

## 7 Chapter 3

# Polystyrene and Styrene-copolymers Applications, Synthesis and Kinetics

Styrene is the main component of all reactions in this thesis. This monomer is chosen as it is versatile and well-known. Styrene is polymerised in the extruder by means of a radical mechanism. In most experiments, one or two comonomers are added to styrene yielding co- and terpolymers. This chapter gives an overview of the applications of polystyrene and styrene copolymers. Furthermore, the polymerisation rates of styrene and styrene-*n*-butylmethacrylate are evaluated theoretically and experimentally.

### 3.1 Applications

#### 3.1.1 Styrene and polystyrene

Polystyrene is one of the most important polymers of today. Its popularity stems from the fact that it possesses many good properties, such as good processability, rigidity, transparency, low water absorbability, and that it can be produced at low costs. However, polystyrene has some disadvantages, such as sensitivity to chemicals and food materials with high oil content, poor UV-resistance and brittleness, which limit its applications. Polystyrene is mainly used in the packaging industry (Ku 1988a, b).

The monomer styrene is a very versatile monomer. It can be polymerised by various mechanism such as free radical-, cationic-, anionic-, and group transfer polymerisation. Moreover, styrene has the capability to create radicals, which makes thermal polymerisation possible. Styrene can also be used in all types of production processes for polymerisation. The most common methods are emulsion-, suspension-, bulk- and solution polymerisation. The type of process determines the properties of the polymer produced. The most economical process for the production of polystyrene is a bulk-continuous process, in which around 10 - 20% ethylbenzene is added as a diluent to ease the flow. For expandable polystyrene, a suspension process is used.

In order to adjust properties, comonomers, chain transfer agents or crosslink agents are added to styrene before it is polymerised. Chain transfer agents are used to regulate the molecular weight, but are rarely used in bulk processes. T-Dodecyl mercaptane is often used as chain transfer agent. To crosslink the styrene polymer, divinylbenzene works very well, although other crosslink agents can also be used. Highly crosslinked polymers can only be produced batch-wise in bulk.

### 3.1.2. Blends of polystyrene

Since styrene is a cheap and versatile monomer, many copolymers and blends are produced with styrene as important component. In this section, some blends of polystyrene will be mentioned.

To improve the impact strength, polybutadiene is generally added to polystyrene, in the amount of 5 to 10 % (La Coste 1996). This reinforced polystyrene is known as high impact polystyrene (HIPS). The rubber component can be divided into two categories: homopolybutadiene and polybutadiene-styrene copolymers. Sometimes, saturated elastomers are used for reinforcement instead of polybutadiene. Polybutadiene can be blended physically to polystyrene, but more often it is added to styrene resulting in some grafting during processing. HIPS is applied for instance in packaging, television- and computer housings, and piping and tubing. SBR (styrene 23 %-butadiene-rubber) is a well-known rubber, which is mainly applied in automobile tyres (Ku 1988b). By changing the butadiene content in the polymer, the properties can be changed from a rubber to a rigid polymer. Block copolymers of styrene and butadiene are synthesised by anionic polymerisation and therefore quite expensive.

In order to improve the thermal properties of polystyrene, poly-2,6-dimethyl-1,4-phenylene oxide (PPE) is added to the polymer. PPE is a polymer with a glass transition temperature of 220 °C and this polymer is miscible with polystyrene. The addition of PPE to PS results in a polymer blend with a higher glass transition temperature than PS (Yee 1977).

### 3.1.3 Co- and terpolymers of styrene

The addition of another monomer to styrene is a second method to adjust the properties of the polymer. The most common copolymers of styrene are described in this section.

A very interesting polymer is obtained after the copolymerisation of styrene with maleic anhydride. The polymer finds applications in waxes and emulsifiers when it concerns a low molecular weight polymer, while the high molecular weight materials are used as engineering plastics, which are mostly rubber modified. The styrene-maleic anhydride copolymers are not only interesting from an industrial point of view, but also from a scientific point of view due to the fact that, after polymerisation, an almost perfectly alternating copolymer is obtained (Dodgson 1976, Ebdon 1986, Klumperman 1993, 1994).

