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Temperature and pH Dependency of Copolymerization Parameters of Acrylic Acid and 2-Hydroxypropyl Acrylate

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Summary: Since copolymerization parameters of acrylic acid (AA) and 2-hydroxypropyl acrylate (HPA) in aqueous solutions are scarcely investigated a new method and different experimental setups were developed to run copolymerization experiments at different temperatures and pH values. The experiments were done with UV- or azo-initiation and analyzed by residual monomer analytics with HPLC and GPC methods. Based on the data obtained the conversion and copolymerization parameters were calculated with different mathematical models.

Keywords: acrylic acid; copolymerization; free radical polymerization; monomer reactivity ratios

Introduction

Copolymerization of different monomers is an important tool to design polymers with specific properties, according to their application. Therefore, it is helpful to know the kinetics of a certain copolymerization to be able to generate a particular polymer for a desired application. For super-absorbent polymers, thickeners and many other applications, where highly hydrophilic properties are needed, especially acrylic acid is a very important comonomer. While the copolymerization of acrylic acid with 2-hydroxypropyl methacrylate is well known for some organic solvents, such as 1,4-dioxane,[1] this copolymerization in aqueous solution has hardly been investigated before. Various applications but only few data in literature make it interesting for both, academia and industry, to investigate this copolymerization in terms of pH and temperature dependencies.

Copolymerization Theory

The research on copolymerization properties is mostly done for binary systems, due to the mathematical complexity of ternary and multi-monomer systems. To characterize the kinetics of a binary copolymerization usually r parameters are calculated on the quotient of the rate constants of the homo- and the cross-propagation reactions. For the determination of these parameters different mathematical models are used. The so-called 'terminal model' is based only on the terminal monomer unit in the growing polymer chain and the following step of chain propagation. This simple model only results in two r parameter r_1 and r_2, where $k_{1,1}$ is the rate constant of homo-polymerization of monomer$_1$, $k_{1,2}$ is the rate constant of the cross-propagation of monomer$_1$, $k_{2,2}$ is the rate constant of the homo-propagation of monomer$_2$ and $k_{2,1}$ is the cross-propagation of monomer$_2$

$$r_1 = \frac{k_{1,1}}{k_{1,2}} \quad \text{and} \quad r_2 = \frac{k_{2,2}}{k_{2,1}} \tag{1}$$

To fit these parameters with experimental data different mathematical models are applied. The most common methods were developed by *Kelen* and *Tüdös* and earlier

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by *Fineman* and *Ross* as well as *Mayo* and *Lewis*. These models are all based on the differential copolymerization equation, where F_1 is the mole fraction of monomer $_1$ in the polymer and f_i the mole fraction of monomer $_i$ in the monomer solution.

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{2}$$

In general, this equation is used for low conversions, because the shift in comonomer composition during the experiment is not taken into account. On the other hand it is necessary to employ integral equations like the *Meyer-Lowry* equation, if the reaction runs to high conversion.

In contrast to the terminal model the 'penultimate model' encloses the last two monomer units of the growing polymer chain, which leads to four r parameters:

$$\begin{array}{ll} r_{1,1} = \frac{k_{1,1,1}}{k_{1,1,2}} & r_{1,2} = \frac{k_{1,2,2}}{k_{1,2,1}} \\ r_{2,2} = \frac{k_{2,2,2}}{k_{2,2,1}} & r_{2,1} = \frac{k_{2,1,1}}{k_{2,1,2}} \end{array} \tag{3}$$

Despite expanding computational capacities and the availability of non-linear methods of great complexity in chemistry, nevertheless, linear methods are preferred.[2]

Experimental Part

Setup

For experiments at 15 °C a setup of four *Schlenk* tubes were placed in a thermostated water bath. The solution with monomers and chain transfer agent was neutralized by sodium hydroxide to a specific pH-level and split to fill each flask. After degassing under vacuum and flushing with argon to purge from oxygen, the initiator was added and an UV lamp was placed above the open *Schlenk* tubes (Figure 1) to start the initiation.

Samples were taken with a intervals of a couple of minutes and well mixed with the prepared inhibitor solution to avoid further polymerization until quantitative analysis by HPLC and GPC measurements.

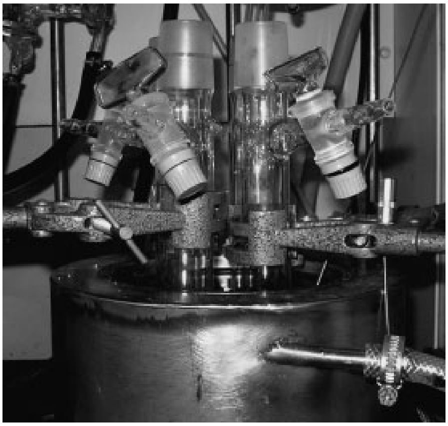

Figure 1.
Experimental setup for copolymerization experiments at 15 °C.

