1. Introduction

In emulsion polymerization, the water phase plays a significant role in controlling the microstructure of the latex [1]. To study the influence of water-phase kinetics in controlling the microstructure and the properties of the final latex particles, the chemical composition distribution (CCD) and molecular weight distribution (MWD) of cooligomers formed in the water phase should be determined. The CCD and MWD of the oligomers in the water phase depend on the rates of propagation in the water phase in combination with the concentrations. The ability of MALDI-ToF-MS to give the full CCD and MWD of cooligomers present in the water phase was demonstrated [2]. This information can be used in the calculation of reactivity ratios in copolymerizations. In order to calculate the reactivity ratios in the water phase, the feed ratios of monomers in this phase should also be known. In emulsion copolymerization, monomers are distributed between the different phases (monomer, water, and particle phases). The concentrations and ratios of the monomers in each phase are determined by thermodynamics [1]. Both theoretical studies and experimental studies have been done on monomer partitioning in emulsion (co)polymerizations. Two equations that have been used so far to calculate partitioning in stages II and III of an emulsion copolymerization are the Vanzo equation [3] and the Morton equation [4].

The Vanzo model [3] is actually a modified version of the Morton model [4]. Both models are based on thermodynamics. These models are based on interactions between monomer and polymer and contain three main terms: the entropic, the enthalpic, and the surface-tension contributions.

Maxwell et al., who derived a simplified solution of the Vanzo equation for the partitioning of sparingly soluble monomers between different phases, stated that for sparingly soluble monomers, which have negligible interaction with each other and with the solvent, the concentration of monomer A in the water phase in the presence of monomer B linearly depends on the molar fraction of monomer A in the droplet phase.
These models are able to calculate the monomer concentration in all three phases. For our calculations of the reactivity ratios in water, we need the accurate feed ratios of the monomers in water. Because we are performing ab initio polymerizations at very low conversions, the initial feed ratios are determined by the initial water-phase solubilities. For this purpose, we have to look at some assumptions that are made in the Vanzo equation.

1. Ratio of the molar volumes of the monomers is close to unity.
2. The monomers in the emulsion polymerization are low to moderately water soluble.
3. The interaction of both monomers with the polymer is similar.
4. Interaction of the monomers with each other and with water does not influence the feed ratio of the monomers in the water phase because the water phase is strongly diluted.

Assumption 4 is especially questionable in the case that we use more water-soluble monomers, but even for moderately water-soluble monomers, the presence of one monomer could affect the solubility of the other monomer. In the case where one monomer is completely water soluble and the other one is partially soluble, the water-soluble monomer can be regarded as a cosolvent for the other monomer [1]. In principle, the addition of monomers can increase (structure makers) or break down (structure breakers) the structure of water (organization of the water molecules) and affect the solubility of the monomers [5]. This means that we cannot simply use the solubilities of the individual monomers in water to calculate the feed ratios; mutual influences must be considered.

To prove our statements, experiments have been done with different monomer combinations based on their solubility in water. The experiments were aimed at determining the feed ratios of monomers in water as a function of the monomer composition. The experiments were done in the absence of particles because we were interested in the initial feed ratio of monomers in the water phase.

2. Methodology

The materials used are as follows. Butyl acrylate (BA), methyl methacrylate (MMA), methyl acrylate (MA), methacrylic acid (MAA), and vinyl acetate (VA) (monomers) were used after passing them over an inhibitor remover column (Sigma Aldrich), used as received.

The methods performed are the following. Two monomers and water were mixed in different ratios (varying only one component, keeping the other constant) in a small reactor. The reactor was heated up to equilibration temperature (70°C) and stirred at 300 rpm for 20 minutes. In order to avoid polymerization, the reactors were shielded from light; polymer formation could be tested for by adding some methanol to the droplet phase (monomer phase) and observing precipitation of the polymer. It was ensured that no polymer was formed during the solubility experiments. After stirring was stopped, both phases separated (monomer droplet and water). After 20–30 minutes, a sample of the water phase has been taken out with a syringe through a tube that was extending underneath the droplet layer (Figure 1) without disturbing the separated droplet phase. The sample was then quickly diluted in water and characterized with UV-Vis spectroscopy.

A sample which was taken from the reactor has been diluted until the absorbance is between 0.1 and 1.5, the optimal range for accurate UV-Vis measurements. The total absorbance of the solution is considered to be the sum of the absorbance of the individual components. A quantitative estimation of each component in the solution is possible if the absorption spectrum is slightly different for the two components. By choosing two wavelengths where the molar absorptivities are different [6], one can calculate the concentration of the two monomers. The expressions for the absorbance at two different wavelengths $A'$ and $A''$ are as follows:

\[
A' = \Sigma'_{1}bc_{1} + \Sigma'_{2}bc_{2},
\]

\[
A'' = \Sigma''_{1}bc_{1} + \Sigma''_{2}bc_{2},
\]

where $\Sigma'_{1}$, $\Sigma'_{2}$, $\Sigma''_{1}$, and $\Sigma''_{2}$ are absorption coefficients of the components 1 and 2 at the two wavelengths and $c_{1}$ and $c_{2}$ are the concentrations of the individual components. These relationships are only valid if Lambert-Beer’s law is followed. The absorption coefficients were determined separately with the aid of aqueous solutions with known concentrations of the individual monomers.

