Modification of polymers in the melt

Gudrun Schmidt-Naake[*], Hinnerk Gordon Becker, Marcus Klak

Institut für Technische Chemie, Technische Universität Clausthal

Erzstraße 18,D-38678 Clausthal-Zellerfeld,Germany

SUMMARY: The kinetics of polymer-analogue reactions in the melt are discussed with the example of conversions of styrene copolymers including anhydride or nitrile groups in the side chain and additives with amino and hydroxyl groups. Poly(styrene-co-maleic anhydride) has been modified with primary alcohols and amines, secondary amines, diamines, amino acids and amino alcohols. Poly(styrene-co-acrylonitrile) has been modified with various amino alcohols.

Introduction

To widen their application window, chemical modifications of the industrial standard polymers are necessary. Polymer modification in the melt can be performed through batch-mixing or extrusion (continuos). The reactive extrusion combines the chemical reaction like, for example, polymerisation or polymer modification (polymer-analogue reactions) with mechanical processes like melting, formation of polymer blends, recreation of hypermolecular structures and the forming process. By way of contrast to chemical reactions in solution or suspension, reactive extrusion needs no solvents or detergents and even no precipitation or removal of the solvent. The reaction velocity is very much higher than in solution due to the high reactant concentration and the higher temperatures in polymer melts. Otherwise a chemical process which should be performed by reactive extrusion or melt-batch-mixing has to achieve special requirements like miscibility of all reaction components, the ability to achieve a homogenous mixture and the control over thermal degradation. An important point is the analysis and control of the molecular weight to avoid serious polymer degradation. Furthermore the transformation of a reaction, well known in solution, into molten state has to take into account, that the processing parameters, which have a high influence on the reaction have to be adapted. Therefore the analysis of the kinetic course of the reaction under the new process conditions is necessary.In the last 15 years the reactive extrusion has obtained more and more industrial acceptance. There are more than 100 patent applications since 1980. The aim of our work [1-6)] is the investigation of polymer analogue reactions between styrene

copolymers with anhydride or nitrile groups in the polymer side chain and additives with hydroxyl- and amino-groups.
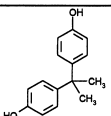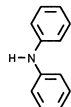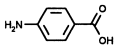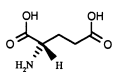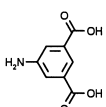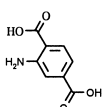
Materials:

a)Conversions with poly(styrene-co-maleic anhydride):

We used four different compositions of poly(styrene-co-maleic anhydride) (S/MA) with 16 wt% MA (S/MA-16), 24wt% MA (S/MA-24), 32 wt% MA (S/MA-32) and with 49wt% MA (S/MA-49). The S/MA-16 showed a glass transition temperature (Tg) of 138 °C, the S/MA-24 of 144°C, the S/MA-32 of 152 °C and the S/MA-49 of 160°C. The polymers were purchased as industrial products and used without further purification. Even the used additives (see Table 1) were not further purified.

b) Conversions with poly(styrene-co-acrylonitrile):

The poly(styrene-co-acrylonitrile) (S/AN) contained 23,8 wt% (38 mole%) acrylonitrile (AN) and had a weight average molecular weight of 102.000 g/mole and a number average molecular weight of 39200 g/mole (polydispersity=2,18) and shows a Tg of 112 °C. The S/AN and all used additives (see Table 1) were used without further purification.
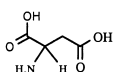
S/MSA					
alcoholes	dodecyl alcohol	phenol	bisphenol A		
amino-alcoholes	3-amino-phenol	5-amino-naphthol	3-amino propanol	2-amino-ethanol	3-amino-benzyl-alcohol
prim. amines	1-amino-dodecane	cyclohexyl-amine	aniline	benzylamine	amino-diphenyl-methane
sec. amines	dioctyl-amine	dicyclo-hexylamine	N-methyl-aniline	diphenyl-amine	
amino acids	amino-acetic acid	3-amino-propanoic acid	6-amino-hexanoic acid	11-amino-undecanoic acid	2-amino-benzoic acid
amino diacids	D, L-aspartic acid	L-glutamic acid	5-amino-isophthalic acid	2-amino-terephthalic acid	
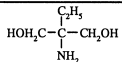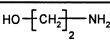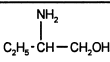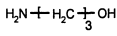
(prim. amines row, 6th column: naphthyl-amine)

(amino acids row, 6th column: 4-amino-benzoic acid)

SAN					
amino-alcohols	OH NH₂ (structure) 2-amino phenol	C₂H₅ HOH₂C–C–CH₂OH NH₂ 2-amino-2-ethylpropane-1,3diol	HO–[CH₂]₂–NH₂ 2-amino-ethanol	H₃C HO⟍NH₂ (structure) 2-amino-1-phenyl-1propanol	NH₂ C₂H₅–CH–CH₂OH 2-amino-1-butanol	H₂N–[H₂C]₃–OH 3-amino-propanol

Table 1: Additives used for modification

Reaction Procedure

For the chemical modification of all polymers we used a BRABENDER W30-EHT batch mixer with two sigma-rotors having a capacity of 30 cm³. The initial mixing temperature was 190 °C (S/AN) respectively 200 °C (S/MA), the rotation speed was 35 r.p.m.

