Multifunctional Coupling Agents. II. Chain Extension and Terminal Group Modification of Polyamides

L. Jakisch,[1] H. Komber,[1] R. Wursche,[2] F. Böhme[1]

[1]*Institute of Polymer Research Dresden, e.V. Hohe Straβe 6, D-10069 Dresden, Germany*
[2]*Degussa AG, Paul-Baumann-Strasse 1, D-45764 Marl, Germany*

Received 28 January 2004; accepted 7 July 2004
DOI 10.1002/app.21159
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: New bifunctional coupling agents possessing one 2-oxazoline group and one 2-oxazinone group were converted in a Haake melt mixer or extruder with PA6 and PA12. It was shown by means of NMR spectroscopic investigations that the 2-oxazoline group reacted mainly with carboxylic groups whereas the oxazinone group reacted preferably with the amino groups. Both reactions proceeded with high selectivity and independent from each other. In the case of carboxy/amino group terminated polyamides, the conversions resulted in increased molecular weights since both reactive terminal groups of the polyamides were addressed simultaneously by the coupling agent. In the case of amino group terminated polyamides, the conversion with the bifunctional coupling agent resulted in oxazoline terminated polymer chains. Unlike PA6, it was possible to convert PA12 in two steps. At lower temperatures (210°C) and short reaction times (2 min), the reaction of the oxazinone group with the amino groups was predominant, whereas the reaction of the oxazoline group with the carboxylic groups proceeded to a sufficient extent only after longer reaction times or at higher temperatures. In the case of PA6, processing temperatures of about 250°C were necessary. Here, a side reaction was observed that resulted in the formation of cyclic quinoxaline structures under evolution of water. This side reaction did not disturb the chain extension significantly. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2170–2177, 2004

Key words: extrusion; modification; polyamides; telechelics

INTRODUCTION

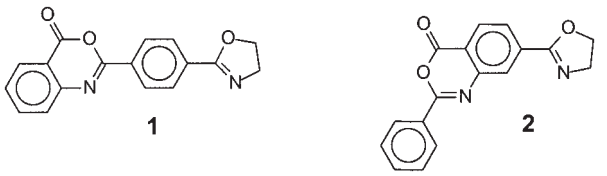
Bifunctional coupling agents such as bisoxazolines,[1–6] bisoxazinones,[7,8] bisoxazolones,[9,10] diisocyanates,[11] bisepoxides,[12] and bislactamates[13] have found broad application in polymer modification and reactive processing. They have proved to be effective chain extenders for various polycondensates and reactive compatibilizers in polymer blends. Their application demands reactive groups in the polymer that are usually hydroxy, amino, and carboxy groups as far as polyesters and polyamides are concerned. Beyond this, polyolefins with carboxy groups or anhydride groups are widely spread and often used in polymer blends.

The application of coupling agents with two reactive groups of the type mentioned above is limited in the case of polymers and polymer blends containing different reactive groups. For example, polyesters possess carboxylic groups, which react very fast with bis-2-oxazolines, whereas the hydroxy groups react with bis-2-oxazinones. Polyamides, the amino groups of which also react preferably with oxazinone groups, show similar behavior. To overcome this problem, mixtures of different coupling agents that address the respective terminal groups or coupling agents having a high reactivity with different groups are used.[13]

The situation in polymer blends is more complicated. The use of coupling agents with reactive groups of the same type causes reactions not only in the interface but also in the single phases. If the coupling agent is more soluble in one of the blend components, the latter can even become predominant. In such cases, complete control of the reaction is hardly possible.

Recently, we introduced a new type of coupling agent with different reactive groups.[14–17] These compounds contain one oxazoline group that reacts with carboxylic groups and one oxazinone group that reacts with hydroxy or amino groups. Two examples of these compounds are shown in Scheme 1. It could be evidenced by means of model reactions that these reactions proceed highly selectively. Moreover, these reactions could be controlled by temperature. In a system containing carboxylic groups and amino groups, the amino groups react first at lower temperatures with the oxazinone group and then, at higher temperatures, the carboxylic groups start to react with the oxazoline group.

Correspondence to: F. Böhme (Boehme@ipfdd.de).



