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The Production of a New Partially Biodegradable Starch Plastic by Reactive Extrusion

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The grafting of polystyrene onto dissolved starch in a twin screw extruder has been studied. This copolymerization was initiated using the thermal initiators benzoyl peroxide and $K_2S_2O_8$. As end product a mixture containing polystyrene-grafted starch, homopolymer of polystyrene and starch was obtained. Parameters like screw rotation rate, fully filled length of the extruder, wall temperature and throughput have been varied in order to obtain information about their influence on conversion, graft percentages and molecular weight of the materials formed. To increase the amount of graft points, maleic acid anhydride (MAH) was added resulting in an increased grafting of polystyrene onto starch. Graft percentages of 60% could be achieved. The total conversion of styrene could be controlled by adjusting extruder parameters like barrel temperature, fully filled length and initiator type. Conversions of 95% were found. Molecular weights of the polystyrene formed could be controlled by adding a chain transfer agent (dodecylmercaptan) to the styrene phase. In this way the molecular weight (M_n) of the styrenic part could be varied from 20,000 to 140,000. The experiments with the chain transfer agent showed that the grafting of polystyrene onto starch is a process occurring at the interface between the dissolved starch and the styrene phase.

INTRODUCTION

Starch is a widely used carbohydrate. Besides its application in the food industry, starch has numerous applications elsewhere. Examples are the paper, textile, and pharmaceutical industries. In order to make starch applicable for these applications, starches are chemically modified to alter their properties. In the last decade, considerable interest in starch modification concerned the grafting of synthetic polymers onto starch (1–4). One application of these grafted starch is as filler for thermoplastics. The hydrophobic grafted branches will make a graft copolymer more compatible with the plastic matrix than unmodified starch. The main reason to perform this type of research is that starch plastics are renewable resources, which do not increase the amount of atmospheric CO_2 at the end of their product life cycles (4). Additionally, because of their biodegradability, starch

plastics can be disposed of without causing a serious landfill problem. Studies have been performed investigating the biodegradability of polymers grafted onto starch (5–7). Parameters such as mass reduction, the amount of CO_2 and water produced, or the amount of O_2 absorbed during the biodegradability tests were measured. These values were compared to known curves of biodegradable materials, leading to the conclusion that the grafted copolymer parts were biodegradable compared to pure synthetic polymers.

The research described examines the feasibility of using a counter-rotating twin screw extruder as a modification reactor for the polystyrene-grafted-starch. Attention is paid to extruder parameters influencing the conversion, the number of graft points during the reaction, and how to control the molecular weights of the polymers formed.

THEORY

Reactions

Different methods for grafting of polystyrene onto starch have been presented. Initiators like potassium persulfate, ceric ammonium nitrate and redox couples

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like ferrous ammonium sulphate-hydrogen peroxide have been studied (8–11). Also simultaneous ^{60}Co -irradiation can be used to create an radical on the starch chain.

All these reactions were performed in a slurry reactor with granular starch. This means that the temperature of the reactor has to be kept low to prevent gelatinization ($T < 330\text{ K}$). If gelatinization occurs serious mixing problems would arise. These problems do not occur when extruders are used (12). Extrusion processes use temperatures in the order of 400 K and processing times of about 4 minutes. This demands a different initiator. In our case we used the thermal initiators $\text{K}_2\text{S}_2\text{O}_8$ (water soluble) and Benzoyl peroxide (BPO, styrene soluble). $\text{K}_2\text{S}_2\text{O}_8$ decomposes in about 1 min at 403 K, while BPO decomposes in about 2 min at 410 K. A radical starting a polymer chain can be formed due to the reaction of $\text{S}_2\text{O}_8^{2-}$ with the styrene monomer and also by radical formation on a starch chain. Due to the very low solubility of styrene (13) in a highly viscous starch gel it is assumed that graft copolymerization only takes place if a radical formed on the starch is situated at the interface between the starch gel and the styrene phase.

