

## Chapter 5

# The influence of the polymer melt viscosity on the working domain in reactive extrusion

Experiments described in chapter 4 indicate that the rate of polymerisation is not sufficient to explain the results of the reactive extrusion experiments. The viscosity of the polymer melt and the increase in viscosity during polymerisation are also very important. To investigate the influence of the polymer melt viscosity on the reactive extrusion process, the styrene-n-butylmethacrylate (St-BMA) copolymer is

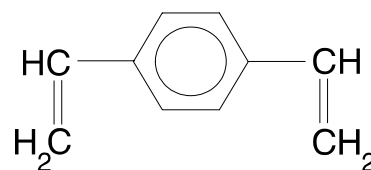


Fig. 5.1 *Divinylbenzene*

crosslinked in order to increase the polymer melt viscosity (section 5.2.2), without influencing the polymerisation rate (section 5.2.3). The crosslink agent used is divinylbenzene (DVB), which influence on product properties is also described in this chapter. Figure 5.1 shows the structure of the molecule.

### 5.1 Introduction

The styrene-n-butylmethacrylate copolymer is investigated several times. Chapter 3 gives a short overview and describes the applications of this polymer. In literature however, not only linear, but also crosslinked polymers that consist of styrene and n-butylmethacrylate are studied (Schellenberg 1993). Generally, the applications of crosslinked polymers lie in the field of optical discs, micro gels for painting, super absorbents and in several medical applications (Tobita 1992). Highly crosslinked polymers are produced in bulk, while emulsion and suspension processes are useful for slightly crosslinked polymers (Ku 1988a). In literature, the extruder is mostly used for the production of linear polymers. Speur (1988) however, did research on the production of nylon 6 from  $\epsilon$ -caprolactam. Not only monofunctional initiators, but also bifunctional initiators were used in these experiments. Although the bifunctional initiator resulted in a high degree of polymerisation, it led to complications, since the polymer melt formed a network due to crosslinking. This resulted in a high polymer melt viscosity. The extremely high viscosity and the large changes in viscosity made the process unstable. Besides, the extruder stopped often because of torque limitations. Crosslinking reduced the operating window of the extruder in this particular application.

Crosslinking however is rather common in reactive extrusion when it concerns modifications of polymers. Coupling reactions, vulcanisation or crosslinking in the presence of peroxides is investigated quite extensively (Xanthos 1992).

## 5.2 The influence of crosslinking on the material properties

The effect of crosslinking on a free radical polymerisation has been studied by several authors. Schellenberg (1993) found that crosslinking leads to higher molecular weights, or to gel formation. As a result of these two effects, the viscosity of the polymer melt increases significantly. The gel formation depends on the type of crosslink agent used. Generally, the product formed is not homogeneous. Schellenberg found also that the glass transition temperatures are relatively constant, irrespective of the concentration of the crosslink agent for copolymers of styrene and BMA.

In recent years, the free radical polymerisation with crosslinking has been modelled several times (Batch 1992, Kurdikar 1994, Tobita 1993, Tobita 1992, Zhu 1993). Tobita (1992) proposed a model that describes the network structure development during the polymerisation. The model can be useful in the production of more homogeneous polymer networks. In 1993, Tobita published a model that describes the network formation in the postgelation period. Batch (1992) developed a kinetic model for crosslinking free radical polymerisation that predicts the effect of temperature, inhibitor, and initiator concentration. This model shows that at higher conversions the effects of a decreased initiator efficiency, a decreased termination rate and radical trapping become important.

### 5.2.1 The influence of DVB on the polymer melt viscosity

The viscosity  $\eta$  of a fluid describes the ratio between the shear stress  $\tau_{xy}$  and the shear rate  $\dot{\gamma}$ :

$$\eta = \frac{\tau_{xy}}{\dot{\gamma}} \quad (5.1)$$

in which for a one dimensional flow, the shear rate is defined as ( $v_y$  is velocity in y-direction):

$$\dot{\gamma} = -\frac{dv_y}{dx} \quad (5.2)$$

The ratio between the shear stress and shear rate is constant for Newtonian fluids. Generally, polymer melts are non-Newtonian fluids, which means that the ratio of the shear stress and shear rate is not constant, but depends on the shear rate. The ratio between the shear stress and shear rate is therefore called the apparent viscosity  $\eta_a$ .

