

Reactive Extrusion of Styrene Polymers

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SYNOPSIS

Reactive extrusion is the term used to denote a plastics processing method in which an extruder is used as a reactor for the continuous synthesis and modification of polymers. This paper describes the manufacture of polystyrene and styrene–isoprene copolymers by a reactive extrusion process: anionic “living” *s*-butyllithium-initiated bulk polymerization was performed in a co-rotating closely intermeshing twin-screw extruder. The results of the process analysis show that living polymerization of styrene can be performed in a screw-type reactor, despite the high reaction temperatures of over 200°C. The polystyrene melt can be modified in bulk with comonomers or coupling reagents immediately after polymer synthesis. Depending on the raw material, formulation, and process parameters, the process variants developed and analyzed at the Institut für Kunststoffverarbeitung for homopolymerization of styrene, copolymerization of styrene–isoprene mixtures, and sequential polymerization of styrene and isoprene resulted in styrene polymers with widely differing structural characteristics and properties. For example, the copolymerization of styrene–isoprene monomer mixtures produced poly[isoprene-*co*-styrene]-*b*-styrene]. The sequential polymerization of styrene and isoprene led to poly(styrene-*b*-isoprene) contaminated with partly cross-linked low molecular weight polyisoprene. The polyisoprene content is presumably formed by side reactions due to the high reaction temperatures. © 1993 John Wiley & Sons, Inc.

1. INTRODUCTION

Polystyrene today offers a spectrum of applications, which, thanks to the variety of different grades including standard polystyrene, expanded polystyrene (EPS), and toughened polystyrene grades (HIPS, ABS, SBS) and the large number of copolymers (SAN, SMMA, styrene- α -methylstyrene copolymer), graft copolymers (ABS, ASA, MABS, MBS), and thermoplastic elastomers (SB, SBS, SBR, SEBS) can be varied within a wide range.^{1–10}

Polystyrene molding compounds can be produced by several methods, whereby the polymerization can be performed in homogeneous phase (bulk and solution polymerization) and in heterogeneous phase (suspension polymerization, precipitation, and

emulsion polymerization).^{1,2,6,7} For standard polystyrene, toughened polystyrene and styrene copolymers, continuous polymerization is primarily performed on an industrial scale in bulk and in solution. Expanded polystyrene (EPS) is preferentially produced by suspension polymerization, and ABS and ASA, by emulsion polymerization.² In these industrial-scale processes, the styrene polymers are generally produced by free-radical polymerization. Anionic polymerization is employed only in the production of copolymers. The cationic and coordinative polymerization, which are also possible, are not employed industrially.²

Tower, plug flow, and stirred tank reactors are predominantly used for bulk polymerization of styrene.^{1,2,6,7} The poor dissipation of the heat of reaction from the highly viscous reaction product and the high pressures and temperatures involved in the processing of the viscoelastic polymers demand technically complex and capital-intensive reactors.¹

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A further difficulty of the predominantly radical-initiated polymerization is the sharp decrease in the polymerization rate at conversions of more than 95%. The continuation of the radical polymerization or the reduction of the high residual monomer content can be performed by subsequent processing of the reaction product in an extruder.^{1,11} Although anionic polymerization supplies the polymer end product after a very short reaction time, the classic reactors such as plug flow and stirred tank reactors do not permit temperature control of this strongly exothermic reaction. The only alternative here is anionic solution polymerization, which, however, due to the technically complex and cost-intensive purification and evaporation of the solvent, is economically less attractive.

This paper presents and discusses the results of a process analysis of the continuous bulk polymerization of styrene polymers in an extruder. The use of an extruder as a reactor for this application has been described in the patent literature to date exclusively for the block copolymerization of styrene and butadiene or isoprene.¹²

The objective of the process analysis presented in this paper is not the development of a new polymerization process for the production of polystyrene. The process analysis performed provides the basis for a large number of potential further development steps, i.e., the results of the fundamental research on the "living polymerization of polystyrene" can be utilized technically for the production of copolymers. The example of the production of styrene-isoprene copolymers proves that further modification of the polystyrene in the melt immediately after polymerization is possible.

2. EXPERIMENTAL

2.1. Materials

The extrusion experiments were performed using the following starting materials:

- Styrene, stabilized with *tert*-butylcatechol. Destabilization is performed in an Al₂O₃-filled column at -10°C in a nitrogen atmosphere (see Section 2.3).
- Isoprene, stabilized with *tert*-butylcatechol. Destabilization is performed as for styrene, but at 20°C.
- *s*-Butyllithium. The initiator is available commercially as a 12% solution in cyclohexane; the concentration of the butyllithium solution is determined by titration using a solution of 1,3-

diphenyl-2-propanone tosylhydrazone in tetrahydrofuran (THF).¹³

- Nitrogen. Preparation and processing of the raw materials was performed in a dry nitrogen atmosphere. The nitrogen specification can be found in Ref. 14.

2.2. Analysis

The following schedule gives an overview of the analytical methods used for the manufactured molding compounds:

Differential Scanning Calorimetry (DSC)

Analysis system: DuPont Thermal Analyzer 9900
 Sample mass: 9–19 mg
 Temperature range: -130–280°C
 Heating-up rate: 20–50°C/min
 N₂/Ar/flow rate: 20–50 mL/min

Dynamic Mechanical Analysis (DMA)

Analysis system: DuPont Thermal Analyzer 9900—DMA 983
 Sample geometry: 30 × 10 mm²
 Temperature range: -120–170°C
 Heating-up rate: 3°C/min
 Frequency: 1 Hz

Gel Permeation Chromatography (GPC)

Columns: Polymer Laboratories PL-GEL 5 μ, 500 Å, 10³ Å, 10⁴ Å and 10⁵ Å
 Solvent: THF
 Polymer concentration: 1–4 mg/mL
 Flow rate: 0.5 mL/min
 Temperature: 20°C
 Detection: RI: Melz Differential Refractometer LCD 201; UV: Waters 990

Nuclear Magnetic Resonance (¹H-NMR and ¹³C-NMR)

Spectrometer: Varian EM-390 90 MHz, Bruker 200 MHz
 Solvent: Deuteriochloroform (CDCl₃)
 Polymer concentration: 40–60 mg/mL (¹H-NMR), 400 mg/mL (¹³C-NMR)
 Internal standard: Tetramethylsilane (TMS)

Ozonolysis

Generator: Fischer 500 M

Solvent: Methylene chloride (CH_2Cl_2)

Temperature: -78°C

Ozone flow: $14.4 \text{ mg/min} \Delta 0.3 \text{ mmol/min}$

Process: The reaction product was precipitated in methanol and, after removal of the methanol by filtration, dried at 50°C for 24 h *in vacuo*.

Transmission Electron Microscopy (TEM)

Microscope: Zeiss EM

Contrasting: OsO_4 , 14 d

Sample thickness: Approx. $80 \mu\text{m}$

2.3. Experimental Setup

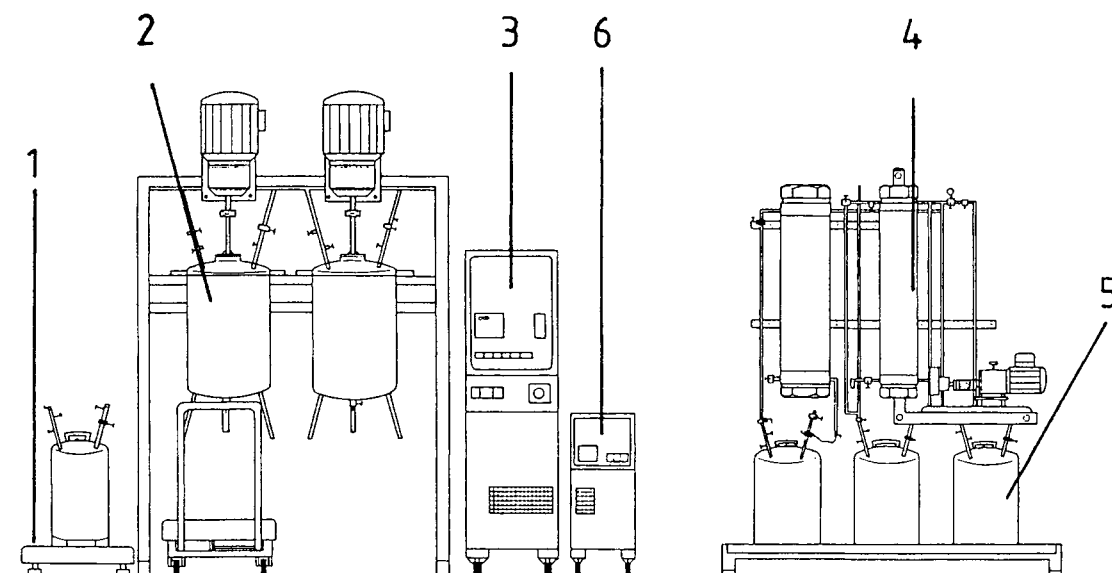
The experimental setup used for the polymerization of styrene consists of three components:

- unit for purification and destabilization of styrene and isoprene;

- stirred tank reactors for the preparation of styrene prepolymers;
- extruder with metering system for performing the bulk polymerization of styrene polymers.