Another copolymer that is often investigated is the styrene-methylmethacrylate copolymer. This polymer has a high transparency, an excellent UV-resistance and it is very suitable for injection moulding. The copolymer is applied in for example lamps, glazing and windows, but due to the high price, the market is limited. The polymer is produced in suspension or in bulk. On laboratory scale, a Lewis acid such as ethyl-aluminium sesquichloride or zinkchloride is added in order to increase the polymerisation rate and the alternating regulation of the polymer formed (Bailey 1972).

Resins of the copolymer styrene-acrylonitril (SAN) are used in applications such as automobile instrument lenses and as an additive to higher cost resins. Besides, the resins are used to modify and improve flow characteristics of ABS, PVC and other resins. Generally, a SAN-copolymer consists of 25 to 30% acrylonitril.

The most well-known terpolymer of styrene is the acrylonitril-butadiene-styrene terpolymer (ABS), which is used in applications such as pipes and fittings. The polymer is produced by dissolving polybutadiene into a monomer mixture of styrene and acrylonitril, which polymerises in an emulsion process. The terpolymer therefore consists of a polybutadiene backbone onto which styrene-acrylonitril copolymers are grafted.

In addition to commercial polymers, many co- and terpolymers of styrene are described in scientific literature. Examples of comonomers are acrylic acid, several acrylates and maleates. Terpolymers described in literature are styrene-methylmethacrylate-maleic anhydride and styrene-methylmethacrylate-maleic imide (Schmidt-Naake 1989).

### 3.1.4 The copolymerisation in this thesis

The copolymerisation described in this thesis is the copolymerisation of styrene (St) with *n*-butylmethacrylate (BMA). The latter component, which is extensively studied by Ganzeveld (1993), increases the rate of polymerisation, and it is chosen for reasons of safety and price. The product of this polymerisation is applied in speciality areas, such as the manufacture of recording tapes and toners for photocopiers. In this study, the St-BMA copolymerisation is the starting point of all experiments described. Changes of polymer melt viscosity or polymerisation rate are related to the St-BMA experiments described in chapter 4. When St and BMA are mixed in the molar ratio 1:1, the polymer formed is transparent and has a glass transition temperature of about 30°C. Figure 3.1 shows the two monomers.

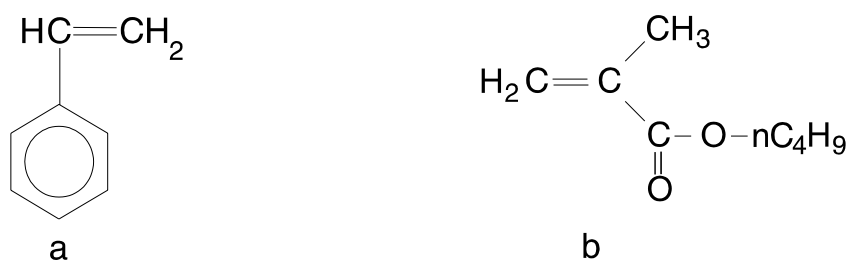


Fig. 3.1 *Styrene (a) and n-butylmethacrylate (b)*

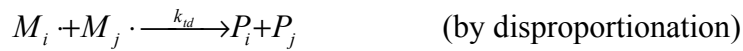
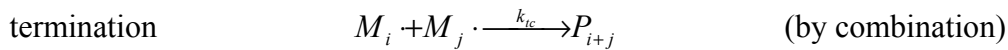
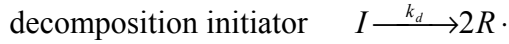
## 3.2 The polymerisation kinetics

### 3.2.1 The homopolymerisation

The polymerisations of styrene described in this thesis are free radical addition polymerisations. This means that after initiation, a polymer chain grows in a rather short time. The termination reaction excludes the polymer chain from further reaction.

