The Influence of Reaction Conditions on the Copolymer Composition in Inverse Miniemulsion

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Summary: Water-soluble poly(2-acrylamido-2-methylpropane-1-sulfonic acid-*co*-1-vinylimidazole) (P(AMPS-*co*-1-VIm)) and poly(2-acrylamido-2-methylpropane-1-sulfonic acid-*co*-2-(dimethylamino)ethyl methacrylate (P(AMPS-*co*-DAMA)) are studied as it is known that the copolymer composition is affected by pH of the monomer phase in inverse miniemulsion. The distribution of the basic monomers in the continuous and dispersed phase changes due to their degrees of protonation. The amounts of the monomers in the cyclohexane phase is determined by gas chromatography, the copolymer composition is studied by elemental and thermogravimetric analysis. An insight into the monomer distribution in the polymer is provided by simultaneous potentiometric and conductometric titration of polymer solutions.

Keywords: copolymer composition; copolymerization; inverse miniemulsion; radical polymerisation; water soluble polymers

Introduction

In recent years new applications were developed for water-soluble, high-molecular-weight polymers, which led to a renewed interest in inverse emulsion polymerization.[1,2] The inverse miniemulsion, using cyclohexane as the continuous phase and water as the dispersed phase, is a way to synthesize those polymers.[3,4] Miniemulsions, prepared by ultrasonication, combine the bulk reaction in nanosized droplets and the advantages of emulsion polymerization. In contrast to the direct miniemulsion there are less publications about inverse miniemulsion polymerization. Monomers like acrylamide[5–7] were often used to investigate the polymerization and copolymerization reactions in inverse miniemulsions. Recently, Matyjaszewski et al. used inverse miniemulsions to obtain well defined polymers by the ATRP technique.[8]

The acid/basic monomer systems 2-acrylamido-2-methylpropane-1-sulfonic acid/1-vinylimidazole (AMPS/1-VIm) and 2-acrylamido-2-methylpropane-1-sulfonic acid/2-(dimethylamino)ethyl methacrylate (AMPS/DAMA) were polymerized at different monomer feed compositions in solution by our working group.[9] Kurenkov et al. studied the kinetics of polymerization of AMPS and its salts and the copolymerization with acrylamide in inverse emulsion.[10,11]

We copolymerized the acceptor monomer AMPS ($Q = 1.0, e = 1.5$) with the donor monomers 1-VIm ($Q = 0.11, e = -0.68$) and DAMA ($Q = 0.6, e = -0.3$)[9] under different conditions in inverse miniemulsion, varying the loci of initiation and pH in the dispersed phase.[3] The distribution of the monomers into both phases of the miniemulsion, caused by deprotonation of the monomer, was followed. To substantiate this observation and its influence on the copolymer composition, the amount of 1-VIm and DAMA in the cyclohexane phase was determined. Also the location of initiation and the location of the monomers at the beginning of the reaction were modified. Monomer solutions were sonicated separately. The results were compared with the conventional system.

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Not only is the absolute copolymer composition affected but also the sequence of the monomer units in the polymer chain. An easy way to get an insight into the assembly of functional groups is the potentiometric and conductometric titration of the polymer solution.[12]

Experimental Part

Materials

1-Vinylimidazole (1-VIm) (Fluka, 99%) was purified by vacuum distillation. 2-(Dimethylamino)ethyl methacrylate (DAMA) (Aldrich, 98%) was treated with an inhibitor remover (Aldrich) to remove MEHQ before use. 2-Acrylamido-2-methylpropane-1-sulfonic acid (AMPS) (Aldrich, 99%), cyclohexane (Riedel-de Haën, 95%) and sodium hydroxide (Fluka) were used as received. Distilled water was used to dissolve the monomers. The initiator 2,2′-azobisisobutyronitrile (AIBN) (Fluka, 98%) was recrystallized from methanol. Ammonium peroxodisulfate (APS) (Fluka, 98%) and the surfactant Addconate WO were used without further purification. Addconate WO, a polyisobutylene succinic anhydride with an average M_n of 2300, was purchased from Lubrizol Co.

