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The Copolymerization of Methacrylates in a Counter-Rotating Twin-Screw Extruder

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The copolymerization of n-butylmethacrylate with 2-hydroxypropylmethacrylate was studied in a closely intermeshing counterrotating twin-screw extruder. The average molecular weight of the product can be increased by increasing the screw rotation rate or the die resistance or by decreasing the throughput or the barrel temperature. The conversion can be improved by decreasing the throughput, increasing the die resistance, and (within limits) increasing the barrel temperature, as well as through post-initiation. Compared with various classical polymerization processes, this situation requires that particular attention be paid to the occurrence of a gel effect, the existence of a thermodynamic ceiling temperature, and the reactivity ratio of the monomers used.

INTRODUCTION

Traditionally, the extruder was primarily used as a plasticating apparatus and in food technology. Recently there has been growing interest in the use of the extruder as a reactor for synthesizing or modifying polymers. The main advantage of the extruder as a polymerization reactor with regard to the conventional polymerization reactors is the ability of the extruder to work without solvents. In order to achieve good mixing and heat transfer in conventional reactors, the increasing viscosity during the polymerization reaction necessitates the use of solvents. In extruders however, the mechanical action of the screws provides mixing and heat transfer even at high viscosities.

In recent years, various investigations have been reported in which reactions were performed successfully in twin-screw extruders (1-3), indicating that reactive extrusion is a rapidly developing field. However, most of these processes concerned homopolymerizations from monomers or prepolymers or modification and grafting reactions. In the present paper, the bulk copolymerization of n-butylmethacrylate with 2-hydroxypropylmethacrylate in a closely intermeshing counterrotating twin-screw extruder is examined.

THE COUNTERROTATING TWIN-SCREW EXTRUDER

The counterrotating twin-screw extruder used in this work 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 (Fig. 1), in

which material is transported towards the die. The maximum volumetric displacement rate or theoretical throughput Q_{th} equals the number of C-shaped chambers transported per unit time multiplied by the chamber volume:

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

where m is the number of thread starts, N is the screw rotation rate, and V_c is the volume of a chamber.

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

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

in which Q_l is the sum of all leakage flows over a cross section of the extruder. Four kinds of leakage gaps can be distinguished (Fig. 2) (4):

- The flight gap is a clearance between the barrel and the flight of the screws.
- The tetrahedron gap originates from a gap between the flight walls. It has approximately the shape of a tetrahedron. This is the only gap that connects chambers on the opposite screws.
- The calender gap is formed by the clearance between the flight of one screw and the bottom of the channel of the other screw, and resembles a calender;
- The side gap is a clearance between the flight walls of the screws, perpendicular to the plane through the screw axes.

Fig. 1. C-shaped chamber.

The leakage flows are driven by inter-chamber pressure differences ΔP_c and conveying of the moving surfaces:

$$Q_l = AN + B \frac{\Delta P_c}{\eta} \quad (3)$$

where A and B are geometrical constants and η is the viscosity.

If a liquid feed, such as a monomer or a prepolymer, is fed to the extruder, two zones can be distinguished in the extruder (Fig. 3):

- a partially filled zone, where the chambers are not yet completely filled with material;

Fig. 2. Leakage gaps in a closely intermeshing counterrotating twin-screw extruder.

- the pump zone or fully filled zone, where pressure is built up to equal the die pressure and where the chambers are fully filled.

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. Depending upon the actual value of these parameters, the reaction could start in the partially filled or in the fully filled zone.

When a polymerization is performed in an extruder, there are five externally adjustable parameters that can influence the reactive extrusion process. These parameters are the screw rotation rate, the throughput, the barrel temperature, the die resistance, and the initiator radical concentration. A reactive extrusion interaction diagram has been presented by Ganzeveld and Janssen (5), from which the influence of the adjustable parameters on other reactive extrusion features can be derived (Fig. 4). Although this

Fig. 3. Schematic representation of the extruder.

diagram has originally been derived for homopolymerizations, it is also helpful for analyzing the machine performance and the general tendencies of the reaction process for copolymerizations in extruders.