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Under the normal assumption that the propagation rate is independent of the polymer chain length, the kinetic scheme for polymerisation is:



where  $k_d$ ,  $k_i$ ,  $k_p$ ,  $k_{tc}$  and  $k_{td}$  are the corresponding rate constants in every reaction step. When it is assumed that the radical concentration is constant (the quasi steady state approximation) the rate of polymerisation is given by (Bamford 1976):

$$v_p = -\frac{d[M]}{dt} = k_p \sqrt{\frac{fk_d[I]}{k_t}} [M] \quad (3.1)$$

in which:

$$k_t = k_{tc} + k_{td}$$

The molecular weight of the polymer formed may change during polymerisation. The molecular weight of the momentarily formed polymer is given by:

$$M_{mom} = \frac{\text{probability of propagation}}{\text{probability of termination}} = \frac{k_p[M \cdot][M]}{k_t[M \cdot]^2} = \frac{k_p}{\sqrt{fk_d k_t}} \frac{[M]}{\sqrt{[I]}} W_m \quad (3.2)$$

Equation 3.2 neglects the effect of chain transfer to the monomer and assumes a termination reaction by combination. Although equation 3.2 gives a good indication of the effect of the initiator concentration on the molecular weight of the momentarily formed polymer, it can not be used for predicting the molecular weight of the polymer formed after complete reaction. The reason is that the ratio of initiator concentration and monomer concentration may change during polymerisation.

When the polymerisation is finished, the number average molecular weight of the polymer can be calculated by means of:

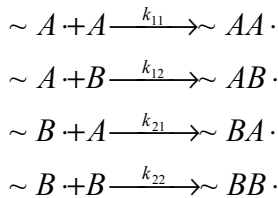
$$M_n = \frac{[M]_0 - [M]}{f([I]_0 - [I])} W_m \quad (3.3)$$

Equation 3.3 also assumes a termination reaction by combination. This equation states that a doubling of the initiator concentration results in a halving of the number average molecular weight of the polymer, when the conversion is not influenced by the initiator concentration. However, since a higher initiator concentration generally results in a higher conversion, the influence of the initiator concentration on molecular weight is reduced.

In bulk polymerisations, deviations from equation 3.1 occur when a certain degree of conversion is reached. These deviations are caused by a strong increase of the viscosity during polymerisation, as a result of which the polymer chain radicals can not diffuse easily through the viscous medium, leading to a decreased termination rate  $k_t$ , since this rate is primarily diffusion controlled. The propagation rate  $k_p$  is, except for very high conversions, independent of the viscosity of the polymer melt, since it is chemically controlled. As a result of these two effects, the overall polymerisation rate increases. This phenomenon is known as the Trommsdorff effect or gel effect (Trommsdorff 1948).

### 3.2.2 The co- and terpolymerisation

In the case of a copolymerisation of two monomers A and B, the propagation step consists of at least four different reactions:



where every reaction has its own propagation rate constant ( $k_{11}$ ,  $k_{12}$  etc.)

When it is assumed that the radical concentrations are constant, the well-known copolymerisation equation can be derived from the mass balance over every component. This equation is:

$$\frac{d[A]}{d[B]} = \frac{[A] r_1[A] + [B]}{[B] r_2[B] + [A]} \quad (3.4)$$

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

$$\begin{aligned} r_1 &= k_{11}/k_{12} \\ r_2 &= k_{22}/k_{21} \end{aligned} \quad (3.5)$$

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, which leads to a continuous shift of the composition of the copolymer formed. To describe the incorporation, a feed ratio and a incorporation ratio are defined as:

$$f_a = \frac{[A]}{[A] + [B]} \quad (3.6)$$

$$F_a = \frac{d[A]}{d[A] + d[B]} \quad (3.7)$$

The incorporation ratio  $F_a$  can be calculated if the values of  $r_1$  and  $r_2$  are known. The values for  $r_1$  and  $r_2$  can be roughly estimated by using the  $Q$ - and  $e$ -values according to Alfrey and Price (Alfrey 1947, Brandrup 1989):

$$r_1 = \frac{Q_1}{Q_2} \exp\{-e_1(e_1 - e_2)\} \quad (3.8)$$

These  $Q$ - and  $e$ -values are monomer properties. For styrene, the values are defined as  $Q_{St} = 1.0$  and  $e_{St} = -0.8$ , while the values for BMA are determined at  $Q_{BMA} = 0.82$  and  $e_{BMA} = 0.28$  (Brandrup 1989). By using equation 3.8, the reactivity ratios can be calculated at  $r_1 = 0.51$  and  $r_2$  is 0.74 (styrene is monomer A).

