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The Working Domain in Reactive Extrusion. Part I: The Effect of the Polymer Melt Viscosity

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This article describes the radical copolymerization of styrene (St) and n-butylmethacrylate (BMA) in a counter-rotating twin-screw extruder. In order to investigate the effect of the polymer melt viscosity on the working domain in reactive extrusion, the copolymer was crosslinked with different amounts of divinylbenzene (DVB). Crosslinking of the polymer resulted in a higher polymer melt viscosity. It was demonstrated that not only the product properties but also the process characteristics were strongly influenced by the addition of divinylbenzene to the reaction mixture. The product properties changed as expected: more crosslink agent led to a higher molecular weight or an increase in gel fraction, and a much higher melt viscosity of the polymer. Besides these effects on the product properties, the addition of DVB resulted in a more stable process, leading to an enlarged working domain.

INTRODUCTION

The copolymerization of styrene with several derivatives of acrylates, especially methylacrylate, methyl-methacrylate, and butylmethacrylate have been studied thoroughly. The importance of the latter copolymerization stems from the fact that this copolymer finds applications in specialty areas, such as in the manufacture of recording tapes and toners for photocopiers (1, 2). Not only linear polymers but also crosslinked copolymers of styrene and n-butyl methacrylate are interesting (3). Generally, the applications of crosslinked polymers lie in the field of optical discs, micro-gels for painting, super absorption and several medical applications (4). Mostly, the polymerization reactions are carried out in suspension or emulsion at relatively moderate temperatures.

In this study, the extruder is used as a polymerization reactor. The main advantage of the extruder over traditional polymerization reactors is its ability to work without a solvent. Moreover, the extruder provides, even at a high viscosity, good mixing and heat transfer. In recent years, several investigations showed that the extruder can be used as a reactor for homo- and copolymerizations (5–8). Jongbloed (8) showed the counter-rotating twin-screw extruder to be the most stable polymerization reactor. Besides, the average shear level in this type of extruder is low, which prevents degradation of the newly formed poly-

mer. Therefore, the counter-rotating twin-screw extruder was used for the copolymerization of styrene (St) with n-butyl methacrylate (BMA). The addition of a crosslink agent leads to a new aspect in the field of reactive extrusion. Not only do product properties change because of the addition of DVB, but also the working domain of the extruder is strongly influenced.

THE COUNTER-ROTATING TWIN-SCREW EXTRUDER

The counter-rotating twin-screw extruder we used is closely intermeshing. This implies that the channel of one screw is blocked by the flight of the other screw. The extruder can therefore be considered as a series of C-shaped chambers, in which material is transported toward the die. The theoretical throughput is defined as the maximum volumetric displacement and equals the number of C-shaped chambers transported per unit time multiplied by the chamber volume:

$$Q_{th} = 2mNV_c \quad (1)$$

in which m is the number of thread starts, N is the screw rotation rate, and V_c is the volume of one chamber. One of the main characteristics of a closely intermeshing twin-screw extruder is that the transport mechanism is not due to drag flow as it is in a single-screw extruder, but due to volumetric displacement. This transport mechanism is relatively independent of the rheological behavior of the material inside the extruder.

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Because of mechanical clearances, the chambers are not completely closed. Leakage flows cause interaction between the chambers. The real volumetric throughput is therefore given by:

$$Q = Q_{th} - Q_l \quad (2)$$

Since these kinds of extruders are fed starved, a partially filled zone arises apart from a fully filled zone before the die. The length of the fully filled zone is mainly determined by the pressure needed to overcome the die resistance and the geometry of the screws (9). The die pressure is determined by the die resistance, the throughput, and the viscosity of the material in the die:

$$P_{die} = \frac{Q\eta}{K} \quad (3)$$

in which K is the reciprocal die resistance.

The length of the fully filled zone can be used for stabilizing the extrusion process. For example, a change in input can be compensated for by a change in the fully filled length. On the other hand, extruder volume is used most beneficially when the extruder is completely filled. When it is used as a reactor, reactions can take place in the total extruder volume. However, stability problems are likely to occur, because the process cannot be stabilized anymore by changes in fully filled length, when the extruder is fully filled. In case of a polymerization taking place in the extruder, the stability of the extruder will also get worse because of the large differences in viscosity of the reaction mixture in the feedzone and at the die end (10).

THE REACTION KINETICS

The bulk copolymerization of styrene with *n*-butyl-methacrylate is a free radical addition polymerization. This means that after initiation a polymer chain grows in a rather short time (propagation) because of a termination reaction the polymer chain is excluded from further reaction.

