Fluorescence spectroscopy and imaging of dynamics and microstructure of acrylic polymer emulsions
Raja, T.N.

Citation for published version (APA):
Raja, T. N. (2011). Fluorescence spectroscopy and imaging of dynamics and microstructure of acrylic polymer emulsions

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (http://dare.uva.nl)
Chapter 3

Repartitioning of Co-solvents in Latex Emulsions

Abstract

Repartitioning of co-solvents between particles of latex emulsions was investigated by means of a fluorescence method, based on the detection of the amount of co-solvent via the solvatochromic shift of the emission maximum of a fluorescent probe, that is built into the polymer in a small quantity.

Complete repartitioning of the co-solvents between particles of latex materials with a low $T_g$ (ca. 25 °C) occurs within minutes. For a hydrophilic latex with a $T_g$ of 68 °C equilibration was achieved in about an hour. For a hydrophobic latex of similar $T_g$, the result of the experiment depended on the history of the sample, which suggests that the presence of the co-solvent causes an irreversible change in the material.
3.1 Introduction

Waterborne polymer emulsions have gained much attention due to their environmental and economical advantages over the solventborne polymer coatings. They have application in various fields such as paints, adhesives, paper, inks, textile, surgical accessories, etc. In order to obtain good mechanical properties of films cast from waterborne polymer emulsions (latex materials) a certain amount of organic co-solvent is often used, which ultimately evaporates from the coating. Extensive research into environmentally more benign waterborne coatings with reduced amounts of such volatile organic compounds (VOC) is in full progress.

Latex film formation is influenced by several factors including the nature of the polymer, particle size and morphology, drying conditions, molecular weight, nature and amount of surfactants, plasticizers and pigments, etcetera. Co-solvents play a vital role in film formation, as they facilitate particle deformation and polymer interdiffusion in the last stages of film formation. A simple experimental characteristic for the formation of a crack-free and homogeneous film is the minimum film formation temperature (MFFT). It is defined as the temperature above which a smooth and coherent film is formed. Above MFFT continuous film formation occurs due to particle deformation and interdiffusion. If a film is cast below the MFFT, however, a discontinuous powdery film is obtained. MFFT and $T_g$ of a polymer are often related. Both are influenced by the same features such as coalescing agents, nature and composition of the monomers, molecular weight, latex particle size, etcetera. Increasing the co-solvent concentration results in an approximately linear reduction of the $T_g$.

The mechanism of latex film formation is a somewhat controversial issue because different authors describe its evolution in two, three, or four stages. The three-stage mechanism, however, appears to be the preferred one in the recent literature. Keddie and Routh stated in their recent book that latex film formation takes place in three stages, which can overlap in time. These stages are (i) drying, (ii) particle deformation and (iii) interdiffusion.

Figure 1 illustrates the various stages involved in latex film formation. Stage I, during which water evaporates from the film, is the transition from the wet initial stage to a more densely packed film, with increased solids content. The rate of evaporation of water in this first stage is similar to the rate of evaporation of pure water or dilute emulsifier solutions. In the second stage particles deform to come into an irreversible contact and forming a closed packed array. This stage is known as particle deformation stage: particles are deformed to polyhedrons if they are soft. Hard particles, however, remain unchanged at this stage. The rate of water evaporation decreases to a great extent at this stage. In the
third stage a continuous film is formed. The film gains its mechanical properties due to the interdiffusion of the polymer chains. Annealing of the particles results in diffusion across particle-particle boundaries and leads to a continuous film. Polymer diffusion occurs across the interfaces of latex particles, which are thought to form a polar barrier due the presence of ionic groups at the polymer surface (a small fraction of acrylic acid in the polymer) and the surfactant that stabilizes the latex.7

Figure 1. Schematic presentation of three stages of latex film formation: aqueous dispersion transforms into a continuous coherent film.5

The function of the co-solvent starts soon after the evaporation of water from the wet latex film (Stage 1). In the case of a water-soluble co-solvent, evaporation of water triggers its entrance into the particles whereby it lowers the $T_g$ and enhances coalescence. The co-solvent should evaporate after film formation so that a high $T_g$ of the dry polymer film can be obtained. An interesting alternative is to use a softening agent that does not evaporate but ultimately becomes part of the polymer network.8 Properties of an ideal co-solvent include: moderate evaporation rate, hydrolytic stability, and compatibility with a wide range of polymers. A co-solvent should obviously evaporate more slowly than water in order to be able to plasticize the particles. Moderately water miscible co-solvents will soften the outer shell of particles already in the wet stage and will penetrate into polymer particles and soften them inside upon film formation.

Waterborne polyvinyl emulsions can be prepared via emulsion polymerization,3-9 yielding emulsified polymer particles in the size range of 20-500 nm in diameter. Formulation of such polymer emulsions with coalescing agents is carried out prior to film formation.
The partitioning of a co-solvent over the aqueous and polymer fractions depends on its relative solubilities in these two compartments. Therefore, knowledge of the distribution coefficients is important. No direct studies on the partitioning of co-solvents in polymeric dispersions can be found in the literature. Toussaint and DeWilde\textsuperscript{10} proposed a model to estimate the distribution coefficients of coalescing agents between polymer particles and aqueous phase of the latex. They calculated the distribution coefficients for different coalescing agents in different latices and compared them with experimental literature values. The agreement was mostly satisfactory. Another model proposed by Toussaint et al. aims at estimating the reduction of the $T_g$ or MFPT on addition of co-solvent to the latex.\textsuperscript{11}

Some other studies investigated the role of co-solvents by employing electrochemical and transmission techniques. In one such study electro-deposition behavior determined the influence of Texanol on the morphology of films of acrylic latices with three different $T_g$s (with low -10, medium 21, and high 101 °C).\textsuperscript{12} The influence of co-solvent was found to be very system specific and depends upon the glass transition temperature of the latex. In another study the role of coalescing agent in the film formation process was investigated by means of a turbidity technique by Zohrehvand and te Nijenhuis.\textsuperscript{13} Texanol and ethylene glycol monobutyl ether were used as coalescing agents to investigate the influence of drying temperature, aging time and aging temperature on film formation.\textsuperscript{14} Lahtinen et al.\textsuperscript{8} described the synthesis of five epoxide based reactive coalescing agents, which can react with the latex polymer and become part of the film, thus simultaneously increasing the solids content of the film as well as crosslinking it. Seebergh et al.\textsuperscript{15} studied the effect of co-solvent concentration on the aggregation stability of a simple coating system.

