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The Self-Wiping Co-Rotating Twin-Screw Extruder as a Polymerization Reactor for Methacrylates

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The self-wiping co-rotating twin-screw extruder was studied as a reactor for two polymerizations in bulk: the homopolymerization of n-butylmethacrylate and the copolymerization of n-butylmethacrylate with 2-hydroxypropylmethacrylate. The influence of the extrusion parameters on the product was analyzed. With both reactions, conversions up to 95% were obtained. Nevertheless, a significant difference was observed in the working domain of both polymerizations, in which a stable reactive extrusion process could be attained wherein the discharge rate is constant and equals the feed rate. In the case of the relatively fast copolymerization, both the throughput and the screw rotation rate could be raised without endangering the stability of the process. This was not the case for the homopolymerization studied. It was determined that the stability of the process depends on the reaction velocity and the product viscosity. Within the boundaries of the working domain, the molecular weight could be influenced by adjustments of the extrusion parameters.

INTRODUCTION

Traditionally, extruders are used to melt, homogenize, pump, and shape polymers into finished plastic products. Nowadays, the use of extruders as continuous flow reactors for polymer modification and even polymer synthesis is growing rapidly. When the reactive extrusion process is compared with the conventional polymerization processes, like the batch process, several advantages can be distinguished. Many conventional polymerization processes require the use of a large amount of solvent in order to decrease the viscosity of the reacting mixture and therewith improve the mixing and heat transfer. In a reactive extrusion process, however, the rotation of the extruder screws ensures mixing and heat transfer even at high viscosities, making the use of solvents for certain polymerizations unnecessary. The synthesis or modification of these polymers may therefore take place simultaneously with the finishing of the product.

In recent years, various investigations were reported in which reactions were performed successfully in twin-screw extruders (1, 2). Most processes concerning the bulk polymerization of (meth)acrylates and similar monomers in extruders were patented.

Stuber (3) and Ganzeveld (4), however, reported respectively, on the homopolymerization of methylmethacrylate (MMA) and of n-butylmethacrylate (BMA) in a closely intermeshing counter-rotating twin-screw extruder. In the same type of extruder the copolymerization of BMA with 2-hydroxypropylmethacrylate (HPMA) was studied (5). On the other hand, not much has been published about the self-wiping co-rotating twin-screw extruder as a reactor. Wielgolinski (6) reported on the self-wiping extruder as a possible reactor for several continuous polymerization processes on a laboratory-development scale, but no results of the different processes are given.

In this paper, the reactive extrusion process in a self-wiping co-rotating twin-screw extruder is examined, for both the homopolymerization of BMA and the copolymerization of BMA with HPMA, which polymerizations differ mainly in reaction velocity and product viscosity. It is determined if instabilities occur in the reactive extrusion process. These instabilities appear as fluctuations in the discharge rate with time while the feed rate is maintained constant. The aim of this study is to get a grasp on the process and investigate the influence of the different process parameters on the product quality.

THE SELF-WIPING EXTRUDER

In the self-wiping fully wiped twin-screw extruder, which was used in this work, one screw wipes its mate, and vice versa (Fig. 1). Except for small clearances between screws and barrel, this wiping action eliminates dead spots where polymer can collect and degrade, making this type of extruder extremely suitable for handling polymers. Because of the requirement that one screw wipe the other, the screw cross section has a unique shape for a given diameter, centerline distance, and number of tips (parallel channels). Booy (7) derived the mathematical expressions from which the geometry of fully wiped co-rotating twin-screw extruders can be calculated. Unlike the counter-rotating twin-screw extruder used in previous studies (3–5), the flight width of the fully wiped screws is small compared to the channel width. The self-wiping extruder can therefore be described as a number of parallel open channels in which material is transported towards the die, by means of drag flow. This transport mechanism strongly depends on the viscosity of the material within the extruder. When a bulk polymerization is performed in an extruder, like the polymerization of methacrylates, the viscosity of

the reacting material strongly increases during the process, roughly ranging from 1 mPa·s at the extruder inlet to 1000 Pa·s in the die. The efficiency of the drag flow mechanism may therefore vary over the length of the extruder, through which instabilities can occur that manifest themselves as variations in output with time.