Scheme 1

In this work our efforts focused on the utilization of the new coupling agents for AB-polyamides such as PA6 and PA12. Both polymers usually possess amino groups and carboxylic groups in equimolar amounts as far as their molecular weights are uncontrolled. This makes them suitable for investigations concerning controlled chain extension and functionalization as shown for compound **1** in Scheme 2. Beside polyamides with uncontrolled molecular weights polyamides with a distinct excess of amino group were also included.

EXPERIMENTAL

Materials

Four different polyamides were used for the investigations: (1) PA6 from BASF (**PA6$_{eq}$**: C_{COOH} = 53 mmol/kg, C_{NH2} = 57 mmol/kg, M_n = 20.000); (2) PA6 (BS 700 D) from BASF (**PA6$_{NH2}$**:C_{NH2} = 83 mmol/kg, C_{COOH} = 25 mmol/kg, M_n = 18.700); (3) PA12 from Degussa (**PA12$_{eq}$**:C_{NH2} = C_{COOH} = 65 mmol/kg, M_n = 15.000); (4) PA12 amino group terminated from Degussa (**PA6$_{NH2}$**: C_{NH2} = 250 mmol/kg, C_{COOH} = 11 mmol/kg, M_n = 5.000). 1,3-Phenylene-bis-2-oxazoline (PBOX) was obtained from Palmarole and used without further purification.

Instruments

The 500.13-MHz ^{1}H-NMR and 125.74-MHz ^{13}C-NMR spectra were recorded on a DRX 500 NMR spectrometer (Bruker). DMSO-d_6 (δ (^{1}H) = 2.50 ppm; δ (^{13}C) = 39.6 ppm) or trifluoroacetic acid-d_1 (TFA-d_1; δ (^{13}C=O) = 164.4 ppm) were used as solvent, lock, and internal standard. The ^{1}H-NMR spectra in TFA-d_1 were referenced on sodium 3-(trimethylsilyl) propionate-2,2,3,3-d_4 (δ (^{1}H) = 0 ppm). Signal assignments were verified by ^{1}H–^{1}H and ^{1}H–^{13}C correlated 2D NMR spectra.

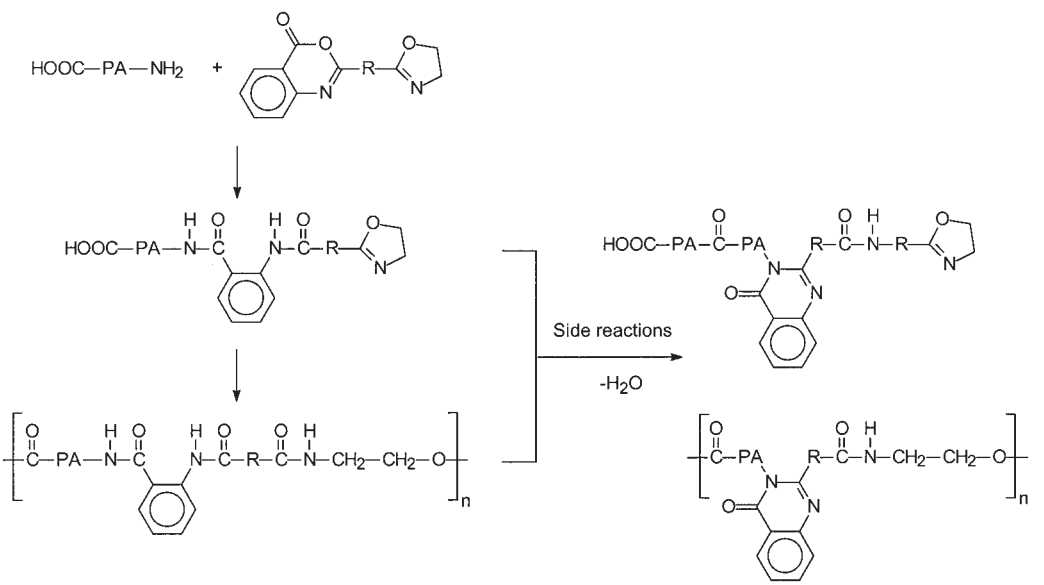
The solution viscosities were measured with an automated Ubbelohde viscosimeter in formic acid (PA6) or *m*-cresol (PA12) at 25°C (0.5 g/dL).