THE REACTION KINETICS

The bulk copolymerization of n-butylmethacrylate (BMA) with 2-hydroxypropylmethacrylate (HPMA), which was carried out in an extruder to investigate the reactive extrusion process, is a free radical addition polymerization. This implies that the polymer chains are formed in a very 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.

The kinetic scheme for polymerization is:

decomposition initiator:

initiation monomer: $R^{\cdot} + M \xrightarrow{k_i} M_1^{\cdot}$

propagation: $M_i^{\cdot} + M \xrightarrow{k_p} M_{i+1}^{\cdot}$

termination:

where k_d , k_i , k_p , k_{tc} , and k_{td} are the corresponding rate constants in every reaction step.

The theoretical polymerization rate v_p can be derived from this scheme and equals:

$$v_p = k_p \sqrt{\frac{fk_d}{k_t}} [I]^{0.5} [M] \quad (4)$$

where $[I]$ and $[M]$ are the initiator and monomer concentration, respectively.

In a concentrated system, however, (as in the bulk polymerization in an extruder) deviations from this equation occur. This is caused by the strong increase in viscosity during polymerization. The polymer chain radicals cannot diffuse easily through the highly viscous medium, so the termination rate decreases. Because the diffusion of the small monomer molecules is not restricted until very high conversions, if the polymerization is carried out above the glass transition temperature (6, 7), the propagation rate does not decrease, resulting in an increase of the polymerization rate. This phenomenon is known as the Trommsdorff effect or gel effect (8). The gel effect results in a higher molecular weight and higher conversion of the reaction than would be expected from conventional kinetics.

In case of the polymerization of methylmethacrylate (MMA), a number of models describing the diffusion limitation of the chain radicals have been presented in the literature (7, 9, 10), but very often these models contain parameters unknown for the copolymerization of BMA with HPMA or for the individual homopolymerizations. However, Malavasic *et al.* (11) have shown for several acrylates and methacrylates, including MMA and BMA, that the intensity of the gel effect decreases and the conversion at the onset of the gel effect increases with increasing length of the alkyl sidegroup. These effects can be explained by considering the process that leads to the termination reaction between two macroradicals. Among others, Benson *et al.* (12) and Dionisio *et al.* (13) describe the termination reaction as a process involving both translational diffusion of the polymer chains and segmental motion of those chains, leading to chemical reaction. The segmental motion improves with increasing length of the alkyl group as a consequence of the shielding of the carbonyl by the alkyl group, and with that the gel effect diminishes. At the same time, the glass transition temperature T_g of the corresponding polymer decreases because the overall flexibility of the polymer chain influences T_g . For the homopolymers of BMA and HPMA, the values of T_g are 20°C and 76°C, respectively (14). Therefore HPMA is expected to have a larger influence on the gel effect than BMA during the copolymerization.

In case of the copolymerization of two monomers A (i.e. BMA) and B (i.e. HPMA) the propagation step of the polymerization consists of four different reac-

Fig. 4. Reactive extrusion interaction diagram: + positive influence; - negative influence.

tions:

where each reaction has its own propagation rate constant.

If one assumes that the radical concentrations are constant, the well-known copolymerization equation can be derived from the mass balances over every component. This equation reads:

$$\frac{d[A]}{d[B]} = \frac{[A]}{[B]} \frac{r_1[A] + [B]}{r_2[B] + [A]} \quad (5)$$

in which r_1 and r_2 are the reactivity ratios defined as usual:

$$r_1 = k_{11}/k_{12} \quad (6)$$

$$r_2 = k_{22}/k_{21}$$

The values of r_1 and r_2 for the copolymerization of BMA with HPMA can be calculated using the Q - and e -values according to Alfrey and Price (14, 15). If BMA is taken as monomer A, this yields $r_1 = 0.29$ and $r_2 = 0.28$. The ratio $d[A]/d[B]$ signifies the ratio of incorporation of monomers A and B, which is not necessarily equal to the monomer feed ratio. Consequently, one of the monomers is consumed more rapidly than the other, and the composition of the monomer feed varies, leading to a continuous shift of the composition of the copolymer formed. The course of the ratio of incorporation is a function of the monomer feed ratio. For the copolymerization of BMA with HPMA, this is illustrated in Fig. 5, in which:

