

Chapter 4

Reactive extrusion of St-BMA

This chapter describes the copolymerisation of styrene-*n*-butylmethacrylate (St-BMA) in a counterrotating twin screw extruder. This extruder has already been used for several other reactive extrusion processes, such as the polymerisation of ϵ -caprolactam (Speur 1988), the grafting of maleic anhydride on polyethylene, the polymerisation of urethanes (Ganzeveld 1992) and the radical polymerisation of several methacrylates (Jongbloed 1995a). The reason for using the counterrotating twin screw extruder in this study is that Jongbloed (1995c) showed this type of extruder to be the most stable polymerisation reactor.

Starting point of the study is the polymerisation of St-BMA in the extruder. Attention is focused on process characteristics as well as product properties, especially the molecular weight. The experiments with St-BMA are described in sections 4.3, 4.5 and 4.6. All other reactive extruder experiments described in the following chapters will be compared and related to the experiments in these sections.

4.1 The extruder as a polymerisation reactor: Working domain

In reactive extrusion processes parameters, such as screw rotation rate and throughput, can not be set freely at any arbitrarily value. Demands for conversion and molecular weight limit the range of the extruder parameters. Furthermore, instabilities can occur more easily in reactive extrusion processes than in normal extrusion processes. This means that the working domain is smaller when the extruder is used as a polymerisation reactor. In this thesis, the working domain of the counterrotating twin screw extruder is defined as the operating window in which a stable extrusion process produces a product with a conversion higher than 90%.

4.2 The extruder as a polymerisation reactor: Experimental set-up

The experimental set-up is schematically shown in figure 4.1. The main aspects of the set-up are listed in this section. The numbers in the list correspond to the numbers in figure 4.1 (1 = extruder, etc.).