Synthesis

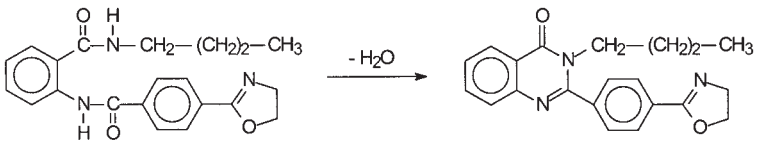
Coupling agents **1** and **2** were prepared as described elsewhere.[16,17]

Model compound **3** was synthesized by reaction of **1** with *n*-butylamine in toluene under reflux (3 h).

3: ^{1}H-NMR (DMSO-d_6): 12.64 (1H, s, NH-Ar), 8.86 (1H, t, NH), 8.63 (1H, d, H_{ar} *ortho* to NH), 8.07 (2H, d, H_{ar} *meta* to Ox), 8.02 (2H, d, H_{ar} *ortho* to Ox), 7.85 (1H, d, H_{ar} *ortho* to CO), 7.59 (1H, t, H_{ar} *meta* to NH), 7.24 (1H, t, H_{ar} *para* to NH), 4.48 (2H, t, OCH_2), 4.03 (2H, t, NCH_2), 3.32 (2H, t, $NHCH_2$), 1.55 (2H, m, CH_2), 1.36 (2H, m, CH_2CH_3), 1.36 ppm (3H, t, CH_3).



Scheme 2



3 **4**

Scheme 3

Model reactions

Model compound **3** was heated for 7 min under nitrogen in a small glass tube at 210 and 250°C. The reaction products were used without further purification for NMR measurements. The reaction at 250°C yielded a mixture of **3** and **4**.

4: ^{1}H-NMR (DMSO-d_6): 8.20 (1H, d, H_{ar} *ortho* to CO), 8.03 (2H, d, H_{ar} *ortho* to Ox), 7.85 (1H, t, H_{ar} *para* to CO), 7.74 (2H, d, H_{ar} *meta* to Ox), 7.68 (1H, d, H_{ar} *ortho* to –N=), 7.58 (1H, t, H_{ar} *meta* to CO), 4.49 (2H, t, OCH_2), 4.04 (2H, t, NCH_2), 3.87 (2H, t, NCH_2), 1.48 (2H, m, CH_2), 1.08 (2H, m, CH_2CH_3), 0.67 ppm (3H, t, CH_3).

Modification reactions

The modification reactions with PA6 and PA12 were carried out in a Haake melt mixer Rheomix 600p (50-mL chamber, 80 rpm) and in a Haake extruder Rheomex PTW 16/25 (corotating twin screw extruder, screw diameter = 16 mm, L/D = 25, 100 rpm) at different temperatures. In case of the melt mixer the