To reduce the amount of homopolymer formed and to increase the grafting efficiency a new method is used. Adding MAH (maleic anhydride) results in two extra reactions. In the first reaction MAH reacts with styrene forming an alternating copolymer of styrene and maleic anhydride.

Assuming that MAH does not homopolymerize (14), under these conditions the reaction mechanism of styrene with MAH can be described according to the penultimate unit model. At low conversions ($< 10\%$) the reaction is diffusion-controlled (15).

In the second fast reaction, MAH reacts under alkaline circumstances with the hydroxyl group of the anhydroglucose units (AGU).

In the case of octenylanhydride, which has a structure similar to MAH, it is measured that the reaction is diffusion limited (1, 16). At low temperatures ($T = 303\text{ K}$), the second order reaction rate constant is in the order of $10\text{ mol}^2\text{ m}^{-3}\text{ s}^{-1}$. The starch ester formed contains an unsaturated bonding, which is able to

react with a growing polystyrene chain. Also, the MAH group in a copolymer between MAH and styrene is able to react with the starch alcohol group. By addition of a chain transfer agent (CTA), the molecular weight of the polymers formed can be controlled. In this work dodecylmercaptan is used.

Experimental

Preliminary experiments were performed in a small 30 cm^3 glass vessel, equipped with baffles and a stirring device. This reactor could be closed using a screw gap equipped with a septum. With this reactor, experiments were performed to investigate the influence of different amounts of chain transfer agent and BPO concentrations on the molecular weight of styrene. The conversion and molecular weight of pure styrene versus the reaction at different temperatures and BPO concentrations were measured. Reactions with starch, styrene and different initiators were performed in the same batch reactor. Additional experiments using DSC were done to investigate in particular the effect of the chain transfer agent on the reaction rate.

The potato starch was a commercial product of "AVEBE B.A. Cooperatieve verkoop en Productie van Aardappelmeel en Derivaten," the Netherlands. Dibenzoylperoxide, potassium persulfate, maleic anhydride, sodium hydroxide, and styrene were commercial products of Merck. Conversions were determined using gravimetry. One gram of the polymer-monomer mixture was weighed and dissolved in acetone. To this solution a small amount of hydroquinone was added to prevent further polymerization on heating. The solution was poured into a petri dish and subsequently heated in a vacuum stove at 393 K. By weighing the remaining polymer, the conversion can be calculated.

Molecular weights were measured using a Gel Permeation Chromatograph (Polymer Laboratories). Isothermal DSC-measurements were at 403 K with styrene (p.a.), BPO and dodecylmercaptane. Using the methods described by Alberda Van Ekenstein *et al.* (17), the $k_p/[k_t]^{1/2}$ of the polymerization reaction could be measured as described above. In case of reactions between starch and styrene, about 4 g of starch was dissolved in 25 cm^3 demineralized water. To this mixture different wt% (water as reference) potassium persulfate and 2.2 cm^3 styrene were added under vigorous stirring. During the experiments everything was kept under nitrogen atmosphere. The reactor was placed in an oil bath in which it reached the desired temperature. After a predefined time the reactor was taken out of the oil bath and quenched with liquid nitrogen. Temperatures used were 353 K and 363 K. The reactor content was analyzed for the amount of polystyrene formed and polystyrene grafted onto starch. Material was washed with methanol and dried to remove water, methanol and styrene. Polystyrene was removed using soxhlet extraction and tetrahydrofuran (THF). After 7 days of refluxing, all the homopolymer polystyrene was dissolved into the THF. Evaporation

of the THF resulted in the homopolymer PS. The remaining starch and polystyrene-g-starch were refluxed for 6 hours using 0.1 N H_2SO_4 hydrolyzing the starch to glucose units. The remaining residue dissolved easily in chloroform and appeared to be polystyrene, as expected. This way, molecular weights and the exact amount of homopolymer and grafted polystyrene formed, as well as the influence of the amount of initiator and the stirring speed on the reaction could be determined.