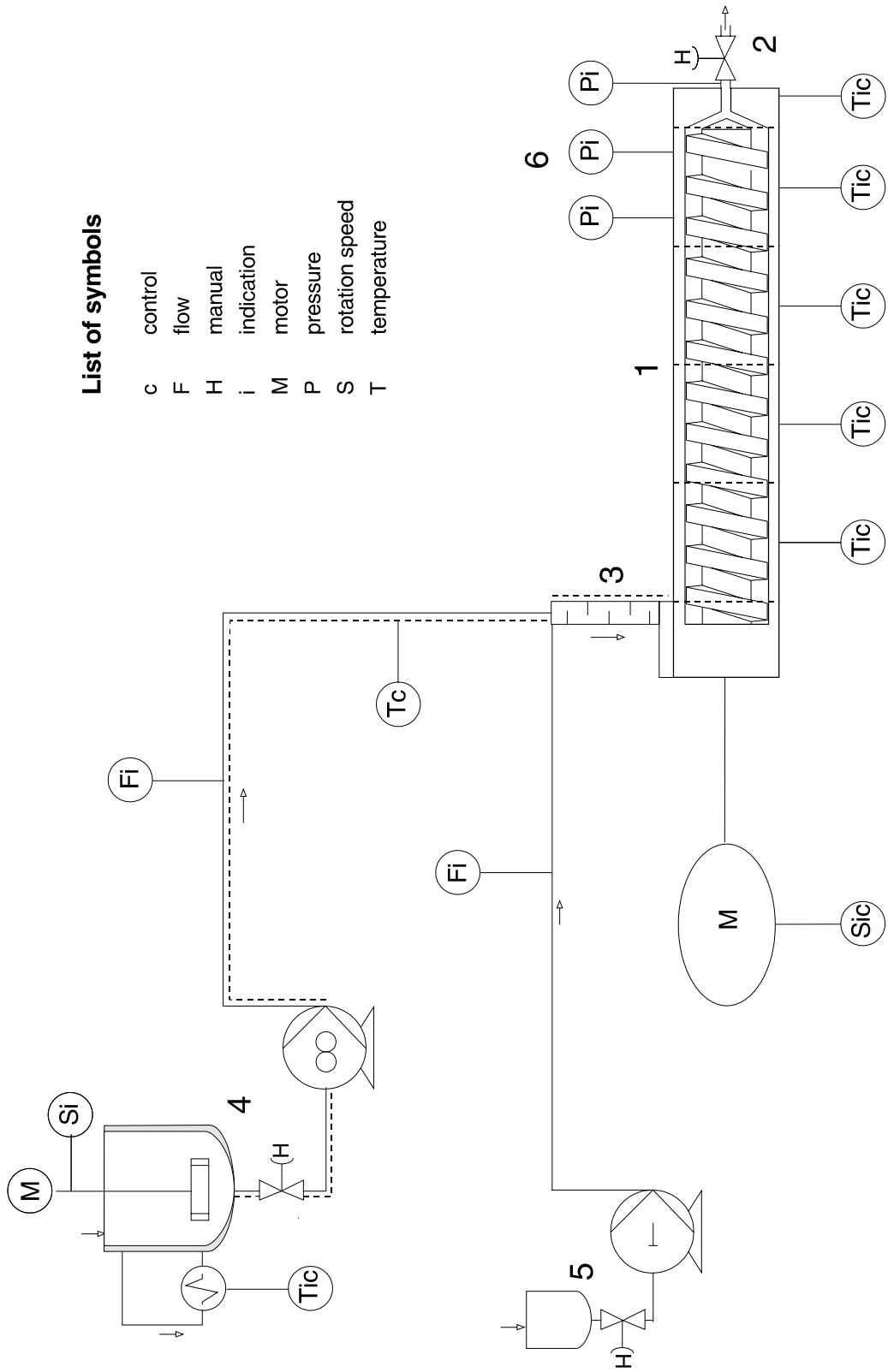


Fig. 4.1 *Experimental set-up*

1. The extruder is a counterrotating, closely intermeshing twin screw extruder (Rollepaal). It possesses screws with a diameter of 40 mm and a length of 600 mm ($L/D = 15$). The pitch of the screw is 2.4 cm, except for the feed zone, in which the pitch is 3 cm. The other geometric constants of the screws are described in chapter 2. The extruder has four heating zones, which are PID controlled. The feedzone can be cooled with water. The motor power of the extruder is 4.5 kW. The screw rotation rate can be varied from 0 to 50 rpm.
2. An important part of the experimental set-up is the die. The die can be heated and is PID-controlled. The die resistance is variable and its reciprocal resistance K can be set between a value of 0 and $6.85 \cdot 10^{-10} \text{ m}^3$. For the meaning of the die resistance, see equation 2.13 and section 2.3.1.
3. The static mixer (Kenics) is connected to the feed zone of the extruder. The mixer has a length 191 mm and an inner diameter of 3.4 mm. Twenty-seven elements are inside the mixer.
4. The stirred tank reactor can be heated and cooled. Due to the heating, a thermal prepolymerisation can be performed, or the monomer mixture can be heated in order to dissolve maleic anhydride (chapter 6) or a polymer (chapter 8). The piping to the static mixer is traced (this means that it can be heated).
5. A separate vessel contains the initiators, which are dissolved in a small amount of monomer. The volumetric flow to the static mixer is roughly 10% of the main volumetric flow that leaves the stirred tank reactor (4). The vessel is not used when the monomer mixture is not heated and the initiator concentration remains constant during an experiment. In that situation, the initiators are added to the monomer mixture in the stirred tank reactor.
6. The pressure transducers measure the die pressure and the pressure at 9 and 15 cm before the die.

4.3 The polymerisation of St-BMA in the extruder

4.3.1 Experimental

The monomer mixture was prepared by mixing the monomers styrene and n-butylmethacrylate (both inhibited) in a molar ratio of 1:1. To this mixture a combination of two or three initiators with different half-life values was added. The number of initiators depended on the temperature profile that was applied over the extruder. In the case of two initiators, the chemicals were dibenzoylperoxide (30%) and Trigonox C (70%). When a steep temperature profile was applied (120-160 °C) half of the Trigonox C was replaced by Trigonox T.

