<td>19.7</td>
<td>19.7</td>
<td>19.7</td>
</tr>
<tr>
<td>Ammonium phosphate (AP)</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>11.8</td>
<td>11.8</td>
<td>11.8</td>
<td>11.8</td>
</tr>
<tr>
<td>Styrene (S)</td>
<td>339.1</td>
<td>473.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-ethylhexylacrylate (EHA)</td>
<td>240.2</td>
<td>105.8</td>
<td>248.3</td>
<td>425.1</td>
</tr>
<tr>
<td>Methyl methacrylate (MMA)</td>
<td>248.3</td>
<td></td>
<td></td>
<td>425.1</td>
</tr>
<tr>
<td>Ethyl acrylate (EA)</td>
<td>331.0</td>
<td></td>
<td>154.2</td>
<td></td>
</tr>
<tr>
<td>isoascorbic acid 5%</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>tert-butyl hydroperoxide (t-BHPO)</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Proxel ultra 10</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

*Another set of four latex batches was prepared with the addition of 0.012 g MFT Compound 1 in order to get labeled latices.

For labeling, compound 1 (6 ppm mol/mol w.r.t. total monomers) was introduced in the monomer feed tank during the emulsion polymerization process. Solid contents of the final latex materials were 40%. Table 3 presents emulsion polymerization recipes of low and high $T_g$ S/EHA and MMA/EA latices.

Emulsion polymerization was carried out in a 2 L reactor equipped with mechanical stirrer with variable speed (100-1000 rpm) and reflux condenser, all under N$_2$ atmosphere. The reactor was charged with water and 1.3% sodium lauryl sulfate (SLS). Ammonium persulfate (APS) 0.12% was used as initiator in the emulsion polymerization. 5% of the monomer was introduced at once to the solution of water and SLS in the reactor at 50 °C and 30% of initiator solution was added to the reactor at once at 70 °C. Then the temperature of the reactor was increased up to 85 °C and the remaining monomer and initiator feeds were added to the reactor over a period of 90 min at this temperature. After finishing monomer and initiator feeds polymerization was allowed to continue for 30 min. Post-reaction treatment was carried out by adding 0.04% solution of iso-ascorbic acid and 0.56% of tert-butyl hydroperoxide (t-BHPO) to the reactor. After 30 min the reaction mixture was cooled down from 85 °C to room temperature. Proxel ULTRA10
(Arch Biocides) was added 1.5 g (containing 10 % of 1,2-benzisothiazolin-3-one (BIT) dissolved with potassium hydroxide). Finally the latex was filtered through a 75 µm filter cloth and stored in clean bottles.

2.5.3 Synthesis of Model Compound

Model compound 2 was synthesized by Michael addition of n-butyl amine to the double bond of 1 (Scheme 1).\(^{39}\) Equimolar quantities of 1 and n-butylamine were dissolved in dichloromethane and the reaction mixture was refluxed over night at 40 °C. The solvent was evaporated, and column chromatography of the crude product provided crystals of adduct 2. Finally it was placed in a vacuum desiccator at 80 °C for two hours to ensure complete removal of solvent. \(^1\)H NMR (400 MHz CDCl\(_3\)), δ (ppm): 8.29 (d, J = 8.3 Hz, 1H), 8.07 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.4 Hz, 1H), 7.73 (ddd, J = 1.2, 6.9, 8.3 Hz, 1H), 7.66 (ddd, J = 1.2, 6.9, 8.3 Hz, 1H), 7.29 (1H, partly overlapping with CHCl\(_3\) signal), 7.18 (AA’ part of AA’BB’ pattern, main splitting 9 Hz, 2H), 6.89 (BB’ part of AA’BB’ pattern, main splitting 9 Hz, 2H), 6.79 (bs, 1H), 4.43 (m, 1H), 4.19 (m, 1H), 3.94 (dd, J = 8.2, 5.1 Hz, 1H), 3.10 (dd, J = 18.0, 8.4 Hz, 1H), 2.96 (d, J = 14 Hz, 1H), 2.79 - 2.68 (m, 3H), 2.55 (d, J = 14 Hz, 1H), 2.31 (d, J = 14 Hz, 1H), 2.1 – 2.2 (m, 2H), 1.9 – 2.05 (m, 2H), 1.6 (m, 3H, partly obscured by H\(_2\)O peak), 1.43 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H).

2.5.4 Coalescing Agents and Formulations

To study the effect of coalescing agent on the latex emulsions formulations of 0, 3, 6 and 9 % w/w were prepared. The pH was raised to 7 – 7.5 using ammonia. Next, the coalescing agent was added slowly with continuous stirring by a mechanical stirrer over 30 min to produce a stable formulation. Physical characteristics of co-solvents are shown in Table 4.

Table 4. Physical properties of the co-solvents.