The mixing (including premixing) procedure of polymer, additive and catalyst was optimized respectively for every polymer-additive group, resulting in different treatment. An example with a torque-time-diagram for solid additives is shown in Figure 1.
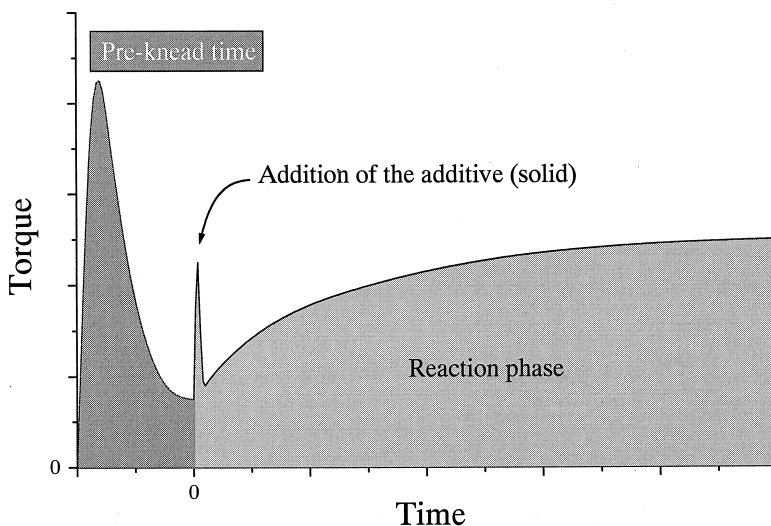
Figure 1: Torque -time-diagram for the addition of solid additives.

We tried to fill the reactor completely in order to get a better mixing. In most cases we used 20 g polymer and varied the amounts of additive and catalyst.

Analysis of the reaction products

The purification of the samples was done by dissolving them in acetone followed by precipitation in methanol or water.

a) Conversions with poly(styrene-co-maleic anhydride):

To determine the solubility, 1g of the product was kept in 100 ml acetone and stirred well for 24 h at room temperature. The sample then was centrifuged for 20 minutes (4500 rpm). The residue was dried under vacuum until its weight was constant and the soluble part was precipitated as described above. The conversion was only determined for the soluble part of the samples. To determine the conversion we used infrared (IR) spectroscopy (Fourier Transform Infrared Spectrometer NICOLET 5DXB) and nitrogen elemental analysis (method of Kjeldahl and VARIO EL from ELEMENTAR). Typical product-IR-peaks were at 1710 cm^{-1} (imid) and 1950 cm^{-1} (ester). For our rheological measures we used a Dynamic Analyser

RDA II from RHEOMETRICS. Our DSC data were generated on a DSC 820/25 from METTLER TOLEDO.

b) Conversions with poly(styrene-co-acrylonitrile):

The nitrile conversion was qualitatively determined by using IR spectroscopy (see above). Therefore the product peaks of the oxazoline at 1660 cm^{-1} (-C=N-) and 1220 cm^{-1} (C-O-C) were used as indicators. Additional specific additive peaks (i.e. OH- for 2-amino-2-ethylpropane-1,3diol (AEPD)) can be equally used. The quantitative determination of the oxygen content was done by elemental analysis (VARIO EL from ELEMENTAR).

Results and Discussions

1. Conversions of S/MA with primary alcohols

In [1] we have already discussed the results of conversions between S/MA with various MA-content (16 and 32wt%) and dodecanol in molten state. The reaction of anhydrides with alcohols is reversible. Scheme 1 shows the reaction mechanism.
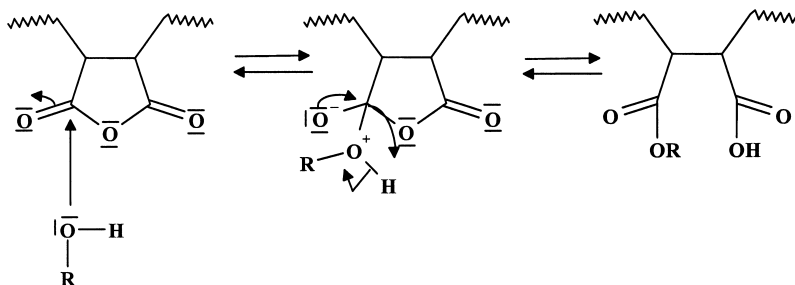
Scheme 1: Alcoholysis of anhydride groups in polymers.

If the reaction is performed in solution there has to be an excess of alcohol and catalyst to achieve a full conversion of the carbonyl groups. Therefore reaction times of more than 100 hours are necessary. In molten state only one of the two anhydride-carbonyl groups reacts. While the reachable conversion limit is not influenced by the anhydride content of the polymer, the reaction velocity increases with an increasing MA-content of the polymer, because of the higher concentration of reactive groups and of the autocatalytic effect of the constituted acid groups. The reaction can be catalysed with dibutyltinn oxide (DBTO) and itaconic acid (ITA) [1].

2. Conversion of S/MA with secondary amines

The reaction of S/MA-copolymers and secondary amines (scheme 2) shows a conversion limit after 10 minutes of reaction time. The limit is due to the steric hindrance of the used additives.
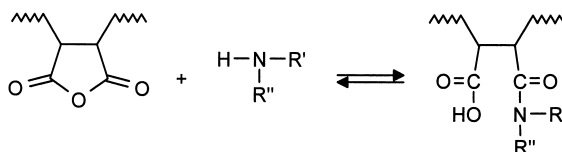
Scheme 2: Reaction of S/MA with secondary amines.