Synthesis

The total monomer concentration was $6.67\,\mathrm{mol}\cdot\mathrm{L}^{-1}$, while the molar ratio AMPS/basic monomer was 1:1. AMPS was dissolved in 4.5 g of distilled water. 1-VIm and DAMA were added dropwise under ice-cooling. For polymerizations in an alkaline dispersion phase, water was partly replaced by a 10 M sodium hydroxide solution to adjust pH. The monomer solution was mixed with 90 g of cyclohexane containing 0.3 g of Addconate WO. After stirring for 30 min under nitrogen, the inverse miniemulsion was prepared by sonication of the mixture for 120 s with a Sonics Vibracell at 90% intensity. The sample was ice-cooled to prevent a temperature rise. The inverse miniemulsion was poured into a double-wall glass reactor heated up to 60 °C, and 0.2 g of AIBN was added. For initiation in the monomer phase, 0.28 g APS was added to the monomer phase prior to sonication. The reaction under continuous nitrogen bubbling was usually complete after 120 min. Samples were taken in certain intervals. The polymer was precipitated with an excess of acetone, filtered off, washed with acetone and dried at 40 °C under vacuum to constant weight.

Analytical Methods

The conversions were determined gravimetrically. Equation (1) was used to calculate the conversions.[3]

$$\text{conversion} = \frac{m_P}{m_M} \times \left(\frac{1}{1 + \frac{m_E}{m_M}} \right) \times \frac{m_{total}}{m_S} \tag{1}$$

where m_P is mass of polymer, m_M mass of monomer feed, m_E mass of emulsifier, m_{total} mass of inverse miniemulsion, m_S mass of taken sample.

The polymers were considered to be composed of the AMPS units, the basic monomer units and water, which is bound to the sulfonic groups. The composition of the copolymers was determined by elemental analysis (Vario EL 2, Elementar Analysensysteme GmbH, Germany) for C, H, N, and S. The conversion data were corrected by subtraction the water content. The elemental analysis results were used to calculate the conversions.

For thermogravimetric analysis a TGA 850 from Mettler Toledo was used. The samples decomposed in nitrogen atmosphere at a heating rate of $20\,\mathrm{K}\cdot\mathrm{min}^{-1}$.

Gas chromatographic measurements were conducted with a Varian GC 3900. An equimolar mixture of AMPS and the basic monomer was dissolved in water or NaOH solution or the basic monomer alone was dissolved in water or HCl solution and cyclohexane was added. The composition was same in the polymerization experiments but the scale was five times smaller. After sonication for 10 s and phase separation

overnight with subsequent centrifugation, the cyclohexane phase was analyzed. To determine the monomer amount, a calibration curve was constructed.

For titration the polymers were dissolved in 1 mM KCl solution (1 mg/mL) and pH was adjusted to 12. Both AMPS and 1-VIm/DAMA units were deprotonated. Then the polymer solution was titrated with 0.1 M HCl. After every titrant addition equilibrium was attained. The titration was conducted until a pH value below 3 was reached to protonate the 1-VIm and DAMA groups. This reversed way of titration was conducted to obtain a uniform starting point where all samples were dissolved completely in the aqueous media. Conductivity was measured with a WinLab Data Line conductivity meter from Windaus. In the course of protonation of the basic groups in the monomer, the conductivity remains constant or the slope strongly decreases, so the beginning and end of the polymer titration can be observed. pH was measured with a WTW pH 521 pH meter. The pK_a value was calculated according to HOARE et al.[12] using the HENDERSON-HASSELBACH equation. The pK_a values were plotted versus the degree of protonation, which was calculated from polymer and blank titration curves.

Results and Discussion

We copolymerized AMPS and 1-VIm and obtained different copolymer compositions for the reactions under acid and alkaline conditions.[3] This suggests, that the weak base 1-VIm is deprotonated under alkaline conditions and therefore is more soluble in the cyclohexane phase, which affects the copolymer composition. To specify these first results, the contents in the cyclohexane phase of 1-VIm and DAMA both protonated and unprotonated, under homo- and copolymerization conditions are determined by GLC.

Table 1 shows a very clear trend regarding the influence of protonation of the basic monomer. Mixed with AMPS (conditions (1)), no basic monomer can be detected in the cyclohexane phase. The H^+-ions of the highly acidic AMPS[13] protonate the nitrogen in 1-VIm and DAMA. Additionally, acid-base-aggregates can be formed by ionic interaction and H-bonds stabilizing the basic monomer in the aqueous phase. In a comparative test with the basic monomers alone, protonated by HCl (2), just 4.3 and 6.0% of the monomer is released into the cyclohexane phase. This can be due to the doubled amount of basic monomer used in this test and/or the missing aggregate formation. However, if the basic monomer is unprotonated, the solubility in the cyclohexane phase increases dramatically. It makes some difference if the deprotonated state predominates naturally (3) or is caused by sodium hydroxide (4). In the case 3 a small amount of 1-VIm or DAMA can still be protonated, which lowers the solubility in cyclohexane. For 1-VIm, the difference is about 5%, for DAMA 15%, which confirms that DAMA is the stronger BRONSTED base that gets protonated easier.[14] Overall, the solubility of unprotonated DAMA in cyclohexane is much higher than of unprotonated 1-VIm.