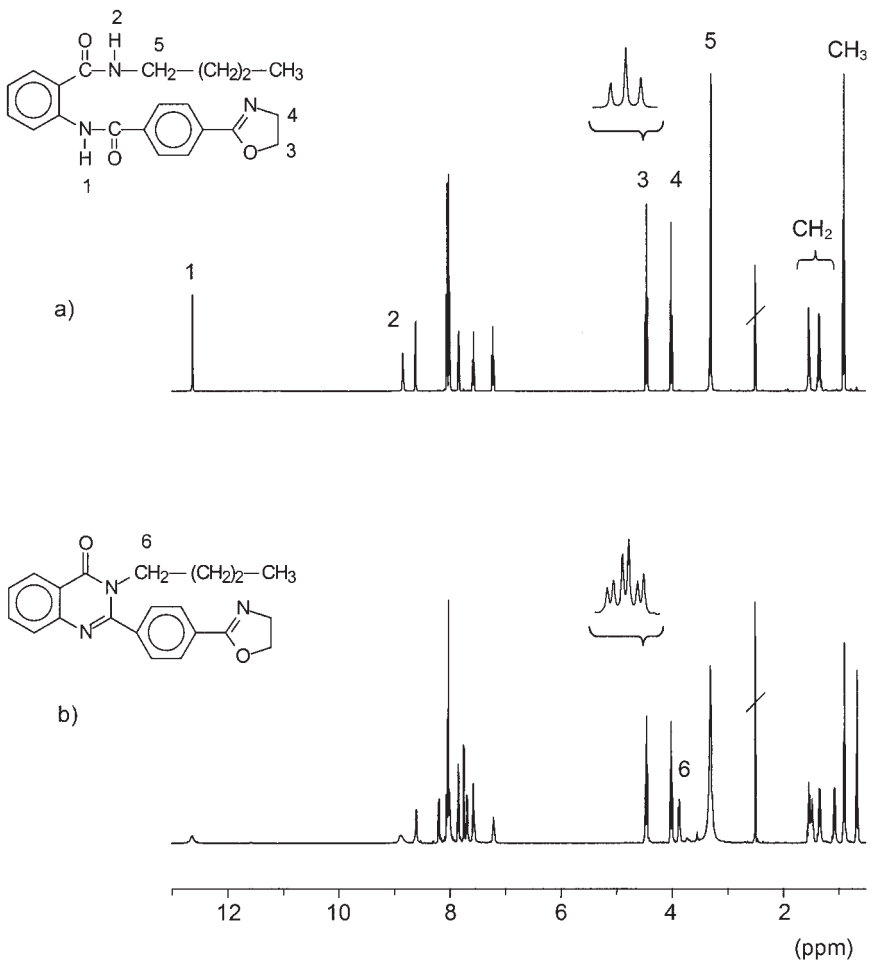


Figure 1 ^{1}H-NMR spectra (in DMSO-d_6) of model compound **3** after 7 min annealing (a) at 210°C and (b) at 250°C (for complete signal assignment, see Experimental).

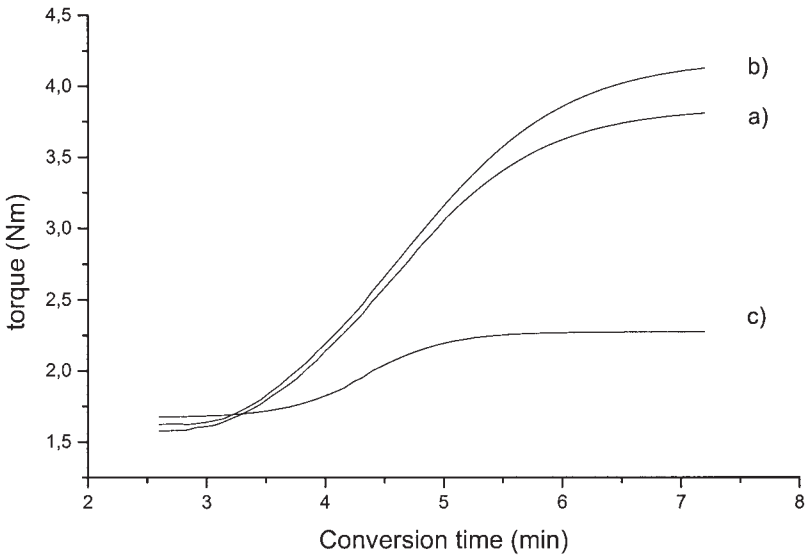


Figure 2 Time–torque curves of the conversion of $\mathbf{PA6_{eq}}$ with (a) **1,** (b) **2**, and (c) PBOX carried out in a Haake mixer at 250°C.

coupling agents were added into the melt after 3 min kneading time. The kneading experiments were stopped after reaching the maximum torque. In the extrusion experiments premixed mixtures of polyamide and coupling agent were processed.

RESULTS AND DISCUSSION

The suitability of coupling agents **1** and **2** was tested on PA6 and PA12. For each kind of polyamide two differend grades were at our disposal ($\mathbf{PA6_{eq}}$ and $\mathbf{PA12_{eq}}$ with equimolar amounts of amino and carboxylic groups; $\mathbf{PA6_{NH2}}$ and $\mathbf{PA12_{NH2}}$ with a distinct excess of amino groups).