Styrene and isoprene were purified and destabilized before processing. This is performed in a dry nitrogen atmosphere in the unit shown in Figure 1.¹⁵ If thermally prepolymerized styrenes are used as starting material for the anionic polymerization, the prepolymer is first produced in a discontinuously operated stirred tank reactor (Fig. 1).¹⁵ If the processing is done without prepolymers, purified styrene can also be metered directly into the extruder.

The reactor is an extruder with co-rotating, closely intermeshing twin screws with a screw diameter D of 30 mm. The maximum screw length L is 29 D . The configuration of the experimental setup employed is shown schematically in Figure 2. The periphery of the extruder [(1) in Fig. 2] comprises three metering systems for the addition of the styrene monomer or prepolymer (3a), the initiator s-



- | | | | |
|---|----------------|---|--|
| 1 | balance | 4 | purification unit for styrene and isoprene |
| 2 | tank reactor | 5 | container |
| 3 | tempering unit | 6 | cooling unit |

Figure 1 Experimental setup for the monomer purification and for the preparation of styrene polymers.

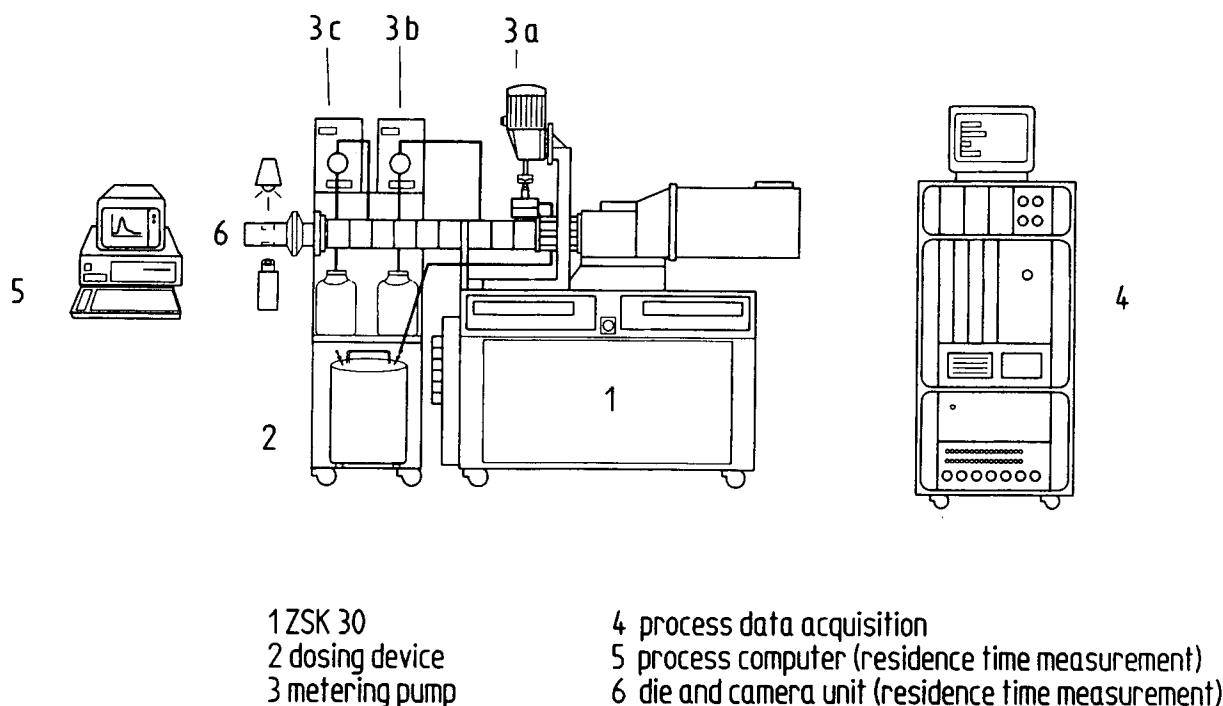


Figure 2 Experimental setup for reactive extrusion of styrene polymers.

butyllithium (3b), and the isoprene (3c). The process-specific data are recorded using a measuring and energy data recording system. A specially developed tool, a camera unit (6), and a separate process computer (5) are available for on-line measurement of the residence time. The co-rotating twin-screw extruder performs the following basic functions during the reactive extrusion of styrene polymers:

- mixing of initiator and monomer or prepolymer;
- anionic polymerization of monomers;
- discharge of the high-viscosity melt.

The screw and barrel temperature profiles corresponding to these functions are shown in Figure 3.

The polymerization zones of screws 1–3 consist predominantly of conveying elements. In line with a recommendation from Ref. 16, no mixing or back-conveying elements are installed in these zones.

The modular design of the twin-screw extruder allows the polymerization zone to be built up starting from the screw tip and to be extended in steps. Products can thus be sampled at various points along the screw for analysis. The complete line operates in a dry nitrogen atmosphere to prevent contami-

nation of the reaction system with oxygen and moisture.

3. RESULTS OF THE PROCESS ANALYSIS AND DISCUSSION

3.1. Performance of the Reaction Extruder

The performance of the reaction extruder is determined by both the choice of raw materials and formulation and by the preset process parameters. The behavior of the screw-type reactor from an energy point of view is influenced to a considerable extent by the strongly exothermic reaction. During polymerization of styrene with an adiabatic temperature increase of approximately 350°C, the bulk temperature increases sharply during the reaction. Because of the efficient heat exchange, approximately 70% of the heat of reaction is drawn from the melt over a short section of the screw. The remaining approximately 30% of the heat of reaction is used to heat up the reaction melt to a polystyrene processing temperature of 200–230°C. Despite this very high reaction temperature for anionic polymerization, the living polymerization of polystyrene can be performed in a screw-type reactor. On leaving the extruder, the melt has an intense red color, a clear

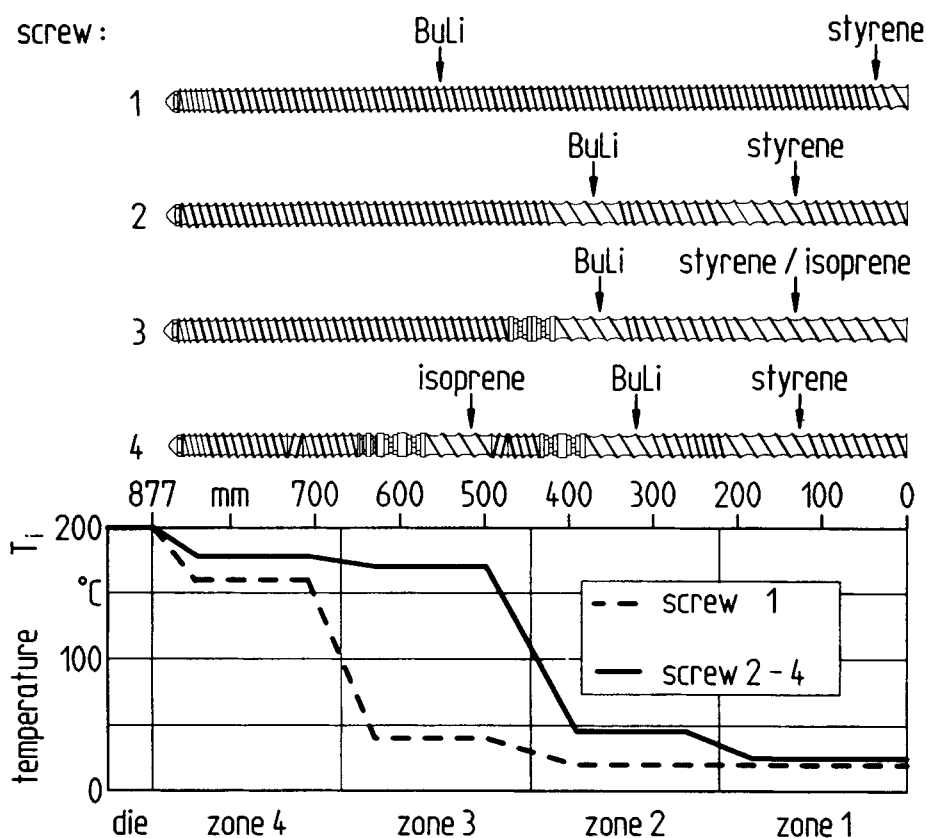


Figure 3 Screw geometries and barrel temperatures for reactive extrusion of styrene polymers.

indication of the presence of reactive polystyryl anions.