Fu et al.\textsuperscript{16} introduced a new strategy referred to as “Designed Diffusion Technology” which concurrently offers enhanced film formation with high mechanical properties and reduction in Volatile Organic Compounds (VOC) of ~ 30 %. Fu et al. used two-polymer systems in which a low $T_g$ (< -5 °C) soft polymer in small amount (15 to 35 %) was added to a high $T_g$ (> 20 °C) hydrophobic polymer, which made the dominant phase (65 to 85 %). Acrylic or styrene-acrylic polymer compositions were used as low $T_g$ soft polymer and Texanol as co-solvent. The selection of polymers was made such that the coalescing agent partitioned selectively into high $T_g$ dominant phase polymer. During film formation, evaporation of water led to the repartitioning of the coalescing agent such that it preferred to migrate from the high $T_g$ polymer to the soft polymer. In the soft phase the co-solvent diffused more rapidly leading to its faster evaporation from the film. Development of hardness was achieved at a faster rate without compromising mechanical properties. The authors did, however, not quantify the coalescent agent distribution.
Vignola et al.\textsuperscript{17} observed that the effect of coalescing agent addition to a surfactant-stabilized latex varies with the nature of the coalescing agent. Paint flocculation was caused by the effect of the coalescing agent on the partitioning of surfactants between the polymer interface and the water phase. Extremely hydrophobic or hydrophilic coalescing agents have a tendency to significantly destabilize an emulsion and medium range hydrophobic solvents have less effect on the stability of the latex.

Fluorescence Resonance Energy Transfer (FRET) was recently used by Schroeder et al. to study the effect of co-solvents ethylene glycol (EG) and propylene glycol (PG) on polymer diffusion in poly(butylacrylate-co-methyl methacrylate) latex films.\textsuperscript{18} They synthesized two similar emulsions except that one was labeled with the energy donor phenanthrene (Phe) and the other with the acceptor aminobenzophenone (NBen). Latices were mixed in a 9:1 (acceptor:donor) ratio to monitor polymer diffusion at early stages of film formation. Schroeder et al. observed that both co-solvents retard polymer diffusion at early times of drying latex film but enhance polymer diffusion at later aging times. This was due to the partitioning behavior ($K = C_W/C_p$) of both coalescing agents: in early drying time both EG and PG partitioned in aqueous phase (where $K > 200$) and retarded coalescence and polymer diffusion. Once water evaporated and film became dry both coalescing agents partitioned in polymer phase, thereby acting as plasticizers enhanced polymer diffusion.

Juhué and Lang used fluorescence energy transfer to monitor interdiffusion of latex particles.\textsuperscript{19} Latices of poly(n-butylmethacrylate) (PBMA) labeled with phenanthrene (energy donor) and anthracene (energy acceptor) were drop cast on a quartz surface and annealed. From the phenanthrene fluorescence lifetime the extent of particle interpenetration could be derived. The best film-forming agents were found to be those with a moderate evaporation rate. They found that increasing the Texanol (TEX) concentration resulted in an increase of the fraction of mixing in the PBMA latex film. The diffusion constant increased with increase in coalescing agent concentration and decreased with increase in fraction of mixing.\textsuperscript{20}

From the above-mentioned examples from the literature it is obvious that co-solvents have an enormous influence on latex film formation. They are an essential part of a latex coating to obtain a crack free, homogeneous film having superior mechanical properties. Water solubility of the co-solvent may be a significant issue for the effectiveness of the co-solvent in the formation of a coherent film. Low and high water soluble co-solvents tend to stay in the co-polymer and the water phase of the emulsion polymer, respectively.

In chapter 2 we have described in detail the determination of the concentration of co-solvents in hydrophobic and hydrophilic latices by using steady-state fluorescence spectroscopy of a solvatochromic fluorescent probe (maleimidofluorotrope MFT)\textsuperscript{21}
covalently linked to the polymer backbone. The addition of co-solvent to the latex leads to a shift of the emission of the probe to longer wavelength, which is caused by the "softening" of the environment of the probe. The same method is applied here to investigate the migration of co-solvent between latex particles in the wet state. We report the investigation of repartitioning of four co-solvents of different water solubility in hydrophobic and hydrophilic acrylic latices. The water solubility of the co-solvents employed in this study ranges from extremely low (0.1 %) to moderate (24 %). The co-solvents used are ethylene glycol ethyl hexyl ether (EEH, 0.2 % water solubility), 2,2,4-trimethyl-1,3-pentanediol mono(2-methyl propanoate) (Texanol) (TEX, 0.1 %), di(propylene glycol) n-butyl ether (DPnB, 5 %) and ethylene glycol ethyl ether acetate (EEA, 24 %). EEH, TEX and DPnB being moderately polar and not well soluble in water were expected to partition predominantly towards the polymer phase of the latex. EEA has substantial water solubility, but the response of the solvatochromic probe was similar to that with the other co-solvents, indicating that EEA also resides mostly in the polymer phase.

Two types of emulsion polymers 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 theoretical $T_g$ (~ 20 °C) and high $T_g$ (~ 60 °C) versions by varying the ratio of “hard” to “soft” monomers. $T_g$-values were predicted using the Fox-equation. In the hydrophobic latex the molar ratios of styrene (“hard monomer”) and 2-ethyl hexylacrylate (“soft monomer”) were 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 : 1 for low and high $T_g$ latices, respectively. In addition to the monomers mentioned all latices contained 2 % acrylic acid (AA). The actual $T_g$s of the prepared latices were found to be few degrees higher than the theoretical values of 20 and 60 °C. For low $T_g$ (20 °C) S/EHA and MMA/EA latices, experimental values were 22 and 26 °C, respectively and high $T_g$ latices exhibited actual values of 69 and 68 °C, respectively. $T_g$s of freshly prepared latex batches were determined using dry state differential scanning calorimetry (DSC). Freshly prepared latex was allowed to air dry for two weeks and $T_g$ was measured without annealing or addition of co-solvent. In the presentation and discussion of results we will use the terms “low” and “high” $T_g$ for the latices in this and further chapters. Each latex was prepared in two batches, one without labeling and the other labeled with copolymerizable MFT. For labeling, MFT (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 %.
Detailed characterization of the materials was described in Chapter 2. It is important to emphasize that co-polymerization of MFT fluorescent label was found to have no influence on the physical and chemical properties of these latices. Formulations prepared to perform the co-solvent repartitioning experiments contained 9% w/w of co-solvent on total weight of the latex.