Polymerization Results

Bulk Polymerization of Styrene in a Batch Reactor

Figures 1 and 2 show results of the styrene bulk reaction at different temperatures and initiator concentrations. Increasing the temperature (Figs. 1 and 2) results in a higher conversion. In the case of $T = 403$ K also higher M_w s are found. The main reason for obtaining higher conversions at higher initiator concentration is that owing to the strong exothermic reaction, the temperature of the mixture rises above the set temperature of the oil bath (Fig. 3). This effect will take place at $c_{\text{BPO}} > 0.1$ mol%. Adding a chain transfer agent (CTA) to the mixture, the M_w could be controlled as can be seen in Fig. 4. The CTA has some influence on the overall reaction rate of the polymerisation (Fig. 5). This effect can be understood when it is realized that the CTA also acts as an initiator starting new chains.

Reaction of Styrene With Starch Using $\text{K}_2\text{S}_2\text{O}_8$ as an Initiator in a Batch Reactor

Figure 6 shows that the reaction is diffusion limited. An increased stirring speed, while all other parameters

Fig. 1. Conversion of styrene versus BPO concentration of styrene at different temperatures. $\diamond T = 383$ K, $\square T = 403$ K, $\triangle T = 423$ K.

Fig. 2. M_w of PS versus the BPO concentration at several temperatures. $\diamond T = 383$ K, $\square T = 403$ K, $\triangle T = 423$ K.

are kept constant, results in an increased graft percentage. This effect is a result of the increased area between the styrene and in water dissolved starch phase. It justifies the contention that grafting mainly occurs at the starch-styrene interface. If the initiator concentration increases resulting in an increase of the radicals formed, also the graft percentages increase (2.5 wt% initiator is the maximum amount of potassium persulfate that dissolves in water). Also, the starch type used has its influence on the reaction rate. This was tested using hydroxyethylated starch (HES) and native starch (S). The graft percentage versus the reaction time for these two different starch

Fig. 3. Temperature profiles of the bulk polymerisation of styrene at several BPO concentrations, $T_{\text{wall}} = 403$ K. — $c_{\text{BPO}} = 0.5$ mol%, -- $c_{\text{BPO}} = 1.0$ mol%, $c_{\text{BPO}} = 0.1$ mol%.

Fig. 4. M_n versus the CTA concentration in the styrene mixture ($T = 403$ K, $t_r = 400$ s, $c_{BPO} = 0.1$ mol%).

Fig. 6. Graft percentage versus the $K_2S_2O_8$ concentration in a starch, styrene and water mixture. $\diamond$: Stirrer speed = 200 rpm, $\triangle$: Stirrer speed = 20 rpm, $T = 353$ K, $m_{starch} = 4$ g, $m_{styrene} = 2$ g, $m_{H_2O} = 25$ g.

types is shown in Fig. 7. In the case of hydroxyethylated starch, the molecular weights of the styrene grafts were slightly lower compared to the molecular weights found of the styrene grafts formed on the native starch. (after 15 min: $M_{wHES} = 13,993$ g mol⁻¹ versus $M_{wS} = 19,789$ g mol⁻¹). A possible explanation for these phenomena is the difference in viscous behavior of both starch types, resulting in a different mixing behavior. After a certain time the graft percentage reaches a maximum because the amount of styrene is exhausted.

GRAFTING OF POLYSTYRENE ON STARCH USING A TWIN-SCREW EXTRUDER

To investigate the influences of various extruder and reaction parameters, experiments were performed in a counter-rotating twin screw extruder. Temperature profiles, screw speed, die pressures and thus the fully filled length of the extruder were changed. In twin screw extruders and especially the closely intermeshing types, the transport takes place by positive

Fig. 5. $k_p/k_i^{0.5}$ of styrene versus the CTA concentration (measured by DSC using the method proposed by Alberda van Ekenstein et al., [22]), $T = 403$ K, $c_{BPO} = 0.1$ mol%.