The main difference between PA6 and PA12 with respect to processability exists in their different melting points. PA12, with an equilibrium melting point of 187°C, can be processed at much lower temperatures than PA6, with an equilibrium melting point of 231°C. From our earlier investigations[16,17] it is known that the reactivity of oxazolines with carboxylic groups strongly differs from that of oxazinones with amino groups. The latter proceeds already in good yields at distinctly lower temperatures. Depending on whether the coupling reactions are carried out at the processing temperature of PA12 (~210°C) or at that of PA6 (~250°C), a more or less pronounced two-step reaction must be assumed, in the course of which at first the coupling agent is bonded to the amino groups and later the chains are connected with each other via the reaction of the carboxylic groups with the oxazoline groups as shown in Scheme 2. Additionally, at elevated temperatures (~250°C) the formation of a cyclic quinoxaline structure under evolution of water has been reported.[18]

Since PA6 is processed in this temperature region, one must be aware of this side reaction. To gain a deeper insight into this reaction, the thermal cyclization of compound **3** to compound **4** according to Scheme 3 was investigated. Compound **3** serves as a model compound for the structural unit formed during the conversion of **1** with an amino terminal group of polyamide.

The ^{1}H-NMR spectra of compound **3** in DMSO after 7 min annealing at 210 and 250°C, respectively, are shown in Figure 1. From spectrum a one can conclude that during annealing at 210°C cyclization is practically negligible. The spectrum corresponds completely to that of compound **3**.

After annealing at 250°C, distinct alterations are visible in the spectrum. Beside the signals of compound **3**, additional signals appear that could be assigned to the cyclized structure, e.g., the H^6 signal of the CH_2 next to the cycle at 3.99 ppm. Both oxazoline group signals H^3 and H^4 are doubled (only shown for H^3) because of the two oxazoline-containing substances **3** and **4** now occurring in the system. From the integral signal intensities, 40% ring formation could be approximated. In TFA-d_1, signal doubling is much more pronounced. Here, two well-separated oxazoline signal groups are observed. Because of proton exchange, the NH group signals are not visible in TFA.

First information about the coupling efficiency of coupling agents **1** and **2** delivered conversions with different polyamides in the melt. $\mathbf{PA6_{eq}}$ with nearly equimolar amounts of carboxylic and amino groups (C_{COOH} = 53 mmol/kg, C_{NH2} = 57 mmol/kg, M_n = 20.000) was converted with **1** and **2** and for comparison purposes with PBOX in a Haake mixer at 250°C. The conversions were carried out in equimolar