### 3.2 Co-solvent Repartitioning Experiment

The co-solvent repartitioning experiments are schematically illustrated in Figure 2. The emission maximum of the fluorescent label attached to the polymer shifts to longer wavelengths with increasing co-solvent concentration in the polymer particle. Thus, when we add a latex formulated with co-solvent to a fluorescently labeled one which does not contain co-solvent, the emission will shift to longer wavelength (bathochromic shift) as the co-solvent diffuses and its concentration in the labeled part of the emulsion increases.

![Figure 2](image)

**Figure 2.** A) Schematic presentation of co-solvent repartitioning experiments; each big circle represents a latex particle of the respective emulsion. Emulsion I: green color displays co-solvent formulated latex particle which contains no dye molecules, Emulsion II: red circles represent co-polymerized dye molecules in the latex particle which contains no co-solvent, Emulsion III contains neither dye nor co-solvent and Emulsion IV contains both. B) Expected trends of wavelength (emission maxima) versus time in the two complementary co-solvent repartitioning experiments.

By monitoring the fluorescence as a function of time we can follow the redistribution of co-solvent between the polymer particles in the mixture. Conversely, when we dilute a fluorescently labeled formulated latex with one that does not contain co-solvent, the concentration of co-solvent in the labeled part of the mixture will decrease, and the fluorescence maximum will shift to the blue (hypsochromic shift). When we mix equal amounts of formulated and non-formulated latex, at equilibrium the co-solvent concentration in the labeled latex should be half of the original value.

In order to perform this experiment, four samples of one kind of latex were used, referred to as “Emulsions I - IV”. Two Emulsions were mixed to get one blend and the fluorescence...
emission of the blend was measured as a function of time. The shift of the emission provided direct information about the repartitioning of the co-solvent between the two crops of polymer particles. Emulsion I was non-labeled and formulated and Emulsion II was labeled but not formulated with co-solvent. Mixing these two yielded a blend whose emission was red shifted compared to the Emulsion II (bathochromic shift).

Emulsion III was non-labeled non formulated, and when mixed with an equivalent amount of Emulsion IV, which was labeled and formulated, yielded a blend whose emission was blue shifted, compared to the spectrum of Emulsion IV. This hypsochromic shift provided evidence of co-solvent leaving the labeled latex particles. Plotting hypsochromic and bathochromic shifts as a function of time, as shown in a hypothetical plot in Figure 2B, provides information about the rate of repartitioning of the co-solvent.

This approach was applied to all four sets of latices, i.e. low and high $T_g$, S/EHA and MMA/EA for monitoring the repartitioning behavior of four different co-solvents. Similar experiments using different latices are described in Chapter 4.

### 3.3 Results and Discussion

Low and high $T_g$ hydrophobic S/EHA and hydrophilic MMA/EA acrylic latices were separately formulated with four co-solvents i.e. EEH, TEX, DPnB and EEA according to the scheme illustrated in Figure 2A. Co-solvent repartitioning was monitored using steady-state fluorescence spectroscopy. The emission measurements were started immediately after mixing equal amounts of the two latex Emulsions in a quartz cuvet. For each experiment two blends were formed and emission spectra of each blend was measured for one hour during which twenty-one spectra were obtained. Integration time of each measurement was 100 sec. Fluorescence emission spectra obtained in this study were fitted with a skewed Gaussian function.

The skewed Gaussian function is a measure of asymmetry of the normal distribution. In skewed curves the peak has a tail either on the left or the right hand side. In our emission data on a wavelength scale we always observed that the tail on the right side was longer than on the left side, and the median, which describes emission maximum, was on the left side in the emission spectra (Figure 3).
Repartitioning of Co-solvents in Latex Emulsions

Figure 3. Skewed Gaussian peak showing asymmetric distribution.

A skewed Gaussian function is described in Equation 1.\textsuperscript{23}

\[
I(\lambda) = I_0 + I_{\text{max}} \exp \left( -\ln 2 \left[ \ln \left( 1 + 2s(\lambda - \lambda_{\text{max}})w \right) / s \right]^2 \right)
\]  

(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 \( s \). Higher skewness value means more asymmetry in the curves, i.e. tail on the right side will be longer and emission maximum will be located more towards the left side of the curve.

The emission curves could be fitted well with the skewed Gaussian function. As an example, Figure 4 displays the emission spectra of low \( T_g \) S/EHA latex with 0, 3, 6 and 9 \% w/w TEX fitted with the skewed Gaussian function as described by Equation 1. The parameters obtained are listed in Table 1.

Figure 4. Fluorescence emission spectra of low \( T_g \) S/EHA formulated with 0, 3, 6 and 9 \% w/w TEX. Emission spectra are fitted with skewed Gaussian function (Equation 1), which yielded emission maximum, intensity, width and skewness listed in Table 1.
Table 1. Emission maximum, intensity, width and skewness obtained by fitting the emission curves in Figure 4 with the skewed Gaussian function (Equation 1).