Table 1.
The content of basic monomer in the cyclohexane phase under acid and alkaline conditions with and without comonomer AMPS.

Conditions	Mixture	Content in the CH phase [wt.%]	
		1-VIm	DAMA
1	AMPS/protonated basic monomer (N−H^+)	0	0
2	protonated basic monomer (N−H^+) (with HCl)	4.0	6.0
3	unprotonated basic monomer (n)	17.3	74.4
4	AMPS/unprotonated basic monomer (N) (with NaOH)	22.3	89.5

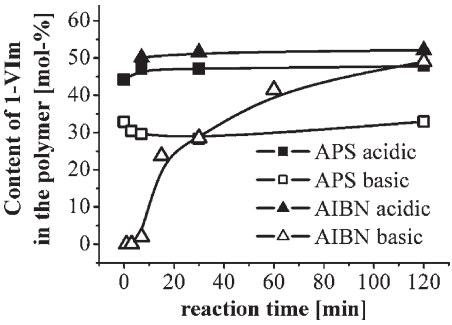

Figure 1.
The 1-VIm content in the polymer during the reaction. Different initiators (squares and triangles) and pH ranges (filled and empty) are compared.

In Figure 1 the content of 1-VIm during the polymerization of AMPS/1-VIm (50/50 mol.%) is compared for different initiations and pH values.

For initiation with AIBN and APS under acid conditions, conditions (1) from Table 1 are effective. That means, no 1-VIm is detected in the cyclohexane phase but AMPS and 1-VIm are available in the 1:1 ratio in monomer droplets. Thus the 1-VIm content in the copolymer is constant over the reaction time. The conversion for AIBN initiation is about 80% after 30 min and 100% after 120 min while the reaction with APS attains full conversion after 30 min. With AIBN initiation, 50–51 mol.% 1-VIm are incorporated, with APS initiation it is slightly less. A possibility is that very small amounts of 1-VIm are dissolved in cyclohexane are not available for APS initiation which takes place in the droplet. This becomes more obvious when the reaction takes place under alkaline conditions, which is related to conditions (4). With APS initiation the content of 1-VIm is constant around 30 mol.% during the whole reaction. The stability is not surprising, since the monomer conversion 78% is constant in time. Both means about 20 mol.% of 1-VIm is missing. This accords well with the 22.3 mol.% 1-VIm determined in the cyclohexane phase by gas chromatography, which is excluded from the polymerization in droplets. With AIBN initiation under alkaline conditions, the amount of 1-VIm in the copolymer increases during the reaction like the conversion, which is 44% after 7 min, 62% after 30 min and 76% after 60 min. The monomer dissolved in the cyclohexane phase can form oligoradicals with AIBN and that way enter the droplets or react on the interface. Thus the final content of 48 mol.% at a final conversion of 90% can be achieved although the 1-VIm is separated in two phases. The results for the AMPS/DAMA system show the same trend of delayed incorporation of under alkaline conditions. It is not possible to obtain results for APS initiation under alkaline conditions for this system, since the monomer solution polymerizes immediately after adding the initiator.

The diffusion of the monomers initially dissolved in the cyclohexane phase can also be displayed with TGA decomposition curves. For this AMPS/1-VIm and AMPS/DAMA copolymers are compared, which were differently prepared:

(A) via conventional inverse miniemulsion polymerization under conditions (1) in Table 1,
(B) via separate preparation and sonication of the monomers – to obtain AMPS droplets and droplets with basic monomer – before the two miniemulsions were polymerized together under conditions (3) in Table 1.

That means for the system AMPS/DAMA that over 70% of DAMA is dissolved in the cyclohexane phase with separate preparation (B).