A more accurate method is the direct determination of the reactivity ratios. In literature, a number of studies is reported, which have studied the copolymerisation of St-BMA. The measurements in these studies show that  $r_1$  ranges from 0.56 to 0.74, while  $r_2$  lies between 0.47 and 0.64 (styrene is monomer A). When these reactivity ratios are compared to the ratios obtained by the method of Alfrey and Price, it can be seen that the  $Q$ - and  $e$ -values give a rather good prediction for St-BMA. However, studies in literature are performed at low temperatures. Since the temperature in the extruder is higher, we determined the reactivity ratios experimentally (section 3.3.2).

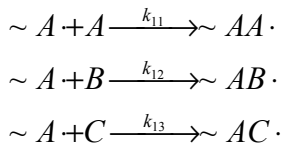
Besides the incorporation of the monomer in the polymer, the reactivity ratios can be used for describing the polymerisation rate. By using equation 3.5 and the propagation rate constants for the homopolymerisation, the average propagation rate constant for the copolymerisation is given by:

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$$k_{p,co} = \frac{1}{4}k_{11} + \frac{1}{4}\frac{k_{11}}{r_1} + \frac{1}{4}k_{22} + \frac{1}{4}\frac{k_{22}}{r_2} \quad (3.9)$$

This model for the copolymerisation described by equation 3.9 is defined as the terminal model. The model needs four propagation steps to describe the rate of copolymerisation, implying that only the last unit in the growing chain determines the reactivity. However, it is known in literature (Fukuda 1987) that for a styrene-methylmethacrylate system the expression for the propagation rate as in equation 3.9 is not sufficient to give a good description of the rate of polymerisation. Not only the last unit, but also the one before the last unit influences the reactivity. This effect is known as the penultimate effect. For a description of the incorporation ratio of the monomers, the reactivity ratios seem to be sufficient.

The theory for homo- and copolymerisation can be extended to the polymerisation in which three components react (Bamford 1976). In that case, the propagation rate consists of nine steps. For component A, the propagation is described by the following equations:



The ratio of the amount of A and B that react at a certain instant time is given by the following equation:

$$\frac{d[A]}{d[B]} = \frac{[A] \left( \frac{[A]}{r_{21}r_{31}} + \frac{[B]}{r_{21}r_{32}} + \frac{[C]}{r_{23}r_{31}} \right) \left( [A] + \frac{[B]}{r_{12}} + \frac{[C]}{r_{13}} \right)}{[B] \left( \frac{[A]}{r_{12}r_{31}} + \frac{[B]}{r_{12}r_{32}} + \frac{[C]}{r_{13}r_{32}} \right) \left( [B] + \frac{[A]}{r_{21}} + \frac{[C]}{r_{23}} \right)} \quad (3.10)$$

in which:

$$r_{12} = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_{21} = \frac{k_{22}}{k_{21}} \quad \text{etc.}$$

For the other components, similar equations can be derived. It should be noted that the quantity  $r_{12}$  means the binary reactivity ratios as obtained in the copolymerisations. In other words  $r_{12}$  is the same quantity as  $r_1$  used in equation 3.5. One more subscript is used to distinguish the several subsystems.

### 3.3 Experimental

Up to now, most of the kinetics studies concerning the copolymerisation of St with n-BMA are performed at low temperatures. Since the temperature in the extruder ranges from 120 to 160 °C, additional experiments were necessary to investigate the kinetics of the reaction and the reactivity ratios of the monomers.

#### 3.3.1 Thermal polymerisation of St-BMA

Styrene is able to polymerise thermally. Through a Diels-Alder-adduct, styrene produces radicals that can create polymer chains (Hui 1972, Husain 1978). Figure 3.2 shows the reaction mechanism.