In order to compare the influence of the several product and process parameters, standard settings were chosen for the parameters. When one parameter was varied, the other parameters were generally set at the standard values. The standard initiator concentration was 8 mmol/mol styrene. The standard screw rotation rate was 28 rpm. The standard

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temperature profile was 120-120-130-140-145 °C; the steeper temperature profile was 120-130-140-150-160 °C. The standard reciprocal die resistance was $7.4 \cdot 10^{-11} \text{ m}^3$. The throughput depended strongly on the reaction mixture used and varied between 4 and 20 g/min. Samples were collected when the extruder reached steady state. In order to stop the reaction immediately, the samples were frozen in liquid nitrogen at the outlet of the extruder.

4.3.2 Product analysis

The conversion of the product was determined gravimetrically. About 1 gram of product was dissolved in tetra-hydrofuran (THF). A small amount of hydrochinon was added to this solution to inhibit further reaction. The solution was poured onto an aluminium dish, which was placed in a vacuum oven at 135 °C for at least 18 hours to remove the THF and remaining monomers. The conversion was determined by weighing and calculated via equation 4.1. The conversion could be reproduced with an accuracy of 1%.

$$\text{conversion} = \frac{\text{weight of remaining polymer}}{\text{weight of sample}} * 100\% \quad (4.1)$$

The molecular weight distribution of the product was determined by Gel Permeation Chromatography. The solvent was THF and two mixed-C columns of Polymer Laboratories were used. The detection method was by refractive index. This detection method needs Mark-Houwink constants. For the copolymer St-BMA, these constants are not known in literature and therefore, it was assumed that these constants were the same as for polystyrene. Some GPC-experiments using light-scattering as detection method showed that the molecular weights given by the refractive index method were a slight underestimation of the actual molecular weight.

Apart from conversion and molecular weight distribution, several other product properties, such as polymer melt viscosity and tensile strength, were determined. The methods and results are described in chapters 5, 6, and 8.

4.3.3 Results

The polymerisation rate of the monomer mixture St-BMA is rather low. This low polymerisation rate resulted in a quite difficult extrusion process, in which the die resistance turned out to be the most important parameter. A stable process and a high conversion could only be obtained if a high die resistance was applied. The high die resistance and the low polymerisation rate resulted in a completely filled extruder at a low maximum throughput. The maximum conversion proved to be 96%, which was probably a result of thermodynamic limitations, as will be explained in chapter 8.

The influence of the die resistance on the conversion is shown in figure 4.2. A reduction of the die resistance results in a decrease in residence time. Therefore, a decrease in conversion is expected. Experimentally, a sharp decrease in conversion was observed at a certain die resistance. This sharp decrease in conversion indicates a certain transition from one regime to another, in which the residence time of the material in the extruder is significant lower. After the drop in conversion, the die pressure is almost zero, which means that no fully-filled

length is present anymore. Figure 4.2 shows also the influence of the screw speed. An increased screw speed results also in a decreased residence time, and therefore in a decreased conversion. The experiments show this decrease, although the decrease is rather small.

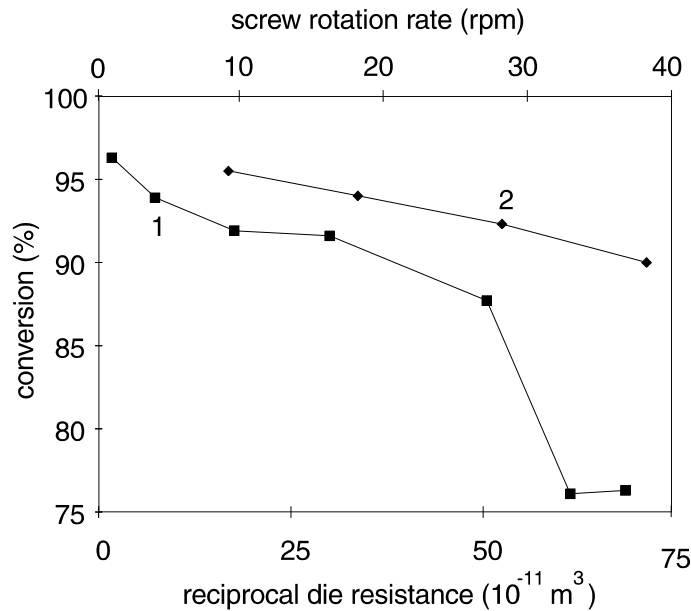


Fig. 4.2 The influence of the die resistance (■) and screw speed (◆) on the conversion. The meaning of the numbers in the figure will be explained in section 4.6. The extruder settings are listed in table 4.1 at the end of this chapter