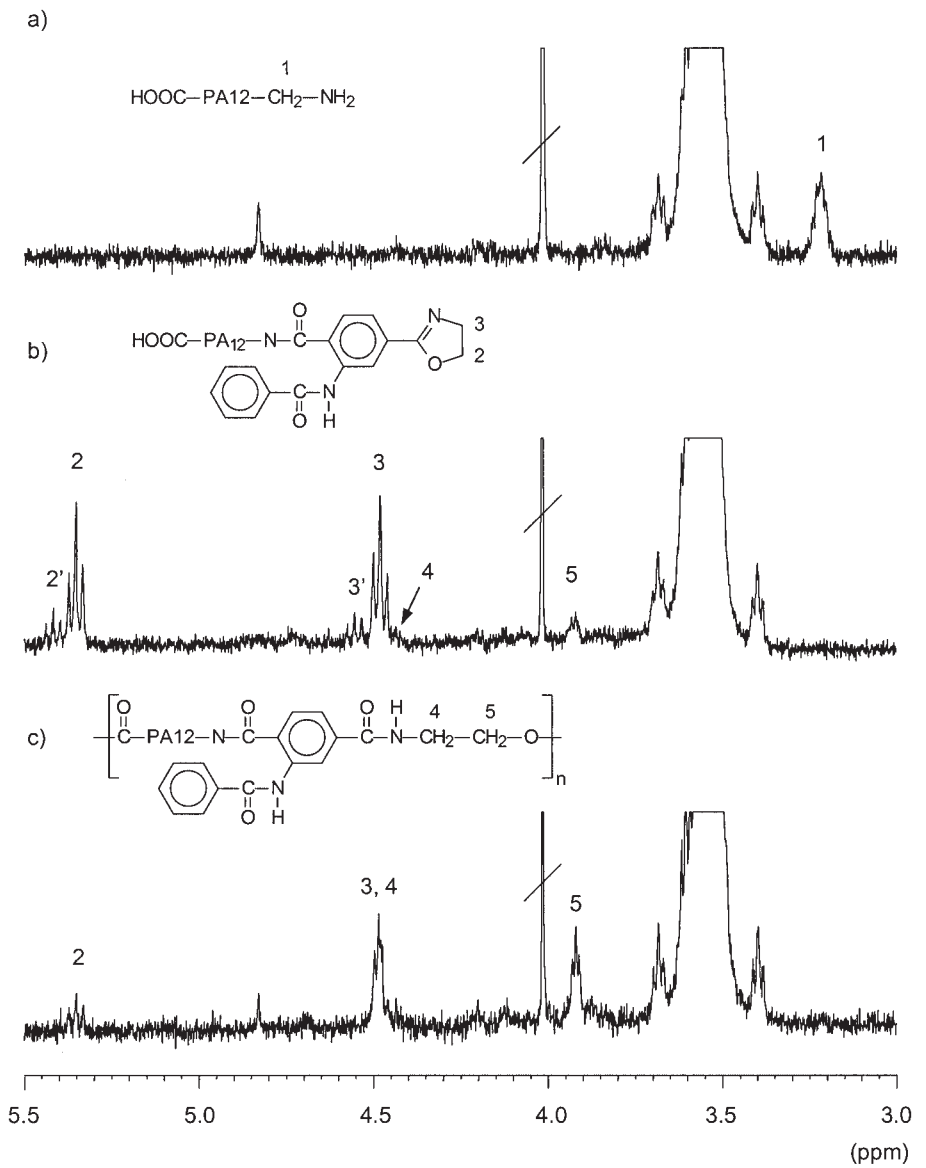


Figure 3 ^{1}H-NMR spectra (in TFA-d_1) of **PA12$_{eq}$**: (a) virgin sample, (b) after conversion with coupling agent **2** at 210°C in a Haake extruder (residence time ~2 min), and (c) after conversion with coupling agent **2** at 230°C in a Haake mixer (residence time ~5).

ratios to the total sum of terminal groups (COOH and NH_2).

As shown in Figure 2, the addition of coupling agents **1** and **2** to PA6 (curves a and b) results in a distinct increase in torque caused by chain extension via the reaction with both the carboxylic and the amino terminal groups. In case of PBOX (curve c) only a moderate increase in torque is observed. This can be explained by the reduced reactivity of oxazolines with the amino terminal groups. Since the amino groups do not react to the same extent as the carboxylic groups, an excess of oxazoline groups referring to the number of carboxylic groups remains in the system, resulting in termination of PA6 with oxazoline groups rather than chain extension.

With coupling agents **1** and **2**, both types of terminal groups are converted due to the presence of the oxazinone groups. This makes coupling agents **1** and **2** more effective with respect to chain extension, resulting in higher molecular weights. These findings are confirmed by the inherent viscosities, which are 0.63 dL/g for the virgin PA6, 0.72 dL/g for PA6 converted with 1,3-PBOX, 0.87 dL/g for PA6 converted with coupling agent **1,** and 0.86 for PA6 converted with coupling agent **2**.

Similar results were obtained for **PA12$_{eq}$** provided that the processing temperature was high enough to allow both reactive groups to react to a comparable extent. At lower temperatures (190–210°C) a steady increase in torque was observed over a long time