$$f_a = \frac{[A]}{[A] + [B]}$$

$$F_a = \frac{d[A]}{d[A] + d[B]} \quad (7)$$

As can be seen in the Figure, this particular copolymerization shows an azeotropic point, in which the incorporation sequence of both monomers does equal the monomer composition, so there is no preferential reaction of one of the monomers. This implies that no shift in compositional distribution of the copolymer will occur if the monomer feed ratio is set to this azeotrope. For the copolymerization of BMA with HPMA, this feed ratio should be 50.3 mol% BMA to 49.7 mol% HPMA. Because a deviation of the monomer feed ratio from this azeotrope will intensify itself during the polymerization, weighing the monomers must be carried out with accuracy.

Most studies in the literature on the kinetics of polymerization reactions have been limited to low degrees of conversion and low reaction temperatures.

Fig. 5. Relation between composition F_a of the copolymer formed and the monomer feed f_a .

At high temperatures, however, another complicating factor arises. Dainton and Ivin (16) have established that for certain systems a depropagation step has to be taken into account, leading to an equilibrium of propagation and depropagation:

in which k_{dp} is the depropagation rate constant. This implies that above a certain temperature no net polymerization occurs. This so-called ceiling temperature T_c satisfies the following equation:

$$T_c = \frac{\Delta H_p}{\Delta S_p + R \ln[M]} \quad (9)$$

Thus, the higher the conversion, the lower the monomer concentration and consequently the lower the ceiling temperature.

For pure MMA, the ceiling temperature has a value of 220°C (17), but, for the polymerizations of BMA and HPMA, no data are known concerning the thermodynamic equilibrium. Elias (18), however, states that the standard molar entropy for the polymerization of liquid monomer to condensed amorphous polymer is practically independent of constitution in the case of compounds with olefinic double bonds. Differences in T_c are therefore caused by the polymerization enthalpy alone. The polymerization enthalpy of the homopolymerizations of BMA and HPMA as given in the literature (14) are 57.5 kJ/mol for BMA at a temperature of 74.5°C and 50.5 kJ/mol for HPMA at 25°C. If the influence of temperature is neglected, an enthalpy of 54.0 kJ/mol can be expected for the copolymerization with azeotropic monomer feed ratio.

If this value is compared with the polymerization enthalpy of MMA, which is 55.5 kJ/mol at 74.5°C, it can be concluded that the occurrence of a ceiling temperature under the working conditions used in reactive extrusion is probable.

Up to now, there have been no kinetic investigations concerning the copolymerization of BMA with HPMA at high temperatures and conversions. Because the temperature of the extruder barrel ranges from 115 to 145°C, resulting in an even higher product temperature due to the heat generated by the reaction, and conversions up to 92% have been obtained, additional experiments were necessary to investigate the course of the copolymerization at high temperatures. The polymerization of HPMA and the copolymerization of BMA with HPMA (both inhibited and with a combination of two peroxide initiators with a total initiator concentration of 0.07 mol/l) were studied using isothermal differential scanning calorimetry (DSC) (11, 19) at temperatures of 110, 120, 130, and 140°C. Although this method gives a good picture of the course of the reaction qualitatively, the variance in the conversions obtained is about 5%. To simulate the situation in the extruder, the inhibitor was not removed from the monomer. The results will be compared with the results of measurements with BMA (5).

To be able to interpret the results adequately and to validate the possible occurrence of a ceiling temperature, the polymerization enthalpy of the copolymerization of BMA with HPMA was determined using DSC and compared with the values for the homopolymerizations of BMA and HPMA given in literature.

RESULTS

The polymerization enthalpy of the copolymerization obtained with DSC equals $\Delta H_p = 60.0 \pm 0.5$ kJ/mol. This value shows a significant discrepancy from the expected value of 54.0 kJ/mol. This difference can be explained by the fact that the polymerization enthalpy of HPMA, as reported in the literature, was determined during emulsion polymerization, in which solvent effects can occur.