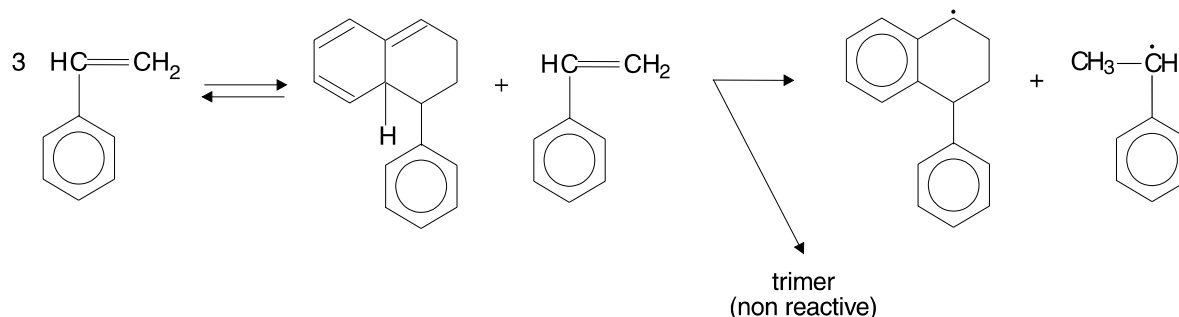


Fig. 3.2 *The formation of styrene radicals*

St-BMA-mixtures can also be polymerised thermally. The rate of thermal polymerisation at 135 °C is shown in figure 3.3, and it is compared to the data for the thermal polymerisation of styrene at 140 °C, as measured by Hui (1972).

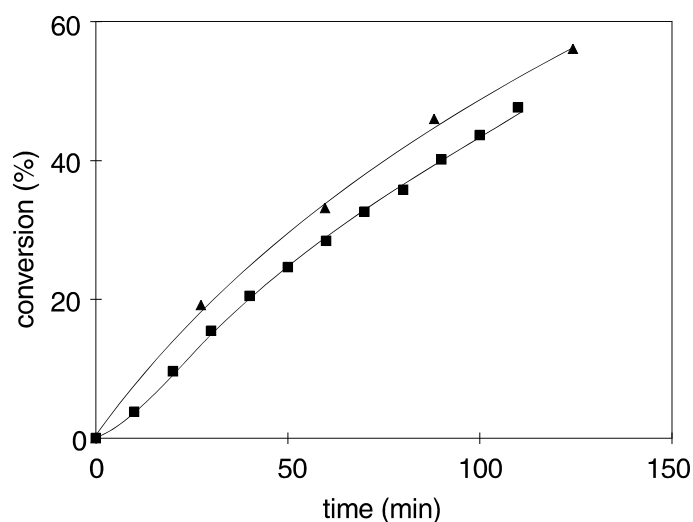


Fig. 3.3 *The thermal polymerisation of styrene (▲) and St-BMA (■)*

It can be seen that the thermal polymerisation rate of St-BMA is comparable to the thermal polymerisation rate of styrene. After one hour, a conversion of around 25% was obtained. The polymer formed at this temperature possesses a weight average molecular weight of 360 kg/mol, with a polydispersity  $P$  of somewhat less than 2. Pure BMA showed no thermal activity.

### 3.3.2 The reactivity ratios of St-BMA

The reactivity ratios were determined by performing a thermal polymerisation at 135 °C of several St-BMA mixtures, in which the mole fraction of styrene varied from 0.1 to 0.9. Except for the mixture with a styrene mole fraction of 0.1, all mixtures showed thermal polymerisation. When these mixtures had reached a conversion of 5 to 10%, the polymerisation was stopped by cooling the mixture rapidly. The polymer-monomer mixture was precipitated in methanol, after which the copolymer was carefully dried in a vacuum oven. The different copolymers were analysed by elemental analysis. The determination of the carbon and oxygen content in the copolymer gave the amount of styrene in the copolymer. The results are shown in figure 3.4.