If a liquid feed like a monomer or a prepolymer is fed to the extruder, two zones can be distinguished in the extruder (Fig. 2):

- a partially filled zone, in which the channels are not yet completely filled with material;
- the pump zone or fully filled zone, where pressure is built up to equal the die pressure.

In the partially filled zone there is no axial pressure gradient. In this zone the monomer or prepolymer is heated to the temperature at which polymerization starts. The starting point of the reaction is therefore determined by the temperature of the barrel, the throughput, and the screw rotation rate. Dependent on the actual value of these parameters, the reaction could start in the partially filled or in the fully filled zone.

The maximum drag flow in the partially filled zone equals (8, 9):

$$Q_d = (2m - 1) \frac{\pi DWH}{2} F_d N \cos \phi \quad (1)$$

where m is the number of thread starts, D the screw diameter, W the channel width, H the channel depth, F_d the shape factor for drag flow, ϕ the pitch angle and N the screw rotation rate. Because of the partial filling, the real throughput is always smaller than Q_d :

$$Q = fQ_d \quad (2)$$

where f is the degree of fill (10).

Fig. 1. Fully wiped screws.

Fig. 2. Schematic representation of an extruder.

In the pump zone, pressure is generated as a result of the resistance of the die:

$$Q = \frac{1}{k} \frac{P}{\eta} \quad (3)$$

where k is the die resistance, P the die pressure, and η the viscosity. This pressure causes a flow in the negative direction (8, 9):

$$Q_p = (2m - 1) \frac{WH^3}{12\eta} \left(-\frac{dp}{dz} \right) F_p \quad (4)$$

where dp/dz is the pressure gradient in the channel direction and F_p the shape factor for pressure flow. The real throughput in this zone equals the sum of the maximum drag flow and the pressure flow:

$$Q = Q_d + Q_p \quad (5)$$

By substituting Eqs 1 and 4 in Eq 5, Q can be written as:

$$Q = (2m - 1) \frac{\pi DWH}{2} F_d N \cos \phi + (2m - 1) \frac{WH^3}{12\eta} \left(-\frac{dp}{dz} \right) F_p \quad (6)$$

For a given extruder geometry and an isoviscous fluid, the amounts of drag and pressure flow are therefore determined by the screw rotation rate and the real throughput.

In a reactive extrusion process, there are five parameters that can be adjusted externally, namely the screw rotation rate, the throughput, the temperature of the extruder barrel, the die resistance and the initiator concentration. By adjusting these parameters, other process aspects, like the average residence time, can be influenced. For the closely intermeshing counter-rotating twin-screw extruder, a steady-state reactive extrusion interaction diagram was presented by Ganzeveld (4). From this diagram the influence of the adjustable parameters on other reactive extrusion features can be elicited. After slight modification, the diagram (Fig. 3) can be used for the analysis of the machine performance and the general tendencies of the reaction process for bulk polymerizations in a self-wiping extruder as well.

THE POLYMERIZATION KINETICS

Both the bulk polymerization of n-butylmethacrylate and the bulk copolymerization of n-butylmethacrylate with 2-hydroxypropylmethacrylate proceed according to a free radical addition mechanism. This implies that the polymer chains are formed in a short time, after which they are excluded from further reaction. Every single polymer chain is initiated and terminated at different points in time, which means that every chain has its own reaction time.

Fig. 3. Reactive extrusion interaction diagram: + positive influence; - negative influence.

The kinetic scheme for polymerization is:

where k_d , k_i , k_p , k_{tc} and k_{td} are the rate constants for each step.

In a copolymerization, there are two monomers A and B involved in the reaction instead of one monomer M, which implies that the propagation step consists of four different reactions.

When a (co)polymerization is performed in bulk, as in a reactive extrusion process, the viscosity of the polymer/monomer mixture strongly increases. The polymer chain radicals, which have to bring about the termination into dead polymer molecules, cannot diffuse easily through the highly viscous medium, so the termination rate decreases. The propagation rate, however, does not decrease until very high conversions if the polymerization is carried out above the glass transition temperature (11, 12), resulting in an overall enhancement of the polymerization rate. This phenomenon is known as the Trommsdorff effect or

gel effect (13). It leads to a higher molecular weight and higher conversion of the reaction than would be expected from conventional kinetics.