In the case of a constant radical concentration (the quasi-steady state approximation), the rate of polymerization is given by (11):

$$v_p = k_p \sqrt{\frac{f k_d [I]}{k_t}} [M] \quad (4)$$

In bulk polymerizations, however, deviations from this equation occur when the conversion of the reaction reaches a certain degree as a result of the Trommsdorff effect or gel effect (12). Because of this effect, greater polymerization rates are obtained when the conversion is increased.

For a copolymerization of two monomers A and B, the propagation step consists of at least four different reactions, in which every reaction has its own propagation rate constant (k_{11} , k_{12} , etc.).

The ratios of propagation rate constants are defined

as the reactivity ratios (11):

$$\begin{aligned} r_1 &= k_{11}/k_{12} \\ r_2 &= k_{22}/k_{21} \end{aligned} \quad (5)$$

The reactivity ratios can be used for describing the incorporation ratio of the monomers and for estimating the rate of copolymerization. However, it is known (13) that for a styrene-methyl-methacrylate system the expression for the rate of propagation as described by Eq 5 is not sufficient for a good description of the rate of polymerization.

The effect of crosslinking on a free radical polymerization is studied several times. Schellenberg (3) 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.

Theoretical studies concerning free radical polymerization with crosslinking have recently been performed quite often (14–17). The studies show that polymer network development during the polymerization is not homogeneous in most situations and that a complete kinetic model for crosslinking is very complicated.

The Reaction Kinetics of St-BMA at High Temperatures

Up to now, most of the kinetic studies concerning the copolymerization of St with *n*-BMA are performed at low temperatures. Because the temperature in the extruder ranges from 120 to 160°C, additional experiments were necessary to investigate the kinetics of the reaction and the reactivity ratios of the monomers. The reactivity ratios were determined by performing a thermal polymerization at 135°C of several St-BMA mixtures, in which the mole fraction of styrene was varied from 0.1 to 0.9. Except for the mixture with a styrene mole fraction of 0.1, all mixtures showed thermal polymerization. When these mixtures had reached a conversion of 5% to 10%, the polymerization was stopped by rapid cooling of the mixture. The polymer-monomer mixture was precipitated in methanol, after which the copolymer was carefully dried in a vacuum oven. The different copolymers were analyzed by elemental analysis. By determining the carbon and oxygen content of the copolymer, the amount of styrene could be calculated. The results are shown in Fig. 1. By use of the method of Kelen and Tüdös (18–20) the reactivity ratios were determined at $r_1 = 0.40$, and $r_2 = 0.86$ (styrene is monomer A).

The rate of copolymerization of styrene with BMA was studied by means of differential scanning calorimetry (DSC). The results of these experiments are shown in Table 1, which gives the quantity $k_p/\sqrt{k_t}$. The quantity $k_p/\sqrt{k_t}$ describes the average rate of polymerization and can be determined within 10% limits (21). Table 1 shows that the copolymerization is faster than the homo-polymerization of styrene, but signifi-

Fig. 1. The relation between the amount of styrene F_{St} in the polymer and the amount of styrene f_{St} in the monomer feed.

Table 1. The Rate of Polymerization for St, BMA and the Copolymerization of St and BMA.

	Temp (°C)	Initiator	[I] (mmol/mol St)	$k_p/\sqrt{k_t}$
Styrene	130	Trigonox C	5.3	0.095
St/BMA	120	Trigonox 29C50	10.0	0.14
St/BMA	130	Trigonox C	10.0	0.24
St/BMA	140	Trigonox 101	9.2	0.37
BMA	130	Trigonox C	4.2 mmol/mol BMA	0.56

cantly slower than the polymerization of BMA. When the terminal model is used to describe the copolymerization of St with BMA, the average rate of polymerization is $0.39 \text{ (l/mol s)}^{0.5}$, when the monomers are mixed in the ratio 1:1. This is significantly more than 0.24 as found by the DSC experiments, which means that also at a higher temperature, the terminal model does not describe the rate of copolymerization accurately.

The Influence of DVB on Kinetics

The addition of a crosslink agent can influence the rate of polymerization, because of the increased viscosity of the polymer melt. This increase can result in an increase in gel effect (15). Figure 2 shows the effect of the addition of DVB on the rate of polymerization in the St-BMA copolymerization. The influence of DVB is rather small. Only at a high conversion, a small difference in polymerization rate could be observed when the polymer was crosslinked.