For thermal initiated copolymerization at 40 °C and 60 °C it was necessary to design a closed equipment due to significant evaporation of the solvent. The modified apparatus was a custom-built gas-sample tube (Figure 2). The tubes were filled with the reaction mixture and placed in a water thermostat. The treatment of the samples was the same as described above.

Figure 2.
Experimental setup for copolymerization experiments at 40 and 60 °C.

Materials

Acrylic acid (AA) and 2-hydroxypropyl acrylate (HPA) were received from *Aldrich* and used without further purification. 3-mercaptopropionic acid (MPA) and sodium hydroxide were received from *Merck*. Furthermore the water soluble initiators 2,2′-azobis[2-(2-imidazolin-2-yl)-propane]dihydrochloride (VA-044) and 2, 2’-azobis{2-[1-(2-hydroxyethyl)-2-imidazol-in-2-yl]propane}dihydrochloride (VA-060) were received from *Wako Chemicals*. Deionized water was used for all experiments.

Polymerization Procedure at 15 °C

40 g of deionized water were mixed with the particular amount of AA, HPA and MPA, and the pH value was adjusted with an aqueous solution of 40 wt-% sodium hydroxide. This reaction mixture was split to fill each of the four reaction vessels (Figure 1). The vessels were first stirred under vacuum for about 5 min and afterwards under argon atmosphere for 40 min. As an initiator 240 mg of VA-044 were added to each vessel. Then an UV lamp was placed above the experimental setup. Samples were taken before adding the initiator and after switching on the UV lamp in the following 3 min, 7 min and 12 min. The samples were quenched in an aqueous solution of 4-methoxyphenol.

Polymerization Procedure at 40 °C

The reaction mixture was prepared as for the prior polymerization (Figure 2). About 200 mg of VA-044 were added to the reaction mixture. In contrast to the procedure at 15 °C the initiator was started thermally. Samples were taken before adding the initiator and after 3 min, 7 min and 12 min and quenched in an aqueous solution of 4-methoxyphenol.

Polymerization Procedure at 60 °C

These experiments were carried out the same way as the polymerization at 40 °C. The only exception was the supply with VA-060 as initiator.

Results and Discussion

Copolymerization at 15 °C

These experiments were carried out at pH 2.9 and pH 5.0 and comonomer concentrations were analyzed by HPLC methods. The copolymerization diagram was calculated from data of residual comonomer composition after 12 min, because the standard deviation of these points is the lowest of the experiments (Figure 3). The relative cross propagation rate constants for the copolymerization of AA and HPA at pH 2.9 are quite similar to each other, so that the differential curve fit with the software “*contours*”[3] is very close to the diagonal. The copolymerization parameters ware calculated to be

$$r_{AA} = 0.69(+0.21 - 0.09)$$

$$r_{HPA} = 0.60(+0.06 - 0.02)$$

The standard deviation is calculated on the measurement errors of the residual monomer analytics, which is given by the individual error of every data point with respect to the chemical composition. Additionally, “*contours*” takes the quality of the curve fitting into account.

Changing the pH value from pH 2.9 to pH 5.0 the copolymerization diagram (Figure 4) and hence the copolymerization

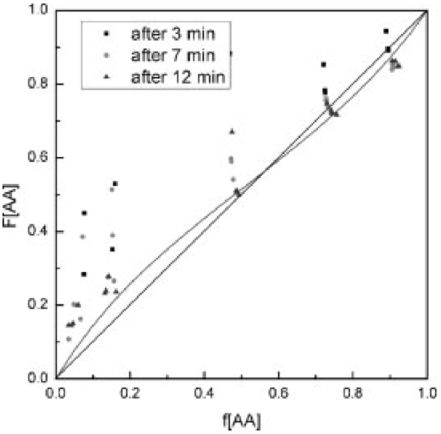

Figure 3.
Copolymerization diagram of AA and HPA at 15 °C and pH 2.9. Reactivity ratios are calculated by a differential curve fit with “*contours*”[3] on data points after 12 min.