Fig. 7. Graft percentage versus the reaction time for unmodified potato starch and hydroxyethylated potato starch $T = 353$ K, $m_{starch} = 4$ g, $m_{styrene} = 2$ g, $m_{H_2O} = 25$ g $\diamond$: MS = 0.5, $\square$: MS = 0.

Table 1. Conversions, Graft Percentages of the Different Graft Reactions.

N [RPM]	ζ_{total} [%]	Graft Percentage [%]	ζ_{graft} [%]	ζ_{homo} [%]
System: Styrene, Starch, Water, $\text{K}_2\text{S}_2\text{O}_8$ Temperature profile: 80-100-130°C / $u_f = 4$				
13	23.20	1.60	1.74	21.46
15	37.00	1.30	7.33	29.67
18	30.70	1.30	11.42	19.28
20	32.30	1.91	14.36	17.94
25	32.00	1.80	14.34	17.66
28	29.00	1.60	12.24	16.76
33	29.90	1.60	13.93	15.97
Increasing the die-pressure/ $u_f = 8$				
15	68.00	4.50	27.00	41.00
20	52.00	2.60	20.00	32.00
Increase of temperature: 80-110-150°C/ $u_f = 4$				
15	46.00	1.30	10.50	35.50
20	48.00	1.30	8.25	39.80
System: Styrene, Starch, Water, BPO/ $\text{K}_2\text{S}_2\text{O}_8$ Temperature profile: 80-120-135°C / $u_f = 4$				
30	76.95	4.88	14.67	62.28
35	75.84	3.17	9.39	66.45
40	73.79	6.23	17.95	55.85
45	70.92	7.66	21.23	49.69
50	69.86	12.08	32.95	36.90
System: Styrene, Starch, Water, MAH, BPO/ $\text{K}_2\text{S}_2\text{O}_8$ Temperature profile: 80-130-145°C / $u_f = 6-8$				
30	94.42	12.00	44.26	50.16
35	94.45	12.83	47.35	47.10
40	93.95	10.55	38.70	55.25
45	93.95	11.17	41.00	52.95
50	94.83	13.60	50.39	44.44

conveying. Therefore, the material cannot rotate with the screw, independent of its properties. This is important when performing reactive extrusion. The throughput is now more or less independent of back-pressure or slip. The counter-rotating twin screw extruder used in this work is closely intermeshing and consists of series of C-shaped chambers in which material is transported towards the die. Three zones can be distinguished from hopper to die. The solids transport zone: The feed material enters the extruder as granules or as powder. The melt zone/partially filled zone: In this zone the starch gelatinizes. This zone begins at the point where the amylose first starts to leach out of the granule and water subsequently diffuses into the starch granule. This zone is partially filled with material. The pump zone/fully filled zone: The pressure on the gel is increased because of completely filled C-shaped chambers. The major part of the mixing, kneading and heat transfer takes place in this zone. Therefore, this zone is of extreme importance for the efficient functioning of the twin screw extruder and is characterized by the number of C-shaped chambers that are fully filled with a starch gel. Experimentally, it is verified that the passage of

Fig. 8. Conversion versus the extruder screw speed. $w_{\text{K}_2\text{S}_2\text{O}_8} = 2.5 \text{ wt\% g}^{-1} \text{ H}_2\text{O}$, $\Phi_{m,\text{starch}} = 25 \text{ g min}^{-1}$, $\Phi_{m,\text{styrene}} = 2 \text{ g min}^{-1}$, $\Phi_{m,\text{water}} = 6 \text{ g min}^{-1}$, $u_f = 4$, $T_{\text{extruder}} (\text{°C}) = 80\text{--}100\text{--}130$, ◇: Total styrene conversion, ■: ζ styrene to PS, △: ζ styrene to grafted PS.

material through high shear and elongation flow fields is necessary to increase the rate of gelatinization of starch (18). These flow fields can be found in the leakage gaps. The number of passages through these gaps is thus an important parameter. This number of passages can be increased by increasing the screw speed and/or the die-resistance (19).