The course of the reaction of the very rapid anionic polymerization of styrene can, as shown in Figures 4 and 5, only be influenced by the production parameters to a very limited extent. When the reaction is started by the addition of the initiator, the melt will contain polystyrene of high molecular weight and with a conversion of 100% after passing through only a short length of the screw.

Increasing styrene prepolymer content and high initiator concentration shorten the polymerization zone. The parameters of speed and throughput determine the residence time spectrum and, thus, the reaction performance of the extruder. This operating point-dependent reactor behavior results in the conversion curves shown in Figure 5. With increasing speed, the polymerization shifts toward the die and the melt throughput has only a minor influence on the conversion.

The calculated lengths of the polymerization zone in Figures 4 and 5 were confirmed experimentally.¹⁵ One hundred percent conversion was observed in all

experiments after a polymerization zone length of 135 mm.

3.2. Material and Structure

The reactive system, which can be varied widely by the choice of raw material and formulation, determines the structure and the end properties of the manufactured styrenes. The following material variations were investigated in greater detail during the course of process development and analysis of the continuous anionic polymerization of styrene polymers:

- homopolymerization of styrene and styrene prepolymers;
- copolymerization of styrene-isoprene monomer mixtures;
- sequential polymerization of styrene and isoprene.

Homopolymerization

Styrene or styrene prepolymers can be used as starting material for the reactive extrusion of poly-

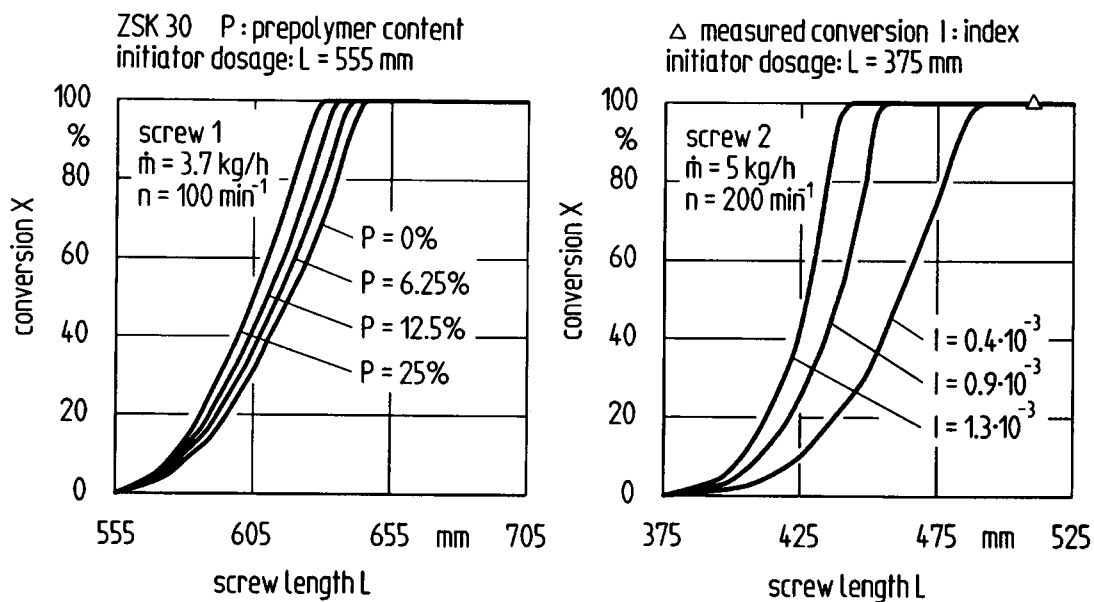


Figure 4 Calculated course of conversion for various raw materials and formulations.

styrene. Conversion and molecular weight are determined by the manufacturing conditions during thermal polymerization in the stirred tank reactor.¹⁵ The model presented in Refs. 17 and 18 allows a very good precalculation of conversion and molecular weight.

The homopolymerization of styrene in the presence of prepolymers permits, e.g., the production of polystyrenes with bimodal molecular weight distributions

(Fig. 6) that contain not only a thermally polymerized component of high molecular weight, but also a component of low molecular weight polymerized anionically in the extruder. Figure 6 shows merely a few of the possible variations in molecular weight distribution. The free choice of the starting components (monomer and prepolymer) and the formulation permits an application-specific setting of molecular weight and molecular weight distribution

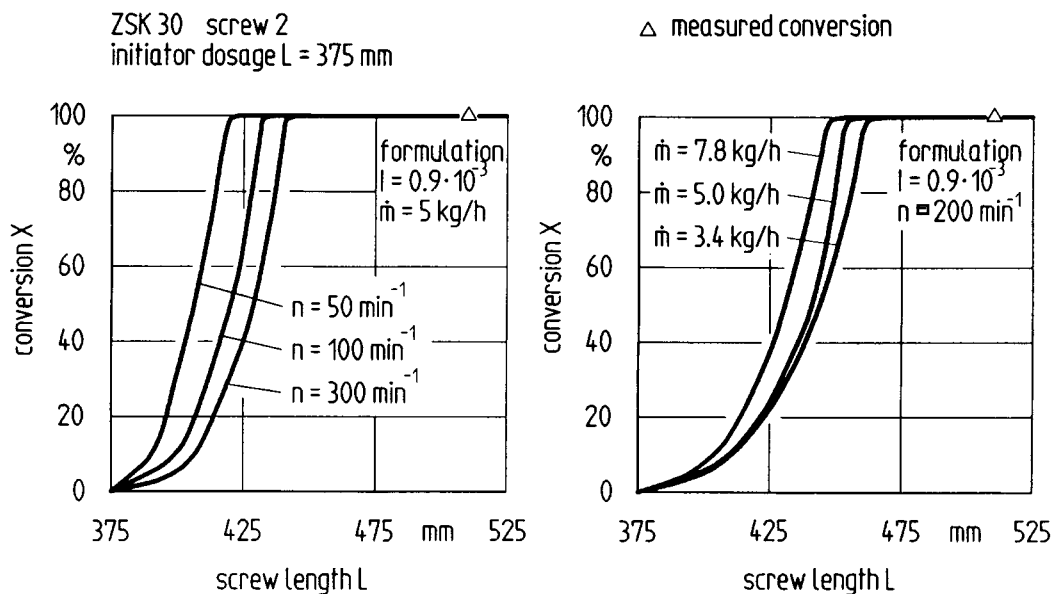


Figure 5 Calculated course of conversion for various screw speeds and throughputs.

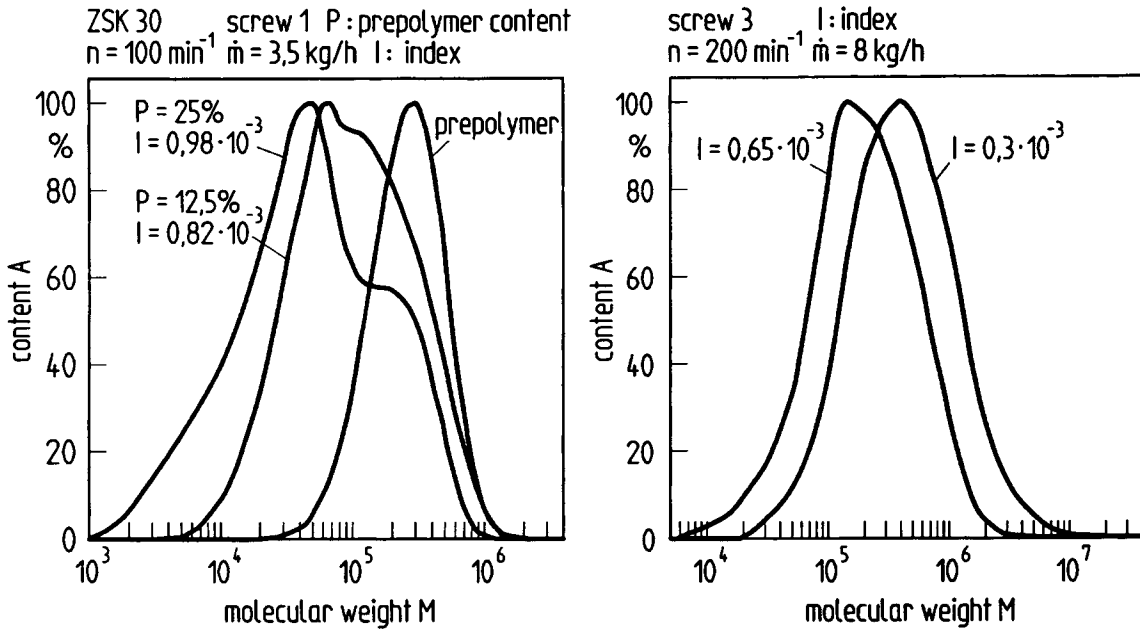


Figure 6 Molecular weight distribution of polystyrene as a function of raw material and formulation.

bution. Figure 7 illustrates this situation once again using the example of the anionic polymerization of monomer styrene in the extruder.