The results of the isothermal experiments are shown in Figs. 6 to 8. Looking at the conversion-time data at low polymerization temperatures (100 and 110°C), one can see a clear transition from conventional kinetics to the gel effect stage. At higher temperatures, a curved profile can be detected, practically indicating an overall enhancement of the polymerization. This curved profile has also been observed by Dube *et al.* (20) in the polymerization of butylacrylate (BA).

The gel effect gets more pronounced in the sequence BMA, BMA/HPMA, HPMA, and the onset of the gel effect occurs at a lower conversion in this order: 70%, 60% and 35% conversion, respectively. This is due to the higher viscosity of the copolymer and the HPMA polymer with regard to the BMA polymer.

In case of the copolymerization, a deviation from

Fig. 6. Conversion curve of the homopolymerization of *n*-BMA (from Ref. 5): ■ $T = 110^\circ\text{C}$; ♦ $T = 120^\circ\text{C}$; ▲ $T = 130^\circ\text{C}$.

Fig. 7. Conversion curve of the homopolymerization of 2-HPMA: ● $T = 100^\circ\text{C}$; ■ $T = 110^\circ\text{C}$; ♦ $T = 120^\circ\text{C}$; ▲ $T = 130^\circ\text{C}$.

the azeotropic monomer feed ratio would cause a consecutive polymerization of the fast reacting HPMA and the slower BMA. This could result in a similar picture of the reaction course as depicted in Fig. 8. However, in our case, a consecutive polymerization is very unlikely because the slope of the conversion-time plot of the copolymerization at the end of the reaction is much steeper than in the case of the homopolymerization of BMA, whereas at high temperatures (120 and 130°C) no separate reaction regimes can be distinguished. Both observations corroborate the expectation of azeotropic polymerization.

THE COPOLYMERIZATION OF BMA WITH HPMA IN AN EXTRUDER

In order to investigate the influence of the adjustable reaction parameters and extrusion parame-

Fig. 8. Conversion curve of the copolymerization of *n*-BMA with 2-HPMA: ● $T = 100^{\circ}\text{C}$; ■ $T = 110^{\circ}\text{C}$; ♦ $T = 120^{\circ}\text{C}$; ▲ $T = 130^{\circ}\text{C}$.

ters on the product and therewith on the process, the copolymerization of BMA with HPMA was carried out in a closely intermeshing counterrotating twin-screw extruder. The rotation rate of the screws, the throughput, the temperature, and the die resistance were varied, the latter having a distinct influence on the fully filled length and therewith on the average residence time in the extruder.

Experimental Setup

The two monomers BMA and HPMA (both inhibited) were mixed in a ratio of 50.3 mol% BMA and 49.7 mol% HPMA, corresponding to the monomer feed ratio in the azeotropic point. Instead of a single initiator, a combination of two peroxide initiators with different half-life values was added to the monomers to prevent a deficiency of radicals towards the end of the reactive extrusion process, where the temperature has increased significantly. The total initiator concentration was 0.07 mol/l. The mixture of monomers and initiators was continuously flushed with nitrogen to prevent further inhibition of the reaction by oxygen and was fed to the extruder at room temperature.

The reactive extrusion took place in a 40 mm Rollepaal closely intermeshing counterrotating twin-screw extruder ($L/D = 15$). The extruder has five heating zones, which can be used to create a temperature profile over the extruder. The barrel wall of the extruder was kept at a uniform temperature in the last four zones ranging from 115°C to 145°C in the different experiments. The first zone (closest to the feed port) was always kept 10°C below the temperature of the other zones. The output of the extruder ranged from 1.2 to 3.6 kg/h. The die resistance could be varied by changing the size of the die outlet. The pressure profile over the extruder was measured with three pressure transducers. The die pressure varied

between 0.1 and 27.5 bar. Samples were collected when the extruder reached a steady state after every adjustment of the reaction and extrusion parameters. 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 300 mbar. If one weighs the remaining polymer, the conversion can be calculated:

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

The disadvantage to 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 2.5%.