<table>
<thead>
<tr>
<th>% w/w TEX</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Intensity (a.u.)</th>
<th>Width (nm)</th>
<th>Skewness</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>449.4</td>
<td>$1.2 \times 10^6$</td>
<td>82.2</td>
<td>0.42</td>
</tr>
<tr>
<td>3</td>
<td>456.1</td>
<td>$9.3 \times 10^5$</td>
<td>88.4</td>
<td>0.39</td>
</tr>
<tr>
<td>6</td>
<td>462.6</td>
<td>$8.2 \times 10^5$</td>
<td>94.6</td>
<td>0.37</td>
</tr>
<tr>
<td>9</td>
<td>469.9</td>
<td>$7.3 \times 10^5$</td>
<td>100.4</td>
<td>0.36</td>
</tr>
</tbody>
</table>

In this study all emission spectra measured for monitoring the co-solvent repartitioning, were similar in shape to those shown in Figure 4. All of these curves were fitted with the skewed Gaussian function. Addition of co-solvent resulted in a shift of $\lambda_{\text{max}}$ to longer wavelength. Emission intensity and skewness decreased and the width of the band increased. This trend was observed for all emission spectra measured in this study.

It is worth to mention that the precision of the data was checked in terms of error in emission measurement by the fluorescence spectrophotometer. In one test we measured the emission of an MFT model compound (see chapter 2) in toluene at room temperature at various times of the day and on different days within a period of two weeks. Between measurements, the sample was taken out of the spectrometer, and the spectrometer was turned off overnight. This provided a measure of the error in the determination of the emission maximum of a representative sample: the standard deviation in $\lambda_{\text{max}}$ was $\pm 0.5$ nm.

On the other hand, the reproducibility of measurements of emission of co-polymerized-MFT in latex is another issue, because the result was found to depend on the age of latex. Freshly prepared and more than one year old latex showed differences in emission maxima of up to 5 nm, which is much larger than the measurement error of the spectrophotometer. Influence of temperature is another potentially significant factor to mention here: co-polymerized MFT in MMA/EA latex exhibited 12 nm shift of emission maximum towards longer wavelength upon increase in temperature from 15 to 35 °C (see chapter 2). This shows that variation in (room) temperature will influence the position of the emission maximum of co-polymerized MFT. The temperature in the laboratory was mostly close to 23 °C, but variations of $\pm 2$ °C may have occurred. By inserting a thermocouple into a latex sample we confirmed that temperature changes upon mixing of two latices and during subsequent 1 hour measurement were negligible.

Next, we will give the results for the four latices under separate headings, followed by an overall discussion at the end.
3.3.1 Low $T_g$ Hydrophilic Latices

The low $T_g$ hydrophilic latex was composed of the co-polymer MMA/EA and 2 % of AA. For the detection of co-solvent repartitioning it was formulated with three co-solvents: TEX, DPnB and EEA.

As explained in section 3.2, blend 1 was formed by mixing Emulsions I and II, which exhibited a bathochromic shift due to the migration of co-solvent into the fluorescently labeled particles. Mixing of Emulsion III and IV yielded blend 2 which showed a hypsochromic shift as a result of migration of co-solvent out of the fluorescently labeled latex particles. Figure 5 presents the fluorescence emission spectra of MMA/EA formulated with DPnB and EEA. With Texanol very similar results were obtained.

![Figure 5](image.png)

Figure 5. Steady-state fluorescence spectra of MMA/EA $T_g$ 20 °C latex formulated with, A) DPnB, B) EEA. Spectra of Emulsion II and IV were measured once and for blends 1 and 2 a series of spectra were measured for 1 hour.

The emission maxima of the non-formulated Emulsion II and DPnB formulated Emulsion IV were observed at 476.3 and 496.1 nm, respectively. Blends 1 and 2 showed the expected bathochromic and hypsochromic shifts, respectively. Within the time it took to prepare the blend and place the cell in the spectrometer the emission maxima coincided at the equilibration point that was at 486 nm, the average of $\lambda_{\text{max}}$ of Emulsions II and IV.

The emission maxima of the spectra were calculated by fitting with the skewed Gaussian function and plotted against time (Figure 6). It is clear that migration of all three co-solvents in this low $T_g$ latex occurred very rapidly, i.e. within the first minute after blend formation.
3.3.2 Low $T_g$ Hydrophobic Latices

A low $T_g$ hydrophobic latex was composed of the co-polymer S/EHA further containing 2% of AA. For the detection of co-solvent repartitioning it was formulated with three co-solvents: TEX, DPnB and EEA. Figure 7 presents the typical emission spectra obtained for blend 1 and 2 for low $T_g$ S/EHA latex formulated with TEX and DPnB co-solvents, respectively.

In TEX formulated S/EHA low $T_g$ latex (Figure 7A) $\lambda_{\text{max}}$ of Emulsion II and IV were observed at 449.4 and 470.0 nm, respectively and both blends exhibited $\lambda_{\text{max}}$ near the average wavelength, i.e. 458 nm. In DPnB formulated S/EHA $T_g$ 20 °C latex (Figure 7B) Emulsion II and IV were observed at 449.4 and 467.0 nm, respectively. Blend 1 and 2 exhibited $\lambda_{\text{max}}$ at 457.0 and 456.0 nm, respectively, corresponding to 4 - 5% of co-solvent in the labeled fraction of the blend. The difference of 1 nm is not considered significant. Results of TEX closely resemble those of DPnB.
Repartitioning of Co-solvents in Latex Emulsions

Figure 7. Steady-state fluorescence spectra of S/EHA $T_g$ 20 °C latex formulated with, A) TEX, B) DPnB. Spectra of Emulsion II and IV were measured once and blends 1 and 2 were measured for 1 hour.

Figure 8 displays the fluorescence emission maxima versus time for the three co-solvent formulations of low $T_g$ S/EHA latex.

Figure 8. Emission maximum versus time upon blending for S/EHA $T_g$ 20 °C latex formulated with A) TEX, B) DPnB and C) EEA.

Like low $T_g$ MMA/EA latex the formulations of S/EHA latices showed a rapid shift of the emission maximum of blend 1 and 2 to the equilibration point for TEX, DPnB and EEA co-solvents. In the experiments with TEX and DPnB the spectra were monitored for ten
Chapter 3

72

minutes. The same experiment was done with EEA for one hour. It is clear that migration of all three co-solvents in this low \( T_g \) S/EHA latex occurred very rapidly, i.e. within the first minute after blend formation.