The number-average molecular weight can be varied within wide limits via the ratio of the mass flow rates of initiator and monomer (index I). The measured number-average molecular weights correlate extremely well with calculated molecular

weights. The number-average molecular weight is calculated from eq. (1):

$$\bar{M}_n = \frac{m_{\text{mono}}}{n_{\text{init}}} = \frac{n_{\text{mono}} M_{\text{init}}}{I M_{\text{mono}}} = \frac{64.06}{I}$$

$$\text{Index: } I = \frac{\dot{m}_{\text{init}}}{\dot{m}_{\text{mono}}}$$

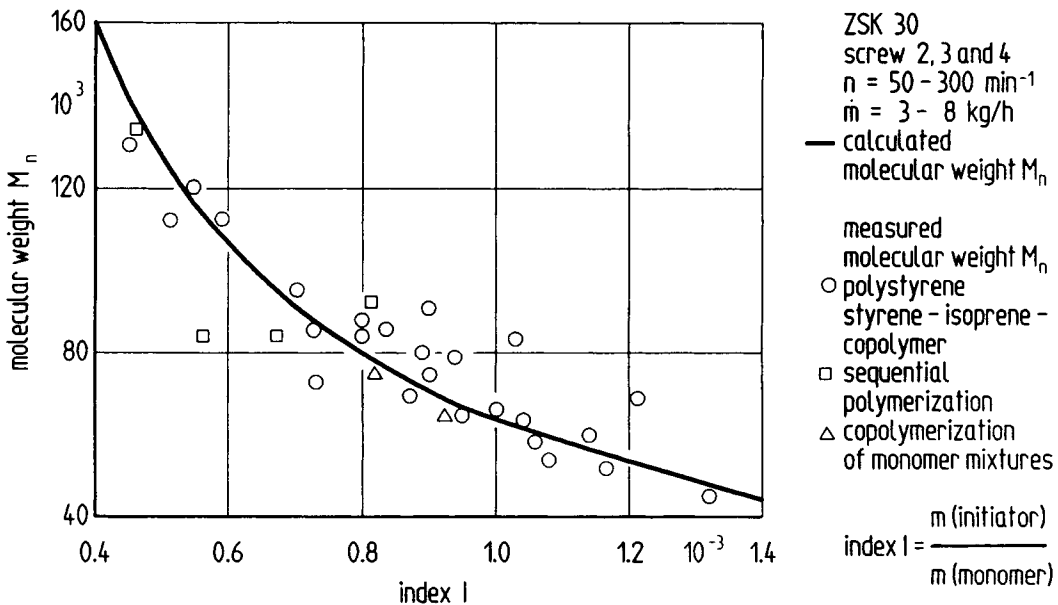


Figure 7 Number-average molecular weight as a function of formulation.

m : mass [g]; n : number of moles; M : molar mass [g/mol]; \dot{m} : mass flow [g/h]; mono: monomer; and init: initiator.

Deviations between calculated and measured weights are attributable to slight impurities and to the not precisely measurable, very low initiator mass flow rate. The weight-average molecular weight and, hence, the nonuniformity cannot be precalculated, as these parameters are influenced by the thermal and mechanical melt load during and after polymerization (see Sections 3.3 and 3.4).

Copolymerization of Monomer Mixtures

Copolymerization of styrene-isoprene mixtures produces diblock copolymers with a statistical styrene-isoprene copolymer block and a long polystyrene block [poly(isoprene-*co*-styrene)-*b*-styrene]. The fact that no styrene-isoprene block copolymers are formed shows that the difference between the copolymerization parameters under the reaction conditions in the extruder is considerably smaller than under the conditions described in Refs. 19 and 20 where the isoprene is polymerized first while the styrene polymerization starts only after consumption of the isoprene.

The existence of a statistical copolymer segment is revealed by the results of nuclear magnetic resonance analysis (NMR) and of ozonolysis. NMR data show a considerable amount of short polystyrene segments (less than 3 monomer units) in the polymer obtained from monomer mixtures, but not in the sequentially polymerized product. The bimodal

molecular weight distribution of the ozonolysis product and the decrease of the molecular weight with increasing isoprene content (Fig. 8) also indicate that the macromolecules consist of a statistical styrene-isoprene block followed by a pure polystyrene block. This diblock structure is also confirmed by the phase separation that is seen in the transmission electron micrograph in Figure 9. The very fine distribution of the polyisoprene phase with particle diameters of approximately $0.05 \mu\text{m}$ leads to transparent styrene-isoprene copolymers.

The analysis of the polyisoprene microstructure using the NMR method showed that the reaction product consists of 50% 1,4-*cis*, 40% 1,4-*trans*, and 10% 3,4-isomer. The number-average molecular weight of the copolymer can, as already shown for the styrene homopolymer, be predetermined by the formulation (see Fig. 7).

In summary, we can conclude from the results of the analyses that in the first phase of polymerization styrene and isoprene polymerize statistically. In the second phase of polymerization (which begins after the consumption of the isoprene), a pure polystyrene block is formed. The lower the initial concentration of the isoprene in the monomer mixture, the longer the polystyrene block.

Sequential Polymerization of Styrene and Isoprene

The sequential polymerization of styrene and isoprene exploits the existence of "living polymer

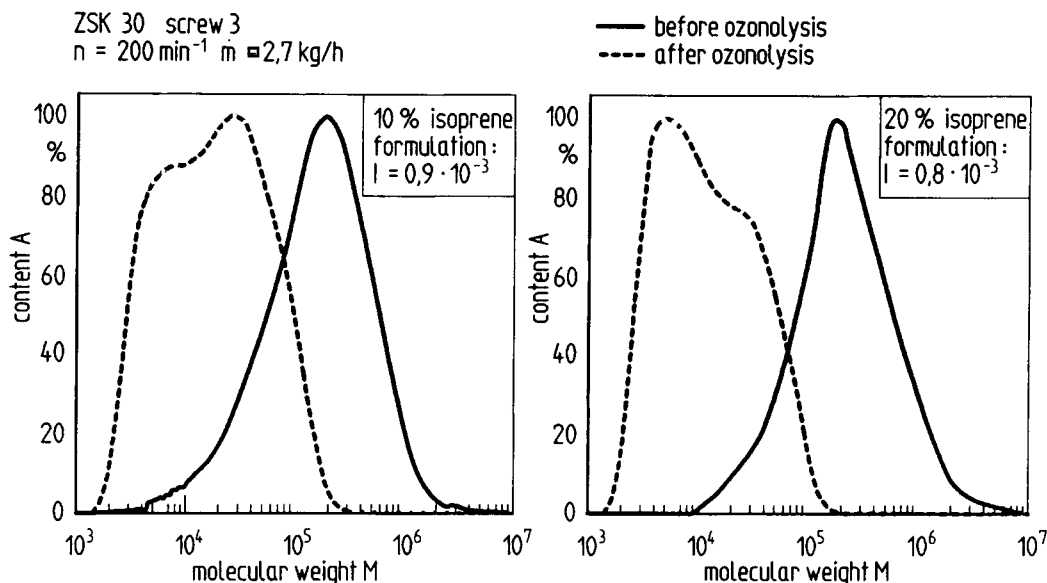


Figure 8 Ozonolysis of styrene polymers (copolymerization of monomer mixtures).

