

Chapter 6

The influence of the rate of polymerisation on the working domain in reactive extrusion

Chapter 5 describes the influence of the polymer melt viscosity on the working domain in reactive extrusion. This chapter describes a more obvious parameter that influences the working domain, namely the rate of polymerisation. The rate of polymerisation is altered by replacing part of the n-butylmethacrylate (BMA) by maleic anhydride (Mah) in a styrene-BMA-copolymer. The effect of Mah on polymerisation rate and polymer melt viscosity is

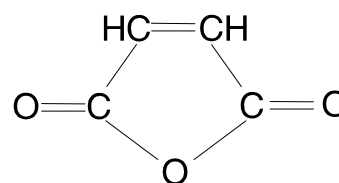


Fig. 6.1 *Maleic anhydride*

quantitatively described in the first paragraph of this chapter. Since the usefulness of the extruder as a polymerisation reactor is also determined by the quality of the product formed, the effect of Mah and several other parameters on the polymer properties are extensively described in this chapter. After that, the effect of Mah on the process of reactive extrusion is studied. Figure 6.1 shows the structure of the Mah-molecule.

6.1 The influence of Mah on material properties

The terpolymerisation described in this chapter is the polymerisation of styrene (St) with BMA and Mah. This terpolymerisation can be considered as a combination of three binary subsystems. The subsystem St-Mah is a well-known copolymerisation. The copolymerisation is very fast and results in an almost perfect alternating copolymer (Ebdon 1986, Klumperman 1994). The copolymerisation of St with BMA is compared to the copolymerisation of St-Mah rather slow (chapter 3). The subsystem BMA-Mah is not investigated in literature yet. Studies of a comparable system, methylmethacrylate-maleic anhydride (MMA-Mah), reveal that the homopolymerisation of MMA is faster than the copolymerisation, as a result of which composition drift occurs during polymerisation (Blackley 1956, North 1965).

The terpolymer St-BMA-Mah is comparable to the terpolymer obtained after the polymerisation of St-Mah-MMA as described by Schmidt-Naake (1989). They found that the kinetic equations for terpolymerisations, as described in chapter 3, predict the terpolymer composition quite accurately, when these equations are based on the reactivity ratios of the several binary subsystems. Furthermore, they found a strong increase in initial polymerisation rate when Mah was added to a mixture of St and MMA. This increase

diminished when the reaction proceeded, but over the whole conversion range, the mixture that contains most Mah gave the highest rate of polymerisation.

As in chapter 5, the copolymerisation of St and BMA is the starting point for investigating the influence of the rate of polymerisation. When certain part of the BMA is replaced by Mah, a faster polymerisation is obtained. The substitution of BMA by Mah turned out to be a good tool for studying the effect of the reactivity on the extruder performance.

6.1.1 The influence of Mah on the kinetics

The copolymerisation of styrene with n-BMA and the terpolymerisation of St-BMA-Mah were studied by using Differential Scanning Calorimetry (DSC). The co- and terpolymerisation were considered as a pseudo homo-polymerisation in order to investigate the effect of replacing BMA by Mah. The terpolymerisation was not described completely, as it was not the goal of this research.

For the copolymerisation of St with BMA, the reactivity ratios were determined at $r_1 = 0.40$ and $r_2 = 0.86$ with St as monomer A (chapter 3). In the case of St-Mah, the reactivity ratios are $r_1 = 0.03$ and $r_2 = 0.00$ (Brandrup 1989). These reactivity ratios account for the fact that the copolymerisation of St with Mah is very fast, although Mah hardly polymerises and the polymerisation of styrene is rather moderate.

The effect of Mah on the rate of polymerisation was investigated with a monomer mixture that was used during reactive extrusion. In these mixtures, the St-content was always 50 mol%. The results of DSC experiments at 140 °C are shown in figure 6.2. It can be seen that the addition of Mah led to a much faster polymerisation.