When the homopolymerization of BMA is compared with the copolymerization of BMA and HPMA (5), the most important differences are the time that is needed to attain a certain required degree of conversion and the intensity of the gel effect. The copolymerization proceeds faster and manifests a bigger gel effect, owing to the higher viscosity of the polymer formed.

THE POLYMERIZATION OF METHACRYLATES IN AN EXTRUDER

In earlier studies (4, 5) the polymerization of methacrylates in a closely intermeshing counter-rotating twin-screw extruder was investigated. It was shown that conversions up to 95% could be obtained without using additional initiator side feed or stripping sections. Owing to the displacement pump mechanism of this type of extruder, which is relatively insensitive to viscosity changes, no instabilities were encountered in the process.

However, this does not mean that the reactive extrusion process in a self-wiping extruder always proceeds in a stable manner. Because of the transport mechanism by drag, the extrusion process may be influenced by the strong viscosity increase during polymerization. Therefore, the homopolymerization of BMA and the copolymerization of BMA with HPMA were studied in a self-wiping co-rotating twin-screw extruder. Because both reactions have the same polymerization mechanism, the only differences are the reaction velocity and the viscosity of the polymer formed.

For the polymerization of BMA, the influence of the rotation rate of the screws and the throughput on the product was investigated. The copolymerization of BMA with HPMA was studied more thoroughly: the screw rotation rate, the throughput, the temperature, and the die resistance were varied, the latter influencing the length of the fully filled zone and thereby the average residence time in the extruder.

Experimental Setup

For the experiments concerning the homopolymerization of BMA in the extruder, the inhibited monomer was mixed with a combination of two peroxide initiators with half-life times of 1 min at temperatures of 126°C and 173°C and concentrations of 0.054 and 0.016 mol/l, respectively. A combination of initiators was used to prevent a deficiency of radicals towards the end of the reactive extrusion process, where the temperature has increased significantly.

The same amount and type of initiator was used for the copolymerization of BMA with HPMA. The initiators were added to a mixture of BMA and HPMA (both inhibited), which had a monomer feed ratio of 50.3 mol% BMA to 49.7 mol% HPMA. This ratio causes an azeotropic copolymerization, which implies that the incorporation ratio of the monomers in the copolymer equals the monomer feed ratio at all times (14).

For both the homopolymerization and the copolymerization the mixture of monomer and initiators was fed to the extruder at room temperature. The reactive extrusion was performed in an APV Baker MPF50 fully wiped co-rotating twin-screw extruder with a screw diameter of 50 mm. The maximum screw length is 25 D (125 cm). In all experiments, however, the utilized length was limited to 14 D by insertion of a seal in the extruder. The extruder has nine heating zones that can be used to create a temperature profile over the extruder. Because of the reduced utilized length, only five heating zones were used.

When the homopolymerization of BMA was performed in the extruder, the barrel wall was kept at a uniform temperature of 130°C in the last four zones. The first zone, closest to the feed port, was kept at a temperature of 120°C. The amount of monomer/initiator mixture fed to the extruder ranged from 1.5 to 4.5 kg/h.

In the case of the copolymerization of BMA with HPMA, the output of the extruder was varied in a wider range, that is, between 1.5 and 8.6 kg/h. Again, the last four zones were maintained at a uniform temperature. In this case, however, the overall barrel temperature ranged from 110°C to 145°C. The first zone was kept at a temperature of 110°C or 120°C. The barrel temperatures used were based on experimental data from the counter-rotating extruder used in Refs. 4 and 5. Two kinds of die outlet were used. In one die, the size of the outlet could be changed, thereby changing the die resistance; the other one had a fixed outlet size. The pressure in the die was measured with a pressure transducer. This pressure varied between 0 and 1.3×10^6 Pa.

After every adjustment of the extrusion parameters, samples were collected when the extruder had reached steady state. In order to stop the reaction immediately, the samples were directly frozen in liquid nitrogen at the outlet of the extruder.