EXTRUDER EXPERIMENTS

During the experiments a counter-rotating closely-intermeshing twin-screw extruder was used with a screw diameter of 50 mm, an L/D of 6 and gaps of 1 mm. The basic settings of the extruder can be found in Table 1. The different parameters were varied one at a time while the other parameters remained those of the basic setting. The pressure profile over the extruder was measured with three pressure transducers. The output of the extruder ranged from 1.8 kg/h to 2.4 kg/h. After preheating the extruder, a composition of starch, water (with dissolved $\text{K}_2\text{S}_2\text{O}_8$), styrene (with or without BPO, MAH and dodecylmercaptane) was fed to the extruder. The starch contained about 15 wt% water. During the experiments the screw speed, the screw type, the die resistance, temperature profile and reactant concentrations were varied. Samples were taken when a stable temperature and pressure profile along the extruder was obtained. To stop the reaction, samples were quenched in liquid nitrogen, ground up, and precipitated in a solution of 100 cm^3 methanol. The opaque precipitated powder obtained was dried in a vacuum oven and analyzed on the amount of homopolymer, graft polymer formed and the molecular weight of both polystyrene polymers.

Fig. 9. Graft percentage and the ratio PS versus the extruder screw speed. $K_2S_2O_8$ is used as initiator. $\diamond$: Ratio homopolymer/graft copolymer, $\blacksquare$: Graft percentage.

EXTRUDER RESULTS

Figures 8 and 9 show the results obtained using $K_2S_2O_8$ as sole initiator. In this system an increasing screw speed results in an almost constant conversion. Initially, this result is surprising, as one expects the conversion of the reaction to decrease with increasing screw speed due to a decrease in the residence time. However, two opposing effects take place. The first is the decrease of reaction time due to the increase of the screw speed (decreasing residence time). The other is that an increased screw speed results in an increased mixing and thus in an increased interfacial area between styrene and the water phase; more radicals are able to initiate a polymerization, resulting in a higher conversion and graft percentage. Both effects seem to balance each other. Increased mixing also results in an increased destructurizing of the starch chains. New radicals are formed as a result of inter-chain scissions (20), which can initiate a polymerization reaction. It should be noted that the extruder temperature could not be changed too much. When the temperature is too high the initiator concentration decays so quickly that the reaction stops. From Table 1 it can be concluded that an increase in the number of filled chambers or/and the temperature results in an increase of the total conversion and the graft percentage. This is logical because an increase in the number of filled chambers results in an increased leakage flow and residence time. A longer residence time means a longer reaction time and thus higher conversions. Also the interfacial area increases owing to the shear as material is pushed through the leakage gaps. An increase in graft percentage is the result. Increasing the temperature of the barrel results in higher conversions. The graft percentage, however, remains the same because the interfacial area does not change.

Fig. 10. Conversion versus the extruder screw speed. $w_{K_2S_2O_8} = 2.5 \text{ wt\% } g^{-1} \text{ H}_2\text{O}$, $w_{BPO} = 2 \text{ mol\%}$, $\Phi_{m, \text{starch}} = 25 \text{ g min}^{-1}$, $\Phi_{m, \text{styrene}} = 2 \text{ g min}^{-1}$, $\Phi_{m, \text{water}} = 6 \text{ g min}^{-1}$, $u_f = 4$, $T_{\text{extruder}} (^{\circ}\text{C}) = 80\text{--}120\text{--}135$. $\diamond$: Total styrene conversion, $\blacksquare$: ζ into homopolymer PS, $\triangle$: ζ into graft copolymer PS.