<table>
<thead>
<tr>
<th>Co-solvent</th>
<th>Mol. Wt. (g/mol)</th>
<th>Water solubility (%)</th>
<th>Viscosity (mPa·s)</th>
<th>Surface tension (dynes/cm)</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EEH</td>
<td>174.3</td>
<td>0.2</td>
<td>7.0</td>
<td>27.6</td>
<td>224</td>
</tr>
<tr>
<td>Texanol</td>
<td>216.3</td>
<td>2</td>
<td>7.0</td>
<td>28.9</td>
<td>244</td>
</tr>
<tr>
<td>DPnB</td>
<td>190.3</td>
<td>5</td>
<td>4.4</td>
<td>28.8</td>
<td>229</td>
</tr>
<tr>
<td>EEA</td>
<td>132.2</td>
<td>24</td>
<td>1.3</td>
<td>28.2</td>
<td>150</td>
</tr>
<tr>
<td>DPM</td>
<td>148.2</td>
<td>100</td>
<td>3.4</td>
<td>29</td>
<td>188</td>
</tr>
</tbody>
</table>
2.5.5 Polymer Characterization

The viscosity of the latex materials was determined by means of a Brookfield viscosity meter LVDV-I. Particle sizes were measured by means of dynamic light scattering using a Malvern Zetasizer. Minimum film formation temperature (MFFT) was measured till formation of crack free and transparent film by Rhopoint bar 90 with the built in WP unit. Wet and dry state \( T_g \) were determined by differential scanning calorimetry (DSC) using a TA Instruments Q1000 from -90 to 150 °C at a heating rate of 1°C/min. The molecular weight distribution of the final latex was determined with gel permeation chromatography (GPC) on a Waters Alliance 2695 with a Styrene/divinylbenzene column and THF as eluent. Free monomer concentration was determined by headspace gas chromatography (GC) (Interscience) equipped with a Triplus HS DAC Rrobotic Autosampler and a flame ionization detector (FID). A column with a stationary phase of medium polarity (CP WAX 52) was used.

2.5.6 Steady-State Fluorescence

The fluorescence emission spectra of model compound 1 and labeled latices were recorded in 1 cm quartz cuvets on a Spex Fluorolog 3 spectrofluorimeter equipped with two double monochromators. Excitation of solutions of the model compound 2 (absorbance ~ 0.1 cm\(^{-1}\)) was done at 360 nm and emission was recorded at a right angle. The excitation wavelength for the latex was 380 nm and emission was measured using a front face geometry. The detector was a Peltier-cooled R636-10 (Hamamatsu) photomultiplier tube. Spectra were corrected for the wavelength dependence of the detection system. Measurements carried out in steady-state fluorescence were at room temperature (20 °C).

The spectral shape was characterized by fitting the spectra \( I(\lambda) \) with a with a skewed Gaussian function (Equation 1). See section 2.2.1. Emission maxima of co-polymerized 1 in latices are presented in Tables 5 and 6.
Table 5. Fluorescence emission $\lambda_{\text{max}}$ of low and high $T_g$ hydrophobic S/EHA latices formulated with coalescing agents.

<table>
<thead>
<tr>
<th>Emission maximum (nm)</th>
<th>% w/w</th>
<th>EEH</th>
<th>Texanol</th>
<th>DPnB</th>
<th>EEA</th>
<th>DPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/EHA20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>453</td>
<td>449</td>
<td>449</td>
<td>449</td>
<td>449</td>
</tr>
<tr>
<td>3</td>
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<td>466</td>
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</tr>
<tr>
<td>9</td>
<td></td>
<td>472</td>
<td>470</td>
<td>468</td>
<td>469</td>
<td>469</td>
</tr>
<tr>
<td>S/EHA60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>449</td>
<td>448</td>
<td>448</td>
<td>445</td>
<td>448</td>
</tr>
<tr>
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<td>6</td>
<td></td>
<td>458</td>
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<td>9</td>
<td></td>
<td>462</td>
<td>460</td>
<td>460</td>
<td>460</td>
<td>450</td>
</tr>
</tbody>
</table>

Table 6. Fluorescence emission $\lambda_{\text{max}}$ of low and high $T_g$ hydrophylic MMA/EA latices formulated with coalescing agents.