The rheology of the polymers formed was studied by using a capillary viscometer. The measurements were performed in a high pressure capillary apparatus (HKV 1000/1600, Göttfert Werkstoff Prämaschinen GmbH). The capillary had a length of 3 cm, a diameter of

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1 mm, and an exit angle of 180 ° (installed die roundhole 30/1.0/180). The measurements were performed at constant pressure and at a temperature of 150 °C. The characteristics of the samples measured are listed in table 5.1. The Rabinowitsch correction is applied in the calculation of the apparent viscosity.

Table 5.1 *Characteristics of the samples used in viscometry. The molecular weight concerns the soluble part of the polymer*

[DVB] (mmol/mol St)	gel fraction (%)	$M_w$ (kg/mol)	$M_w/M_n$
0	0	78	2.6
2	3	155	3.6
3	38	146	3.8
4	55	148	3.6
5	62	82	3.0

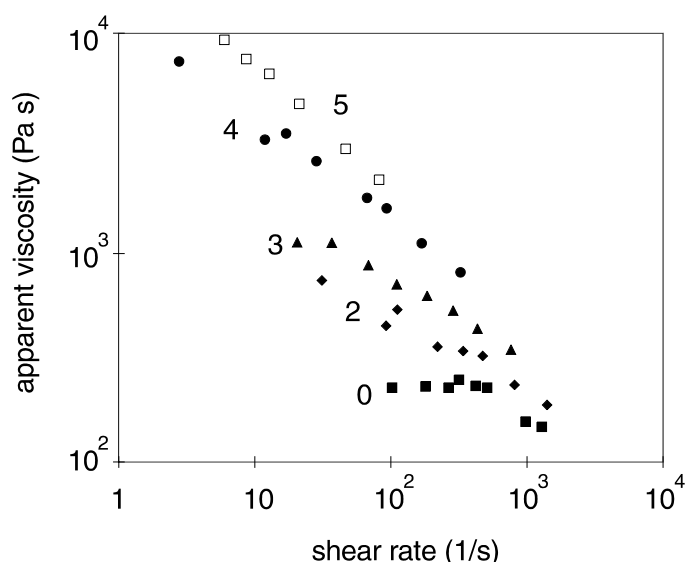


Fig. 5.2 *The shear rate versus the apparent viscosity. The numbers in the figure refer to the amounts of DVB (mmol/mol St) added*

Figure 5.2 shows the shear rate versus the apparent viscosity for the different samples. The addition of DVB results in a higher polymer melt viscosity. Furthermore, figure 5.2 shows that the apparent viscosity of all polymers decreases at higher shear rate. At lower shear rates, the linear polymer shows a Newtonian behaviour, which is normal for linear polymers. The individual polymer chains behave as rigid spheres, which do not have much conformational interaction. When the polymer chains are crosslinked, the Newtonian behaviour at low shear rate was not observed. Due to crosslinking, the individual polymer chains have large interaction with each other, even at very low shear rates.

### 5.2.2 The influence of DVB on the kinetics

The addition of a crosslink agent can influence the rate of polymerisation, due to the increased viscosity of the polymer melt. This higher viscosity can enhance the gel effect (Batch 1992). Figure 5.3 shows the effect of the addition of DVB on the rate of polymerisation for St-BMA. The rate of polymerisation was determined by using DSC as in chapter 3. It can be observed that DVB hardly influences the rate of polymerisation in these experiments.