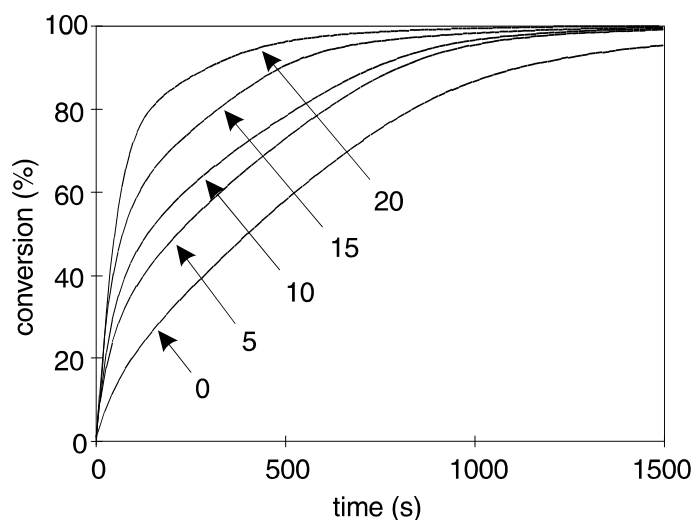


Fig. 6.2 *The influence of Mah on the rate of polymerisation. The number next to the arrow refers to the percentage of Mah in the feed*

The question that now rises is whether the reaction is only accelerated in the low conversion range, or the polymerisation is accelerated over the whole conversion range. One possible reaction mechanism is that styrene first reacts very fast with Mah, after which the remaining

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styrene polymerises rather slowly with BMA. In that case, a mixture of two polymers is formed. Another possibility is that styrene mainly reacts with Mah, but that in the low conversion range also some BMA will react. As a result of this, Mah will be present during a larger part of the polymerisation, leading to a higher reaction rate in a larger conversion range. Therefore, the polymerisation rate, which is given by the quantity $k_p/\sqrt{k_t}$ ($= k_{ov}$, see chapter 3), is determined quantitatively by DSC-experiments. Table 6.1 shows the results of these calculations. The DSC-experiments were performed at 130 °C and only 1 initiator was used (10 mmole Trigonox C per mole styrene).

Table 6.1 $k_p/\sqrt{k_t}$ ($l^{0.5} mol^{-0.5} s^{-0.5}$) at different conversions, temperature 130°C.

| % Mah | at 30 % conversion | at 40 % conversion | at 50 % conversion |
|-------|-----------------------|-----------------------|-----------------------|
| 0 | 0.24 | 0.28 | 0.33 |
| 5 | 0.38 | 0.34 | 0.33 |
| 10 | 0.59 | 0.58 | 0.51 |
| 15 | 0.83 | 0.78 | 0.68 |
| 20 | 0.49 | 1.29 | 1.29 |

The addition of Mah led to a strong increase in polymerisation rate compared to the copolymerisation of St-BMA, but the increase diminished when the reaction proceeded. However, Mah increased the polymerisation rate in a larger conversion range than would be expected if St only reacts with Mah in the beginning of the polymerisation. After the addition of 20% Mah, the increase in reaction rate was more than a factor 4 (the lower value at 30% conversion was due to the fact that at high Mah-concentrations the polymerisation started before the desired reaction temperature of 130 °C was achieved. This implied that the value for the reaction rate at 30% conversion corresponded with a lower temperature than 130 °C). The results obtained by the DSC-experiments were comparable to those obtained by Schmidt-Naake for the St-MMA-Mah system. The DSC-experiments showed that mainly the St-Mah-copolymer will be synthesised in the low conversion region, but during the whole polymerisation some Mah will present in the monomer mixture, resulting in a higher reaction rate during the whole polymerisation.

From the DSC-experiments, it can be concluded that the bulkpolymerisation of St-BMA-Mah can be controlled easily in contrary to the St-Mah-copolymerisation, which mostly results in a run away. It seems that the presence of BMA reduces the polymerisation rate. Therefore, the terpolymer of St-BMA-Mah can be a promising precursor for the synthesis of ionomers that can be produced by for example reactive extrusion.

6.1.2 The influence of Mah on the polymer melt viscosity

Since the experiments described in chapter 5 show that the polymer melt viscosity is a important parameter in reactive extrusion, the viscosity of the terpolymers had to be studied. The apparent viscosity of the terpolymers St-BMA-Mah was described as the ratio between the shear stress and shear rate:

$$\eta_a = \frac{\tau_{xy}}{\dot{\gamma}} \quad (6.1)$$

The rheology of the polymer was studied by using a capillary viscometer. The measurements were performed in a high pressure capillary apparatus (Rheograph 2003, release 2.1, Göttfert Werkstoff Prämaschinen GmbH). The capillary used had a length of 3 cm, a diameter of 1 mm, and an exit angle of 180 ° (installed die roundhole 30/1.0/180). The temperature, at which the viscosity was determined, was 140 °C. The measurements were performed at constant pressure. The characteristics of the samples used are given in table 6.2.