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 $K = 4.37 \cdot 10^{-5} \text{ dl/g}$ and $a = 0.80$ (14). For poly-HPMA these values are unknown, so it was assumed that they are the same as for poly-BMA. The deviation in molecular weights obtained was about 500 g/mol, if the influence of possibly inaccurate Mark-Houwink constants was neglected.

The composition of one series of samples was analyzed using element analysis. The copolymer was purified by removing the remaining monomer. For this purpose, a concentrated solution of the copolymer in acetone was poured out in petroleum-ether (40/60). The precipitated copolymer was filtrated and dried in a vacuum stove.

RESULTS AND DISCUSSION

The properties of the reactive extrusion product are fixed by the reaction temperature, residence time, and mixing. These can be varied by changing the adjustable reaction and extrusion parameters. Thus, the analysis of the influence of each parameter on the product is an important resource in investigating the reactive extrusion process qualitatively.

The Screw Rotation Rate

The screw rotation rate was varied between 0.2 and 0.8 rps at various values of the throughput. Figure 9 shows the results of these experiments. Though an increase in rotation rate involves a decrease in resi-

Fig. 9. Influence of screw rotation rate on conversion at $T = 130^\circ\text{C}$ and three different throughputs: ■ 19 g/min; ◆ 41 g/min; ▲ 61 g/min.

dence time through which a decrease in conversion is expected, it has no influence on the conversion of the polymerization. In all probability this is due to better mixing upon increasing the screw rotation rate, both through an increase in leakage flows and through a direct improvement, thereby increasing the heat transfer coefficient.

In the feed zone of the extruder, the monomer is heated by the extruder barrel to the temperature at which polymerization starts. At a high screw rotation rate, where the heat transfer coefficient is high, the monomer will reach the reaction temperature much faster than at a low screw rotation rate. Although an increase in screw rotation rate causes a decrease in the overall residence time, the time in which the material can react (the effective residence time) does not decrease accordingly, as a consequence of the earlier starting point with regard to low rotation rates.

After the polymerization has started, heat will be produced by the exothermic reaction. When the heat transfer coefficient is high and the mixing is good, the temperature of the material within the screw chambers is relatively low and any possible temperature inhomogeneities are small. The low temperature will cause the material at the end of the extruder, where the conversion is high, to be very viscous, resulting in a diffusion limitation of the long polymer chain radicals. The gel effect will therefore appear, causing a higher conversion than expected. Both the earlier starting point of the reaction as the appearance of the gel effect will counterbalance the reduction in true residence time.

These observations are in agreement with the results obtained by analyzing the average molecular weight shown in Fig. 10. Temperature inhomogeneities at a low screw rotation rate cause the decomposition rate of the initiator to increase, resulting in a low molecular weight. At a high rotation rate,

Fig. 10. Influence of screw rotation rate on number average molecular weight at $T = 130^\circ\text{C}$ and three different throughputs: ■ 19 g/min; ◆ 41 g/min; ▲ 61 g/min.

the gel effect will bring about an increase in molecular weight.

The Throughput

From the results of the experiments, as shown in Fig. 11, an increase in the throughput appears to decrease the conversion of the polymerization quite dramatically. Although an increase in the throughput does somewhat decrease the residence time, this effect is not big enough to account completely for the conversion decrease. The same reasoning as with the influence of the screw rotation rate can be used. Along with the decrease in residence time, a decrease in the heat transfer coefficient and mixing occurs. These effects cause the monomer to reach its reaction temperature further down the extruder, so the effective residence time decreases even more while

Fig. 11. Influence of throughput on conversion at $T = 130^\circ\text{C}$ and $N = 0.5 \text{ l/s}$.

increasing the throughput. The average temperature of the material will be higher, so the polymerization rate will increase through an increase in reaction rate constants. At the same time, the viscosity of the material and therewith the intensity of the gel effect and the conversion decrease. The increase in the polymerization rate obviously does not counterbalance the decrease in conversion consequent on the decrease in the gel effect.

Through the effects mentioned above, the average molecular weight decreases with increasing the throughput (see Fig. 12).