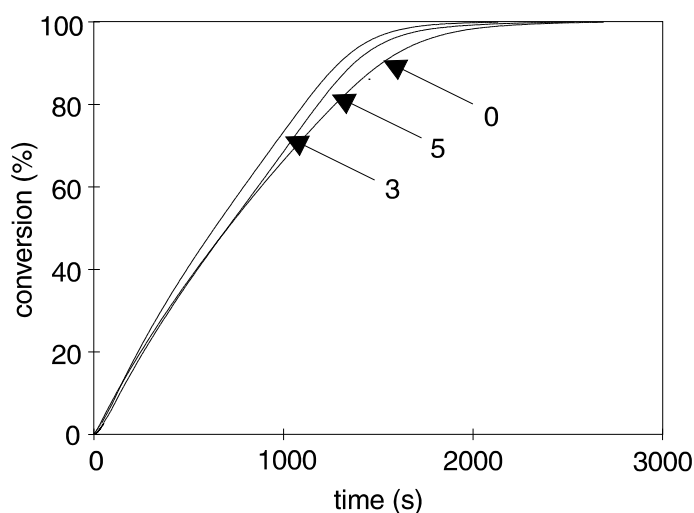


Fig. 5.3 Conversion curves for the copolymerisation of St with BMA with 0, 3 or 5 mmol DVB/mol St added to the monomer mixture ( $T = 130\text{ }^{\circ}\text{C}$ )

Table 5.2 gives the rate of polymerisation at 10 % conversion for several monomer mixtures, while figure 5.4 presents  $k_{ov}$  for the whole conversion range (for the definition of  $k_{ov}$  see chapter 3). The copolymerisation was assumed to be pseudo homogeneous when calculating  $k_{ov}$ . At low conversion, there is no increase in reaction rate due to the addition of DVB. Only at high conversion, a small increase in gel effect could be observed when the polymer was crosslinked (figure 5.4).

Table 5.2 The influence of the crosslink agent on the rate of polymerisation

[DVB] (mmol/mol St)	$T$ ( $^{\circ}\text{C}$ )	initiator	[I] (mmol/mol St)	$k_{ov}$ $\sqrt{(\text{l/mol s})}$
0	130	Trigonox C	10	$0.24 \pm 0.02$
3.0	130	Trigonox C	10	$0.26 \pm 0.02$
5.0	130	Trigonox C	10	$0.22 \pm 0.02$

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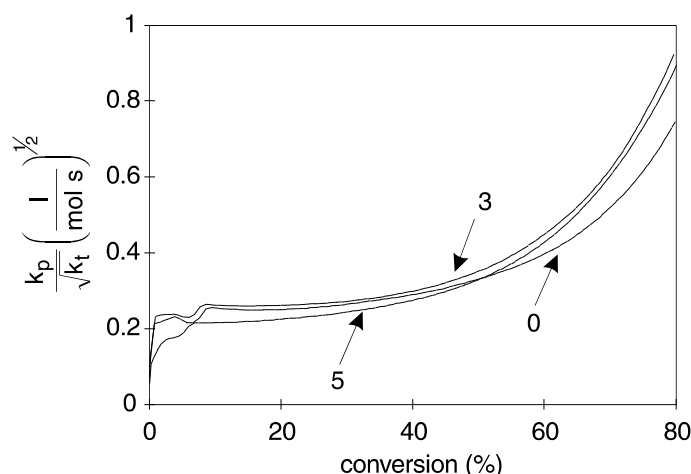


Fig. 5.4 The pseudo first-order reaction rate "constant" for the mixtures given in figure 5.3

## 5.3 The extruder experiments

### 5.3.1 Experimental

The experimental set-up is described in chapter 4.

The monomers styrene and n-butylmethacrylate (both inhibited) were mixed in the ratio 50-50 mol%. 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. The two initiators were dibenzoyl peroxide (mole fraction of 0.3) and Trigonox C. When a steep temperature profile was applied (120-160 °C) half of the Trigonox C was replaced by Trigonox T. The standard temperature profile was 120-125-130-140-145 °C; the steep profile was 120-130-140-150-160 °C. The standard die resistance was  $7.4 \cdot 10^{-11} \text{ m}^3$ . To the monomer mixture, DVB was added in the amount of 0 to 5 mmol/mol St. The DVB used was of mixture of o-, m- and p-divinylbenzene, which was supplied as a 50 wt% solution in ethyl-vinylbenzene.

The conversion was determined as described in chapter 4, except for the fact that the amount of crosslinked polymer used for the determination was somewhat less than the amount of linear polymer (about 0.4 gram). The molecular weight distribution was determined by GPC as in chapter 4. However, from samples that contained a non-soluble part due to crosslinking, only the molecular weight distribution of the soluble part was determined. The non-soluble fractions (gel fraction) of the samples were examined by using Soxhlet extraction.