The reachable conversion limit in Figure 2 shows the influence of increasing anhydride-concentration in the used S/MA-polymers. In Figure 3, the influence of the batch ratio of additive groups and MA-groups is shown. An increase of the temperature (+ 20 °C) does not result in a higher conversion limit. The MFI increases with increasing rate of conversion.
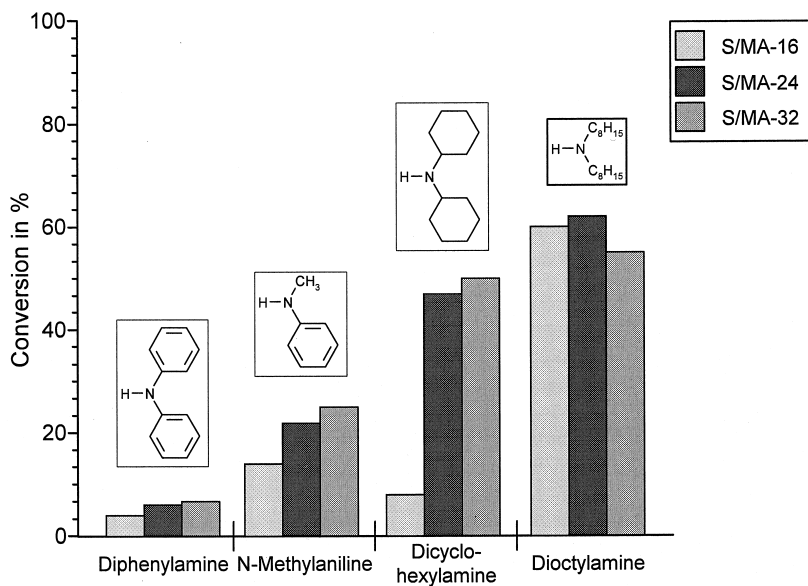
Figure 2: Reaction of S/MA with secondary amines ,ϑ = 200 °C, [MA]:[amine] = 1:1
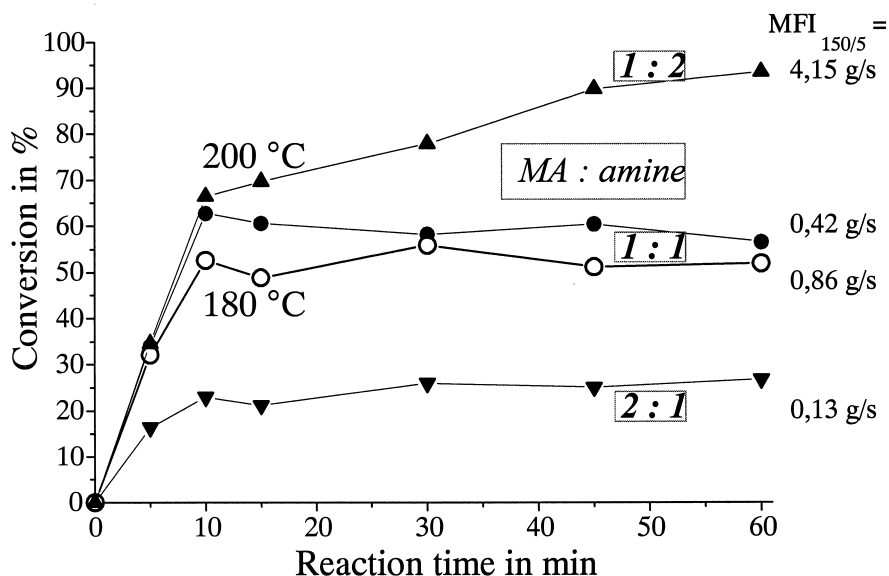
Figure 3: Conversion-time behaviour during the conversion of S/MA-16 with dioctylamine under variation of the MA:amine-ratio and at different temperatures.

3. Conversion of S/MA with primary amines and amino acids

The reaction of S/MA-polymers with primary alcylamines [8] and ammonia [9-14] in the melt, using batch-mixer and corotating extrusion has already been published. The imidisation of the anhydride group of S/MA runs in a heterocyclic manner resulting in cyclic imids after 5 minutes at 200 °C. The conversion with amino acids is done in an analogous way.
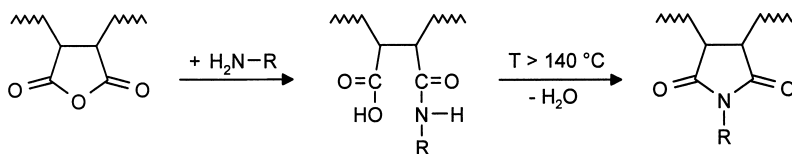
Scheme 3: Conversion of S/MA with primary amines and amino acids