An increase in maximum throughput was expected, when the polymerisation rate was increased by raising the reactor temperature. When the temperature of the extruder barrel was changed, also one or more initiators has to be replaced, because the initiators are very temperature sensitive. However, the maximum throughput did not increase when the temperature of the barrel was increased. Moreover, the output of the extruder became irregular. These instabilities are probably caused by the decreased polymer melt viscosity because of the higher extruder temperature. The effect of the polymer melt viscosity is described in chapter 5.

4.4 Prepolymerisation

Prepolymerisation can improve the process for several reasons. First of all, the heat, due to the polymerisation reaction in the extruder decreases, since part of the heat of polymerisation is already released in the prepolymerisation reactor. This decreased heat is important, since the initiator efficiency is strongly influenced by the reaction temperature, which implies that the temperature control is important. If the temperature inside the

extruder can not be controlled, a run-away may occur. In the case of a radical polymerisation, run away conditions will not result in a too high reactor temperature leading to polymer degradation, but run-aways will generally limit the maximum conversion. This limitation in conversion is caused by a strong decreasing initiator efficiency at too high temperatures. In the extruder used in this thesis, no severe heat problems are likely to occur, due to the low throughputs, but for faster reactions, or in large extruders, the removal of the heat of polymerisation can become a problem (Ganzeveld 1990). In those situations, the decrease of released heat of polymerisation is very important.

A second effect of prepolymerisation is an increase in feed viscosity. Since extruders are not very suitable for handling low viscous materials, a feed with low viscosity can result in several problems, such as instabilities in output. After prepolymerisation, a feed is obtained that is more suitable for the extruder, resulting in a process that is easier to control.

Finally, prepolymerisation increases the molecular weight of the polymer formed in reactive extrusion. It is therefore a good tool to adjust the molecular weight of the polymer formed (Michaeli 1993).

4.4.1 Experimental

The prepolymerisation was performed in a stirred tank reactor (figure 4.1). About 2.5 kg of St and BMA (molar ration 1:1) was put in the reactor and heated to 135 °C. When the prepolymerisation started, the tank reactor had to be cooled to maintain a temperature between 135 and 140 °C. The prepolymerisation was stopped by cooling the tank reactor rapidly to 60 °C when the conversion was estimated to be 25% by using figure 3.3. A sample was taken to determine the conversion precisely. After prepolymerisation, the extruder was operated as described in section 4.2 and 4.3.1. Samples were analysed as described in section 4.3.2.

4.4.2 The effect of prepolymerisation on the process

Prepolymerisation influenced the process strongly. Although the conversion after prepolymerisation was only 20-25%, the maximum throughput could be increased with at least a factor 2 (14 g/min compared to 7 g/min), without a severe loss of conversion. Furthermore, the dependence on extrusion parameters, such as die resistance, was much smaller (figure 4.3). Although the throughput was higher in the case of the prepolymerisation, the conversion did not decrease when a prepolymerised mixture was added to the extruder, while the conversion decreased sharply when no prepolymerisation was performed. After prepolymerisation, a steeper temperature profile could be applied, without obtaining irregularities in the output. This steeper temperature profile is desirable, because it simulates the process in industrial extruders, in which not all the heat of reaction can be removed easily.

The increase in maximum throughput and the decreased dependence on the die resistance can be explained as a result of three effects. First of all, the time needed to obtain a high conversion is decreased because of the prepolymerisation. Secondly, the increased molecular weight of the polymer leads to an increase in polymer melt viscosity. An increase in melt viscosity stabilises the process, which also results in higher throughputs (chapter 5). The

third effect is the increased viscosity of the feed, which also stabilises the process. This effect will be explained in chapter 7.