To investigate the effect of DVB better, the quantity $k_p/\sqrt{k_t}$ is calculated. Table 2 gives the rates of polymerization at 10% conversion for the polymerization of different monomer mixtures. At low conversion, there is no increase in reaction rate due to the addition of DVB.

The Influence of DVB on the Polymer Melt Viscosity

The viscosity of a fluid describes the ratio between the shear stress and the shear rate:

Fig. 2. Conversion curves for the copolymerization of St with BMA under the addition of 0, 3, or 5 mmol DVB/mole St to the monomer mixture ($T = 130^\circ\text{C}$).

Table 2. The Influence of the Crosslink Agent on the Rate of Polymerization.

[DVB] (mmol/mol St)	Temp (°C)	Initiator	[I] (mmol/mol St)	$k_p/\sqrt{k_t}$
0	130	Trigonox C	10.0	0.24 ± 0.02
3	130	Trigonox C	10.0	0.26 ± 0.02
5	130	Trigonox C	10.0	0.22 ± 0.02

$$\eta = \frac{\tau_{xy}}{\dot{\gamma}} \quad (6)$$

in which the shear rate is defined as:

$$\dot{\gamma} = -\frac{dv_y}{dx} \quad (7)$$

The ratio between the shear stress and shear rate is constant for Newtonian fluids. Generally, polymer melts are not Newtonian fluids. This means that the ratio of the shear stress and shear rate is not constant, but dependent on the shear rate. The ratio is called the apparent viscosity η_s .

The rheology of the polymer was studied using a capillary viscometer. The measurements were performed in a high pressure capillary apparatus (HKV 1000/1600, Göttfert Werkstoff Prüfmaschinen GmbH). The capillary used had a length of 3 cm, a diameter of 1 mm, and an exit angle of 180° (installed die round-hole 30/1.0/180). The temperature at which the viscosity was determined was 150°C . The measurements were performed at constant pressure. The characteristics of the samples used are given in Table 3. The Rabinowitsch correction was applied in the calculation of the apparent viscosity.

Figure 3 shows the shear rate versus the apparent viscosity for the different polymers. The addition of DVB results in a higher polymer melt viscosity. Moreover, Fig. 3 shows that the apparent viscosity of all polymers decreases at higher shear rate. At lower shear rates, the linear polymer shows a Newtonian

Table 3. Characteristics of the Samples Used in Viscometry.

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. 3. The shear rate vs. the apparent viscosity for the polymers. The numbers in the Figure refer to the amounts of DVB (mmol/mol St) added.

behavior, which is normal for linear polymers when their molecular weight is not too high. The individual polymer chains behave as rigid spheres, which do not interact very much. When the polymer chains are crosslinked, Newtonian behavior was not observed. Because of the crosslinking the individual polymer chains have large interactions with each other, even at very low shear rates.

By summarizing the kinetic and rheological measurements, we can conclude that the crosslink agent DVB barely influences the rate of polymerization, but that DVB strongly increases the polymer melt viscosity.

EXPERIMENTAL SETUP

The extruder used in this study was a counter-rotating closely intermeshing twin-screw extruder with a screw diameter of 40 mm and an L/D of 15. The pitch of the uniform screw was 24 mm. The extruder had four heating zones and a heated die. The die resistance could be adjusted.

The monomers styrene and n-butyl-methacrylate (both inhibited) were mixed in the ratio 50-50 mol%. To this mixture, DVB was added in the amount of 0 to 5 mmol/mol St. The DVB used consisted of a mixture of o-, m- and p-divinylbenzene, which was supplied as a 50 wt% solution in ethyl-vinylbenzene. Apart from DVB, 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. The two initiators were benzoyl 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. This liquid reaction mixture is pumped into the feedzone of the extruder.

The standard temperature profile was 120-125-130-140-145°C; the steep profile was 120-130-140-150-160°C. In most experiments, the reciprocal die resistance was $7.4 \times 10^{-11} \text{ m}^3$, while the screw rotation rate was generally set to 0.47 s^{-1} . The actual extruder settings belonging to the experiments outlined in the figures are listed in Table 4.

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. The conversion was determined gravimetrically. About 1 gram of product was dissolved in THF. A small amount of hydrochinon was added to this solution to inhibit further reaction. The solution was poured onto an aluminum dish, which was placed in a vacuum oven at 135°C and $2 \times 10^4 \text{ Pa}$ for at least 18 hrs. The experiments showed a variance in conversion of 1%.