It is noteworthy that there is an increase of the conversion limit with primary amines compared with secondary amines if S/MA-24 is used instead of S/MA-16, but a decrease with higher MA contents due to the increase of steric hindrance of the MA-groups. The conversion limit of reactions with primary amines decreases in the line 1-amino dodecane>amino diphenylmethane>benzyl amine>aniline>cycohexyl amine>naphthylamine (see Figure4). This can be explained with the higher steric room solidity.
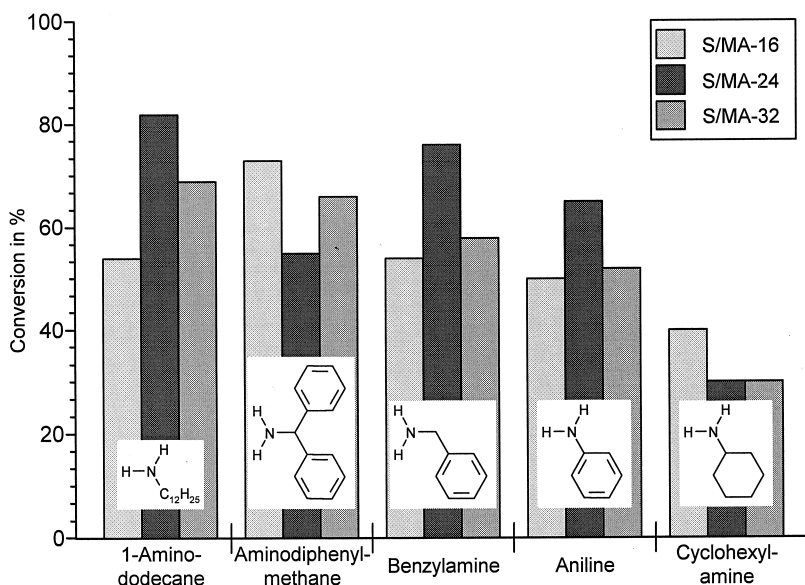
Figure 4: Conversion of S/MA with primary amines, ϑ=200 °C, MA:amine=1:1.

The conversion limit decreases with an increase of additive concentration. The influence of temperature is small. Polymers with imid structures on side chains show an increase of the thermal shape stability, a good adhesion on metal surfaces and good electro-isolating properties. The glass transition temperature which can be used as expression for the thermal shape stability is shown in Figure 5 with variation of the imid content and imid structure.
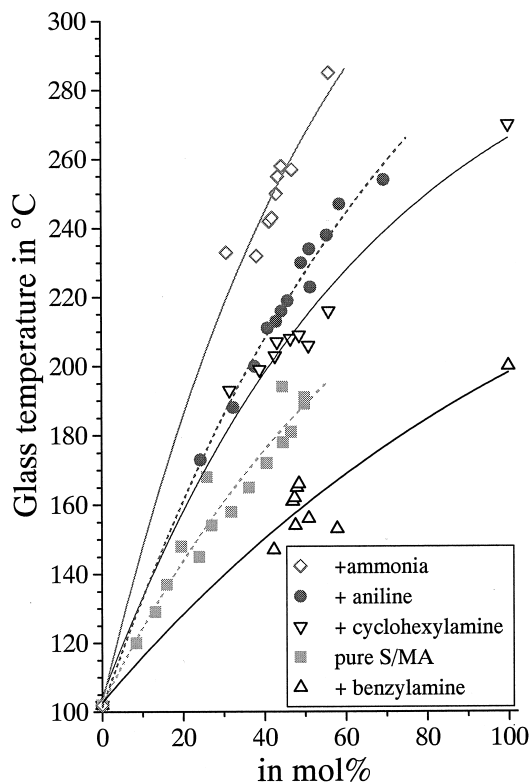
Figure 5: Coherence of glass transition temperature (Tg), imid structure and imid content of styrene-maleicimide copolymers.

The conversion of S/MA in solution [10-12] and in molten state results in comparable products [13]. In Figure 6 the similarity of reactions with S/MA and aniline in solution and in the molten state is shown on the example of Tg-increase during the reaction.
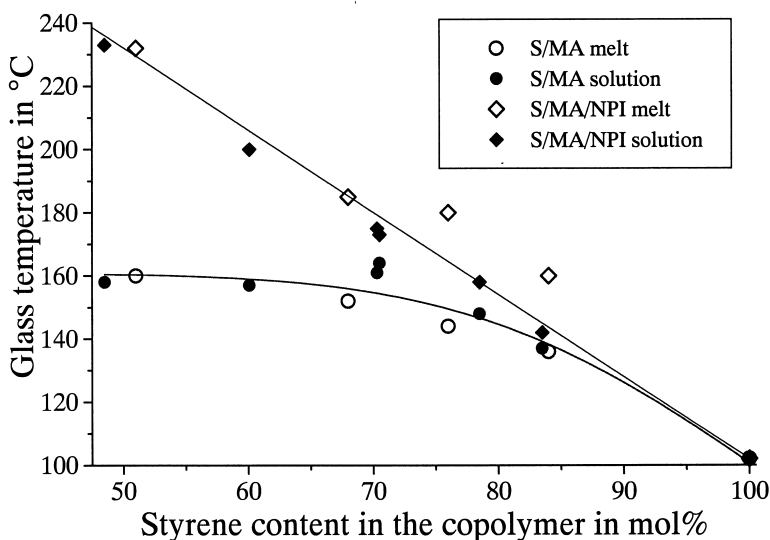
Figure 6: Glass temperatures of the reaction products from the conversion of
S/MA copolymers and aniline in melt and solution.

Reactions of S/MA with amino acids result in products with aliphatic or aromatic carbonyl-groups in the side chain of the polymer [4,5]. These polymers can be transferred into water soluble products (polyelectrolytes) by the use of NaOH. Another noteworthy possibility is the transformation into acid chlorides and the use for reactive blending i.e. with polyamides. The chain length of the aliphatic amino acids does not influence the conversion limit (about 80 %). An exception is the reaction behaviour of amino acetic acid which transforms into 2,5-diketo piperazine if heated (Scheme 4).
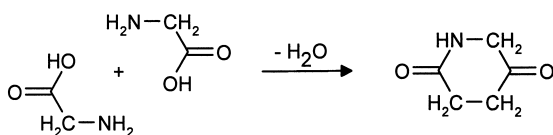
Scheme 4: Side reaction of amino acetic acid.