The Barrel Temperature

On increasing the temperature of the extruder barrel the conversion initially increases, but above a temperature of about 125°C it decreases again (Fig. 13). The conversion increase is caused by an increase in the polymerization rate. Because of the relatively low temperature, the gel effect will still be present. The decrease in conversion above 125°C originates from three effects. In the first place, an increase in temperature causes a decrease in viscosity towards the end of the extruder and in the die. Therefore the number of fully filled chambers falls off, causing a decrease in residence time. This effect was experimentally observed: above a temperature of 130°C, a large pressure drop occurred. Stuber (21) derived a model for the polymerization of MMA, in which the temperature and conversion of the polymer-monomer mixture are related to the viscosity. It can be concluded from this model that at high conversions the temperature does have a fairly large influence on the viscosity. This affirms the above chain of reasoning.

The second cause for the decrease in conversion is a decrease in gel effect as a result of the high temperature and low viscosity. At the same time, a lowering of the initiator efficiency at a high temperature and a possible occurrence of a thermodynamic equilibrium

Fig. 13. Influence of temperature on conversion at $N = 0.5$ l/s and $Q = 41$ g/min.

could also bring about the conversion decrease. The higher the temperature, the higher the equilibrium monomer concentration and thus the lower the conversion.

Because a rise in the temperature causes an increase in the decomposition rate of the initiator, the average molecular weight of the polymer decreases with increasing temperature (Fig. 14). Both the decrease in molecular weight and the temperature rise result in a lower viscosity, so the gel effect reduces, intensifying the effect of temperature on molecular weight.

The samples of this series of experiments were used to determine the copolymer composition with element analysis. Should a non-azeotropic copolymerization occur after all, the composition of the samples should be influenced by the differences in temperature and degrees of conversion. The results

Fig. 12. Influence of throughput on number average molecular weight at $T = 130^\circ\text{C}$: ■ $N = 0.2$ l/s; ♦ $N = 0.5$ l/s; ▲ $N = 0.8$ l/s.

Fig. 14. Influence of temperature on number average molecular weight at $N = 0.5$ l/s and $Q = 41$ g/min.

visualized in Fig. 15 show that the composition is almost constant and corresponds fairly well to the expected monomer incorporation ratio.

The Die Resistance or Fully Filled Length

The die resistance can be varied by changing the size of the die outlet. An increase in the die resistance increases the fully filled length and therewith the residence time, while all other parameters remain constant. The conversion therefore increases too (Fig. 16). However, the maximum attainable conversion appears to be limited to a value of 92%, indicating that the residence time is not the only factor determining the conversion. At high conversions, the depropagation reaction might play an important role, so the conversion is limited by the thermodynamic equilibrium.

Fig. 15. Influence of temperature on fraction of HPMA in the polymer.

Fig. 16. Influence of die pressure on conversion at $N = 0.8$ l/s, $T = 130^\circ\text{C}$, and throughputs of: ■ 51 g/min; ▲ 61 g/min.

Fig. 17. Influence of post-initiation on conversion at varying the main throughput at $N = 0.5$ l/s and $T = 130^\circ\text{C}$: ■ without initiator side feed; ◆ with initiator side feed.

librium. Moreover, the amount and efficiency of the initiator could be a limiting factor.

To investigate the possibility of increasing the maximum attainable conversion by enlarging the amount of initiator, a concentrated solution of 1.2 mol/l initiator in monomer was continuously fed through a side feed to the third zone of the extruder during the reactive extrusion process. The amount of the side feed was adjusted so as to ensure a constant ratio of monomer and initiator within the extruder. Figure 17 shows the results of these experiments. At a throughput of 20 g/min, the conversion was raised from 92% to 96%, which means that an extra reduction of 50% of the remaining monomer was attained with regard to the process without initiator side feed. The amount of initiator is therefore a significant parameter in the reactive extrusion process.