Figures 10 and 11 give results obtained during experiments where BPO and $K_2S_2O_8$ are added to the styrene phase. Because the decay of BPO is slower at the same temperature in comparison to $K_2S_2O_8$ a higher temperature is chosen for the last extruder zone and the die. The final conversion obtained appeared in the order of 80%, which is an improvement compared to the experiments using $K_2S_2O_8$ as initiator. Again, higher screw speeds result in higher graft percentages, while the total conversion shows a slight

Fig. 11. Graft percentage and the ratio PS versus the extruder screw speed. $K_2S_2O_8$ and BPO are used as initiators. $\diamond$: Ratio homopolymer/graft copolymer, $\blacksquare$: Graft percentage.

Fig. 12. Conversion versus the extruder screw speed. $w_{K_2S_2O_8} = 2.5 \text{ wt\% g}^{-1} \text{ H}_2\text{O}$, $w_{BPO} = 0.3 \text{ mol\%}$, MAH is used as extra component in the styrene phase. $T_{\text{extruder}} (^{\circ}\text{C}) = 80\text{--}120\text{--}135$, $\Phi_{m,\text{starch}} = 25 \text{ g min}^{-1}$, $\Phi_{m,\text{styrene}} = 2 \text{ g min}^{-1}$, $\Phi_{m,\text{water}} = 6 \text{ g min}^{-1}$, $u_f = 6\text{--}8$, $\diamond$: Total styrene conversion, $\blacksquare$: ζ into homopolymer PS, $\triangle$: ζ into graft copolymer PS.

decrease at increasing screw speed. This last effect can be explained as being due to the decreasing residence time at increasing screw speeds. The increased mixing due to the increased screw speed no longer balances the decreased residence time.

In Figs. 12 and 13 results of the effect of MAH on the graft percentage versus the screw speed is shown. The graft percentage and the total conversion have

Fig. 13. Graft percentage and the ratio PS versus the extruder screw speed. $K_2S_2O_8$ is used as initiator, MAH is used as extra component in the styrene phase. $\diamond$: Ratio homopolymer/graft copolymer, $\blacksquare$: Graft percentage.

Fig. 14. M_n of the grafted copolymer polystyrene for the three initiator systems used versus the screw speed (without chain transfer added), Table 1. $\triangle$: $K_2S_2O_8/BPO/MAH$, $\diamond$: $K_2S_2O_8/BPO$, $\square$: $K_2S_2O_8$.

increased considerably. The increased conversion is due to the gel effect that occurs at conversions over 70%. Also the exothermic reaction between styrene and MAH ($\Delta H_{\text{styrene-styrene}} = 50 \text{ kJ/mol}$ and $\Delta H_{\text{MAH-styrene}} = 70\text{--}80 \text{ kJ/mol}$) causes an increased temperature jump in comparison to Fig. 3. The molecular weights of the systems measured are given in Figs. 14 and 15, as a function of the screw speed. An increase in the screw speed results in a slight increase of the shear imposed on the starch, which gives rise to a higher temperature. As can be seen from Fig. 2, an increase in the temperature means that the M_n increases. The differences in M_n between the three systems is mainly due to the difference in processes conditions like temperature and initiator concentrations. Adding a chain transfer agent (CTA) to the mixture results in a decrease of the M_n of the formed polystyrene as can be seen in Figs. 16 and 17. The CTA not only influences the formation of the homopolymer but also the formation of the graft polymer in exactly the same way. This is in accordance with the shape of the curves. Because the CTA used does not dissolve in water, the conclusion can be drawn that the formation of grafted polystyrene occurs presumably at the boundary between the starch and the styrene phase. In Fig. 16 the M_n versus the screw speed is shown for a system with 0.4 mol% CTA added. The M_n increases as well for the homopolymer as for the grafted copolymer as the screw speed increases. An increased screw speed results in more shear opposed on the starch, which causes a different mixing behavior as a result the M_n increases in this case.