Table 6.2 *Characteristics of the samples used in the viscosity measurements*

| % Mah | M_n (kg/mol) | M_w (kg/mol) |
|-------|-------------------|-------------------|
| 0 | 43 | 99 |
| 5 | 45 | 105 |
| 10 | 47 | 103 |
| 15 | 58 | 143 |

Figure 6.3 shows the shear rate versus the apparent viscosity. In the calculation of the apparent viscosity, we applied the Rabinowitsch correction. It can be seen that the substitution of 15% BMA by Mah increases the apparent viscosity by two orders of magnitude.

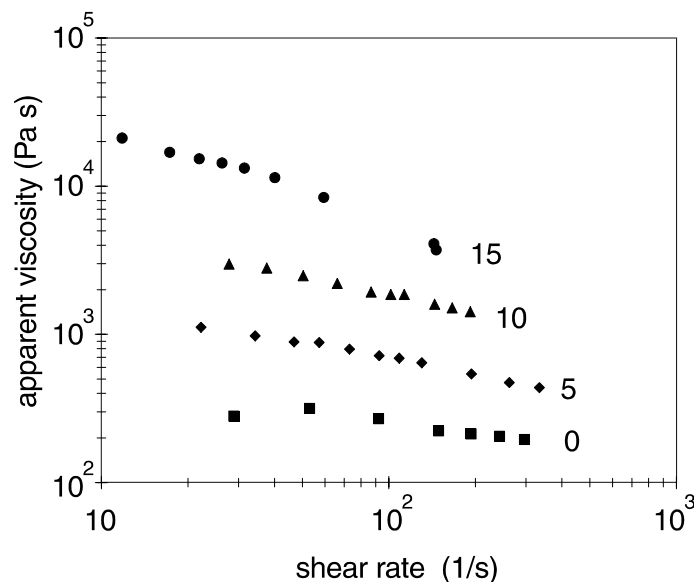


Fig. 6.3 *The apparent viscosity versus the shear rate. The numbers in the figure refer to the amount of Mah in the sample*

6.2 The extruder experiments

6.2.1 Experimental

The extruder and its equipment are described in chapter 4. In most experiments, the stirred tank reactor was slightly heated (40 °C) to dissolve all the Mah in the liquid monomers styrene and BMA. The monomer mixture consisted of 50 mole% styrene. The other 50 mole% consisted partly of n-butylmethacrylate and partly of maleic anhydride. The initiators used were the same as in chapters 4 and 5, just as the standard settings of the extruder.

The conversion of the samples collected at the die end were determined gravimetrically. The molecular weight of the product was determined by Gel Permeation Chromatography as described in chapters 4 and 5. Sometimes, a small part of the terpolymer did not dissolve in the THF, which means that only the molecular weight of the soluble part could be measured. As in chapter 4, the molecular weights are relative molecular weights, and they are also a slight underestimation of the actual molecular weights.

6.2.2 The effect of Mah on product properties

The styrene-n-butyl-methacrylate copolymer was a homogeneous polymer. Although the reactivity ratios indicate that some composition drift is likely to occur, the polymer formed was completely transparent. No phase separation occurred. When maleic anhydride was added to the reaction mixture the polymer became pale white, indicating some sort of phase separation, although this separation could not be observed with optical microscopy.

As described in paragraph 6.1, Mah increased the polymerisation rate. This increase in reaction rate (the ratio $k_p/\sqrt{k_t}$) results in an increased molecular weight (equation 3.2).