In the same way as the conversion, the average molecular weight increases initially and reaches a maximum value further on. In most polymerization systems, diffusion limitation of the monomer does not take place until very high conversions if the polymerization is carried out above the glass transition temperature. Even when the amount of active initiator has reached zero at high conversions, the chances are that there are still polymer chain radicals present as a result of the diffusion limitation of these chains. The limitation in molecular weight therefore should not occur as a result of lack of radicals or monomer diffusion limitation. The most likely explanation, therefore, is the appearance of an equilibrium, which tends to limit both the conversion and the average molecular weight (Fig. 18).

SUMMARY AND CONCLUSIONS

The use of an extruder as a polymerization reactor is not only restricted to homopolymerizations, such as the polymerization of MMA (21) and BMA (5), but

Fig. 18. Influence of die pressure on number average molecular weight at $N = 0.8$ 1/s, $T = 130^\circ\text{C}$, and throughputs of: ■ 51 g/min; ▲ 61 g/min.

can be extended to copolymerizations as well. The copolymerization of BMA with HPMA works out very well in the closely intermeshing counterrotating twin-screw extruder. Other radical addition copolymerizations may be carried out in an extruder equally well. Care has to be taken, however, in choosing the types of copolymerizations performed. The polymerization time needed to attain a certain required degree of conversion should not exceed the economical residence time of the material in the extruder. Besides, choosing any monomers with different reactivity ratios in a copolymerization could cause a drift in the composition distribution of the product.

The course of the polymerization and the properties of the product are strongly dependent on the adjustment of the reaction and extrusion parameters, such as the screw rotation rate, throughput, temperature, and die resistance. An investigation was carried out with the azeotropic copolymerization of BMA with HPMA to unravel the effects of these parameters on the reactive extrusion product. The following results were obtained.

- The screw rotation rate has no influence on the conversion of the polymerization. On increasing the rotation rate, the decrease in residence time is counterbalanced by an increase in effective reaction time and gel effect.
- An increase in screw rotation rate causes an increase in average molecular weight, because of a lessening of temperature inhomogeneities and an increase in gel effect.
- The conversion of the polymerization decreases with increasing throughput as a result of a shorter residence time and effective reaction time.
- Temperature inhomogeneities on increasing the throughput cause the average molecular weight to decrease.
- An increase in temperature initially causes an in-

crease in conversion as a result of an increase in reaction rate constants, then causes a decrease in conversion as a result of a decrease in filled length and gel effect and the appearance of a thermodynamic equilibrium.

- Owing to an increase in the decomposition rate of the initiator, the average molecular weight decreases when increasing the temperature.
- An increase of the die resistance and therewith the fully filled length positively affects the conversion as a result of an increased residence time. Initiator deficiency and a thermodynamic equilibrium limit the conversion.
- The average molecular weight increases when increasing the fully filled length.

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NOMENCLATURE

- A = Geometrical constant (m^3).
 a = Mark-Houwink constant ($-$).
 B = Geometrical constant (m^3).
 D = Diameter (m).
 ΔH_p = Polymerization enthalpy (J/mol).
 I = Initiator
 K = Mark-Houwink constant ($-$).
 k_d = Initiator decomposition rate constant (1/s).
 k_{dp} = Depropagation 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 ($\text{m}^3/\text{mol}\cdot\text{s}$).
 L = Extruder length (m).
 M = Monomer
 M_i = Growing radical of chain length i
 m = Number of thread starts ($-$).
 N = Screw rotation rate (1/s).
 ΔP_c = Inter-chamber pressure gradient (Pa).
 Q = Throughput (m^3/s).
 Q_l = Total leakage flow (m^3/s).
 Q_{th} = Theoretical throughput (m^3/s).
 R = Gas constant ($\text{J/mol}\cdot\text{K}$).
 R^* = Initiator radical
 r_1 = Reactivity ratio ($-$).
 r_2 = Reactivity ratio ($-$).
 ΔS_p = Polymerization entropy ($\text{J/mol}\cdot\text{K}$).
 T_c = Ceiling temperature (K, $^\circ\text{C}$).
 V_c = Chamber volume (m^3).
 v_p = Polymerization rate ($\text{mol}/\text{m}^3\cdot\text{s}$).
 η = Viscosity ($\text{Pa}\cdot\text{s}$).
 $[]$ = Concentration (mol/m^3).

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