### 5.3.2 The effect of DVB on the product properties

Crosslinking combines polymer chains. When the degree of crosslinking is low, the crosslinking results in higher molecular weights of the polymer formed. When the amount of crosslink agent in the reaction mixture is increased, part of the polymer will form a polymer network, which does not dissolve, but only swells in a solvent. More crosslink agent leads to

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a complete polymer network. The fact that highly crosslinked polymers have lost their thermoplastic properties makes the extruder not suitable for producing these materials. In the experiments described in this chapter, the amount of DVB added is limited to a maximum of 5 mmol/mol St.

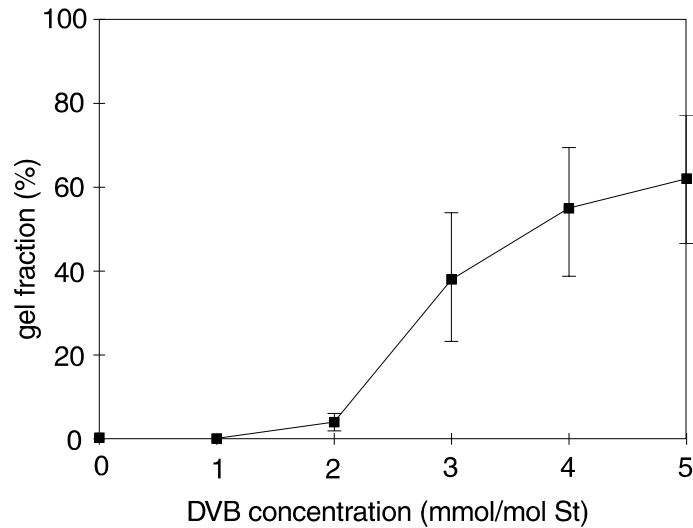


Fig. 5.5 *The influence of the amount of DVB on the gel fraction in the polymer formed*

Figure 5.5 gives the amount of gel formed during reactive extrusion. It turned out that it was possible to synthesise a slightly crosslinked polymer via reactive extrusion. Only when more than 2 mmol DVB was added, gel fraction started to occur. The shape of the curve in figure 5.5 is comparable to curves described by Schellenberg (1993).

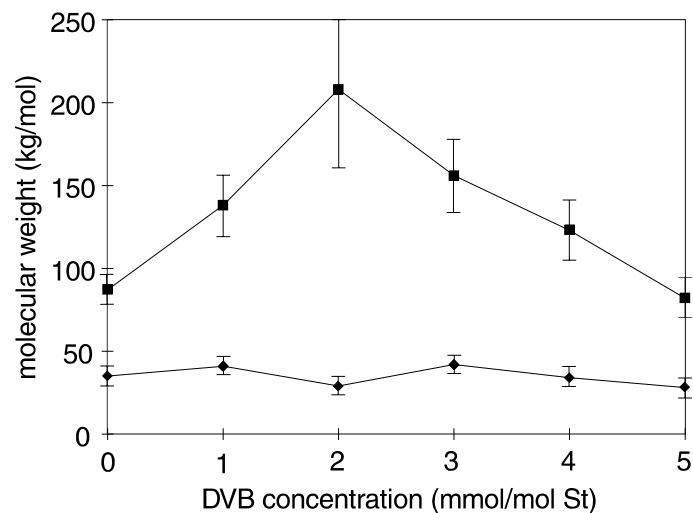


Fig. 5.6 *The influence of DVB on the molecular weight of the polymer (■  $M_w$ , ♦  $M_n$ )*

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The effect of crosslinking on the molecular weight is given in figure 5.6. It should be noted that only the molecular weight could be measured from that part of the polymer that still dissolved. That is why a maximum in the molecular weight occurs. Low DVB-concentrations leads to an increase in molecular weight, while more DVB leads to gel formation, as a result of which the length of the remaining polymer chains decreases.

Figure 5.7 shows a typical molecular weight distribution of a crosslinked polymer. When the distribution is compared to the distribution of the unbranched polymer (figure 4.4), a broadening can be observed. Furthermore, the distribution shows two local maximums, which is a result of doubling, tripling, etcetera the normal molecular weight distribution of the unbranched polymer. This effect was predicted in a theoretical study performed by Yan (1979).