Analysis

The conversion of the polymerization reaction was determined gravimetrically. About 1.5 g of the polymer/monomer mixture was weighed precisely and dissolved in acetone. A small amount of hydroquinone was added to this solution to prevent further polymerization on heating. The solution was poured into a petri dish. Acetone and monomer were evaporated in a vacuum stove at 150°C and 3×10^4 Pa for about 60 min. By weighing the remaining polymer the conversion can be calculated:

$$\text{conversion} = \frac{\text{weight of polymer}}{\text{weight of mixture}} \times 100\%$$

The disadvantage of this method is that monomer could be prevented from evaporation by the formation of a polymer film. Therefore, the film was kept very thin, and reproducibility experiments were performed. These experiments showed a variance in conversion of 1%.

The average molecular weight of the reactive extrusion product was determined by gel permeation chromatography using chloroform as a solvent and polystyrene as a standard. The Mark-Houwink constants for poly-BMA at 25°C are $K = 4.37 \cdot 10^{-5}$ dl/g and $a = 0.80$ (15). For poly-HPMA these values are unknown, so it was assumed that they are the same as for poly-BMA. If this assumption is valid, the deviation in molecular weights obtained was about 500 g/mol. However, should the possibly inaccurate Mark-Houwink constants for poly-HPMA cause the absolute values of the molecular weight to be somewhat different from the values found, the trends observed would still be the same.

RESULTS AND DISCUSSION

For a clear apprehension of the reactive extrusion process in a self-wiping extruder, the influence of the extrusion parameters on the product was analyzed. The adjustment of each parameter determines the average residence time, the mixing, and the temperature of the material within the extruder and how it affects the quality of the product. The results obtained were compared with the reactive extrusion interaction-diagram, thus providing insight into the extrusion process.

The Polymerization of BMA in the Extruder

At three values of the throughput, namely 25, 50, and 75 g/min (respectively, 1.5, 3, and 4.5 kg/h), the rotation rate of the screws was varied between 0.16 and 7.2 1/s. The results of these experiments are shown in Fig. 4. At the lowest value of the throughput, the influence of the screw rotation rate on the conversion seems to be negligible. With increasing throughput, though, the conversion decreases drastically when the rotation rate is increased.

From theoretical relationships (Eq 6), an increase in screw rotation rate causes a shortening of the fully filled zone and hence a decrease in average residence time. As a result, a decrease in conversion is ex-

pected. The results of the experiments at the two higher throughputs correspond to this. When the screw rotation rate is increased at a throughput of 75 g/min, the conversion decreases in such a way that at screw rotation rates higher than 5.4 1/s the product leaves the die as a mixture of scarcely converted monomer and vapor. Obviously, the average residence time in the extruder is too short for the reaction to take place. This is not the case at a throughput of 25 g/min, where the slight variation in conversion falls between the limits of accuracy. It appears that at such a low throughput, the average residence time is long enough to ensure a high degree of conversion at every value of the screw rotation rate.

According to theory, increasing the throughput causes a direct reduction in average residence time on the one hand, but an increase in die pressure (Eq 3) and lengthening of the fully filled zone on the other hand. As a result, the average residence time and therewith the conversion of the reaction should hardly be influenced by a change in throughput. In practice, however, the throughput does influence the average residence time. Rauwendaal (16), for example, found the average residence time to be inversely proportional to the throughput for a counter-rotating extruder. Indeed, a dramatic decrease in conversion is observed on increasing the throughput, especially at high values of the screw rotation rate. Clearly the average residence time does depend on the throughput, in spite of theoretical expectations; otherwise, the conversion would have remained constant.

During all experiments, the stability of the process was checked by measuring the throughput leaving the die at regular intervals and comparing it with the amount of material fed to the extruder. This way it could be determined whether the reactive extrusion process reached a stable situation for every adjustment of throughput and screw rotation rate or not.

At a throughput of 25 g/min, no instability problems occurred. At higher throughputs, however, the screw rotation rate could not be raised indefinitely. A screw rotation rate of 5.4 1/s (throughput 50 g/min) involved small fluctuations in output, and increasing the rotation rate even further caused an unstable process. At a throughput of 75 g/min, this was already the case for a rotation rate of 5.4 1/s. Although the output of the extruder seemingly reached a steady state 15 min after the adjustment of the rotation rate, the actual value of 75 g/min was not reached: The output measured did not exceed 60 g/min, indicating that the rotating screws did not succeed in transporting the reacting mixture sufficiently.