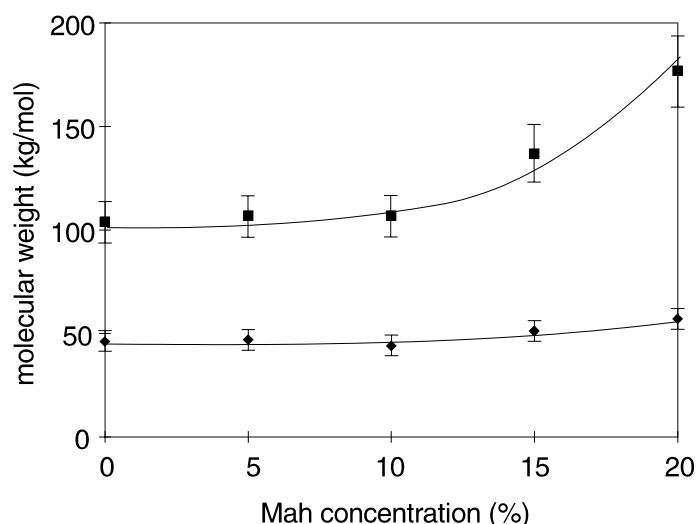


Fig. 6.4 The influence of Mah on the molecular weight of the polymer ($\blacksquare M_w$, $\blacklozenge M_n$)

At standard conditions, the results shown in figure 6.4 were obtained. The weight average molecular weight increased from 100 to 170 kg/mol, although the increase was only significant if a high percentage (more than 10 mole%) Mah was added to the mixture. The polydispersity M_w/M_n increased from 2.4 to 3.6 when more Mah was added. This increased polydispersity can be explained as a result of the decreased polymerisation rate at higher conversion. The polymer formed in the high conversion range will therefore have a lower molecular weight, which leads to an increased ratio between M_w and M_n . The experiments indicates that the amount of Mah added is a tool to adjust the molecular weight of the polymer formed, although it influences also other product properties.

6.2.3 The influence of the initiator concentration and extrusion parameters on the molecular weight

A real tool to adjust the molecular weight of the polymer is the initiator concentration. In chapter 4, the effect of the initiator concentration on the molecular weight was studied for the St-BMA copolymerisation. This paragraph describes the effect on the molecular weight of the terpolymer. Special interest is focused on the highest molecular weight that can be achieved, since only high molecular weight polymers when based on styrene can be used as engineering plastics.

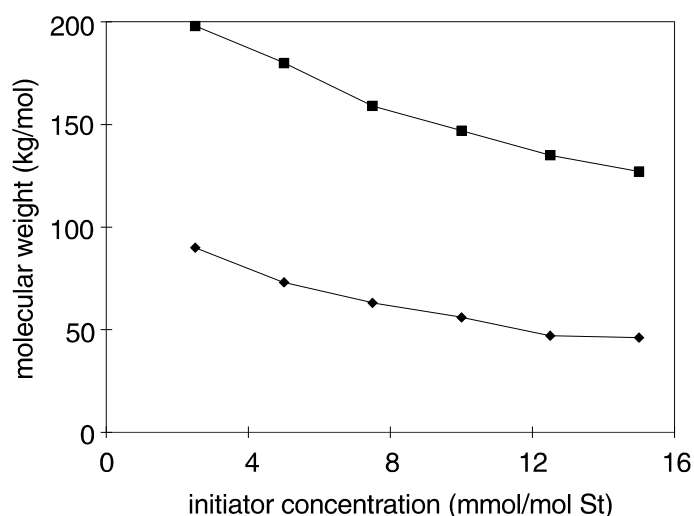


Fig. 6.5 *The influence of the initiator concentration on the molecular weight (■ M_w , ◆ M_n)
The extruder settings are listed in table 6.3 at the end of the chapter*

Figure 6.5 shows the effect of the initiator concentration on the molecular weight for a terpolymer, which consisted of 15% Mah. The extruder was operated under standard conditions. It can be seen that the molecular weight was strongly influenced by the initiator concentration. At a low initiator concentration, a molecular weight M_w of almost 200 kg/mol was obtained, which makes the polymer suitable as an engineering plastic.

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Although the influence of the initiator concentration was larger than in the case of St-BMA (chapter 4), the influence is still rather small. The ability of styrene to polymerise thermally probably accounts for the small influence of the initiator concentration.

It should be noted that the conversion of the product decreased with decreasing initiator concentration. When 2.5 mmole initiator per mole styrene was added to the mixture, the conversion became 77%, while with a higher initiator concentration (> 12 mmol/mol St), conversions of 95% could be obtained. In summary, the initiator concentration is a rather powerful tool to adjust the molecular weight of the polymer, but the conversion may decrease at too low initiator concentrations.