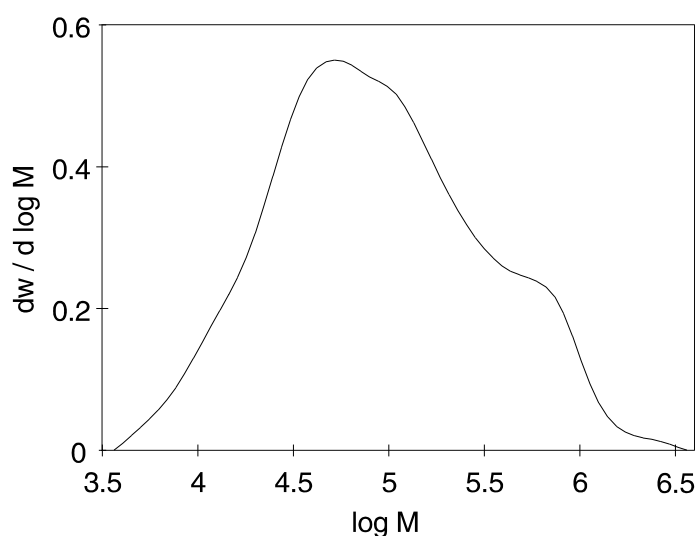


Fig. 5.7 *A typical molecular weight distribution of a crosslinked polymer. The extruder settings at which this polymer is obtained are listed in table 5.3*

#### **5.3.3 The effect of DVB on the process.**

As already described in chapter 4, the reactive extrusion process of St-BMA was quite difficult due to the low polymerisation rate. Irregularities in the output of the extruder occur quite often. An extreme example of instabilities in the output of the extruder is given in figure 5.8. With a period of roughly 15 minutes, the output reached a maximum, after which the extruder started to refill itself.

As already stated, the situation described in figure 5.8 was quite extreme. However instabilities in the output occurred more often. These instabilities indicated that a minimum residence time was reached for a sufficient conversion, as could be proven by changing the die resistance. This effect will be discussed below.

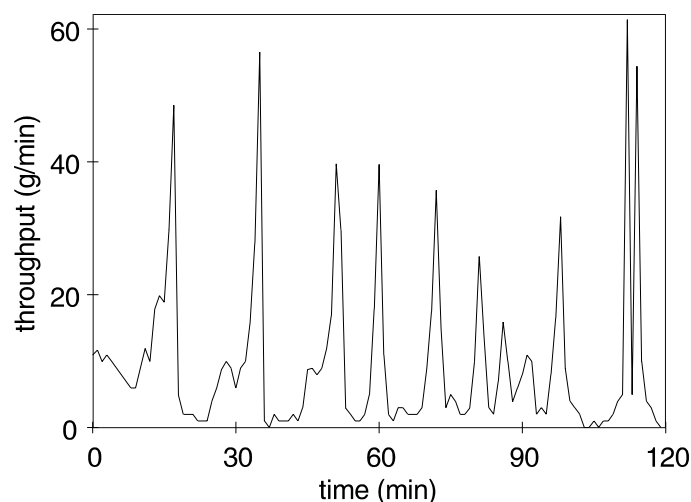


Fig. 5.8 *Instabilities in the output of the extruder*

To overcome the instabilities, the die resistance could be increased or decreased. When it was decreased, the residence time was decreased, which resulted in a significantly lower conversion. However, the output of the extruder became stable again. Nevertheless, this situation is not desirable due to the low conversion. When instabilities in the output are observed, the die resistance has to be increased in order to obtain a stable process, with sufficiently high conversion.