Vermeesch [8] reported a linear coherence between the chain length of the allylic side chains, that means the chain length of the used amines, and the Tg in reactions of aliphatic amines with the terpolymer MA/MMA/S (25 mol% MA, 7mol% MMA, 68 mol% S) in the melt. This can be explained with an increase of the free volume simultaneous with reduced packing density and decreased steric hindrance of the segmental mobility.
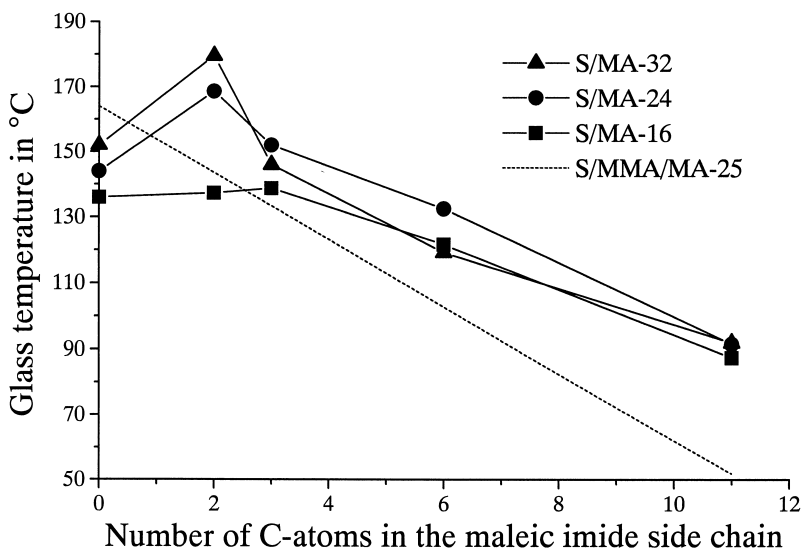
Figure 7: Glass transition temperatures (Tg) of the reaction products compared with the number of carbon atoms in the ω-amino acids used.

Figure 7 shows that the reaction of S/MA and ω-amino acids with various chain length results in similar products. An exceptance is again amino acetic acid (see above). The aromatic amino acids show a similar reaction behaviour with conversion limits of about 70 % and glass transition temperatures which are placed about 20 °C higher compared with the analogue non-substituted imides [4,5)].

4. Conversion of S/MA with diamines

Polymer modification of S/MA in the melt using diamines results (even with low additive concentrations of MA: additive = 100:1) in highly crosslinked products (see Scheme 5). The melt transforms into solid powder in a very short time. The crosslinked products can be sulfonated and used as ion exchange media in water conditioning processes.
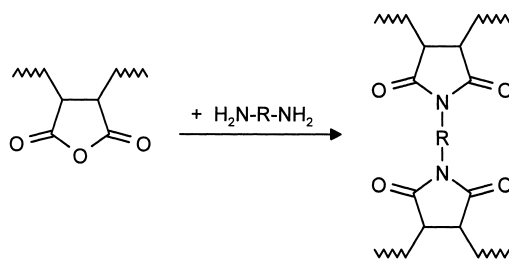
Scheme 5: Reaction of S/MA with diamines.

5. Conversion of S/MA with amino alcohols

The reaction of S/MA with amino alcohols should result in a fast imidisation which is followed by a slower alcoholysis (see Scheme 6). Since the alcoholysis results in a intra- and intermolecular crosslinking the degree of crosslinking should increase with the reaction time, that means the crosslinking should be controllable and lead to products with various crosslinking density in which the crosslinking can be completed in line with the forming process.
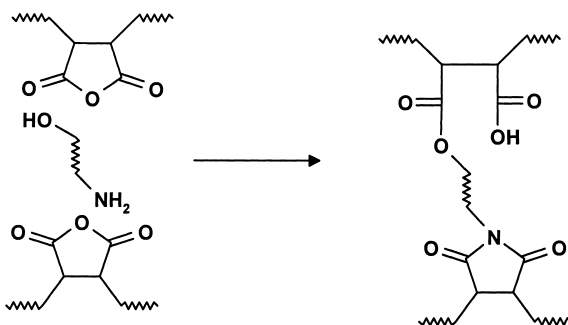

Scheme 6: Reaction of S/MA with amino alcohols.

The rheological analysis of the crosslinked products (see Table 2) shows a strong increase of the complex viscosity and the storing module G' i.e. an increase of the steadiness compared to the pure S/MA. Simultaneously there is a strong decrease of the loss factor tan δ i.e. a decrease of the viscous material properties. These results are a further indication of the increasing degree of crosslinking. A completely crosslinked product should show a solid-sphere viscosity ($> 10^{-7}$ P) and a tan δ of nearly 0.

	S/MA (84/16)	S/MA(84/16) + 3-amino-propanol (MA:NH$_2$=1:0,5)	Δ
Complex Viscosity η* (T= 120 °C) [P]	216200	518800	+ 140 %
Loss Factor tan δ (T=120 °C)	0,99	0,21	- 80 %
Storing Module G` (T=120 °C) [dyn/cm^2]	966200	3185800	+230 %

Table 2: Rheologic Data from the reaction of S/MA(84/16) with 3-amino-propanol (APr).