In previous chapters, it was already concluded that the molecular weight of the polymer formed is hardly influenced by extruder parameters. For the terpolymer St-BMA-Mah comparable results were obtained. For example, a change in screw rotation rate hardly influences the molecular weight of the polymer (figure 6.6).

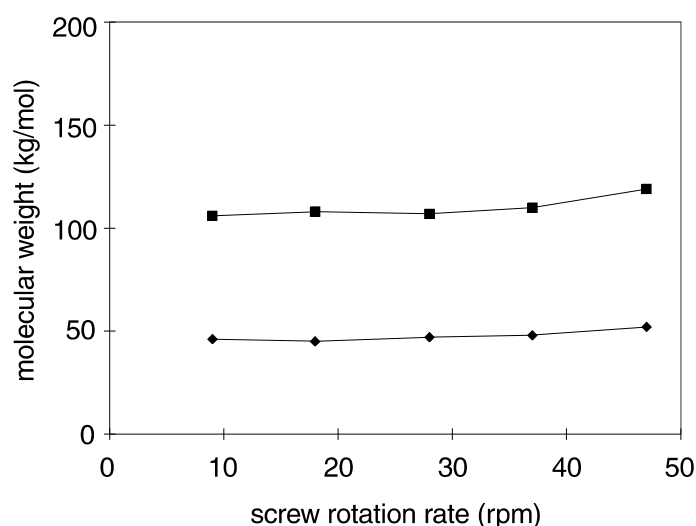


Fig. 6.6 *The influence of the screw rotation rate on the molecular weight (■ M_w , ♦ M_n)*

6.2.4 The effect of Mah on the process

To investigate the effect of Mah on the process of reactive extrusion, the process will be compared to the reactive extrusion process of St-BMA, which is described in chapter 4. The polymerisation of St with n-BMA was rather slow, which made the extrusion process rather difficult. A high die resistance was needed to obtain a high conversion. Due to the high die resistance, the extruder became already completely filled with liquid at a very low maximum throughput of roughly 7 g/min.

The addition of Mah led to a faster polymerisation and a more viscous polymer melt. Therefore, the partial substitution of BMA by Mah influenced the process of reactive extrusion strongly. Higher throughputs were obtained, and the dependence on extruder parameters, such as die resistance and screw rotation rate, was reduced. Therefore, an increase in polymerisation rate combined with an increased polymer melt viscosity enlarges the working domain of the counterrotating twin screw extruder.

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Figure 6.7 shows the effect of Mah on the maximum throughput of the extruder. The extruder worked under standard conditions. The maximum throughput was obtained if the extruder was fully filled with liquid or if the conversion became lower than the required conversion of 95 %. We could obtain this conversion under standard conditions, except for the St-BMA copolymer. The conversion in that situation was at most 94%. When figure 6.7 is compared with figure 5.9, it can be observed that the increase in throughput is larger than the increase in throughput due to an increased polymer melt viscosity. Therefore, it was concluded that not only the polymer melt viscosity is important, but that also the polymerisation rate of the monomer mixture enlarges the working domain.