Looking at Fig. 4 again, the above observations can be properly accounted for. At high values of the screw rotation rate and the throughput, the average residence time of the material within the extruder is short. Therefore the conversion of the reaction is low, as has already been concluded, implying a low viscosity of the material. This implies that the die pressure will be too low to bring on back flow, and as a result there will be no fully filled zone, reducing the average

Fig. 4. Influence of screw rotation rate on BMA-conversion at $T = 130^\circ\text{C}$ and three different throughputs: ■ 25 g/min; ♦ 50 g/min; ▲ 75 g/min.

residence time even more. Because there is no fully filled zone, there is no material blocking the die and preventing vaporized monomer from leaving the extruder at the die outlet; this was indeed observed. At certain values of throughput and rotation rate, the average residence time and thus also the viscosity will be so low as to deteriorate the pump mechanism considerably, because the drag flow is strongly dependent on the viscosity of the material. This implies that the discharge rate is lower than the feed rate. Because the feed rate remains constant, the hold-up in the extruder increases and thereby the average residence time in the extruder increases, which allows the material to react and the viscosity to build up. At a certain degree of viscosity, the material can be dragged towards the die again and pushed out of the extruder in a short time, so the throughput increases temporarily. After that, the discharge rate decreases again.

The foregoing implies that any combinations of throughput and screw rotation rate cannot be chosen freely. At a fixed screw rotation rate, the maximum feasible throughput is determined by whether the process is stable or not. And vice versa, when the throughput is fixed, the screw rotation rate is limited. This relationship between throughput and screw rotation rate suggests that a working domain exists in which a stable reactive extrusion process can be created. The limits of the domain are determined by the residence time needed to realize a required degree of conversion on the one hand and by the pump capacity of the screws on the other hand: At low screw rotation rates only a limited amount of material can be transported. Figure 5 illustrates this. The solid line is determined by the pump capacity and therefore by the screw geometry: For a certain extruder this line is fixed. The dashed line, however, is determined by the minimum residence time needed and therefore mainly by the reaction kinetics and the viscosity of the material, which both are influenced by the barrel temperature (3, 5). The shape and the position of this line vary for different reactions in the same extruder.

When the present results are compared with earlier studies in a closely intermeshing counter-rotating extruder (4, 5), the latter shows a more stable behav-

Fig. 5. Working domain of a reactive extrusion process.

ior. This can be attributed to the fact that the screw of an intermeshing extruder can be described as series of C-shaped chambers. Material is "locked" in these chambers and is transported towards the die by positive displacement, not by drag. This is a more stable transport mechanism, which implies that the reaction velocity and product viscosity in a reactive extrusion process in this type of extruder can be lower than in a self-wiping extruder before instabilities occur.

The Copolymerization of BMA with HPMA in the Extruder

The experiments concerning the homopolymerization of BMA in the self-wiping extruder showed that only a small working domain exists in which a stable process can be obtained for this reaction. A more thorough study of the influence of reaction and extrusion parameters on the product quality and on the process should therefore be carried out using a different polymerization. Because it was assumed that instabilities in the process occur because of a low reaction velocity and low viscosity of the polymer/monomer mixture during reaction, the new reaction should be faster, and the resulting product should have a higher viscosity. The copolymerization of BMA with HPMA, which was studied before (5), meets these requirements. With this reaction, the influences of screw rotation rate, throughput, barrel temperature and die resistance were studied.

Screw Rotation Rate

The influence of screw rotation rate on the product was studied with both a constant die resistance (i.e. die size) and a constant die pressure. The barrel temperature was kept at 140°C.

For iso-viscous fluids at constant throughput, the screw rotation rate merely influences the pressure gradient, not the die pressure. However, increasing the rotation rate in the reactive extrusion process turns out to lower the die pressure from 10^6 to 3×10^5 Pa, if the die resistance is constant (Fig. 6).

Fig. 6. Die pressure and product temperature as a function of screw rotation rate; BMA/HPMA copolymerization at $T = 140^\circ\text{C}$ and $Q = 75$ g/min.

This can be caused only by a decrease in the viscosity of the material in the last zone of the extruder.