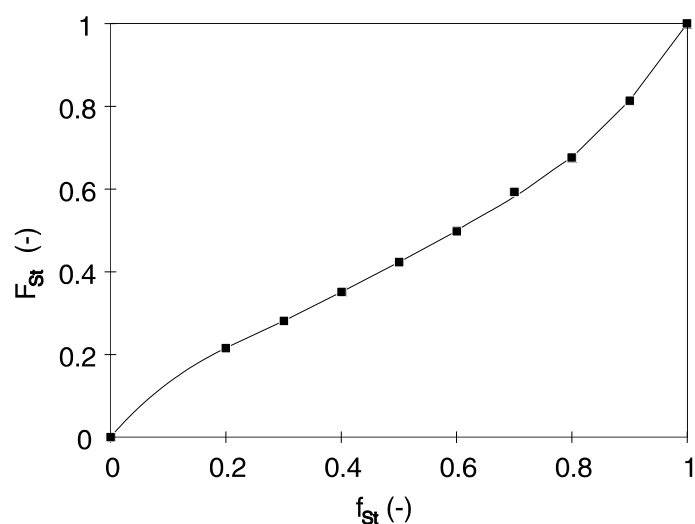


Fig. 3.4 *Influence of the fraction styrene in the monomer feed on the fraction styrene in the copolymer formed*

By using the method of Kelen-Tüdös (Kelen 1975, 1980, Tüdös 1976), the reactivity ratios were determined at  $r_1 = 0.40 \pm 0.03$ , and  $r_2 = 0.86 \pm 0.03$  (styrene is monomer A).

When St and BMA are mixed in equal molar ratio, some composition drift is likely to occur during polymerisation. However, in all bulkpolymerisations, a transparent polymer was obtained, indicating no severe phase separation.

### 3.3.3 The polymerisation kinetics of St-BMA

The rate of copolymerisation of styrene with BMA was studied by using isothermal Differential Scanning Calorimetry (DSC). The conversion of the monomer was obtained by using the following expression:

$$\zeta(t) = \frac{\int_0^t \Delta H_r(t) dt}{\int_0^\infty \Delta H_r(t) dt} \quad (3.11)$$

By using equation 3.11, it was assumed that the maximum conversion was 100% and that the heat of polymerisation was linearly dependent on the conversion. Probably, these assumptions are not completely valid, but nevertheless the DSC-experiments are useful for comparing the rates of polymerisation of the different monomers and monomer mixtures.

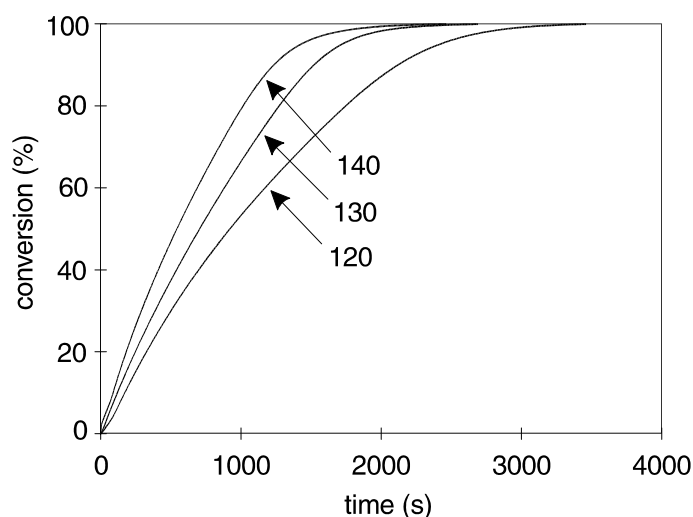


Fig. 3.5 The polymerisation of St-BMA at different temperatures

The results of the DSC experiments with a St-BMA monomer mixture are shown in figure 3.5. The amount of initiator added was about 5 mmol/mol monomer (table 3.1). The initiators used were Trigonox 29C50 (120 °C), Trigonox C (130 °C) and Trigonox 101 (140 °C). As expected, a higher temperature resulted in a faster polymerisation. Figure 3.6 is derived from figure 3.5. The quantity  $k_p/\sqrt{k_t}$ , also indicated as  $k_{ov}$ , is a pseudo-first order polymerisation rate constant when it concerns a homopolymerisation. The quantity gives an averaged polymerisation rate in case of a copolymerisation. The expression for  $k_{ov}$  can be derived from equations 3.1 and 3.11, and equals:

$$\frac{k_p}{\sqrt{k_t}} = k_{ov} = \frac{d\zeta}{dt} \frac{1}{\sqrt{fk_d[I]}} \quad (3.12)$$

The decomposition rate constant  $k_d$  can be calculated via:

$$k_d = k_{d0} e^{-E_d/RT} \quad (3.13)$$

in which the temperature T is expressed in Kelvin. The initiator efficiency is assumed to be 1. The value for  $k_d$ , which differs for every initiator, can be calculated from relations given by Akzo-Nobel, the supplier of the initiators (table 3.2).