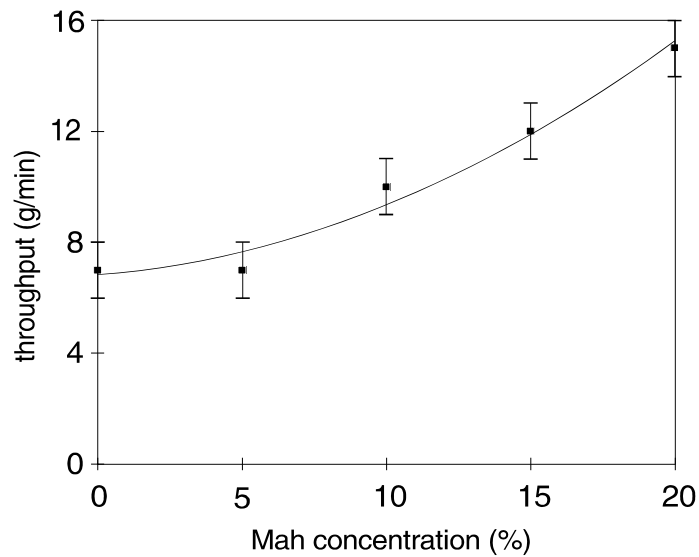


Fig. 6.7 *The influence of Mah on the maximum throughput*

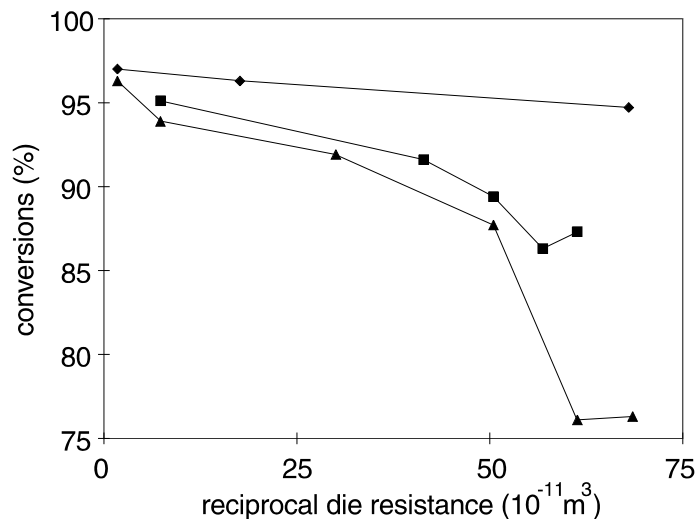


Fig. 6.8 *The influence of the die resistance on the conversion (◆ 20 % Mah, ■ 10 % Mah, ▲ 0 % Mah)*

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Figure 6.8 shows the effect of the die resistance on the conversion of the product that leaves the extruder. In these experiments, the extruder operated under standard conditions, but when 20% Mah was added, the steep temperature profile was applied. The throughput was 7 g/min when no Mah was added, 10 g/min when 10 % Mah was added, and 13 g/min when 20% Mah was added to the reaction mixture. It can be seen that the addition of Mah stabilised the process, since the influence of the die resistance decreased at higher Mah-contents. The effect of stabilising was even enhanced when taking into account the larger throughput at higher Mah-concentrations, since at higher throughputs a stronger effect of the die resistance was expected.

Figure 6.9 shows the effect of the screw rotation rate on the conversion. The St-BMA-copolymerisation showed a decrease in conversion. When Mah was added to the monomer mixture, the influence of the screw rotation rate on the conversion was diminished. This means that the magnitude of the effect of the screw speed was also dependent on the material inside the extruder.

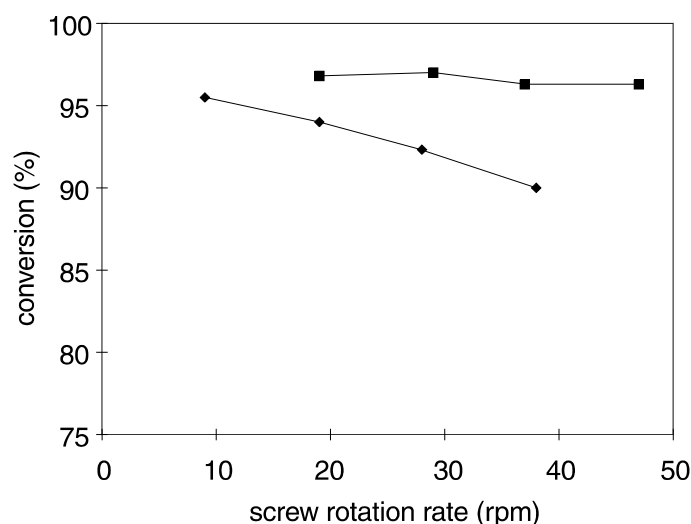


Fig. 6.9 *The influence of the screw rotation rate on the conversion (■ 20 % Mah, ◆ 0 % Mah)*

The effect of screw rotation rate was also influenced by the die resistance. At a high die resistance, a change of screw rotation rate hardly influenced the conversion, while at a low die resistance, the loss of conversion was significant at higher screw speed (figure 6.10).