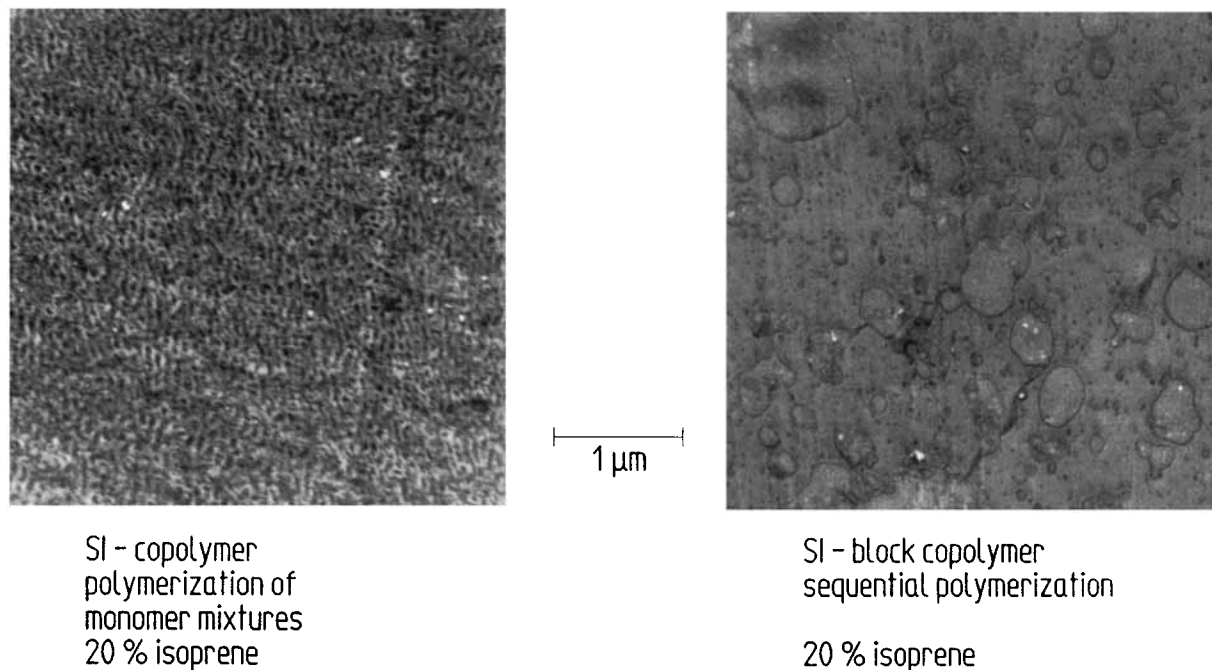


Figure 9 Morphology of various styrene polymers.

chains” to attach further monomers. If the sequential polymerization is performed in the extruder, a blend of styrene-isoprene block copolymers [poly(styrene-*b*-isoprene)] and partly cross-linked low molecular weight polyisoprene is produced. Both the synthesis and the cross-linking of polyisoprene is a result of the high reaction temperatures, which obviously lead to side reactions.

The existence of copolymer blocks is confirmed by the results of the ozonolysis (Fig. 10). The lowering of the molecular weight of the polymers upon ozonolysis while leaving the molecular weight distribution more or less unchanged indicates that the polymers have an AB block structure. This assumption is further backed up by the observation that the molecular weight of the ozonolyzed polymer is

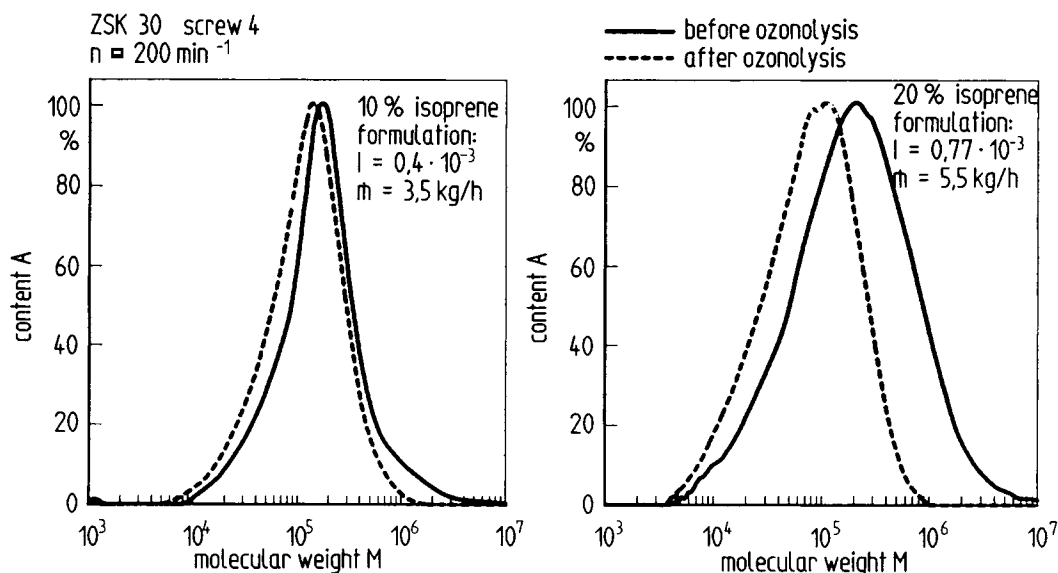


Figure 10 Ozonolysis of styrene polymers (sequential addition of styrene and isoprene).

lower the higher the isoprene content of the original polymer was.¹⁵

NMR measurements show that the block lengths are considerably more uniformly distributed than after copolymerization of monomer mixtures. Furthermore, the recorded NMR spectra also provide information on the microstructure of the polyisoprene sequences. After sequential polymerization in the extruder, the polyisoprene consists of approximately 60% 1,4-*cis*, 30% 1,4-*trans*, and 10% 3,4-isomers. 1,2-Linkages are not found.¹⁵ These results correlate the results quoted in Ref. 21. The polyisoprenes of low molecular weight not bound to polystyrene were detected by gel permeation chromatography (GPC). The tests of solubility and the ¹H-NMR spectra indicate a partial cross-linking of the polyisoprene content. Figure 9 shows the transmission electron micrograph of an ultrathin section of a sequentially polymerized sample. Compared with the copolymerization of monomer mixtures, the sequential polymerization results in a polymer with a coarser two-phase structure. The dark polyisoprene phase contrasted with OsO₄ forms particles with a diameter of 0.1–0.7 μm. As a result of these larger particle diameters, the sequentially polymerized molding compounds are white and not transparent. The number-average molecular weight of the styrene–isoprene block copolymer is determined by the percentage of added initiator (see Fig. 7).

3.3. Residence Time and Structure

The average residence time and residence time distribution are both determined by the production pa-

rameters of screw speed, and mass flow rate, by the screw geometry, and by the rheological behavior of the melt. In view of the complex and time-consuming determination of residence time spectra during these experiments, the calculated average residence time offers a simple method of determining the influences of the residence time on the product quality.

The relationship between the average residence time, the weight- and number-average molecular weight, and the polydispersity U ($U = M_w/M_n - 1$) is shown in Figure 11. To distinguish between the effect of shear and residence time, the data in this figure are all for samples that have been subjected to a comparable shear stress. With practically constant mechanical melt loading, the anionically polymerized styrene exhibits no degradation phenomena over the varied residence time range.

Investigations to clarify the relationship between residence time distribution and molecular weight distribution have shown that there is no relationship between these two parameters.¹⁵ The molecular weight distribution is determined primarily by the shear stress on the reaction melt during and after polymerization.

3.4. Shear and Structure

An important process parameter influencing the shear is the amount of material in the extruder. In conjunction with the screw geometry and the selected variables of speed and mass flow rate, it determines the shear energy applied to the material.