There are three factors that can bring about this effect: shear rate, temperature, and molecular weight. As can be seen in Fig. 7, the molecular weight increases, so this would bring about the contrary effect, an increase in die pressure. The shear rate does increase when the rotation rate is raised, and this will induce a viscosity drop of the material in the extruder. But this does not imply that the viscosity of the material in the die decreases along with this. The main cause for the viscosity drop should therefore be sought in the temperature increase of the product from 142°C to 158°C (Fig. 6).

Although it may seem contradictory, this last factor is the key to the increase in molecular weight. Figure 8 shows a qualitative illustration of the temperature of the material over the length of the extruder. In the first zone, the monomer/initiator mixture is heated to the temperature at which polymerization starts. As soon as the reaction starts, heat will be produced, causing the temperature of the material to rise above the barrel temperature. When the polymerization is almost completed, the material will be cooled by the extruder barrel.

As the screw rotation rate increases, the forward drag flow also increases. In the partially filled zone,

Fig. 9. Influence of screw rotation rate on conversion; BMA / HPMA copolymerization at $T = 140^{\circ}\text{C}$ and $Q = 75 \text{ g/min}$.

the material will be transported faster towards the die, decreasing the temperature gradient over the length of the extruder in that zone; in the fully filled zone, a high screw rotation rate causes a good mixing in the axial direction (Eq 6), so in this zone the overall temperature could be lower. In short, the mean temperature of the material in the extruder will be lower with an increase in the screw rotation rate, although the temperature of the product is higher as a result of the shift of the cooling zone. The reaction velocity will be lower and the average residence time shorter, causing a decrease in conversion (Fig. 9).

If the die pressure is kept constant at 10^6 Pa , the molecular weight is not influenced by the screw rotation rate (Fig. 10) and is equal to the molecular weight at low rate in Fig. 7. When the die pressure is kept constant, no big changes in filled length and temperature occur, so the molecular weight will indeed be the same over the whole range of screw rotation rates. In Fig. 7 the die pressure at low screw rotation rate had a value of 10^6 Pa , which is in accordance with the observations in Fig. 10.

Fig. 7. Influence of screw rotation rate on weight average molecular weight and polydispersity; BMA / HPMA copolymerization at $T = 140^{\circ}\text{C}$ and $Q = 75 \text{ g/min}$.

Fig. 8. Temperature of a reacting mixture over the length of the extruder; — low screw rotation rate; ---- high screw rotation rate.

Fig. 10. Influence of screw rotation rate on weight average molecular weight; BMA / HPMA copolymerization at $T = 140^{\circ}\text{C}$, $P = 10^6 \text{ Pa}$; ■ $Q = 50 \text{ g/min}$; ▲ $Q = 75 \text{ g/min}$.

Fig. 11. Influence of throughput on conversion; BMA/HPMA copolymerization at $N = 3.6$ 1/s and $T = 120^\circ\text{C}$.

Fig. 12. Influence of throughput on weight average molecular weight and polydispersity; BMA/HPMA copolymerization at $N = 3.6$ 1/s and $T = 120^\circ\text{C}$.

Throughput

The influence of the throughput on conversion and molecular weight was studied in two different situations.

In the first situation, the temperature of the barrel was 120°C and the screw rotation rate was 3.6 1/s. The size of the die outlet was kept constant. The results of this series of experiments are shown in Figs. 11 and 12.

According to Eq 3, an increase in die pressure is expected when the throughput is increased. However, the pressure falls from 7×10^5 to 4×10^5 Pa in the measured range of the throughput. Obviously, this can only be caused by a decrease of the viscosity of the product leaving the die. As can be seen from Fig. 12, the weight average molecular weight of the product decreases drastically, so the viscosity decreases accordingly. This can be explained as follows. When the throughput is increased, the amount of heat produced by the reaction in the extruder will also in-

crease. Because the heat transfer to the barrel per unit mass of product decreases, the temperature of the reacting material will be higher, resulting in an enhancement of the initiator decomposition and a decrease in molecular weight. This decrease is intensified by the fact that the gel effect, which increases the molecular weight, becomes less important as the viscosity diminishes. In Fig. 11 it can be seen that the conversion diminishes slightly, from 92.5% to 88.7%. Like the decrease in molecular weight, this could be caused by a lessening of the gel effect and a shorter average residence time.