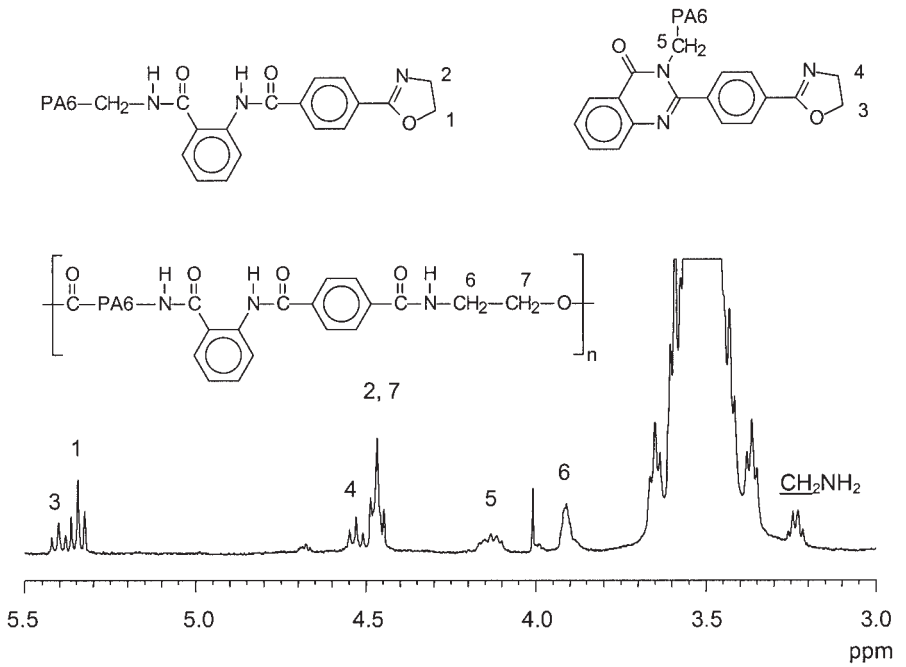


Figure 4 ^{1}H-NMR spectrum (in TFA-d_1) of **PA6$_{eq}$** after conversion with coupling agent **1** at 250°C in a Haake extruder (residence time ~2 min).

when coupling agents **1** and **2** were used. Indications for a two-step character of the coupling reactions as shown in Scheme 2 could not be found in the torque–time curves of **PA6$_{eq}$** or in those of **PA12$_{eq}$**. In this regard, a ^{1}H-NMR terminal group analysis was more informative.

^{1}H-NMR spectra of **PA12$_{eq}$** before and after reaction with coupling agent **2** are shown in Figure 3. The conversion was performed first at 210°C in a Haake extruder in equimolar ratio. The residence time was approx. 2 min. The spectrum of the virgin polyamide (Fig. 3a) shows a distinct signal at 3.23 ppm (H^1) belonging to the CH_2-NH_2 terminal group. This signal disappears after conversion with **2** (Fig. 3b), showing that the reaction of the oxazinone groups with the amino groups proceeded completely. However, the signals of the unreacted oxazoline groups (H^2, H^3) are still visible. Small signals at 3.92 and 4.47 ppm (H^4, H^5) indicate that only small amounts of the oxazoline groups reacted with carboxylic groups. The signals $H^{2'}$ and $H^{3'}$ belong to the oxazoline group of unreacted coupling agent **2**, showing that the coupling agent was slightly overdosed. From the terminal group analysis one can conclude that the conversion of **PA12$_{eq}$** with **2** under the relatively mild reaction conditions chosen resulted in the formation of an oxazoline terminated polyamide, the carboxylic groups of which remained unreacted. For comparison purposes, a blind sample of PA12 without coupling agent was extruded. Comparing the inherent viscosities of the three samples, 0.46 dL/g for the virgin sample, 0.47 dL/g for the blind sample, and 0.45 dL/g for the sample converted with **2**, one can conclude that the conversion with coupling agent **2** under these conditions did not result in a significant increase of the molecular weight of PA12.

For the conversion of the carboxylic groups, higher temperatures and reaction times are necessary. Therefore, the same conversion was carried out in a Haake mixer at 230°C with a residence time of approx. 5 min. The ^{1}H-NMR spectrum of the conversion product is shown in Figure 3c. It can be seen that the oxazoline signals nearly disappear whereas the signals of the moiety formed during the reaction of the oxazoline groups with the carboxylic groups (H^4, H^5) increase distinctly. From the signal intensities, an 80% conversion of the oxazoline groups could be approximated. The respective inherent viscosity of the sample was 0.54 dL/g. Cyclization reactions as shown in Scheme 3 play a secondary role under the reaction conditions chosen.