Figure 2 shows that the resulting AMPS/DAMA copolymers (thin lines) do not differ in their decomposition behavior. The high amount of DAMA dissolved in the cyclohexane phase diffuses into AMPS droplets and the copolymerization can proceed conventionally. It is possible that the rest of DAMA also dissolves in cyclohexane and copolymerizes. For the AMPS/1-VIm (broad lines) the decomposition curves differ. Apparently, a mixture of P(AMPS-*co*-1-VIm) and the homopolymer P(1-VIm) is formed when separate

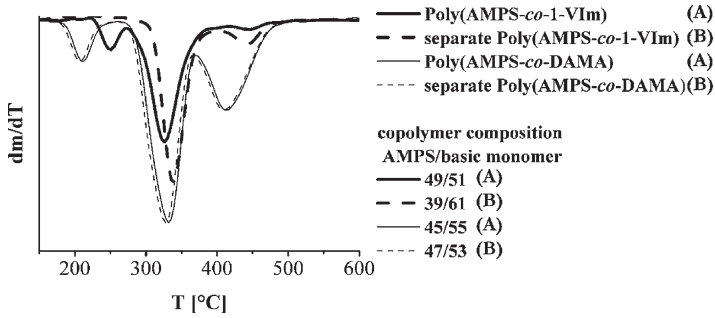

Figure 2.
Differentiated TGA curves, compositions of AMPS/1-VIm and AMPS/DAMA copolymers. The monomers were prepared and sonicated together (solid line) and separately (dashed line) before polymerization.

preparation (B) was used. The decomposition peak around 440 °C corresponds to the decomposition peak of P(1-VIm). Other peaks at lower temperatures for the decomposition of the copolymer and homopolymer overlap. The homopolymerization of 1-VIm is possible since less monomer is dissolved in the cyclohexane phase - compared to DAMA - according to gas chromatography. A measurable part stays in the droplets where the nucleation can take place. In addition, the overall copolymer compositions are given. For the AMPS/DAMA system also no crucial difference is observed; the copolymer composition reflects the monomer feed composition 1:1. For AMPS/1-VIm the amount of 1-VIm in the polymer increases when separate preparation (B) was used. The decrease in the AMPS content in the polymer mixture can also be seen in the missing first decomposition peak at 250 °C for the separate preparation of AMPS/1-VIm, which is related to P(AMPS) decomposition.

The kind of the basic monomer and its partitioning in both phases of the inverse miniemulsion not only affects the overall copolymer composition but also the distribution of monomer units in the polymer chain. For the determination, potentiometric and conductometric titration with subsequent calculation of the degree of protonation and effective pK_a value is used. The slope of the effective pK_a value of the polymer during the titration differs when the basic monomer is well distributed or cumulated in the polymer due to the polyelectrolyte effect.

In Figure 3 AMPS/1-VIm and AMPS/DAMA copolymers and AMPS/1-VIm synthesized under different conditions are exemplarily compared. The protonation of DAMA and 1-VIm is hindered during the titration by increasing electrostatic repulsion if the monomer groups are accumulated in the polymer chain. Thus, the effective pK_a value decreases. For well distributed basic monomer units the electronic environment does not change and the effective pK_a value remains constant. It can be seen in Figure 3a, that the AMPS/DAMA copolymer is fully protonated over a narrow pH range while it takes more acidic titrant to protonate the 1-VIm groups. This already indicates a good distribution of the DAMA monomeric unit in the polymer and the flat pK_a value exhibited in Figure 3b clarifies this result. For P(AMPS-*co*-1-VIm) the pK_a value decreases during the titration, which means that 1-VIm monomer units are located over the whole polymer chain.

Figure 3c and d show for P(AMPS-*co*-1-VIm) that not only the kind of monomer and the involved copolymerization parameters have an impact on the monomer unit distribution in the polymer chain. The titration curves of the polymers, overall copolymer compositions of which are already discussed in Figure 1, are different for varied initiators and pH values. For