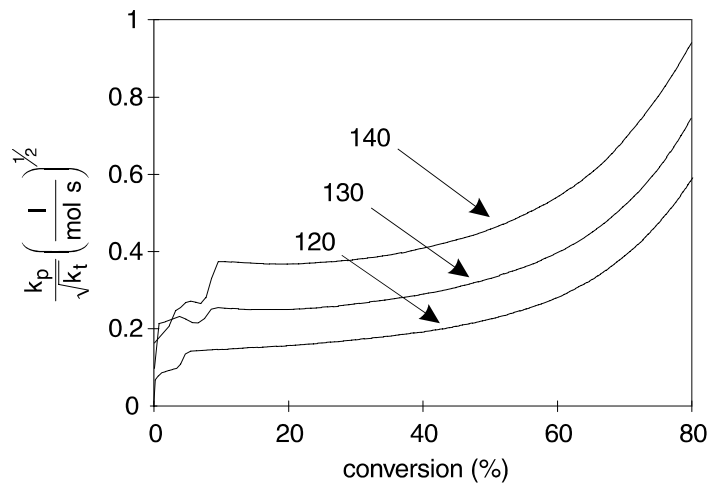


Fig. 3.6 The polymerisation rate constant versus the conversion

Figure 3.6 shows the  $k_{ov}$  versus the conversion of the monomers for the St-BMA copolymerisation. It can be observed that  $k_{ov}$  is not only dependent on temperature, but also on the conversion. The increase in polymerisation rate at higher conversion is a result of the gel effect. At low conversion, the rate of polymerisation is rather low, which is probably a result of the inhibitor, which was not removed in the DSC- and extruder experiments. Figure 3.6 shows that the effect of inhibitor is more pronounced at higher temperatures.

Figure 3.7 compares the rates of polymerisation for styrene, BMA and the copolymerisation. It can be seen that the copolymerisation is faster than the polymerisation of styrene, but significantly slower than the homopolymerisation of BMA. Just as in figure 3.6, the fastest reaction is mostly hindered by inhibitor effects. The gel effect is most pronounced in the case of BMA. The gel effect of styrene is comparable to the effect of the copolymerisation.

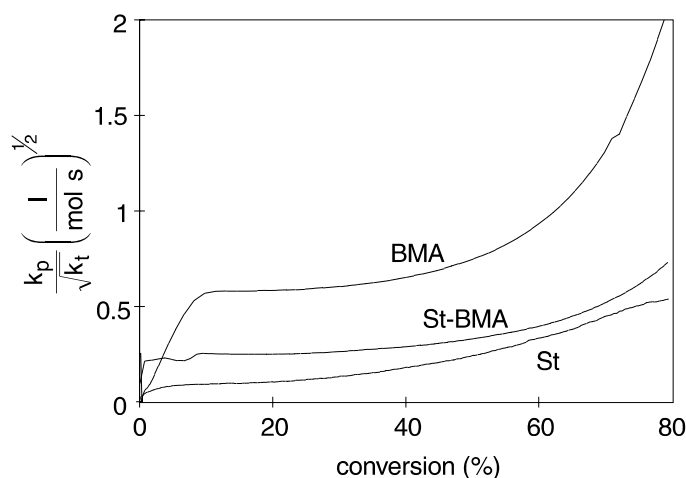


Fig. 3.7 Comparison of styrene, St-BMA and BMA

Table 3.1 shows the values for  $k_{ov}$  after 10% conversion for the polymerisation described in figures 3.6 and 3.7. After 10% conversion, the effect of the inhibitor can be neglected and the gel-effect is not important yet. The data for the  $k_{ov}$  for St and BMA, combined with the values for  $r_1$  and  $r_2$  can be used for a prediction of a value for the  $k_{ov}$  for the copolymerisation by using the terminal model. This  $k_{ov}$  can be calculated via:

$$k_{ov,co} = \frac{1}{4} k_{St,ov} + \frac{1}{4} \frac{k_{St,ov}}{r_1} + \frac{1}{4} k_{BMA,ov} + \frac{1}{4} \frac{k_{BMA,ov}}{r_2} \quad (3.14)$$