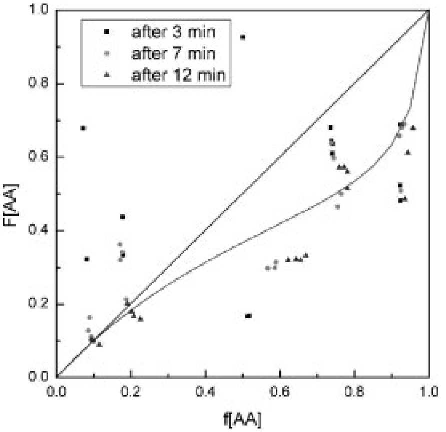

Figure 4.
Copolymerization diagram of AA and HPA at 15 °C and pH 5.0. Reactivity ratios are calculated by differential curve fit with "*contours*"[3] on data points after 12 min.

parameters differ significantly, which was expected, because the rate constant of AA is depending a lot on the pH value.[4] The propagation rate constant of the AA homo polymerization is high at pH 2 and pH 10, but has a minimum at pH 6.

Consequently, the increase in pH value from 2.9 to 5.0 causes a significant decrease in the propagation rate constant, which considerably affects the copolymerization diagram (Figure 4) as well as the monomer reactivity ratios:

$r_{AA} = 0.1(+0.28)$

$r_{HPA} = 0.89(+0.37 - 0.14)$

The parameter r_{AA} is significantly smaller at pH 5.0 than at pH 2.9 whereas the parameter r_{HPA} is much higher. This means, the rate constants for the homopolymerization of HPA and the cross-propagation of AA with HPA are increasing in relation to the rate constants of the cross-propagation of HPA with AA and the homopolymerization of AA.

Copolymerization at 40 °C

Also at this temperature, the experiments were carried out at pH 2.9 and 5.0. The residual comonomers were analyzed by HPLC methods after 12 min. The obtained data were used to calculate the copolymerization parameters with the software "*COPOINT*".[5] Due to higher conversion least square fitting to the integral copolymerization equation was required. Subsequently, *COPOINT* was quite appropriate for these conditions. At pH 2.9 the copolymerization parameters were estimated to be

$r_{AA} = 2.51$

$r_{HPA} = 0.99$

and for pH 5.0 keeping to the same conditions

$r_{AA} = 0.22$

$r_{HPA} = 1.19$

As shown in Figure 5 and 6 the monomer reactivity ratios for the copolymerization of AA and HPA at pH 2.9 and pH 5.0 differ significantly, which was expected in accordance with the experimental results obtained at 15 °C. Differences in the reactivity ratios at pH 2.9 and pH 5.0 can be explained by the dissociation of the acrylic acid. At pH >3.5 the acrylic acid exists predominantly as acrylate ion which has a different

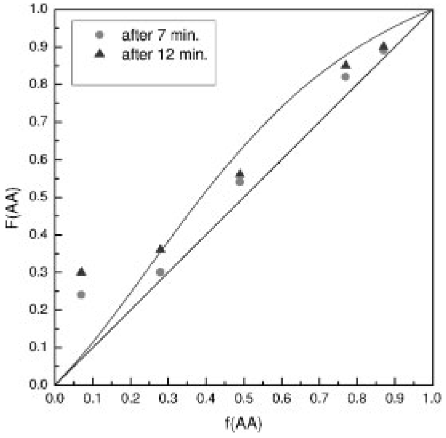

Figure 5.
Copolymerization diagram of AA and HPA at 40 °C and pH 2.9. Values are given as average value. Reactivity ratios are calculated by an integral curve fit with *COPOINT*[5] from data points after 12 min.

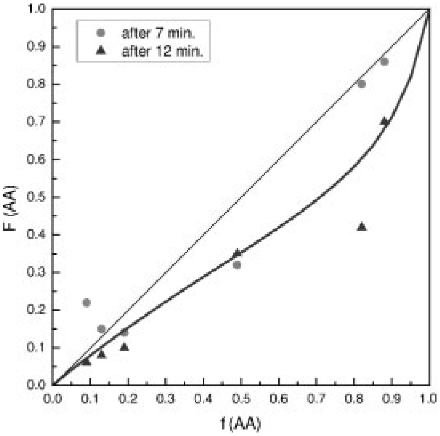

Figure 6.
Copolymerization diagram of AA and HPA at 40 °C and pH 5.0. Values are given as average value. Reactivity ratios are calculated by an integral curve fit with *COPOINT*[5] from data points after 12 min.

reactivity resulting in a change in the copolymerization parameters.

As in copolymerization at 15 °C the copolymerization parameters differ significantly. The propagation rate constant decreases because of changing pH from 2.9 to 5.0. This affects the copolymerization diagram (Figure 5) as well as the monomer reactivity ratios.