To characterize the influence of the screw geometry on the mixing effect, screw 2 (see Fig. 3)

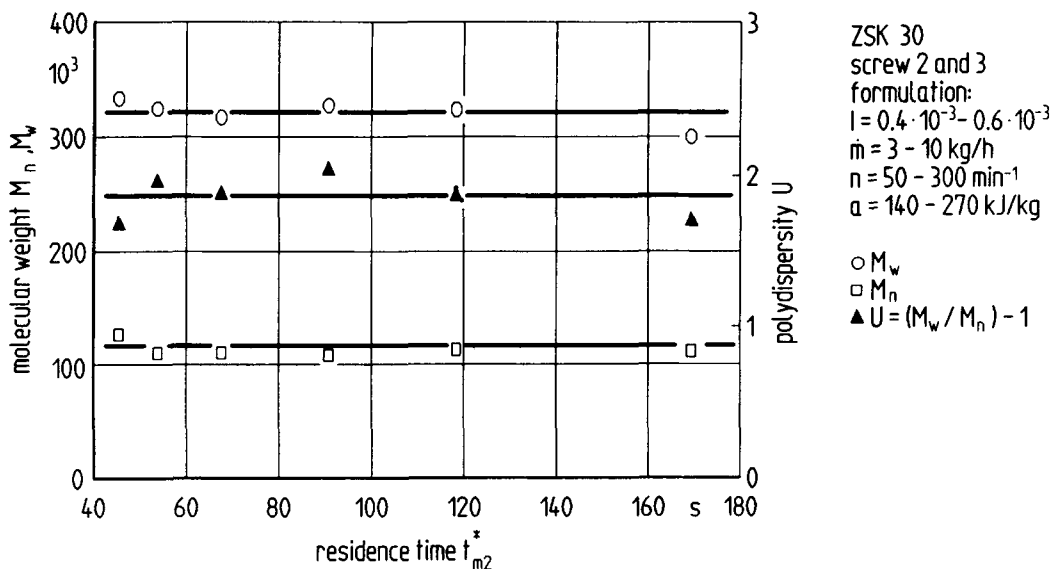


Figure 11 Effect of the residence time on the molecular weight distribution of polystyrene.

was configured with different transport and mixing elements in the first part of the polymerization zone. Samples were taken at the end of the polymerization section after a screw length of 135 mm. We deliberately dispensed with a subsequent long metering zone in order to avoid an additional shear load after polymerization. The elements with a pitch of $H = 20$ mm showed the most homogeneous mixing results over the varied speed range (Fig. 12). Kneading blocks KB 28 45°R with a forced conveying action produced the styrene polymers with the fewest inhomogeneities.¹⁵

Apart from the mixing homogeneity of initiator and monomer, the influence of the mechanical load on the melt with increasing shear grows in importance, particularly after polymerization. As the results of the process analysis show, constituents of a high molecular weight, in particular, are preferentially degraded where mechanical loads are imposed on the melt, resulting in a more homogeneous product. GPC analyses of styrene polymers show a noticeable decrease in the weight-average molecular weight with increasing shear load (Figs. 13 and 14). In contrast to the weight-average molecular weight, the number-average molecular weight is not influenced by the mechanisms of the mechanical melt load. The process parameters, shear deformation (distributive mixing), and specific drive power or specific energy conversion (dispersive mixing) can be used to describe the melt load, since they illustrate comparable functional relationships between shear and structure (Figs. 13 and 14).

If we consider the inhomogeneities of the styrene polymers produced in the extruder, it is noticeable that a distribution very close to the Poisson distribution ($U = 0.02-0.2$), as in the ideal case of the anionic styrene polymerization, could not be shown for any of the examined samples.

The broader molecular weight distribution of the polymers produced in the extruder is attributable to the fact that side reactions cannot be ruled out at melt temperatures of 200°C. A less than ideal mixing of monomer and initiator (see Fig. 12) and a deactivation of the initiator due to impurities can also lead to a broader molecular weight distribution.

3.5. Mechanical Properties

The material polystyrene owes its significance to the fact that, e.g., via elastomer modification, its general properties can be varied within wide limits. The all-important factor for the use of toughened polystyrenes is the ideal combination of rigidity and toughness. A very wide range of polystyrene types can be adapted to particular applications through a specifically selected composition.

This adaptation, however, demands intensive material development. As the objective of this project was to concentrate on the further development of the continuous polymerization process for styrene polymers, we do not intend to go into a detailed structure/property analysis here. Only such mechanical and thermal performance characteristics of the material are discussed below that lead to a

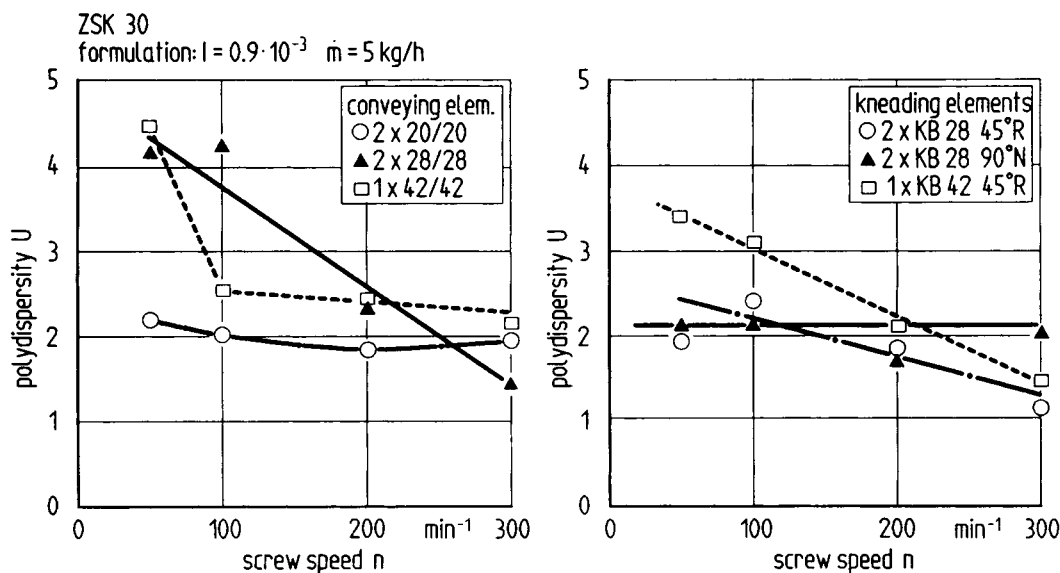


Figure 12 Effect of the screw geometry and the shear stress on the polydispersity of polystyrene.

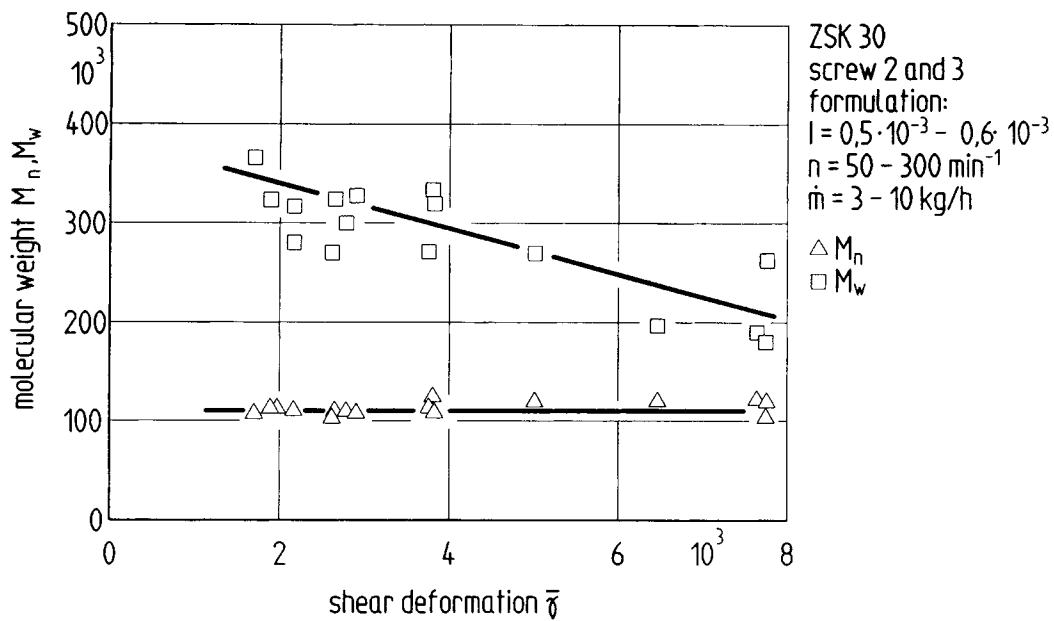


Figure 13 Molecular weight of polystyrene as a function of the shear deformation.

further clarification or confirmation of the structure of the styrene-isoprene copolymers produced.

The curve of the Young's modulus (E') measured using dynamic mechanical analysis provides very good insight into the mechanical performance characteristics of multiphase systems. Comments can be made as to the multiphase structure on the basis of these curves. According to Ref. 22, the curve of the modulus E' for a copolymer with the components A

and B varies with temperature between the limiting values a and d (Fig. 15).