The molecular weight 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 was performed by determining the refractive index. This detection method needed Mark-Houwink constants, but for the copolymer St-BMA these constants were not known in literature, so 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. The gel fraction was determined by using soxlet extraction.

Table 4. 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^3)	N (s^{-1})
6 ■	8	0	120–145	6	var	0.47
6 ♦	8	0	120–140	5	7.4	var
9	10	3	120–150	11	7.4	0.63
10	8	3	120–150	—	50	0.47
11 ♦	10	var	120–145 or 120–160	var	7.4	0.47
11 ■	10	var	120–145 or 120–160	var	30	0.47
12 ■	8	0	120–145	5	var	0.47
12 ♦	10	4	120–160	12	var	0.47
13 ■	8	0	120–140	6	7.4	var
13 ♦	10	4	120–160	7	7.4	var

RESULTS

The Extruder Experiments Without Crosslinking

The properties of the reactive extrusion product are fixed by temperature, initiator concentration, and residence time. The average residence time is not only determined by process parameters, such as screw rotation rate and die resistance, but also by the properties of the reactive medium in the extruder. The die resistance plays an important role in the process of reactive extrusion.

The polymerization of St with BMA was rather slow. As a result of the low polymerization rate, the extrusion process was rather difficult to perform. A high die resistance was needed to obtain a high conversion. As a result of the high die resistance, the maximum throughput was low (7 g/min). Although an increase of the barrel temperature resulted in a higher polymerization rate, the maximum throughput did not increase (22). Moreover, the output of the extruder became irregular when a steep temperature profile was applied.

An increase in screw rotation rate or a decrease in die resistance led to a decrease in conversion resulting from reduction in residence time. The influence of the die resistance was larger than the influence of the screw rotation rate (Figs. 4 and 5). The molecular weight was only slightly influenced by a change in extruder parameters such as screw rotation rate and die resistance. Under standard conditions the weight average molecular weight of the polymer was about 100 kg/mol, with a ratio of M_w/M_n of 2.4.

The Extruder Experiments With Crosslinking: Effect on Product Properties

Crosslinking combines polymer chains. When the degree of crosslinking is low, the crosslinking results in a higher molecular weight of the polymer formed. When the amount of crosslink agent in the reaction mixture is further increased, part of the polymer will

Fig. 5. The influence of the screw rotation rate on the conversion for St-BMA.

form a polymer network, which does not dissolve, but only swells in a solvent. More crosslink agent leads to 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, the amount of DVB added is limited to a maximum of 5 mmol/mol St.

Figure 6 gives the amount of gel formed during reactive extrusion. It turned out that it was possible to synthesize a slightly crosslinked polymer via reactive extrusion. The form of the curve in Fig. 6 was comparable to curves described by Schellenberg (3). The effect of crosslinking on the molecular weight is given in Fig. 7. It should be taken in mind that only the molecular weight could be measured from that part of the polymer that still dissolved in THF. That is why a maximum in the molecular weight occurred. Initially crosslinking led to an increase in molecular weight, but after the addition of more DVB, gel formation occurred, as a result of which the length of the re-

Fig. 4. The influence of the die resistance on the conversion for St-BMA. All extruder settings are listed in Table 4.

Fig. 6. The influence of the amount of DVB on the gel fraction in the polymer formed.

Fig. 7. The influence of DVB on the molecular weight of the polymer (■ M_w , ♦ M_n).

maintaining polymer chain decreased, which is shown in Fig. 7. It should be noted that when a polymer is branched, the results of the GPC measurements can become unreliable. Nevertheless, Fig. 7 shows the effect of DVB quite well, although the actual value of the molecular weight can be different from that which is outlined in the Figure.

Figure 8 shows a typical molecular weight distribution of a crosslinked polymer. When the distribution is compared with the distribution of the unbranched polymer, a broadening can be observed. Moreover, the distribution shows two local maximums, which is probably a result of doubling and tripling the normal molecular weight distribution. This effect was predicted in a theoretical study performed by Yan (23).

The Extruder Experiments: The Effect of Crosslinking on the Process

The working domain in reactive extrusion is determined by the maximum throughput and by the rate of dependence on the extruder parameters. A sufficient

Fig. 8. A typical molecular weight distribution of a crosslinked polymer.

throughput and a stable process can lead to an economically beneficial process. In our experiments, we observed that the polymer melt viscosity influenced both the throughput and the stability of the process.