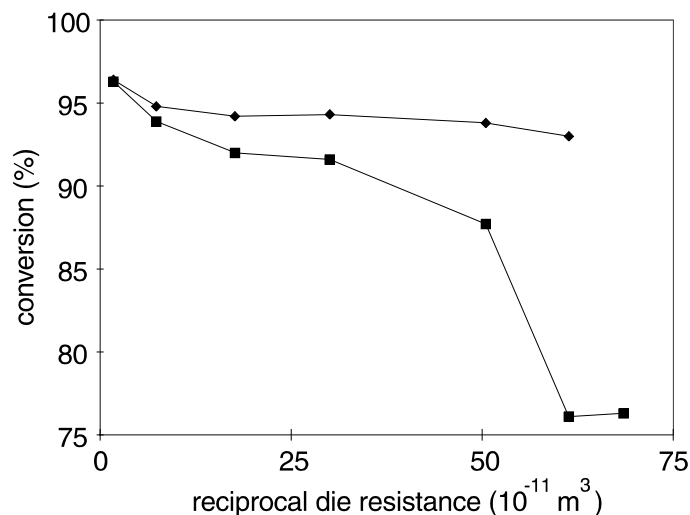


Fig. 4.3 The effect of the die resistance on the conversion (◆ prepolymerisation, ■ no prepolymerisation)

4.4.3 Comparison with the patent written by Kelley (1993)

The reactive extrusion process with prepolymerisation as described in this section resembles very much the process described by Kelley (1993). In that patent, styrene is polymerised through a radical mechanism in a two-steps process. The first step is a thermal prepolymerisation or a prepolymerisation with peroxides, in which a conversion of 20 to 40% is obtained. After prepolymerisation, the mixture is polymerised and devolatilised in a corotating twin screw extruder (Berstorf ZE180). A conversion of 98.5% was obtained. In the latter step, the polymerisation is initiated by peroxides similar to the initiators used in our study. Initiator concentrations are roughly 2 mmol/mol St. During the polymerisation, temperatures of 260 to 310 °C can occur in the extruder, when a throughput of 8 tons per hour is applied. Not only styrene, but also various copolymers, such as styrene-maleic anhydride and styrene-methylmethacrylate can be produced via the same process.

The results as claimed by Kelley do not correspond with the results described in this chapter. First of all, the throughput is much higher than the throughput obtained in the extruder used in this study. When the scaling rules as developed by Ganzeveld (1990) are applied, we should be able to obtain a throughput of 80 kg/hour, which corresponds roughly to 1 kg/min. Due to the higher screw speed, the throughput in corotating machines is higher than in counterrotating extruder, but it can not explain the large differences. Besides the higher throughput, Kelley obtained a high conversion under run-away conditions. We never obtained a conversion higher than 90 % in flask polymerisation, when a significant temperature rise was observed.

Concluding, I will be very surprised if ever a polymerisation plant will be built based on the process as described by Kelley.

4.5 The molecular weight of the polymer

Without prepolymerisation, the weight average molecular weight of the polymer formed was about 90 kg/mol when the extruder was operated under standard conditions. The molecular weight distribution was smooth for the samples obtained by reactive extrusion (figure 4.4).

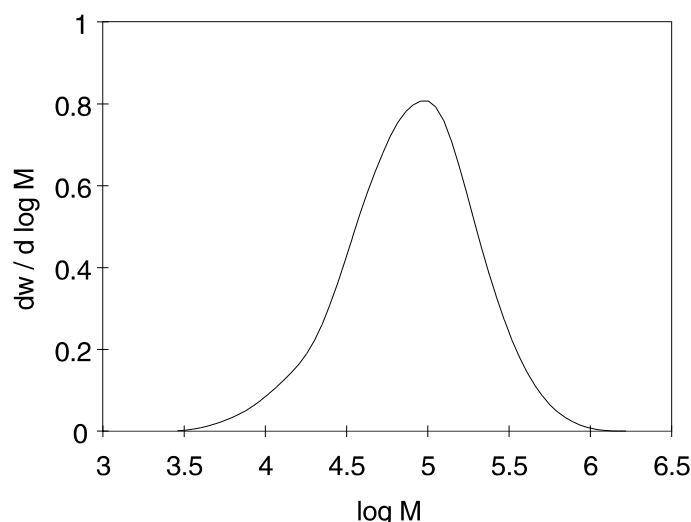


Fig 4.4 *A typical molecular weight distribution for St-BMA when polymerised in the extruder*