### 3.3.3 High \( T_g \) Hydrophilic Latices

Co-solvent repartitioning experiments were carried out with a hydrophilic MMA/EA latex with high \( T_g \). As an example, emission spectra of DPnB and TEX formulated latices are shown in Figure 9. In non-formulated latex Emulsion II and DPnB formulated Emulsion IV, emission maxima were at 466.5 and 482.2 nm, respectively. In blends 1 and 2, the emission maximum gradually moved towards longer and shorter wavelengths, respectively, as expected. After an hour both of them coincided at 472 nm. Similarly in the case of TEX Emulsion II and IV had \( \lambda_{\text{max}} \) at 466.0 and 478.0 nm, respectively, and blends 1 and 2 showed emission at 470 nm after one hour.

![Figure 9](image)

**Figure 9.** Steady-state fluorescence spectra of MMA/EA \( T_g \) 60 °C latex formulated with A) TEX, B) DPnB. Spectra of Emulsions II and IV were measured once and blends 1 and 2 were measured for 1 hour.

Emission maxima versus time plots of high \( T_g \) MMA/EA latex formulated with four co-solvents EEH, TEX, DPnB and EEA are shown in Figure 10. For a quantitative description of the repartitioning of co-solvent we fitted the emission maximum versus time plots with exponential, biexponential and stretched exponential functions. Stretched exponential did not show a reasonable fit for any of the plots, but simple mono and biexponential functions showed good fits. The data obtained by fitting with exponential functions are presented in Table 2. Two time constants were obtained from biexponential fitting of the hypsochromic shifts for the emission versus time plots of EEH, TEX and DPnB formulations. One time constant was large (9 to 14 min) with a contribution of 1.7 to 2.9 nm while the other one was short (0.4 to 1.1 min), with a larger contribution. Unlike these three co-solvents EEA showed a good fit of the monoexponential model for the hypsochromic shift i.e., ca. 0.6 min.
Repartitioning of Co-solvents in Latex Emulsions

Figure 10. Emission maximum versus time plotted for MMA/EA $T_g$ 60 °C latex formulated with A) EEH, B) TEX, C) DPNB and D) EEA. Hypsochromic and bathochromic shifts in these plots were fitted with (bi)exponential functions, (blue and red lines).

Table 2. Data obtained with exponential fitting of hypsochromic and bathochromic shifts in the emission maximum versus time plots of MMA/EA $T_g$ 60 °C latex formulated with EEH, TEX, DPNB and EEA. Fits are shown in Figure 10.

| MMA/EA $T_g$ 60 °C formulation | Time constant 1 | | Time constant 2 |
|-------------------------------|----------------|----------------|
|                               | $\tau_1$ (min) | $A_1$ (nm)    | $\tau_2$ (min) | $A_2$ (nm) |
| EEH-hypsochromic              | 14 ± 2         | 2.9 ± 0.4     | 1.1 ± 0.1      | 7.4 ± 0.4  |
| EEH-bathochromic              | 4.4 ± 0.6      | 5.1 ± 0.3     |               |            |
| TEX-hypsochromic              | 13 ± 1         | 2.5 ± 0.1     | 0.51 ± 0.04    | 3.6 ± 0.1  |
| TEX-bathochromic              | 21 ± 6         | 1.9 ± 0.5     | 3.7 ± 0.5      | 4.1 ± 0.6  |
| DPNB-hypsochromic             | 9 ± 2          | 1.7 ± 0.4     | 0.4 ± 0.1      | 6.9 ± 0.4  |
| DPNB-bathochromic             | 12 ± 3         | 4.4 ± 1.6     | 3 ± 1          | 2.8 ± 1.7  |
| EEA-hypsochromic              | 0.6 ± 0.1      | 9.1 ± 0.5     |               |            |
| EEA-bathochromic              | 17 ± 1         | 6.5 ± 0.2     |               |            |
Bathochromic shifts for EEH and EEA co-solvents exhibited one time constant: 4.4 and 17 min, respectively. For the bathochromic shift for TEX and DPNB formulations a biexponential fit was slightly better than a monoexponential fit. The longer time constants are 21 and 12 min and the shorter ones are 3.7 and 3 min, for TEX and DPNB, respectively. Because of the smaller amplitude of the slow component, the average time constant of the bathochromic shift is smaller for TEX (6 min) than for DPNB (8 min).

In high $T_g$ hydrophilic latex we observed a gradual shift of the emission maxima of blends 1 and 2 towards a common equilibration point, which determines the migration of co-solvent into and out of latex particles. For EEH the equilibration point was observed 20 minutes after blend formation whereas for DPNB and TEX it took about 40 minutes. EEA took longer than the three co-solvents and the equilibration point was observed after 60 minutes.

Apart from the emission maximum, two more parameters that might be helpful in understanding the diffusion of co-solvent in aqueous and polymer phase of the latex are width and skewness.

![Figure 11. Width and skewness versus time plotted for MMA/EA $T_g 60 \degree C$ latex formulated with TEX: A) width B) skewness; DPNB: C) width and D) skewness.](image)

Addition of co-solvent to the co-polymerized MFT results in an increase of width and decrease in the skewness (Figure 4). Therefore we expect an increase in the widths of the
bands for blend 1 and a decrease for blend 2. Figure 11A and 11C presents plots of width versus time for TEX and DPNB formulated latex, respectively. Width and skewness plots of all four co-solvents show similar trend, therefore as an example only results for DPNB and TEX are shown in Figure 11.

The width of the emission bands obtained in blend 1 increased, while in blend 2 it decreased for all the co-solvents studied. As described earlier entrance of co-solvent into non-formulated latex results in the increase of peak width and a decrease in skewness.

Width and skewness of TEX formulated MMA/EA presented an equilibration point around 20 minutes, which is similar to the emission maximum versus time plot with the same co-solvent. In DPNB formulated MMA/EA latex in approximately 20 minutes width of blends 1 and 2 coincided at the same point, which is similar to the emission versus time plot. Skewness, however, did not show coincidence of both blends at the same time as observed for emission and width.