Figure 9 shows instabilities in the output of the extruder. With a periodic period of roughly 20 min, the output reached a maximum, after which the extruder started to refill itself. The situation described in Fig. 9 is quite extreme, but instabilities in the output occurred often. These instabilities indicated that a minimum residence time was reached for a sufficient conversion. When the residence time was decreased by lowering the die resistance, the conversion decreased significantly. After the decrease in conversion, the die pressure was almost zero, indicating that the fully filled length was small or even absent, but the output of the extruder became stable again. However, this situation is, because of the low conversion, not desirable. When instabilities in the output are observed, the die resistance should therefore be increased in order to obtain a stable process with sufficient high conversion.

Figure 10 shows the effect of DVB on the throughput. The throughput could be increased by almost a factor of 2 when going from 0 to 4 mmol DVB per mol St. The maximum throughput was limited by two restrictions. The extruder could be fully filled, or the conversion of the product was lower than 90%. All experiments satisfied these requirements, except the experiment in which 1 mmole DVB was added at a reciprocal die resistance of $3 \times 10^{-10} \text{ m}^3$. The conversion was only 88% in that experiment. In all other situations, the conversion ranged from 92% to 95%.

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

Fig. 9. Instabilities in the output of the extruder.

Fig. 10. The influence of DVB on the maximum throughput of the extruder.

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.

Apart from the influence on the maximum throughput, the addition of DVB led to a decreased dependence on the extruder parameters. The effect of the die resistance on the conversion is shown in Fig. 11. When no DVB was added, the conversion decreased rapidly when the die resistance was lowered. This decrease was caused by a decreased residence time. When 4 mmole DVB per mole styrene was added, a decrease in conversion was not observed. From Fig. 11, 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

Fig. 11. The influence of the die resistance on the conversion for the linear polymer (■) and the crosslinked polymer (◆).

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.

A comparable effect to that described above is obtained by changing the screw speed (Fig. 12). By the addition of DVB, the effect of the screw speed on the conversion is significantly reduced.

The results indicated in Figs. 10, 11, and 12 show that the working domain in reactive extrusion is enlarged by crosslinking the St-BMA-copolymer. Not only can the throughput 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.

CONCLUSIONS

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

The effect of the crosslinking on the product properties was as expected. The polymer melt viscosity increased as a result of an increase in the molecular weight of the polymer chains. When more than 2 mmole DVB per mole styrene was added to the reaction mixture, gel formation started. Except at a high conversion, the rate of polymerization was not influenced by crosslinking.

Crosslinking of the St-BMA copolymer leads to an enlarged working domain, which means a higher max-

Fig. 12. The influence of screw rotation rate on the conversion for the linear (■) and the crosslinked polymer (◆).

imum throughput and a decreased dependence on the extruder parameters.

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NOMENCLATURE

- f = Initiator efficiency.
 f_a = Mole fraction of monomer A in the feed.
 F_a = Mole fraction of component A in the polymer.
 I = Initiator.
 k_d = Initiator decomposition rate constant, $\text{m}^3/\text{mol s}$.
 k_i = Initiation rate constant, $\text{m}^3/\text{mol s}$.
 k_p = Propagation rate constant, $\text{m}^3/\text{mol s}$.
 k_t = Termination rate constant, $\text{m}^3/\text{mol s}$.
 K = Reciprocal die resistance, m^3 .
 m = Number of thread starts.
 M = Monomer.
 M_i = Growing radical of chain length i .
 M_n = Number average molecular weight, kg/mol .
 M_w = Weight average molecular weight, kg/mol .
 N = Screw rotation rate, s^{-1} .
 P_{die} = Die pressure, Pa.
 P_i = Polymer of chain length i .
 Q = Throughput, m^3/s .
 Q_l = Leakage flows, m^3/s .
 Q_{th} = Theoretical throughput, m^3/s .
 r_1, r_2 = Reactivity ratios.
 R = Initiator radical.
 v_p = Polymerization rate, $\text{mol}/\text{m}^3 \text{ s}$.
 v_y = Velocity in the y -direction, m/s .
 V_c = Volume of a C-shaped chamber, m^3 .
 η = Viscosity, Pa s.

- η_s = Apparent viscosity, Pa s.
 $\dot{\gamma}$ = Shear rate, $1/\text{s}$.
 τ_{xy} = Shear stress, Pa.
 $[]$ = Concentration, mol/m^3 .

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