Feed ratios of monomers in water are calculated for several monomer combinations. In the first three monomer combinations, BA is a common monomer and the other...
monomer varied from hydrophobic (case I) to very hydrophilic (case III).

(i) Case I (MMA-BA). It can be seen from Figure 2 that the amount of MMA monomer in the water phase linearly increases with the fraction of MMA in the droplet phase coupled with a decrease in the amount of BA in the water (aqueous) phase.

(ii) Case II (VA-BA). First of all, in Figure 3 a small deviation from linearity of the water-phase concentration of VA versus the feed ratio in the droplet phase can be seen. Secondly, with increased feed ratio of VA in the droplet phase (Dataset Item 2 (Table)), the BA amount in water is decreased.

(iii) Case III (MAA-BA). To understand interaction of monomers with each other and with water better, another monomer combination MAA-BA was studied where MAA is completely miscible with water (Dataset Item 3 (Table)). One can observe in Figure 4 that more MAA in the droplet phase means more in the water phase (with a small deviation from a linear dependence). The absolute concentration of BA in the water phase in the presence of already small amounts of MAA is much higher than the saturation concentration of BA in water alone and also of BA in water in the presence of VA (case II).

Until now, in all combinations of monomers, BA was kept the same and the other monomer was varied (based on solubility in water). Another set of monomers has been analyzed where MMA is the constant factor, and other monomers varied again based on their water solubility.

(i) Case IV (MA-MMA). For this combination also, there is a deviation from the linear dependence of the water-phase concentration on the droplet phase (Dataset Item 4 (Table) and Figure 5).

(ii) Case V (MAA-MMA). In case V, high solubility of MMA in water (higher than in the case of MMA-BA and MA-MMA) is observed (Dataset Item 5 (Table) and Figure 6). This was also observed in the combination MAA-BA (case III) for BA. The solubility trends are deviating from linearity.

3. Dataset Description

The dataset associated with this Dataset Paper consists of 5 items which are described as follows.
Figure 5: Concentration of MA (blue) and MMA (red) in the water phase versus the mole fraction of MA in the droplet phase.

Column 5: BA Final Concentration (mol dl⁻¹)
Column 6: MMA Final Concentration (mol dl⁻¹)

Dataset Item 2 (Table). Fraction of VA and BA in the droplet layer (droplet mole fraction) and the resulting amounts in the water phase (final concentration).

Column 1: VA Droplet Mole Fraction
Column 2: BA Droplet Mole Fraction
Column 3: Absorbance at 200 nm
Column 4: Absorbance at 210 nm
Column 5: BA Final Concentration (mol dl⁻¹)
Column 6: VA Final Concentration (mol dl⁻¹)

Dataset Item 3 (Table). Fraction of VA and BA in the droplet layer (droplet mole fraction) and the resulting amounts in the water phase (final concentration).

Column 1: VA Droplet Mole Fraction
Column 2: BA Droplet Mole Fraction
Column 3: Absorbance at 200 nm
Column 4: Absorbance at 210 nm
Column 5: BA Final Concentration (mol dl⁻¹)
Column 6: VA Final Concentration (mol dl⁻¹)

Dataset Item 4 (Table). Fraction of MA and MMA in the droplet layer (droplet mole fraction) and the resulting amounts in the water phase (final concentration).

Column 1: MMADroplet Mole Fraction
Column 2: MADroplet Mole Fraction
Column 3: Absorbance at 200 nm
Column 4: Absorbance at 215 nm
Column 5: MA Final Concentration (mol dl⁻¹)
Column 6: MMA Final Concentration (mol dl⁻¹)

Dataset Item 5 (Table). Fraction of MAA and MMA in the droplet layer (droplet mole fraction) and the resulting amounts in the water phase (final concentration).

Column 1: MMADroplet Mole Fraction
Column 2: MAADroplet Mole Fraction
Column 3: Absorbance at 200 nm
Column 4: Absorbance at 210 nm
Column 5: MAA Final Concentration (mol dl⁻¹)
Column 6: MMA Final Concentration (mol dl⁻¹)

4. Concluding Remark

As concluding remarks, one can be sure that the solubility of one monomer is definitely affected by the solubility of the
other monomer especially in case of water-soluble monomers. This means that we cannot simply use the solubility of the individual monomers in water to calculate the feed ratios; mutual influences must be considered.

Dataset Availability

The dataset associated with this Dataset Paper is dedicated to the public domain using the CC0 waiver and is available at http://dx.doi.org/10.1155/2013/610329/dataset.

Disclosure

The authors declare that they have no competing financial interests.

Acknowledgment

The authors would like to acknowledge BASF for sponsoring this project.

References