CONCLUSIONS

The performance of graft copolymerization in twin screw extruders depends on several extruder

Fig. 15. M_n of the homopolymer PS formed for the three initiator systems used versus the screw speed (without CTA added). $\triangle$: $K_2S_2O_8/BPO/MAH$, $\diamond$: $K_2S_2O_8/BPO$, $\square$: $K_2S_2O_8$.

parameters. A good understanding of the reaction kinetics, mixing mechanisms as well as the influence of extruder parameters on the process is necessary to obtain a stable process. According to the kinetics, the grafting of polystyrene onto starch can be described by a two step mechanism, in which a radical first must be produced on the starch (radical inducing step), after which a normal homopolymerization can take place if the radical is situated in the neighborhood of the interface between the water and styrene.

Fig. 16. M_n of the homopolymer and the grafted copolymer PS formed versus the screw speed, $w_{BPO} = 0.1 \text{ mol\%}$, $w_{K_2S_2O_8} = 2.5 \text{ wt\% g}^{-1} \text{ H}_2\text{O}$, $w_{CTA} = 0.4 \text{ mol\%}$, $u_f = 2$, $\Phi_{m\text{starch}} = 25 \text{ g min}^{-1}$, $\Phi_{m\text{styrene}} = 2 \text{ g min}^{-1}$, $\Phi_{m\text{water}} = 6 \text{ g min}^{-1}$, $T_{\text{extruder}} (^{\circ}\text{C}) = 90\text{--}120\text{--}135$, $\diamond$: Grafted copolymer, $\square$: Homopolymer PS.

Fig. 17. M_n of the grafted polystyrene and the formed homopolymer PS versus the CTA amount, $u_f = 2$, $w_{BPO} = 0.1 \text{ mol\%}$, $w_{K_2S_2O_8} = 2.5 \text{ wt\% g}^{-1} \text{ H}_2\text{O}$, $F_m \text{ starch} = 25 \text{ g min}^{-1}$, $\Phi_{m\text{styrene}} = 2 \text{ g min}^{-1}$, $\Phi_{m\text{water}} = 6 \text{ g min}^{-1}$, $T_{\text{extruder}} (^{\circ}\text{C}) = 90\text{--}120\text{--}135$, $\diamond$: Grafted copolymer PS, $\square$: Homopolymer PS.

The radical inducing step is influenced by the initiator concentration and the temperature. Mixing influences the number of radicals present at the interface. Focusing on the extruder experiments the following conclusions can be drawn:

- The *in situ*-grafting of polystyrene onto starch can be carried out in a counter rotating twin screw extruder. During the reaction the conversion, the molecular weight and the graft efficiency can be controlled.
- Mixing during the graft copolymerization of styrene onto starch is very important as the reaction is diffusion limited. Increasing the screw speed and the number of fully filled chambers are possible routes to increase the interfacial area and in this way increase the graft percentage.
- From the experiments performed with the chain transfer agent it is concluded that the reaction takes place at the interface between the starch and the styrene phase.
- Choosing the right amount of initiators gives rise to higher conversions, graft percentages and molecular weights.
- Adding MAH and NaOH to styrene and the starch phase respectively results in higher grafting percentages and conversions.
- Adding a chain transfer agent to the styrene phase not only influences the M_n of the homopolymerization but also the M_n of the grafted polystyrene.

NOMENCLATURE

m	= Number of screws.	[-]
m	= Mass.	[kg]
M	= Molar mass.	[kg kmol ⁻¹]
M_n	= Average molecular weight by number.	[kg kmol ⁻¹]
M_w	= Average molecular weight by weight.	[kg kmol ⁻¹]
N	= Screw speed.	[s ⁻¹]
T	= Temperature.	[K]
t	= Time.	[s]
V_c	= Volume of a C-shaped chamber.	[m ³]
Φ_v	= Volumetric feed rate.	[m ³ s ⁻¹]
ξ	= Conversion.	[%]
h	= Viscosity.	[Pa s]
u_f	= Number of fully filled chambers.	[-]

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