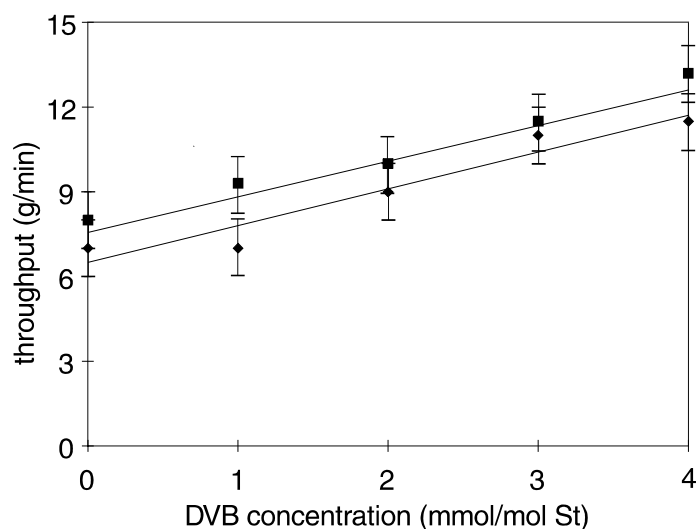


Fig. 5.9 *The influence of DVB on the maximum throughput of the extruder*  
 (■  $K = 3 \cdot 10^{10} \text{ m}^3$ , ◆  $K = 7.4 \cdot 10^{-11} \text{ m}^3$ , the other extruder parameters are listed in table 5.3)

Figure 5.9 shows the effect of DVB on the process. The throughput could be increased by almost a factor 2 when going from 0 to 4 mmole DVB per mole St. The maximum

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throughput was defined as the throughput at which the extruder was fully filled, and the conversion of the product was higher than 90%.

A conversion higher than 90% was achieved in all experiments, except in the experiment in which 1 mmole DVB was added at a reciprocal die resistance of  $3 \cdot 10^{-10} \text{ m}^3$ . The conversion of that sample was only 88%. In all other situations, the conversion ranged from 92-95%.

Figure 5.9 shows that the maximum throughput is strongly influenced by the rheological behaviour of the material in the extruder, since the rate of polymerisation is hardly influenced by the addition of DVB. This implies that the residence time is not the only limiting factor in reactive extrusion. The rheological behaviour of the material inside the extruder also influences the operating window of the extruder.

For a good comparison of the various experiments, all extruder settings should be identical. Because of stability reasons, this was not completely possible. The desired temperature profile, for example, ranged from 120 to 160 °C to simulate an industrial extruder, in which not all heat of reaction can be removed. When some DVB was added to the mixture, a stable extrusion process was obtained when this temperature profile was applied. In the case of the linear polymer, this steep temperature profile led to irregularities in the output of the extruder. Therefore, the standard temperature profile was applied, which is comparable to an increased die resistance. On the other hand, when more than 4 mmole DVB was added, the maximum throughput could only be increased by increasing the die temperature to 170 °C.

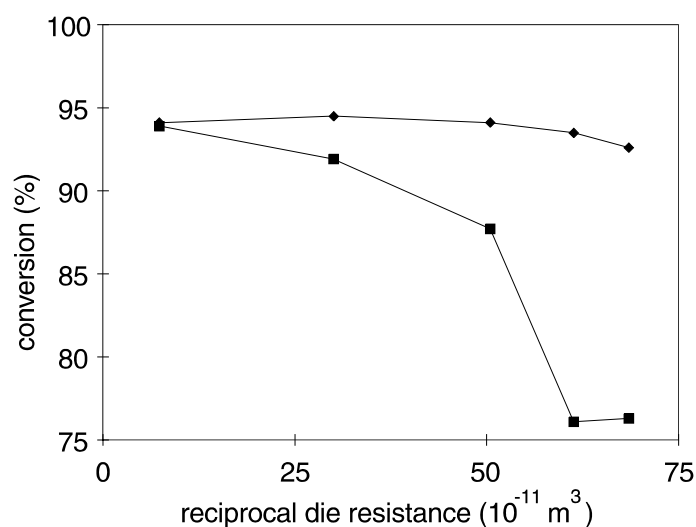


Fig. 5.10 *The influence of the die resistance on the conversion for the linear polymer (■) and the crosslinked polymer (◆)*

Apart from the influence on the maximum throughput, the addition of DVB led also to a decreased dependence on the extruder parameters. The effect of the die resistance on the conversion is shown in figure 5.10. When no DVB was added, the conversion decreased rapidly when the die resistance was lowered, due to a decreased residence time. When 4 mmole DVB per mole styrene was added, a decrease in conversion was not observed. From figure 5.10, two conclusions can be drawn. The first conclusion is that a conversion of 95%

is more or less a maximum conversion in this situation. The second conclusion is that the reactor volume is large enough to obtain this maximum conversion. Apparently, by crosslinking the polymer, the extruder volume is used more effectively. It is quite difficult to understand the underlying mechanism, but obviously the linear polymer needs a high die resistance to obtain sufficient conversion, while in the case of the branched polymer, the die resistance could be lowered. In that situation, a high die resistance resulted only in an unnecessary energy input in the crosslinked material.