With the aromatic amino alcohols 3-amino phenol (3AP) and 5-amino naphthol (5AN) we got different results under similar reaction conditions. Amino phenol is the simplest aromatic amino alcohol. The meta-form (3AP) was chosen to avoid the steric hindrance of the ortho-form and the chinoid structures of the para-form of amino phenol. The conversion of S/MA-16 with 3AP results in completely soluble products. Even the infrared spectroscopy shows only the imid peak at 1710 cm-1 as product peak so that we suggest that only the aminolysis has taken place. The conversion limit was reached after a few minutes and amounted to 60 % (MA:NH$_2$= 1:1; maximum conversion=100 %) and 30 % (MA:NH$_2$=1:0,5; maximum conversion=50%). The glass transition temperatures (Tg) of the reaction products are similar to the glass transition temperatures of poly(styrene-co-N-phenylmaleimide) (S/NPI) which was produced by radical polymerisation (see Figure 8).
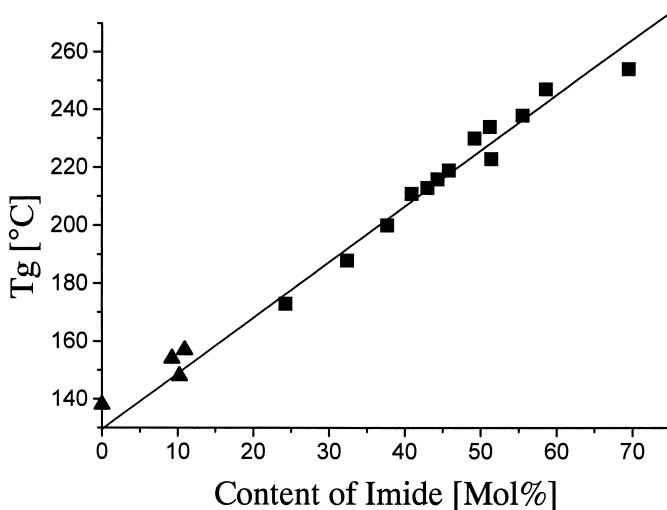
Figure 8: Tg-comparison of products from reactions with
S/MA(84/16) and 3AP[▲] and products of S/NPI-copolymerisation[■]

Under the reported reaction conditions only the aminolysis can be observed when the additive 3AP is used. This is due to the low reactivity of the hydroxyl group. The use of 5AN enables to control aminolysis and alcoholysis. Its obvious that this reaction behaviour is due to the different nucleophile of the additives. 5AN reacts with both S/MA-16 and S/MA-32 in the expected way i.e. the alcoholysis is slower than the aminolysis. We found that the solubility is a good indicator for the degree of crosslinking. The decrease of the solubility is a function of the reaction time and the additive concentration (see Figure 9).
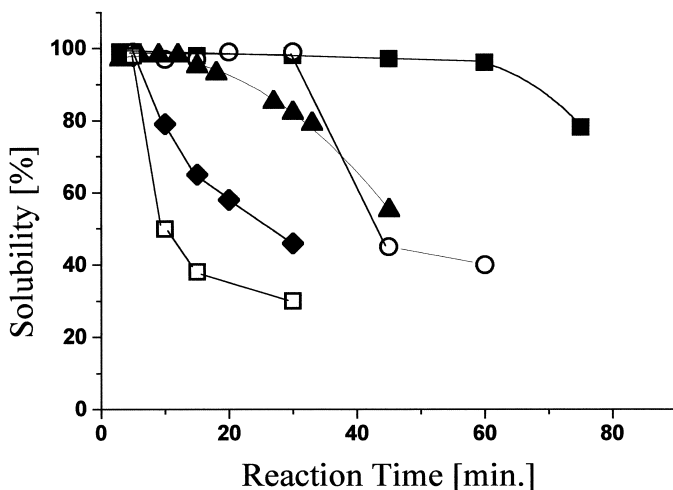
Figure 9: Solubility of reaction products from reactions with S/MA (84/16) and 5AN

[■]MA:NH$_2$=1:0,25; [⭘]MA:NH$_2$=1:0,5; [▲]MA:NH$_2$=1:1;

[◆]MA:NH$_2$=1:1,5; [□]MA:NH$_2$=1:2

6. Conversion of poly(styrene-co-acrylonitrile) (S/AN) with amino alcohols

The introduction of heterocyclic structures in polymers can be used as a basis for various further modification and treatment. Examples are reactive blending as well as the use of the new reactive centerpoints for draft polymerisation or as a basis for coatings or reactive paints.
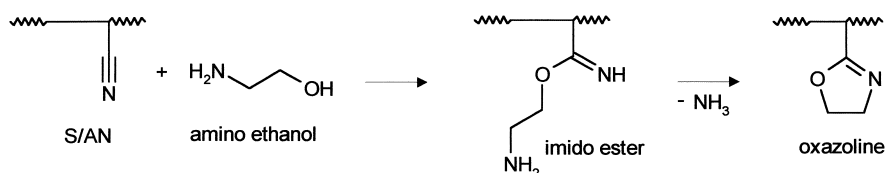
Scheme 7: Reaction of S/AN with amino ethanol leading to oxazoline products.