### 3.3.4 High T\textsubscript{g} Hydrophobic Latices

Emission spectra of blend 1 and blend 2 of high T\textsubscript{g} S/EHA latex formulated with DPNB and TEX are presented in Figure 12. In non-formulated Emulsion II and DPNB formulated Emulsion IV (Figure 12A) emission maxima were at 445.2 and 459.5 nm, respectively. After one hour, blend 1 and 2 exhibited λ\textsubscript{max} at 453.1 and 451.0 nm, respectively. In both blends, the emission maxima seemed to shift towards constant values, but the maxima in the two blends remained approximately 2 nm apart at the end of the 1 h measurement period. Similarly, in TEX formulated high T\textsubscript{g} S/EHA latex blends 1 and 2 exhibited λ\textsubscript{max} 451.8 and 454.4 nm, respectively, and both wavelengths remained 2.6 nm apart.

![Figure 12. Steady-state fluorescence spectra of S/EHA T\textsubscript{g} 60 °C latex formulated with, A) TEX, B) DPNB. Spectra of Emulsions II and IV were measured once and blends 1 and 2 were measured for 1 hour.](image)

Figure 13 presents the λ\textsubscript{max} versus time plot for high T\textsubscript{g} S/EHA latex formulated with EEH, TEX, DPNB and EEA.
Figure 13. Emission maximum versus time plotted for S/EHA $T_6$ 60 °C latex formulated with A) EEH, B) TEX, C) DPnB and D) EEA. Bathochromic and hypsochromic shifts were fitted with exponential functions (red and blue lines show the fit).

Table 3. Data obtained with exponential fitting of hypsochromic and bathochromic shift in the emission maximum versus time plots of S/EHA $T_6$ 60 °C latex formulated with EEH, TEX, DPnB and EEA. Fits are shown in Figure 13.

<table>
<thead>
<tr>
<th>S/EHA $T_6$ 60 °C formulation</th>
<th>Time constant 1</th>
<th>Time constant 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_1$ (min)</td>
<td>$A_1$ (nm)</td>
</tr>
<tr>
<td>EEH-hypsochromic</td>
<td>$6 \pm 1$</td>
<td>$2.1 \pm 0.3$</td>
</tr>
<tr>
<td>EEH-bathochromic</td>
<td>$17 \pm 2$</td>
<td>$4.7 \pm 0.3$</td>
</tr>
<tr>
<td>TEX-hypsochromic</td>
<td>Not fit</td>
<td></td>
</tr>
<tr>
<td>TEX-bathochromic</td>
<td>$27 \pm 1$</td>
<td>$4.15 \pm 0.05$</td>
</tr>
<tr>
<td>DPnB-hypsochromic</td>
<td>Not fit</td>
<td></td>
</tr>
<tr>
<td>DPnB-bathochromic</td>
<td>$27 \pm 3$</td>
<td>$4.1 \pm 0.1$</td>
</tr>
<tr>
<td>EEA-hypsochromic</td>
<td>Not fit</td>
<td></td>
</tr>
<tr>
<td>EEA-bathochromic</td>
<td>$31 \pm 7$</td>
<td>$4.4 \pm 0.4$</td>
</tr>
</tbody>
</table>

Fitting of the hypsochromic shifts in case of TEX, DPnB and EEA plots was not successful,
but the EEH formulation showed a good monoexponential fit with a time constant of 6 min (Table 3). The bathochromic shifts showed a good fit with biexponential models. The time constants obtained by these fits describe the diffusion of co-solvent into the non-formulated latex particle.

For bathochromic shift of these four formulations one time constant was longer (17 to 31 min) with a large contribution (4.1 to 4.7 nm) while the other was shorter (0.7 to 1.5 min) with a small contribution (1.5 to 2.9 nm).

Unlike these three co-solvents, EEA showed good fit of monoexponential model for the bathochromic shift with a time constant of ca. 16 min.

Width and skewness of the emission spectra are plotted against time and as an example shown for TEX and DPnB in Figure 14. In all four formulations of high $T_g$ S/EHA a change in the width of band was observed in the first 10 minutes i.e., it increased and decreased for blend 1 and 2, respectively. For instance non-formulated fraction II of high $T_g$ S/EHA and TEX formulated fraction IV, exhibited widths of 82.5 and 102.5 nm, respectively. After blend formation migration of co-solvent started to occur and a change in the width of the band was observed. After an hour the blends exhibited widths of 92.1 and 94.7 nm, respectively.

![Figure 14](image_url)

Figure 14. Width versus time plotted for S/EHA $T_g$ 60 °C latex formulated with A) TEX, B) DPnB.
Figure 14B and 14D present skewness versus time plots for the high $T_g$ S/EHA latex formulated with TEX and DPnB, respectively. We observed increase in skewness for blend 1 and decrease in blend 2. This holds true for all the formulations in high $T_g$ S/EHA latex.

In Figure 13 two features are commonly observed in the plots for all four co-solvents: (i) coincidence of $\lambda_{\text{max}}$ at a common equilibration point was not observed in the first hour of blend formation (ii) escape of co-solvent was much more rapid and abrupt than the entrance which progressed gradually. However, no more change in $\lambda_{\text{max}}$ was detected after approximately 40 minutes after blending. This was contrary to the low $T_g$ latices, which showed coincidence of hypsochromic and bathochromic shifts at the equilibration point in first minute of blend formation. Also the plots of width and skewness (Figure 14) did not show coincidence of the values in the complementary experiments.

### 3.4 Discussion

An important result that emerges from our experiments is that the rate of co-solvent repartitioning is strongly dependent on the $T_g$ of the latex material, irrespective of the co-solvent. In low $T_g$ latices repartitioning was found to be very rapid, whereas in high $T_g$ latices it was much slower. Still, it occurred within an hour for the high $T_g$ hydrophilic material. For the styrene-based copolymer of high $T_g$, the results for the two complementary measurements did not show convergence on the same emission wavelength, but most of the changes in the position of the emission maximum after blending occurred within an hour, as for the hydrophilic high $T_g$ material.

In the repartitioning process, the viscosity of the polymer particles appears to play a key role. In the low $T_g$ latices equilibration was observed in the first minute after mixing both pairs of emulsions, and the actual kinetics could not be resolved. Diffusion of co-solvent is much faster when the free volume is high, which is the case at $T > T_g$. The polymer in the particles of the lower $T_g$ latices has a low viscosity and addition of co-solvent further reduces it. Hydroplasticization may contribute to a further lowering of the $T_g$ especially of the hydrophilic latex particles.