The molecular weight of the polymer determines its usefulness. Therefore, we tried to influence the molecular weight both by process and by product parameters. The main tools for adjusting the molecular weight are initiator concentration (equations 3.2 and 3.3) and the temperature at which the polymerisation proceeds (Jongbloed 1995a). Generally, the influence of screw speed and die resistance is quite small and often unpredictable. Since it is very likely that the molecular weight of the polymer formed changes when the polymerisation proceeds (gel effect), molecular weights should only be compared at the same conversion, which should be preferably higher than 95%. For samples with different conversions, the molecular weight increases generally with the conversion.

Figure 4.5 shows the effect of the initiator concentration on the molecular weight and the effect of prepolymerisation. The conversion was slightly influenced by the initiator concentration in these experiments and varied between 90 and 95%. As shown in figure 4.5, prepolymerisation increases the molecular weight and also the ratio M_w/M_n . After prepolymerisation, a weight average molecular weight of roughly 190 kg/mol could be obtained at low initiator concentration. This increase in molecular weight means that the product quality is improved by prepolymerisation.

The effect of the initiator concentration is predicted by equations 3.2 and 3.3. A doubling of the initiator concentration results in a decrease in momentarily formed molecular weight

with a factor $\sqrt{2}$, while if the conversion is not influenced by the initiator concentration, a doubling in initiator concentration can result in a halving of the number average molecular weight after polymerisation. Experiments, however, show a much smaller influence. From figure 4.5, it can therefore be concluded that prepolymerisation is a better tool to obtain higher molecular weights, than lowering the initiator concentration without prepolymerisation.

Chapter 8 describes the effect of very high initiator concentrations in order to obtain low molecular weights.

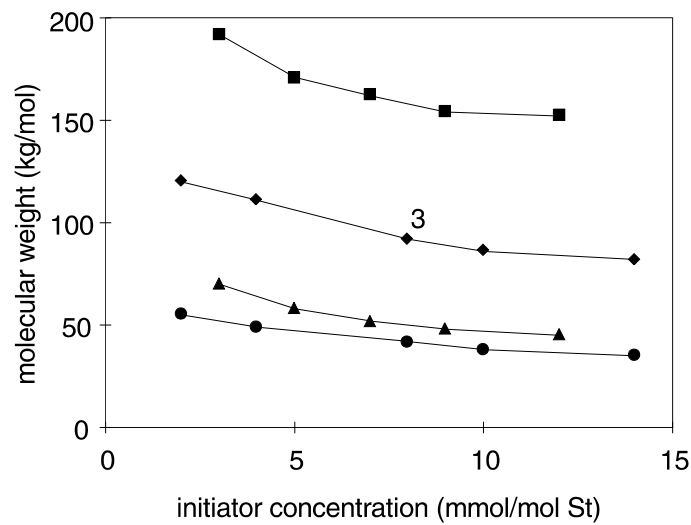


Fig. 4.5 The effect of the initiator concentration on the molecular weight of the polymer formed, with (■ M_w , ▲ M_n) and without prepolymerisation (◆ M_w , ● M_n)

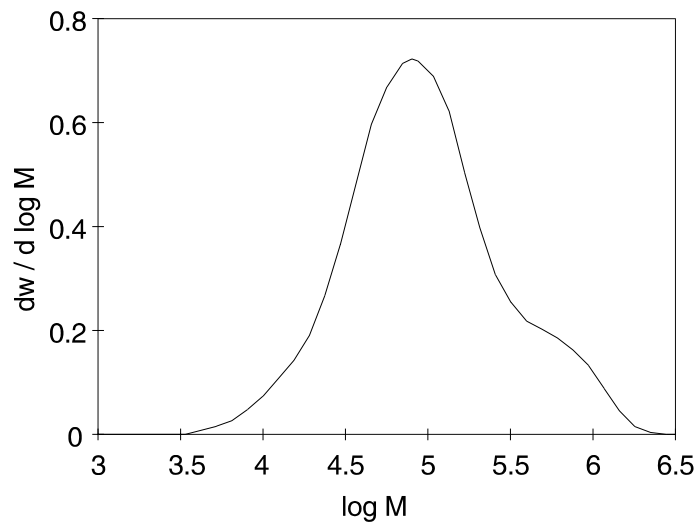


Fig. 4.6 A typical molecular weight distribution after prepolymerisation

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The effect of prepolymerisation on the molecular weight distribution can be observed, when comparing figures 4.4 and 4.6. Prepolymerisation resulted in a tail associated with high molecular weight fraction formed during prepolymerisation.