Seeliger and Witte [15,16] gave detailed descriptions of the reaction of nitriles and 2-amino alcohols to oxazolines (see Scheme 7). Polymer analogue reactions on the nitrile groups (AN) of S/AN in solution were realised from Hseigh et al. [17,18]. The transfer of this reaction into molten state eas done by Hu et al [19] and in our workgroup [2,3]. For aceotropic poly(styrene-co-acrylonitrile) we found that a reaction temperature of 190 °C is ideal. Even though Hu et al[19] favoured zinc acetate for the catalysis of the reaction, we found that dibutyltinn oxide gives

higher yields. The used additives are arranged in Table 1. We put special interest in the influence of the following reaction parameters:

=>   **additive concentration**

=>   **catalyst concentration**

=>   **reaction performance**

=>   **structural influences of the additives**.

In Figure 10 the example of the additive 2-amino-2-ethylpropane-1,3diol (AEPD) shows that an increase of additive concentration results in an increase of conversion limit. The batch ratio of additive to catalyst was constant.
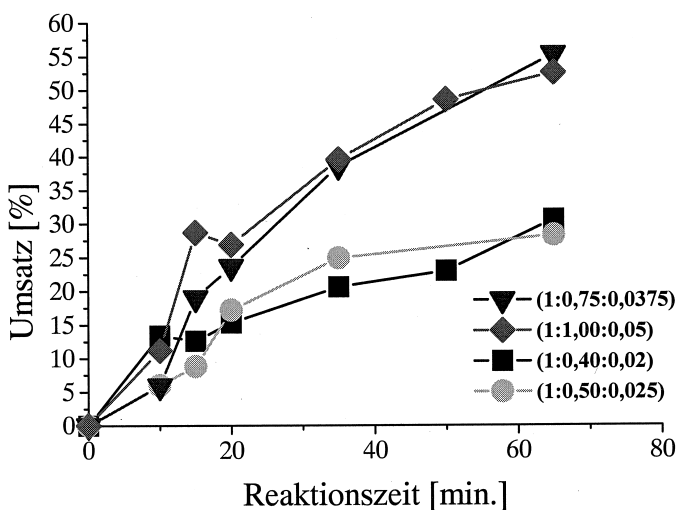
Figure 10: Reactions of S/AN with AEPD using various batch ratios [AN]:[additive]

As one of the most important reaction parameters we found the catalyst concentration.

The maximum conversation of reactions with S/AN and AEPD (AN:AEPD=1:1, catalyst concentration is varied) as a function of the catalyst concentration is shown in Figure 11. It is noteworthy that the coherence of maximum yield and catalyst concentration shows a maximum. This can be due to a deactivation of the nitrile group by excessing DBTO.
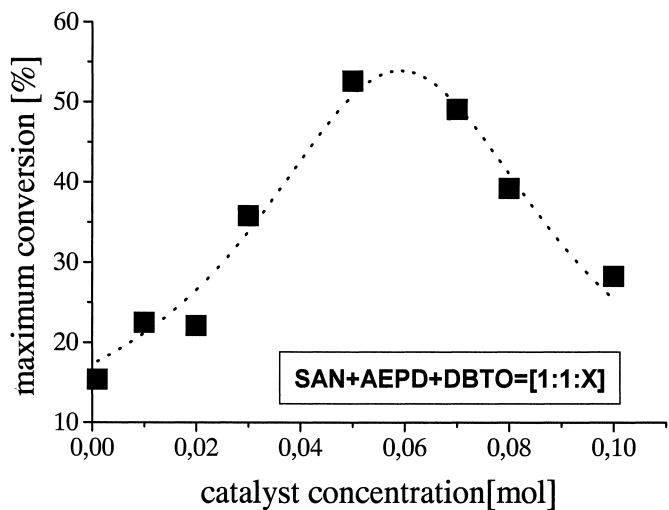
Figure 11: Coherence of maximum yields and catalyst concentrations of several DBTO-catalysed reactions of AN (S/AN) with AEPD.

Through an improved reaction performance, that means a stepwise addition of the additive, even additives with a low boiling point, like for example, 2-amino ethanol (AE) (b_p=170 °C) which shows a conversion limit of 17-31 % under standard conditions [2,19] can yield up to 50% [6] (see Figure 12). Therefore the reaction performance is changed from batch to semi-batch.
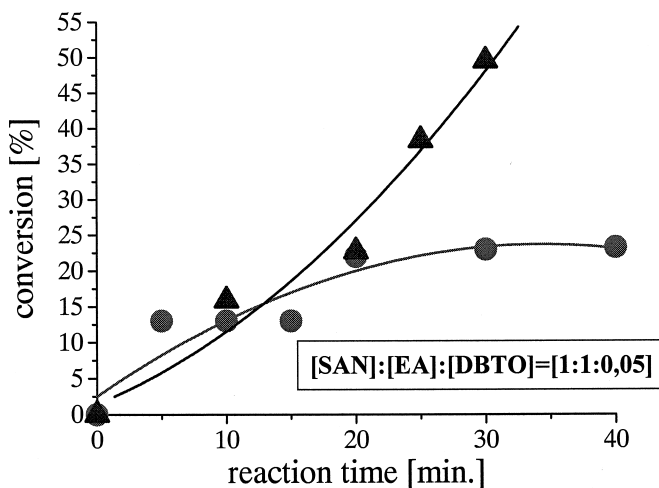
Figure 12: Influence of the addition mode of the additive on the conversion in DBTO-catalysed conversions of S/AN with AE (batch ratio: [AN:AE:DBTO]=[1:1:0,05]).