In the second situation, the die pressure was kept constant at 10^6 Pa by adjusting the die resistance; the barrel temperature was kept at 140°C to ensure a high reaction velocity, and the screw rotation rate was set at 5.4 1/s. The influence of the throughput on the conversion seems to be almost negligible (Fig. 13), while in this series of experiments the molecular weight is increased from about 25,000 to 30,000 in the measured throughput range. The polydispersity has a constant value of 2.3.

The high value of the screw rotation rate improves the heat transfer with respect to the first series (17). This means that at low values of the throughput the material fed to the extruder reaches a high (reaction) temperature very quickly, especially at the high barrel temperature used in this series. The initiator will therefore decompose instantly, causing the molecular weight to be low. Increasing the throughput implies that the heating of the material takes place in a more gradual way, so there is more time for the mixture to react at a temperature that is lower than the barrel temperature; this accounts for the rise in molecular weight.

The same chain of reasoning justifies the almost constant conversion. The more gradual heating of the material at higher throughputs implies that the biggest part of the reaction takes place further on in the extruder. The temperature of the material at the end of the extruder will therefore be higher and the viscosity lower. Because the die pressure was kept constant at 10^6 Pa, this results in a lengthening of the fully filled zone (Eq. 6) and therefore an increase in the average residence time. As a consequence the conversion hardly decreases.

Again the trends in both series seem to be contradictory, yet the results are reconcilable. In the second series, the barrel temperature and the screw rotation rate are high, ensuring a high material temperature and thereby a low molecular weight by means of heat transfer. In the first series, however, a high material temperature can be reached only through heat production of the reaction.

Die Resistance

Besides the influence of screw rotation rate and throughput, which both affect the length of the fully filled zone, the direct influence of the length of the fully filled zone was studied by varying the die resis-

Fig. 13. Influence of throughput on conversion and weight average molecular weight; BMA/HPMA copolymerization at $N = 5.4$ 1/s, $T = 140^\circ\text{C}$ and $P = 10^6$ Pa.

tance. Screw rotation rate, throughput and temperature, were kept at 3.5 1/s, 75 g/min, and 140°C , respectively.

Figure 14 shows the results of this series of experiments as a function of die pressure. The conversion remains almost constant, varying only between 91.1% and 92.1%. This implies that even with a short fully filled zone the average residence time is long enough to ensure a high conversion. When the die pressure increases, the molecular weight seems to decrease slightly. This is in agreement with the interpretation of the influence of the screw rotation rate (see also Fig. 8). Because the amount of material having a high temperature will be larger on increasing the fully filled length, the overall temperature of the material in the extruder will be slightly higher. With that the molecular weight decreases.

Temperature

In order to validate the explanations given above, the last parameter studied was the temperature of

the barrel. This was done in two different situations: In the first situation the throughput was set at 50 g/min, the screw rotation rate at 3.6 1/s and the die resistance was kept constant, while in the second situation the throughput was 75 g/min and the die pressure was kept at a constant value of 10^6 Pa. The influence of the temperature on the molecular weight was analyzed. The results are shown in Fig. 15.

In both situations the molecular weight decreases when the temperature is increased. However, at a throughput of 50 g/min, the value of the molecular weight at low temperature is much higher than at 75 g/min, and the decrease with a rise in the temperature is more intense. When comparing this with the results obtained by varying the throughput, the explanations used before seem to be correct. At a low value of the throughput, the amount of heat produced by the reaction is small, so the heating of the material is mainly achieved through the barrel; this results in a high molecular weight at low temperature and a low molecular weight at high temperature. Increasing the throughput, however, causes an increase in heat production at the same time, so the temperature of the material will not be fixed by the barrel temperature alone. This implies that the temperature of the material will be higher than the barrel temperature so that the influence of the barrel temperature will be smaller, resulting in only a small decrease in molecular weight.

SUMMARY AND CONCLUSIONS

The results obtained in this study show that the self-wiping co-rotating twin-screw extruder can be used as a polymerization reactor for methacrylates. It should be noted, however, that for machines with much higher diameter than the one studied, removal of the heat generated by the reaction could be a serious problem (18).