<table>
<thead>
<tr>
<th>Emission maximum (nm)</th>
<th>% w/w</th>
<th>EEH</th>
<th>Texanol</th>
<th>DPnB</th>
<th>EEA</th>
<th>DPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA/EA20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>479</td>
<td>477</td>
<td>477</td>
<td>478</td>
<td>477</td>
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<tr>
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<td>485</td>
<td>482</td>
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<td>479</td>
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<td>481</td>
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<td>MMA/EA60</td>
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<tr>
<td>0</td>
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<tr>
<td>9</td>
<td></td>
<td>484</td>
<td>479</td>
<td>486</td>
<td>484</td>
<td>470</td>
</tr>
</tbody>
</table>

2.5.7 Time-Resolved Fluorescence

Fluorescence decay profiles of the co-polymerized 1 in latices were measured at room temperature (20 °C) in 1 cm quartz cuvets by means of time correlated single photon counting (TCSPC). Samples were excited at 380 nm with excitation pulses supplied by a Coherent Chameleon titanium sapphire laser. The repetition rate of laser was
Detection of Co-solvents in Polymer Latices

reduced to 4 MHz by an APE pulse-picker PulseSelect. The output at 760 nm was frequency doubled using a 1 mm BBO doubling crystal. The decay was measured in the range of 400-650 nm with polarizations of excitation and emission set at the magic angle (54.7°). A micro channel plate was used as a detector. The instrument response function (IRF) was measured using Raman scattering of doubly demineralised water. Decay curves of each sample were collected at different wavelengths in 4000 channels and > 3000 counts. For the decay time measurements of 2 a Hamamatsu Streak camera system was used, with the same excitation source. Time profiles were fitted with multiexponential decay functions with convolution with the IRF using procedures implemented in Igor Pro 6.0.

2.5.8 Time-Resolved Fluorescence of Neat Hydrophobic S/EHA Latex (Non-Labeled Latex)

Fluorescence decays of blank samples of S/EHA low and high $T_g$ non-labeled and non-formulated latices were measured by means of TCSPC (Figure 10). It is worth to mention that both of these unlabeled latices exhibited fluorescence in the region of interest, i.e. 400-600 nm, with two lifetimes (longer lifetime with small amplitude and shorter lifetime with larger amplitude) showing that the latices contained some impurity. For low $T_g$ neat (non-labeled) latex at 440 nm time components were: $\tau_0$ 2.9 ns ($A_0$ 30%) and $\tau_1$ 0.5 ns ($A_1$ 70%). For high $T_g$ latex it was $\tau_0$ 7.2 ns ($A_0$ 48%) and $\tau_1$ 1.4 ns ($A_1$ 50%) showing that while measuring labeled latices at this particular wavelength fluorescence decay could have an inaccuracy due to lifetime component impurities present in the latex. Due to this impurity it can be expected that values of lifetime of labeled latex at $\lambda_{max} = 440$ nm would be slightly higher than the actual.

![Figure 10](image_url)

Figure 10. Fluorescence decay of S/EHA $T_g$ 20 and 60 °C blank samples (no fluorescent probe, no co-solvent), A) time-resolved fluorescence ($\lambda_{exc} = 375$ nm measured at 440 nm wavelength), B) steady-state fluorescence ($\lambda_{exc} = 380$ nm).
2.5.9 Gel Permeation Chromatography of MFT-Co-Polymerized S/EHA and MMA/EA Latices

The distribution of copolymerized MFT in the copolymer in S/EHA and MMA/EA latices was analyzed with gel permeation chromatography (GPC) using a Waters Alliance Gel Permeation Chromatograph coupled with a Waters 410 dRI refractive index detector and a Shimadzu RF 10a XL fluorescence detector (excitation 380 nm; detection 570 nm). Tetrahydrofuran (THF; stabilized HPLC grade, 99.8% pure) containing 1% acetic acid at a flow rate of 1.0 ml/min was used as eluent. One guard column PLgel 10 µm (50 × 7.5 mm) and three PLgel 10 µm Mixed-B (300 × 7.5 mm) columns were used. Polymer standards were Polystyrene MP 160-10 000 000.

![A) Refractive index and fluorescence signals of S/EHA T_g 20 °C.](image)

![B) Refractive index and fluorescence signals of S/EHA T_g 60 °C.](image)

![C) Refractive index and fluorescence signals of MMA/EA T_g 20 °C.](image)

![D) Refractive index and fluorescence signals of MMA/EA T_g 60 °C.](image)

Figure 11. GPC chromatograms showing refractive index and fluorescence signals of A) S/EHA T_g 20 °C, B) S/EHA T_g 60 °C, C) MMA/EA T_g 20 °C, D) MMA/EA T_g 60 °C.

GPC traces of S/EHA and MMA/EA T_g 20 and 60 °C latices are presented in Figure 11. Neat latices were also measured and they showed no fluorescent signal at this retention time. It is quite obvious from Figure 11 that the peaks of refractive index and fluorescence emission emerge at the same retention time. This shows that MFT is homogeneously distributed over the whole molecular weight range of the copolymer. The fluorescence signal for MMA/EA T_g 20 °C (Figure 11C) was weaker than the other three due to a smaller amount of copolymerized MFT (6 ppm vs. 18 ppm).
2.6 References


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