In the high $T_g$ latices, the emission maxima shifted more slowly, and the rates of the shift could be characterized in terms of exponential functions. A common observation is that the overall diffusion rate in blend 1 is slower than in blend 2 (Figures 10 and 13). The hypsochromic shift, caused by the escape of co-solvent from the fluorescently labeled particles, occurred rapidly. In this case, the latex particles have a low $T_g$ due to the presence of co-solvent, as schematically illustrated in Figure 15B. The fluorescently labeled particles in blend 1 do not contain co-solvent and have a high $T_g$. 

---

78
Repartitioning of Co-solvents in Latex Emulsions

Figure 15. Situation of latex particle in Emulsion II and IV is presented by the left and right hand cartoon images, respectively. Small spheres present co-solvent molecules and one big sphere is latex particle having polymer chains in its core. A) Migration of co-solvent into fluorescently labeled particle in Emulsion II, $T_g$ of the latex particle is not yet affected by the co-solvent B) migration of co-solvent out of a fluorescently labeled latex particle in Emulsion IV, here plasticization due to the presence of co-solvent has lowered $T_g$ of the particle and polymer chains are unwound.

In the repartitioning of co-solvent the molecules need to exit from the solvent-enriched polymer particles, enter into the water phase, diffuse through it and enter into the co-solvent-deficient polymer particles. A simple description of the process in terms of a chemical equilibrium is given in Equation 2:

$$
\begin{align*}
&\text{A} \xrightleftharpoons[k_{\text{out}}]{k_{\text{in}}} \text{W} \xrightleftharpoons[k_{\text{out}}]{k_{\text{in}}} \text{B}
\end{align*}
$$

In this equation, A and B are the concentrations of the co-solvent in the two polymer compartments, W represents the concentration in the water phase. Since the polymer compartments are chemically identical, the same rate constants for entry ($k_{\text{in}}$) and exit ($k_{\text{out}}$) of the co-solvent will apply. Before blending, the co-solvent containing emulsions are in equilibrium. After blending equal volumes of A+W and W+B, the aqueous phase contains the same concentration of co-solvent as at the final equilibrium, but the concentration in compartment A is twice the equilibrium value and that in B is zero. If this simple model applies, the concentration in the aqueous phase is constant, that in A decreases exponentially, and that in B increases exponentially with the same time constant. The experimental data, however, clearly show different time constants and in many cases biphasic behavior.

Given the importance of the internal viscosity of the polymer particles, one should expect a rate that depends on the ability of plasticization by the co-solvent and its actual concentration in the particles. Because the concentration of co-solvent is changing, we should expect the rate to change with time. This could lead to stretched exponential behavior. The data, unfortunately, did not allow a meaningful fit to this function: many more data points are needed to determine the time constants and the stretch constants.
individually with a useful accuracy. We therefore used fits with simple exponential or a biexponential function.

Even without any data fitting it is obvious from figures 10 and 13 that the escape of co-solvent from the formulated particles is faster than the entrance into the non-formulated ones. Such behavior can be modeled by making $k_{\text{out}}$ dependent on the concentration of co-solvent in the particle. Initially, co-solvent escapes from the formulated particles, enriching the water phase in co-solvent. In the next phase, the co-solvent in the water phase and the non-formulated particles slowly equilibrate. This is particularly clearly seen in the case of MMA/EA with EEA as the co-solvent: dilution of the formulated latex with the non-formulated one leads to rapid loss of co-solvent from the formulated particles ($\tau = 0.6$ min), and much slower increase of the co-solvent concentration in the non formulated MFT-labeled particles ($\tau = 17$ min).

At this stage, we prefer to treat the observations more qualitatively. An important reason is that the change in the shapes of the emission bands, exemplified in figures 12 and 14, occurs more rapidly than the change in the emission maxima. This can be attributed to heterogeneity of the co-solvent distribution within the latex particles. The migration of co-solvent out of the enriched particles will first occur from the outer shell, and likewise, entry into the non-formulated particles will first shift the emission of the probe’s fluorescence in the outer shell. This may explain the rapid shift (with small amplitude) in the first minutes of most of the experiments with the high $T_g$ materials. As a result of this heterogeneity, the emission maximum as observed during the redistribution process does not necessarily agree with the equilibrated values (figure 4), and it cannot be taken as a precise quantitative measure of co-solvent concentration.

In the case of the high $T_g$ MMA/EA latices clear differences between the dynamics for the co-solvents are observed. For EEH equilibration was observed after ~ 20 minutes of blend formation whereas for DPnB and TEX it took ~ 40 minutes. EEA took longer than the three co-solvents and equilibration was observed at 60 minutes. This behavior correlates with the hydrophilicity of these co-solvents, measured by the water solubility or the octanol/water partition coefficient ($\log P_{o/w}$). Texanol is the least water-soluble (0.1 %) and has highest $\log P_{o/w}$ (3.74).\textsuperscript{26} The water solubility of EEH is 0.2 % and has the $\log P_{o/w}$ 2.73.\textsuperscript{27} DPnB (5 %) being the moderately water-soluble has, has lower $\log P_{o/w}$ value (1.13).\textsuperscript{28} EEA (24 %) is quite water-soluble and has a lowest $\log P_{o/w}$ of 0.24.\textsuperscript{29} Whereas release of co-solvent from the formulated particles is fast in all cases, the uptake in the non-formulated particles is faster when the water solubility is smaller, that is, when the distribution coefficient favors the polymer phase more.
Calculation of the wet state \( T_g \) of co-polymers for low and high \( T_g \) latices was carried out by using Fox equation. This was done in the similar way as the dry state \( T_g \) was predicted by using this equation (Chapter 2). The only difference in the calculation of wet and dry state \( T_g \)s was that \( T_g \) value of the third monomer, acrylic acid, was taken as -98 °C for the former and 105 °C for the latter case. These calculations indicated that the wet state \( T_g \)s of MMA/EA latex were ca. 5 and 43 °C, when dry state values were 20 and 60 °C, respectively. Similarly, for S/EHA latex wet state \( T_g \)s were 15 and 53 °C when dry state values were 20 and 60 °C, respectively. These facts reveal that in general MMA/EA latex is more hydroplasticized than S/EHA latex and for low \( T_g \) MMA/EA latex this effect was even more pronounced i.e., three times more than its hydrophobic counterpart.