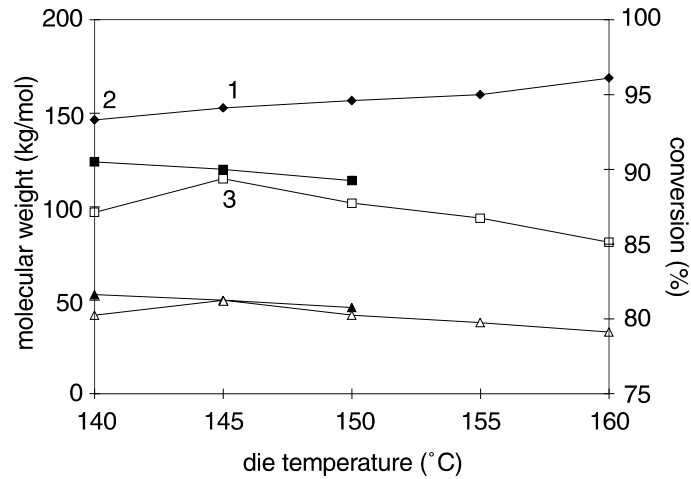


Fig. 4.7 The effect of the temperature on the molecular weight and conversion (\blacklozenge conversion, \blacksquare M_w , \blacktriangle M_n)

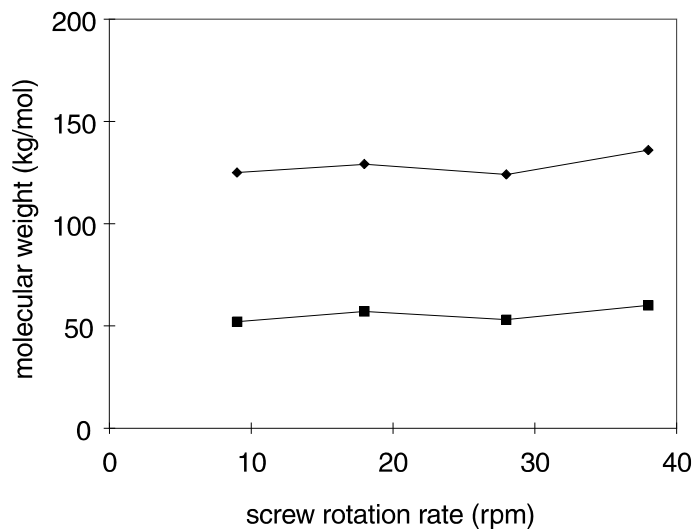


Fig. 4.8 The effect of the screw rotation rate on the molecular weight (\blacklozenge M_w , \blacksquare M_n)

Figure 4.7 shows the effect of the barrel temperature on the molecular weight of the polymer formed. In these experiments, the temperature of the first heating zone was kept at 120 °C, while the die temperature is indicated in the figure. The temperature of the other heating zones was increased with steps of 5 or 10 °C from first heating zone temperature to die temperature. Only two initiators were added (BPO and Trigonox C), except for the

experiments with a die temperature of 160 °C in which half of the Trigonox C was replaced by Trigonox T. It was demonstrated that a higher barrel temperature resulted in a lower molecular weight, although the effect was quite small. The conversion increased slightly with temperature.

A change in extruder parameters, such as die resistance and screw speed, also influences the molecular weight of the polymer formed. The most reasonable explanation is that by changing an extruder parameter, the thermal treatment of the material inside the extruder alters, due to the temperature profile along the barrel. Hornsby (1994) suggested that also the amount of shear stress influences the molecular weight. Although Hornsby found a very strong influence on the molecular weight in the case of polyamide 6, in radical polymerisations the influence is rather weak and often unpredictable (figure 4.8, Jongbloed 1995a).