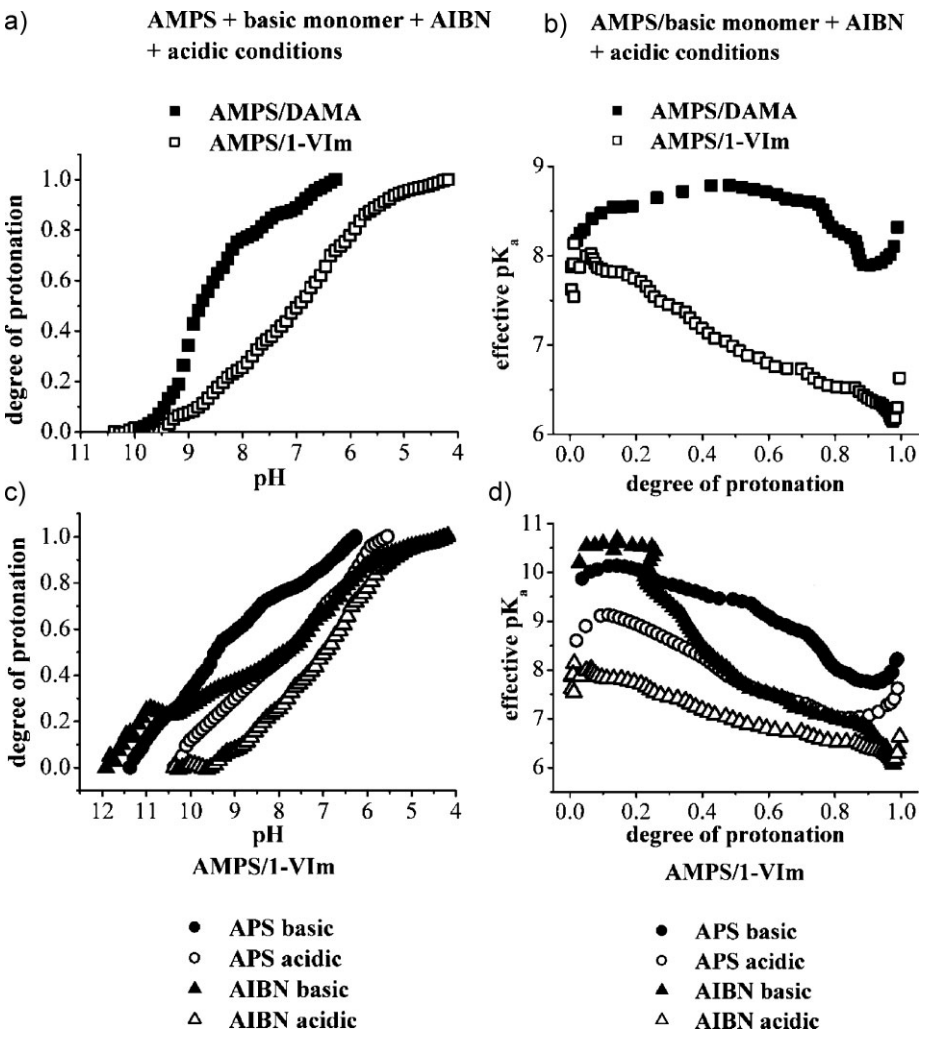

Figure 3.
Degree of protonation versus pH profiles (a and c), slope of the effective pK_a value versus the degree of protonation (b and d). AMPS/1-VIm and AMPS/DAMA copolymer (a and b) and AMPS/1-VIm copolymer with different initiators and pH values (c and d) are compared.

AIBN initiation and under alkaline condition, the pH range for protonation is the broadest and the slope of the pK_a value is the steepest. This is coherent with the results in Figure 1. A large amount of AMPS is already polymerized when 1-VIm is incorporated step by step. This leads to large sequences of 1-VIm monomer units in the polymer chain and therefore to a high chemical diversity of the polymer chains. Because of large 1-VIm sequences the electrostatic hindrance during protonation is increased. The plateau at the beginning of the titration may indicate that the 1-VIm units are very long so the protonation of two 1-VIm groups does not take place in the direct neighborhood and electrostatic repulsion has no influence below 25% protonation. The other polymers show decreasing pK_a values as well, but the slopes are not that steep and are very similar. That means the distribution of 1-VIm units in the polymer chain is not affected by the kind of initiation or pH

alone but by the interaction of both of them. For selected samples, also titrations from acidic to basic conditions were conducted. No differences in the titration curves and the resulting p*K*a intervals are obtained. That means that interactions of Na^+ cations with the polymer are negligible for the titrations. But it makes a difference for the the pH ranges and resulting pK_a intervals. This is due to the different initial pH of the polymer solutions and the amount of NaOH needed to obtain a starting point of pH 12. Also the accessibility of the functional groups has an influence on the effective pK_a value, so that physical interactions and entanglements of polymer chains can shift the overall position.

Conclusion

The change of pH of the monomer phase causes deprotonation of the basic monomers 1-VIm and DAMA. This leads to an increased solubility in the cyclohexane phase, which could be observed by gas chromatographic analysis. This also shows that the basic monomer is also deprotonated and more soluble in the cyclohexane phase when it is solely present in the droplet. Depending on the place of initiation (APS in the monomer droplets, AIBN in cyclohexane) the monomer in the cyclohexane phase is excluded from the reaction or is incorporated decelerated. By using different preparation procedures the strong influence of diffusion of monomer dissolved in cyclohexane can be observed. Finally, conclusions about the distribution of the monomers in the polymer chain can be made by simultaneous potentiometric and conductometric titration of the polymer solution. As expected, different monomers and the changes in the reaction conditions strongly influence the sequence of monomer units in the polymer chain, which becomes apparent by the change in the pK_a value. The results of the titrations correspond with the further results.

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