When the terminal model is used for describing the copolymerisation of St with BMA the average polymerisation rate constant is  $0.39 \text{ (l / mol s)}^{0.5}$ , when the monomers are mixed in the ratio 1:1. This is significantly more than 0.24 as found by the DSC experiments. This means that the terminal model does not describe the rate of copolymerisation correctly at high temperatures. To describe the rate of polymerisation more accurate, a penultimate model should be used (Fukuda 1987).

### 3.4 Conclusions

The copolymerisation of St-BMA is slower than the polymerisation of BMA, but significantly faster than the homopolymerisation of styrene. The terminal model is not sufficient for the description the copolymerisation when using the reactivity ratios measured. The reactivity ratios indicate that when St and BMA are mixed in equal molar amounts, some composition drift is likely to occur. However, the St-BMA-copolymer was completely transparent in all experiments, indicating no severe phase separation due to composition drift. The rate of thermal polymerisation of St-BMA is comparable to that of styrene itself. The BMA used showed no thermal activity.

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Table 3.1 *The rate of polymerisation for St, BMA and St-BMA-copolymerisation.*

	T (°C)	initiator	[I] (mmol/mol M)	$k_{ov}$ (at 10% conversion)
Styrene	130	Trigonox C	5.3	0.095
St-BMA	120	Trigonox 29C50	5.0	0.14
St-BMA	130	Trigonox C	5.0	0.24
St-BMA	140	Trigonox 101	4.6	0.37
BMA	130	Trigonox C	4.2	0.57

Table 3.2 *Decomposition rate constants and temperatures belonging to the half life time  $t_{1/2}$  indicated for the initiators used in this thesis*

	$k_{d0}$ (1/s)	$E_a$ (kJ/mol)	$t_{1/2} =$ 0.1 hr	1 hr	10 hr
BPO (Lucidol)	6.94 e13	122.35	113 °C	91 °C	72 °C
Trigonox 29C50	7.59 e13	127.52	128	105	85
Trigonox C	2.26 e16	151.59	142	122	103
Trigonox 101	1.68 e16	155.49	156	134	115
Trigonox T	1.17 e15	146.98	159	136	115

## Nomenclature

$e$	constant for determining reactivity ratios	-
$E_a$	activation energy	J/mol
$f$	initiator efficiency	
$f_a$	mole fraction of monomer A in the feed	-
$F_a$	mole fraction of component A in the polymer	-
$\Delta H_r$	heat of polymerisation	J/kg
$I$	initiator	
$k_d$	initiator decomposition rate constant	1/mol s
$k_{d0}$	pre-exponential factor for the decomposition of the initiator	1/s
$k_i$	initiation rate constant	1/mol s
$k_{ov}$	pseudo first order polymerisation rate constant	$\sqrt{(1/\text{mol s})}$
$k_p$	propagation rate constant	1/mol s
$k_t$	overall termination rate	1/mol s
$k_{tc}$	termination by combination rate constant	1/mol s
$k_{td}$	termination by disproportionation rate constant	1/mol s
$M$	monomer	

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$M\cdot$	total amount of growing polymer chains	
$M_i\cdot$	growing radical of chain length $i$	
$M_n$	number average molecular weight	kg/mol
$M_w$	weight average molecular weight	kg/mol
$P$	polydispersity $M_w/M_n$	-
$P_i$	polymer of chain length $i$	
$Q$	constant for determining reactivity ratios	-
$r_1, r_2$	reactivity ratios	-
$r_{11}$	reactivity ratio used in the terpolymerisation kinetics equations	-
$R$	gas constant (8.314)	J/mol K
$R\cdot$	initiator radical	
$t$	time	s
$T$	temperature	K
$v_p$	polymerisation rate	mol/l s
$W_m$	molecular weight of monomer M	kg/mol
$\zeta$	conversion	-
[ ]	concentration	mol/l
[ ] <sub>0</sub>	concentration before polymerisation	mol/l

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