4.6 Reproducibility

In this section the reproducibility of the extruder experiments is studied. This is done by comparing identical extruder settings, which are obtained by changing different extruder parameters. The main objective is to investigate the possibilities of a multiple steady state taking place in the extruder.

The experiments described in this chapter show a good reproducibility in conversion. For example, the points indicated with an "1" in figures 4.2 and 4.7 are obtained at identical extruder settings. However, the settings of the extruder are obtained in experiments in which other parameters were altered. In figure 4.2 the die resistance is changed, while in figure 4.7 the temperature profile was altered. The values for conversion were respectively 93.9 and 94.1%. Another examples is given by the values for the conversions indicated with a "2" figures 4.2 and 4.7. These conversion values are respectively 92.3 (figure 4.2) and 93.3% (figure 4.7). In general, the conversion could be reproduced with an accuracy of about 1%.

The reproducibility in molecular weight was less good. For example, the values for the experiments indicated with a "3" are respectively 92 kg/mol (figure 4.5) and 115 kg/mol (figure 4.7) at identical extruder settings.

The differences in molecular weight can be a result of some kind of hysteresis in the process of reactive extrusion. However, some errors in measurements of the process are more likely because of the slow polymerisation. Due to this slow polymerisation, long residence times were needed, as a result of which the steady state will be obtained just after long waiting times. For better results concerning the molecular weight, one should use a faster polymerisation, as in chapter 6 or feed the extruder batch wise as in chapter 8.

4.7 Conclusions

The copolymer St-BMA can be produced via reactive extrusion. A conversion of 96% is possible in one step. However, due to the low polymerisation rate, the throughput is limited. Prepolymerisation enlarges the working domain of the counterrotating twin screw extruder. It results in higher maximum throughputs and a decreased dependence on the extruder parameters. Prepolymerisation leads also to higher molecular weights. The rate of conversion after prepolymerisation seems to be a good tool to adjust the molecular weight of the product formed. For slow polymerisations such as St-BMA a prepolymerisation is strongly recommended in reactive extrusion.

References

- Ganzeveld K.J., Janssen L.P.B.M., Pol. Eng. Sci., vol. 30, no. 23, p. 1529-36 (1990)
- Ganzeveld K.J., Janssen L.P.B.M., Pol. Eng. Sci., vol. 32, no. 7, p. 467-474 (1992)
- Hornsby P.R., Tung J.F., Taverdi K., J. of Appl. Pol. Sci., vol. 53, no. 7, p. 891-7 (1994)
- Jongbloed H.A., Mulder R.K.S., Janssen L.P.B.M., Pol. Eng. Sci., vol. 35, no. 7, p. 587-97 (1995a)
- Jongbloed H.A., PhD thesis, University of Groningen, the Netherlands (1995c)
- Kelley J.M., U.S. patent, no. 5,270,029 (1993)
- Michaeli W., Berghaus U., Frings W., J. of Appl. Pol. Sci., vol. 48, p. 871-86 (1993)
- Speur J.A., Ph.D. thesis, University of Groningen, the Netherlands (1988)

Table 4.1 *Extruder settings. The initiator concentration is expressed as mmol/mol St*

figure	[I]	conv. after prepol. (%)	temp. profile (°C)	Q (g/min)	K (10^{-11} m ³)	N (rpm)
4.2 ■	8	0	120-145	6	var	28
4.2 ◆	8	0	120-140	5	7.4	var
4.3 ■	8	0	120-145	6	var	28
4.3 ◆	9	22	120-160	10	var	28
4.4	8	0	120-145	5	7.4	28
4.5 ■ ▲	var	25	120-160	9	7.4	28
4.5 ◆ ●	var	0	120-145	7	7.4	28
4.6	8	21	120-140	9	17.7	28
4.7 ◆ □ △	8	0	var	7	7.4	28
4.7 ■ ▲	8	0	var	4	7.4	28
4.8	8	0	120-140	4	7.4	var