Fig. 14. Influence of die pressure on conversion and weight average molecular weight; BMA/HPMA copolymerization at $N = 3.6$ 1/s, $T = 140^\circ\text{C}$ and $Q = 75$ g/min.

Fig. 15. Influence of temperature on weight average molecular weight; BMA/HPMA copolymerization; $\blacksquare$ $N = 3.6$ 1/s and $Q = 50$ g/min; $\blacktriangle$ $N = 3.6$ 1/s, $Q = 75$ g/min and $P = 10^6$ Pa.

Two polymerizations, namely the homopolymerization of BMA and the copolymerization of BMA with HPMA, which differed only in reaction velocity and product viscosity, were carried out in the extruder. Conversions up to 95% were obtained with both reactions, while the molecular weight could be adjusted by varying extrusion parameters like screw rotation rate, throughput, die resistance, and barrel temperature.

However, because of the pump mechanism of the extruder studied, instabilities, consisting of a variable discharge rate in the reactive extrusion process, can occur. This implies that for every single polymerization, the working domain in which a stable extrusion process can be attained is limited. The boundaries of this domain are fixed by a maximum in both throughput and screw rotation rate, depending on the viscosity of the product and the reaction velocity. The polymerization time needed to attain a certain required degree of conversion should not exceed the residence time of the material in the extruder. Moreover, the viscosity of the reacting mixture should be high enough to ensure a stable drag mechanism.

Because the reactive extrusion process and as a result the product quality is strongly dependent on the adjustment of the extrusion parameters, an investigation was carried out to determine the influence of these parameters on the conversion and the molecular weight of the product. The following results were obtained.

Polymerization of BMA:

- The conversion is hardly influenced by the screw rotation rate at low values of the throughput and at low values of the screw rotation rate it is scarcely influenced by the throughput. However, if one of them is increased while the other has a high value, the conversion decreases dramatically, eventually leading to instabilities in the process.

Copolymerization of BMA with HPMA:

- An increase in screw rotation rate causes a small decrease in conversion. This is the result of an overall lowering of the material temperature in the extruder, which causes a lower reaction velocity.
- When the die resistance is kept constant, the weight average molecular weight increases as a function of screw rotation rate, resulting from the decrease in material temperature. When the die pressure is kept constant, the molecular weight remains constant on increasing the screw rotation rate.
- Both the influence of the throughput and of the barrel temperature are based on the same principle. If the temperature of the barrel is low, the course of the polymerization within the extruder is mainly determined by the production of polymerization heat. This implies that at low values of throughput, the temperature of the material in the extruder is lower and the molecular weight higher

than at high throughput values. If the temperature of the barrel is high and the heat transfer is good, that is, at high values of screw rotation rate, then the effect of the heat of reaction is of less importance to the material temperature than the heating through the barrel.

- The die resistance has only a small effect on both conversion and molecular weight.

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NOMENCLATURE

a	Mark-Houwink constant.
D	Diameter (m).
F_d	Shape factor for drag flow.
F_p	Shape factor for pressure flow.
f	Degree of fill.
H	Channel depth (m).
I	Initiator.
K	Mark-Houwink constant (dl/g).
k	Die resistance (m^{-3}).
k_d	Initiator decomposition rate constant (1/s).
k_i	Initiation rate constant ($\text{m}^3/\text{mol} \cdot \text{s}$).
k_p	Propagation rate constant ($\text{m}^3/\text{mol} \cdot \text{s}$).
k_{tc}	Termination by combination rate constant ($\text{m}^3/\text{mol} \cdot \text{s}$).
k_{td}	Termination by disproportionation rate constant ($\text{m}^3/\text{mol} \cdot \text{s}$).
M	Monomer.
M_i	Growing radical of chain length i .
m	Number of thread starts.
N	Screw rotation rate (1/s).
P	Die pressure (Pa).
p	Pressure (Pa).
Q	Throughput (m^3/s).
Q_d	Drag flow rate (m^3/s).
Q_p	Pressure flow rate (m^3/s).
$R \cdot$	Initiator radical.
T	Temperature ($^{\circ}\text{C}$).
W	Channel width (m).
z	Coordinate in channel direction (m).
η	viscosity (Pa $\cdot$ s).
ϕ	pitch angle (rad).

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