With regard to the structure, the following information can be drawn from the curves in Figure 15:

- Curve a: Components A and B are completely compatible; no phase separation takes place.
- Curve b: Intermediate stage at which the partly

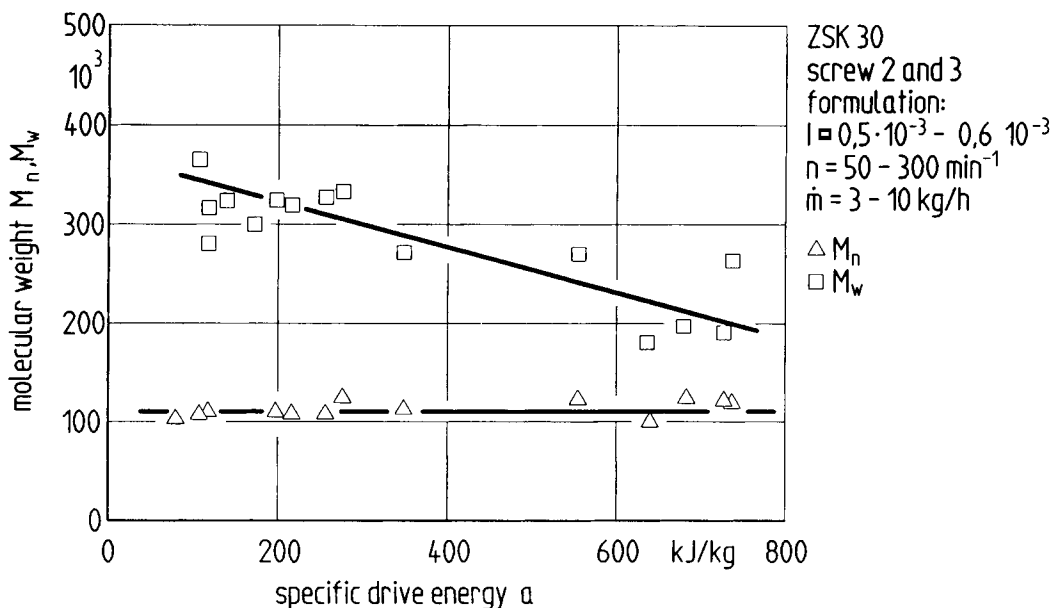


Figure 14 Molecular weight of polystyrene as a function of the specific drive energy.

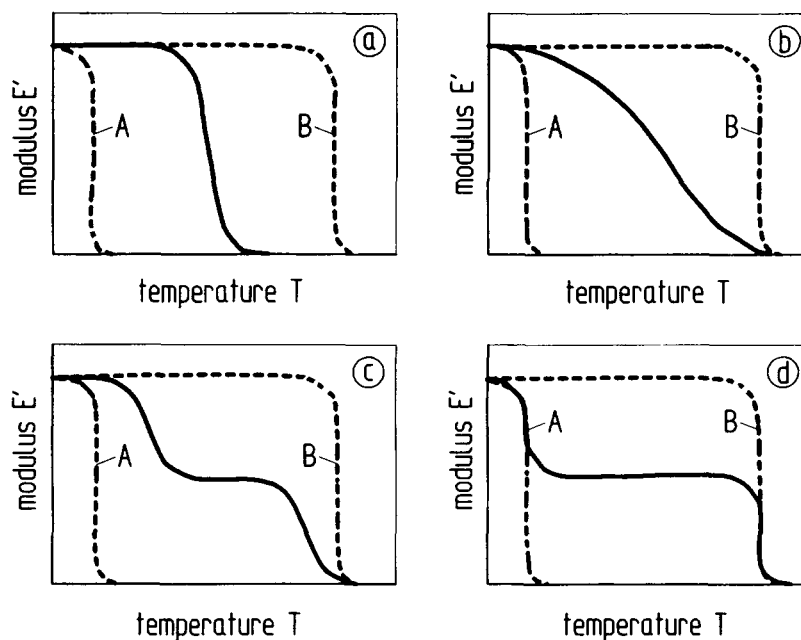


Figure 15 Temperature dependence of the storage modulus E' for different copolymers.

compatible components exist without phase separation.

Curve c: Intermediate stage with phase separation, but with diffuse phase boundary. The narrower the horizontal curve of the modulus, the more diffuse are the phase boundaries.

Curve d: Components A and B are completely incompatible and a complete phase separation with sharp phase boundaries takes place.

Figures 16 and 17 show the functional relationship between modulus E' and temperature for styrene polymers produced by different methods. The polymerization of monomer mixtures results in materials that exhibit a behavior that is to be classified between cases b and c (Fig. 15). With increasing isoprene content, the modulus shifts toward curve c.

The modulus curves for the samples synthesized by sequential polymerization lie between curves c and d (Fig. 15), whereby with increasing isoprene content, they approach the limiting curve d. As far as the copolymer structure is concerned, this is a confirmation of the results presented in section 3.2.

The polymerization of monomer mixtures results in diblock copolymers with a statistical styrene copolymer block and a long polystyrene block. The sequentially produced polymers consist predominantly of styrene-isoprene block copolymers. A further component of the polymer is a polyisoprene of low molecular weight.

For the statistical copolymers, glass transition temperatures are obtained that lie between those of the corresponding homopolymers (Fig. 18). Consequently, in this case, material combinations can be set only hard/brittle or soft/tough. The achievement of a very high toughness while at the same time maintaining the hardness is not possible.²³

This combination of toughness and rigidity that is ideal for many applications can only be achieved using block or graft copolymers. In contrast to the statistical copolymer, the storage modulus for block copolymers produced in the extruder drops in two stages, in each case in the area of the glass transition temperatures between the hard and soft phases. With isoprene contents of up to 15%, the material rigidity drops only slightly when the toughness is increased (Fig. 17).

3.6. Thermal Properties

Because of their different structure characteristics, the styrene copolymers produced in the extruder using various methods exhibit different behavior on exposure to heat. With isoprene contents of up to 15%, the diblock copolymers with a statistical styrene-isoprene copolymer block and a long polystyrene block exhibit only one glass transition temperature, which, as was to be expected, shifts toward lower temperatures with increasing rubber content. With isoprene contents of more than 20%, both glass

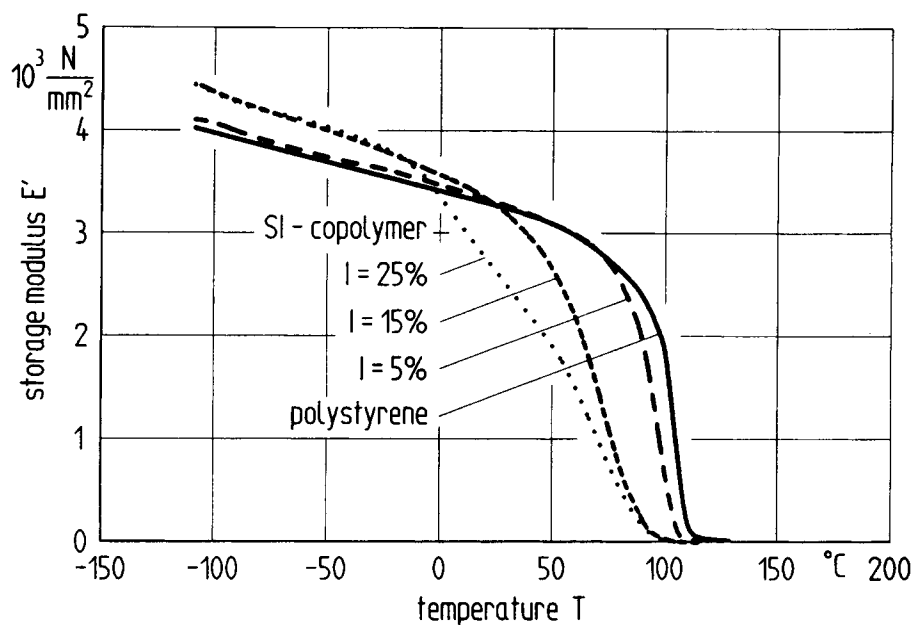


Figure 16 Temperature dependence of the storage modulus E' for various SI-random copolymers.

transition temperatures of the diblock copolymer can be seen (Fig. 18). With an isoprene content of 25%, the glass transition temperature of the statistical styrene-isoprene copolymer block is already 100°C below the glass transition temperature of polystyrene. The second glass transition tempera-

ture of the polystyrene block lies approximately 25°C below that of the pure polystyrene. This allows us to conclude that the polystyrene blocks contain small quantities of isoprene. In contrast to the statistical copolymers, the styrene-isoprene block copolymers exhibit two quite separate glass transition