This effect shown in figure 6.10 can be explained by the following reasoning. The maximum conversion that can be obtained in these extruder polymerisations turned out to be about 97%. At the high die resistance, this conversion was obtained. Due to the high die resistance, the residence time in the extruder was larger than the reaction time needed for a conversion of 97%. A decrease in residence time, due to an increase in screw rotation rate hardly influences the conversion, because the residence time was still larger than the reaction time needed. At low die resistance, the maximum conversion could not be obtained. The

maximum conversion was 92% at a screw rotation rate of 9 rpm. This means that the monomer mixture was still able to polymerise and the residence time was in fact too short to obtain the conversion of 97%. In this situation, a decrease in residence time due to an increased screw speed resulted in a decrease in conversion. Why the conversion remained constant when the screw speed was varied between 19 and 39 rpm is not quite clear yet. This effect, a constant conversion lower than the maximum conversion at varying screw speed was also observed by Ganzeveld (1993) and Jongbloed (1995a).

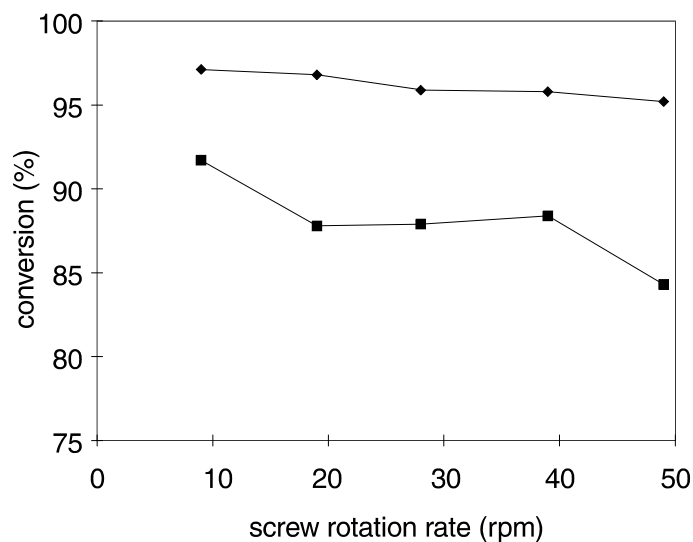


Fig. 6.10 The influence of the screw rotation rate at high (◆) and low (■) die resistance

6.3 Conclusions

The closely intermeshing counterrotating twin screw extruder is a suitable polymerisation reactor for the terpolymerisation of St-BMA-Mah. When compared to the St-BMA-copolymerisation, the addition of Mah led to a faster polymerisation and a more viscous polymer melt. As a result of these two effects, the extrusion process stabilised, which implied that the dependence on extruder parameters, such as die resistance was diminished. Besides, the maximum throughput could be increased significantly. It can be concluded that a faster polymerisation results in a larger working domain in reactive extrusion.

The influence of extruder parameters is influenced by the other extruder parameters. This study showed that at a high die resistance, the influence of the screw rotation speed was negligible, while at low die resistance, an increasing screw speed resulted in a lower conversion.

The molecular weight of the polymer formed is mainly dependent on product parameters such as initiator concentration and Mah-content. The initiator concentration influences the molecular weight, but the influence is somewhat smaller than theoretically expected. The

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addition of Mah leads to a higher molecular weight. The influence of process parameters tested on the molecular weight is quite small and seems unpredictable.

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Table 6.3 *Extruder settings: [I] initiator concentration (mmol/mol St), Q throughput, K reciprocal die resistance, N screw rotation rate*

| figure | [I] | Mah (%) | temperature profile (°C) | Q (g/min) | K (10 ⁻¹¹ m ³) | N (rpm) |
|--------|-----|---------|--------------------------|-----------|---------------------------------------|---------|
| 6.4 | 8 | var | 120-145 | var | 7.4 | 28 |
| 6.5 | var | 15 | 120-145 | 16 | 1.7 | 28 |
| 6.6 | 9 | 5 | 120-145 | 7 | 1.7 | var |
| 6.7 | 8 | var | 120-145 | var | 7.4 | 28 |
| 6.8 ▲ | 8 | 0 | 120-145 | 5 | var | 28 |
| 6.8 ■ | 8 | 10 | 120-145 | 10 | var | 28 |
| 6.8 ◆ | 8 | 20 | 120-160 | 13 | var | 37 |
| 6.9 ◆ | 8 | 0 | 120-140 | 6 | 7.4 | var |
| 6.9 ■ | 8 | 20 | 120-160 | 13 | 17.7 | var |
| 6.10 ◆ | 9 | 5 | 120-145 | 7 | 1.7 | var |
| 6.10 ■ | 9 | 5 | 120-150 | 7 | 30 | var |