In Figure 13 three features were observed in the plots for all four co-solvents with the high \( T_g \) S/EHA latex: (i) escape of co-solvent from formulated fluorescently labeled particles was more rapid than the entrance, (ii) in the bathochromic shift a fast rise occurred and (iii) coincidence of \( \lambda_{max} \) at a common equilibration point was not observed within one hour, although no more change in emission maximum was detected after \( \sim 40 \) minutes of blend formation. Comparison of co-solvent partitioning plots of S/EHA \( T_g \) 60 °C latices with the calibration curves revealed that release of co-solvent from the fluorescently labeled particles (hypsochromic shift) was faster reached to the equilibration point. Only the uptake of co-solvent by the fluorescently labeled particles (bathochromic shift) was slow and it was slightly behind the equilibration point, however it was not far from the equilibrium. Because of no co-solvent in the non-formulated fluorescently labeled particle (Emulsion II) no free volume is available which in turn slower down the entrance of co-solvent. Free volume between the polymer chains, to much extent is responsible for the rate of repartitioning of the co-solvent in latices.

The first observation is similar to that made with the hydrophilic latex materials. The fast rise of the bathochromic shift (\( \tau \ 0.7 - 1.5 \) min) can be attributed to the entry of the co-solvent in the outer shell of the particles, which is followed by slower equilibration (\( \tau \ 17 - 31 \) min). For most co-solvents, the hypsochromic shift is a bit smaller than the bathochromic one. It is conceivable that the presence of a high concentration of the co-solvent in the latex (9% w/w on the total weight, i.e. up to 24% in the polymer phase) causes a structural relaxation of the polymer particles. As a result, the two polymer compartments A and B (Equation 2) are no longer identical on the time scale of the experiment. The relaxation of compartment A may have increased its affinity for the co-solvent, or it may have increased the sensitivity of the solvatochromic fluorescent probe to the presence of the co-solvent. Further research will be needed to shed more light on this issue.
3.5 Conclusion

Repartitioning of co-solvents was monitored as a function of time in low and high $T_g$ hydrophobic S/EHA and hydrophilic MMA/EA acrylic latices. Low $T_g$ latices of both types displayed rapid migration of co-solvent across the aqueous and polymer phase of the latex, and equilibration was observed within the first minute of blend formation.

In high $T_g$ MMA/EA latex repartitioning of co-solvent smoothly progressed towards equilibration, which was achieved within an hour of blending. The equilibrium was attained faster with less water-soluble co-solvents than with more water-soluble co-solvents. In high $T_g$ S/EHA latex repartitioning of co-solvent was slower than in the MMA/EA latex of similar $T_g$. This may be due to a lower wet state $T_g$ in the latter as a result of some hydroplasticization.

Remarkably, a common equilibration point was not reached in the complementary experiments starting with the co-solvent in the labeled or in the non-labeled S/EHA latex. This suggests that the presence of a high concentration of the co-solvent in the latex causes a change of the material that is not reversible on the time scale of the present experiments.

Biexponential fits provided two time constants for entry of the co-solvent in the nonformulated particles in both high $T_g$ latices, which demonstrate that diffusion occurs in two different stages: a fast component with small amplitude, which is particularly pronounced in the case of the hydrophobic material, is probably caused by diffusion of co-solvent molecules into the outer shells of the latex particles, and the second, slower component is related to further penetration of co-solvent molecules into the cores of the particles.

3.6 Experimental details

3.6.1 Co-solvents and Formulations

The four co-solvents were employed in this study were ethylene glycol ethyl hexylether (EEH), 2,2,4-trimethyl-1,3-pentanediol(2-methylpropanoate) (Texanol), di(propylene glycol) n-butyl ether (DPnB) and ethylene glycol ethyl ether acetate (EEA) (Figure 16).

In the co-solvent experiments listed in this chapter, formulated fractions of latex contained 9% w/w co-solvent. The pH of latex as prepared (see Chapter 2) 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. To prepare 100 g of 9% w/w DPnB formulated S/EHA latex, 9 g of DPnB was slowly added to 91 g of S/EHA latex at pH 7 and stirred for 30 min by a mechanical stirrer.
3.6.2 Blend formation

1 ml of each Emulsion (i.e., Emulsion I and II or Emulsion III and IV) was added into the quartz cuvet and the whole amount was sucked once in and out of the pipette to ensure the thorough mixing of the two Emulsions. Emission measurement was started within a minute after blending and emission spectra were recorded for one hour. The acquisition of each spectrum (200 points, 0.5 s/point) took 100 seconds. As the results show that the dynamics of interest are either much faster or much slower than the acquisition time, the small distortion of the spectrum due to changes occurring during a scan can be neglected.

A trivial explanation of the fact that some of the trend lines of the two complementary experiments do not meet could be that the amounts of the two Emulsions that are blended are not well controlled. We carefully checked this by weighing the sample cell with one emulsion and again with the mixture. The error in the pipetting was < 0.05 %. Another possibility that we considered was that some heat could be generated during the co-solvent repartitioning, which will affect the emission maximum (see chapter 2). Measurement of the temperature inside the blend during the experiment allowed us to exclude this as well. Each experiment was repeated three times to ensure the reproducibility. First time experiment was carried out as such i.e., without any extra monitoring whereas in second and third attempt amount of Emulsions added for blending and temperature inside the cuvet were monitored, respectively. Repetition produced similar results and in this chapter those results are reported which were obtained in first attempt when latex was fresh.
3.7 References

Repartitioning of Co-solvents in Latex Emulsions


26. Screening Information Data Sheet (SIDS) of 2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol). **1994**, Organisation for Economic Co-operation and Development (OECD). High Production Volume Chemicals Programme, USA.

27. Chemical Information Profile for Ethylene Glycol 2-Ethylhexyl Ether (EEH). **2008**, National Toxicology Program USA.