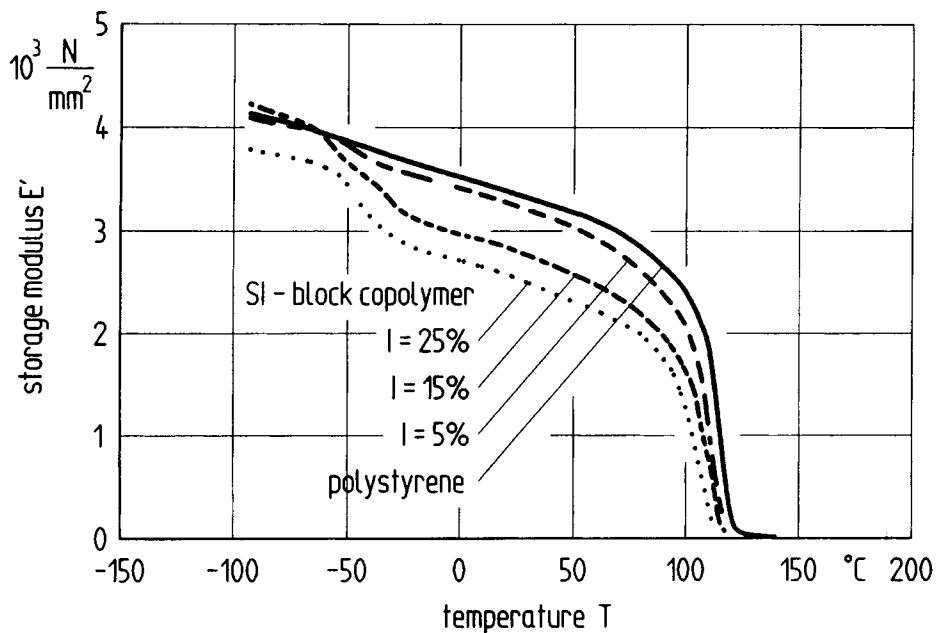


Figure 17 Temperature dependence of the storage modulus E' for various SI-block copolymers.

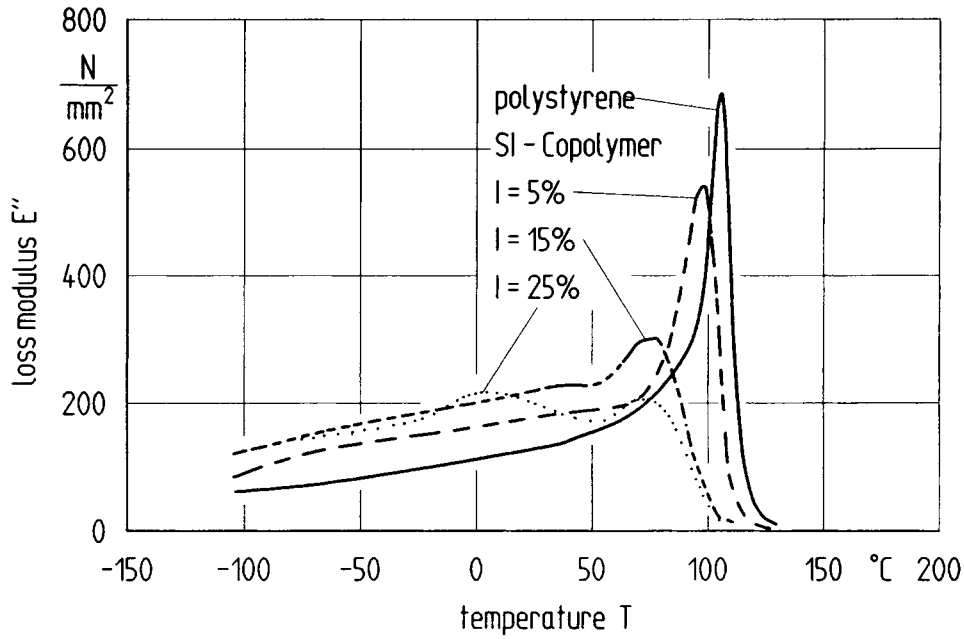


Figure 18 Glass transition temperature for various SI-random copolymers.

temperatures between hard and soft phases. With increasing isoprene content, only the signal identifying the polyisoprene glass transition becomes more intense. The glass transition temperature of the polyisoprene soft phase for all sequentially polymerized samples is -50°C ; that of the polystyrene hard phase is 110°C (Fig. 19).

4. FUTURE PROSPECTS

Using the production of styrene polymers as an example, the process development presented here illustrates the wide range of potential applications offered by reactive extrusion. Thanks to the variety of possible comonomers and bifunctional or multi-

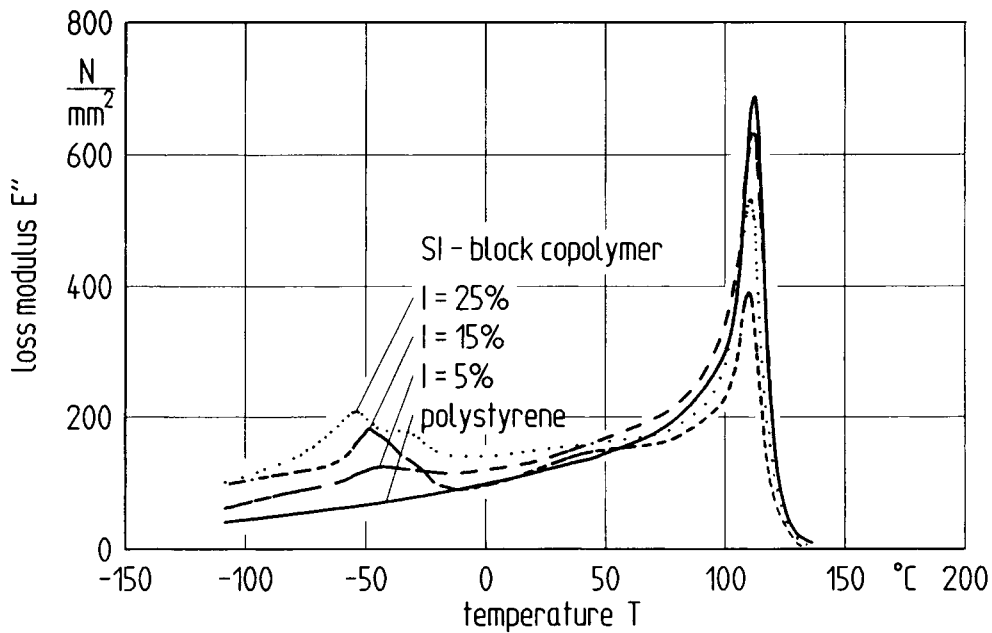


Figure 19 Glass transition temperatures for various SI-block copolymers.

functional coupling reagents, this basic investigation on the "living polymerization of polystyrene" offers technically and economically interesting aspects for the production of copolymers and/or modified homopolymers. The technical and economic aspects of the industrial application can be summarized as follows:

The polymer synthesis and modification can be performed without the use of solvents (*in situ*). The technically complex and costly evaporation and refining of the solvents is eliminated. Modification of the polystyrene can be performed after synthesis directly in the melt. The material only has to be melted once, i.e., the polymer melt has only one thermal history.

The combination of individual processing steps or the immediate linking of further processing steps to the continuous polymer synthesis or modification results in more favorable production conditions with respect to energetical aspects. The production process can be streamlined and carried out more quickly as the remelting of intermediate products is eliminated.

As with conventional extrusion processes, the product properties can also be influenced during reactive extrusion by the choice of appropriate machine and process parameters. The additional parameter "material" allows the product properties to be adapted specifically to the application by the use of different raw materials, formulations, and additives even with small material batches.

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ABBREVIATIONS

a	specific drive energy	kJ/kg
A	polymer content (GPC)	%
E'	storage modulus	N/mm ²
E''	loss modulus	N/mm ²
γ	shear deformation	
I	index: m (initiator)/ m (monomer)	
I	isoprene content	%
L	screw length	mm
m	mass	kg
m	mass flow, throughput	kg/h

M	molecular weight	g/mol
n	screw speed	L/min
P	prepolymer content	%
t_{m2}	residence time, calculated	s
T	temperature	°C
U	polydispersity: $\bar{M}_n/\bar{M}_w - 1$	
X	conversion	%

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