Figure 13 shows the structural influence of the additive. Reactions with S/AN and substituted 2-amino alcohols result in higher yields than with unsubstituted (AE). The highest yield was reached with 2-amino phenol (2AP) while the conversions with AEPD and 2-amino-1-phenyl-1-propanol (APP) showed a similar course. We note the reason for this in the aromatic stabilisation of the reaction product of AN and 2AP. Actually the product is not an oxazoline but an oxazole.
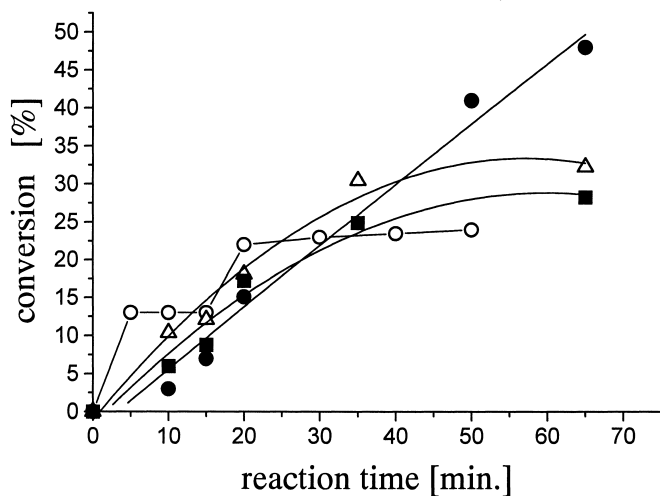
Figure 13: Coherence of conversion and reaction time in DBTO-catalysed reactions of AN (SAN) with AE,APP,AEPD and AP in the batch ratio of

[AN : additive : DBTO] = [1:0,5:0,025] (O)AE/(△)APP/(■)AEPD/(●)2AP

The maximum yields of the reactions with the batch ratio of [AN:additive:DBTO]=[1:0,5:0,025] (Figure 13) show the following increasing line dependent to their product structure (Scheme 8):
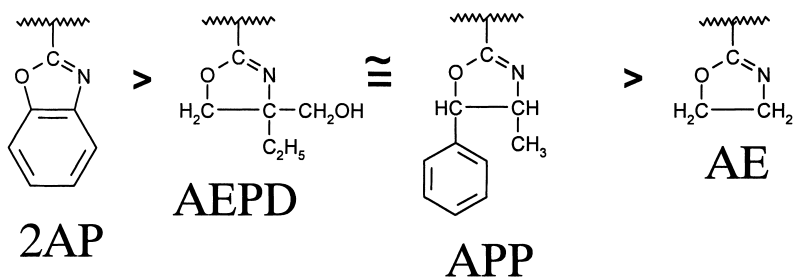
Scheme 8: Reaction products and their formation propabilities (experimental).
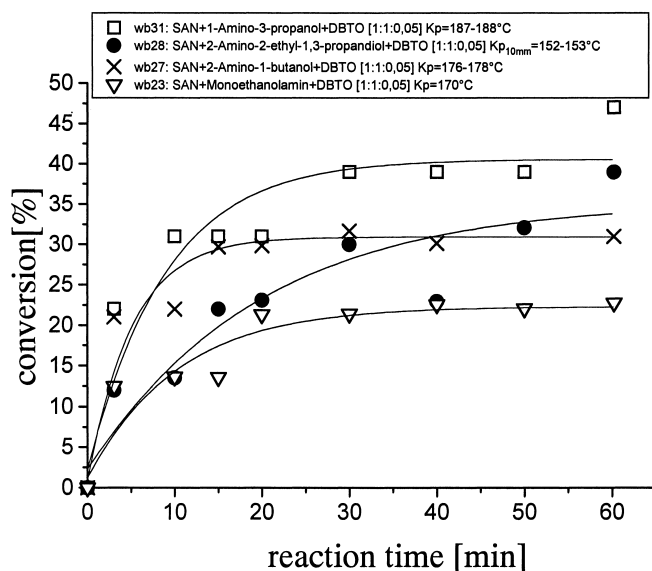
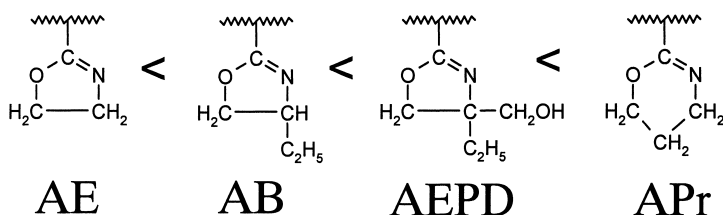**Figure 14**: Conversion-time curve by variation of the additive

[AN:additive:DBTO]=[1:1:0,05].

Using only aliphatic additives (Figure 14) results in the following decreasing line (Scheme 9):

Scheme 9: Reaction products and their formation propabilities

(experimental/aliphatic additives).

Therefore we can state that even if the forming of substituted 5-ring-systems compared with unsubstituted is favoured, it is topped by the formation of 6-ring-systems (additive 3-amino propanol (APr)).

Conclusion

Through the variation of the additives and catalysts during polymer modification the material properties of polymers can be changed in various manner. On the example of S/MA-modification, it can be shown that polymer modification has the tools to develop products with various new properties (for example with high thermal shape stability, polyelectrolytic

and crosslinked products) out of simple industrial polymers. The introduction of heterocyclic structures in (S/AN) can be used as a basis for various further modifications and treatment leading to new polymer products with fascinating possibilities in use which have been only poorly investigated yet.

References

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