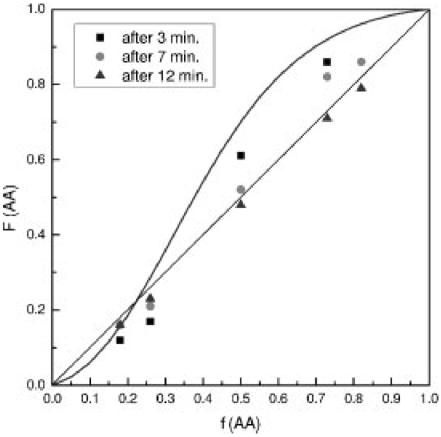

Figure 7.
Copolymerization diagram of AA and HPA at 60 °C and pH 2.9. Values are given as average value. Reactivity ratios are calculated by an integral curve fit with *COPOINT* from data points after 7 min.[5]

On the one hand the r_{AA} parameter is considerably smaller at pH 5.0 than at pH 2.9, on the other hand the parameter r_{HPA} is higher at pH 5.0.

This has effect on the assembling of the copolymer. From this it follows that there is an increased integration of AA-sequences in the copolymer at pH 2.9.

Copolymerization at 60 °C

In this series of copolymerization experiments besides the temperature only the initiator was changed from VA-044 to VA-060. The copolymerization diagram was calculated from data of residual comonomer composition after 7 min alternatively 12 min. Again, a pH dependency was detected but less than in the experiments at 15 °C and 40 °C. The monomer reactivity ratios for pH 2.9 were determined to be:

$r_{AA} = 9.22$

$r_{HPA} = 3.36$

and at pH 5.0 (Figure 8):

$r_{AA} = 0.35$

$r_{HPA} = 1.10$

The integral curve fit of AA and HPA at 60 °C and pH 2.9 was calculated from data

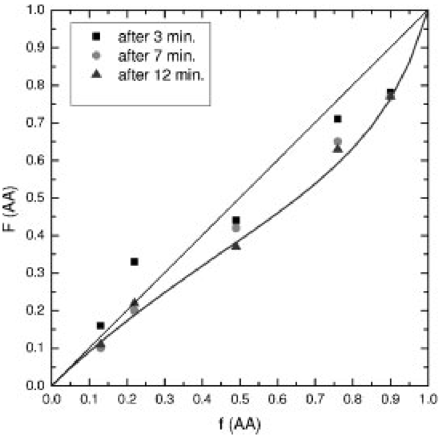

Figure 8.
Copolymerization diagram of AA and HPA at 60 °C and pH 5.0. Values are given as average value. Reactivity ratios are calculated by an integral curve fit with *COPOINT* from data points after 12 min.[5]

of residual comonomer after 7 min due to very high conversion in this experiments after 12 min. There is an inexactness of COPOINT while calculating with monomer conversion over 80%. The integral curve fit in Figure 6 does not match well with the experimental points because of the before discussed problems with COPOINT. The program associates the conversion with different priorities so that experiments with low conversions have a higher weighting in the calculating and can distort the integral fit.

The r-parameters at 60 °C and at pH 5.0 are similar to the experimental results at 40 °C or 15 °C and at pH 5.0. Only the r-parameters at pH 2.9 can hardly be compared to the values at 40 °C or 15 °C.

Though one can see the general tendency of the homo polymerization rate of AA to be greater as the cross-propagation rate of AA with HPA. Also the rate constant for the homo polymerization of HPA is greater than the cross-propagation of HPA with AA.

Conclusion

Investigations on the copolymerization behavior of acrylic acid and 2-hydroxypropyle acrylate at reaction temperatures of 15 °C, 40 °C and 60 °C have been carried out.

Differences in reaction temperature, use of differential or integral mathematical methods, and use of low conversion in contrary to high conversion for the copolymerization model are reasons for the difference in results. However to reach high conversion becomes more and more important for industry.

Comparing the experimental series with the same pH value but different temperatures shows that the value of the mole fractions are marginal changing. This means that there is a negligible influence of the temperature on the copolymerization parameters.

Also including the results of M. Möller[6] reaction temperature does not severely affect the copolymerization parameters, whereas the pH value is of major influence. This was expected and can be explained by the dependence of the homo-propagation rate constant of AA on the pH value. Thus, the copolymerization parameter r_{AA} is at pH 2.9 always bigger than at pH 5.0 regardless of the reaction temperature.

The analysis of the pH dependencies shows that a pH >3.5, in this case pH 5.0, decreases the r- parameters of AA and increases the r-values of HPA. This result can be explained with the existence of a higher amount of the less reactive acrylate ion and for this reason the more often integration of the 2-dihydroxypropyle acrylate compared to the acrylic ion. The r-parameters are located in the range of the non-ideal Copolymerization.

For non-aqueous solutions Daly and Lenz[1] basically determined copolymerization parameters similar to ours.

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