The effect of the screw rotation rate is shown in figure 5.11. An increase in screw rotation rate led to a decrease in the mean residence time. The decrease in residence time could result in a lower conversion if the time necessary for conversion was more or less equal to the mean residence time. A constant conversion with increasing screw rotation rate implied that the residence time was larger than the reaction time needed for the maximum conversion. Figure 5.11 shows a decrease in conversion for the linear polymer, while the conversion was hardly influenced when the polymer was crosslinked. Because the polymerisation rate was not influenced by crosslinking, it is concluded that in the case of St-BMA an increased viscosity results in a better use of the reaction volume in the extruder.

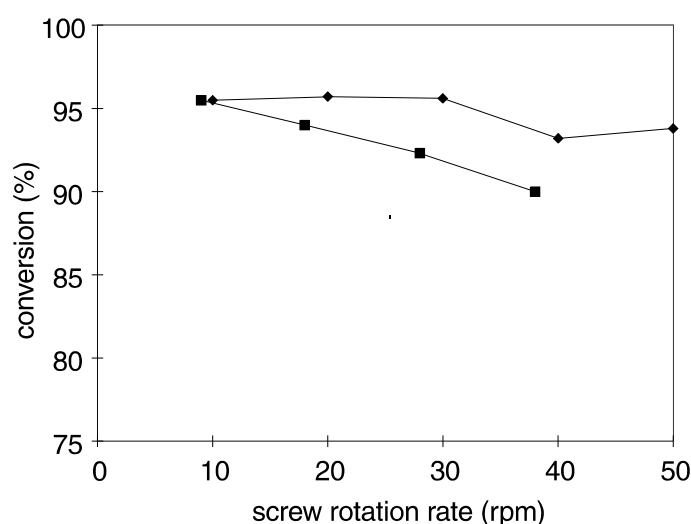


Fig. 5.11 *The influence of screw rotation rate on the conversion for the linear (■) and the crosslinked polymer (◆)*

The results indicated in figures 5.9, 5.10 and 5.11 show that the working domain in reactive extrusion is enlarged by crosslinking the St-BMA-copolymer. Not only the throughput can be increased, but the extruder parameters can also be chosen in a wider operating window. Besides, by applying a higher temperature profile or a lower die resistance, even higher throughputs can be obtained. Chapter 7, in which the results are generalised, gives an optimisation procedure for the extruder when it is used as a polymerisation reactor

## **5.4 Conclusions**

The use of an extruder as a polymerisation reactor is not only restricted to linear polymers, but it can be extended to crosslinked polymers. The degree of crosslinking has to be limited, but a certain gel formation is allowed. If the degree of crosslinking is too high, the polymer is not a thermoplast anymore, as a result of which the extrusion of the material is not possible.

In the case of the St-BMA, crosslinking leads to an enlarged working domain, which means higher maximum throughputs and a decreased dependence on the extruder parameters

The effect of the crosslinking on the product properties was as expected. The polymer melt viscosity increases due to an increase of the molecular weight of the polymer chains. When more than 2 mmole DVB per mole styrene is added to the reaction mixture, gel formation starts. Except when the conversion is higher than 60%, the rate of polymerisation is not influenced by crosslinking.

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Table 5.3 *Extruder settings. The initiator concentration and the concentration of DVB are expressed as mmol/mol St*

figure	[I]	[DVB]	$T$ (°C)	$Q$ (g/min)	$K$ ( $10^{-11}$ m <sup>3</sup> )	$N$ (rpm)
5.7	10	3	120-150	11	7.4	38
5.8	8	3	120-150	-	50	28
5.9 ■	10	var	120-145 or 120-160	var	30	28
5.9 ◆	10	var	120-145 or 120-160	var	7.4	28
5.10 ■	8	0	120-145	5	var	28
5.10 ◆	10	4	120-160	12	var	28
5.11 ■	8	0	120-140	6	7.4	var
5.11 ◆	10	4	120-160	7	7.4	var