Because of the higher processing temperature, a different coupling behavior was expected for PA6. Figure 4 represents the ^{1}H-NMR spectrum of **PA6$_{eq}$** converted in equimolar ratio with coupling agent **1**. The conversion with coupling agent **2** delivered similar results. The conversion was carried out in a Haake extruder at 250°C with a residence time of ~2 min. Unlike the spectrum of **PA12$_{eq}$** processed under similar conditions only at lower temperatures (210°C, see Fig. 3b), the spectrum of **PA6$_{eq}$** in Figure 4 shows signals of both the unreacted (H^1, H^2) and the reacted

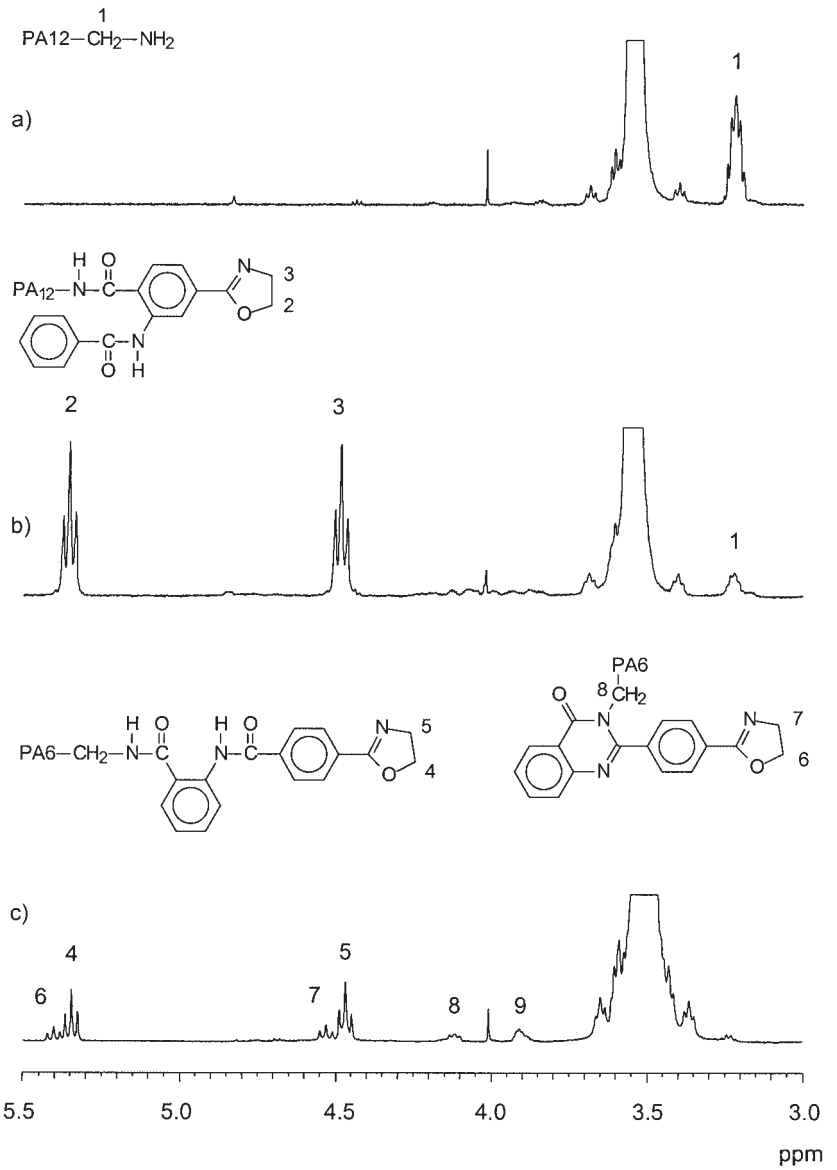


Figure 5 ^{1}H-NMR spectra (in TFA-d_1) of $\mathbf{PA12_{NH2}}$: (a) virgin sample, (b) after conversion with coupling agent **2** at 210°C in a Haake extruder (residence time ~2 min), and (c) of $\mathbf{PA6_{NH2}}$ after conversion with coupling agent **1** at 250°C in a Haake extruder (residence time ~2 min).

oxazoline (H^6, H^7). Additionally, the signals for H^3, H^4, and H^5 indicate a distinct extent of cyclization as shown in Scheme 3. In comparison to the spectrum in Figure 1b the signals of Figure 4 are shifted because of the different solvents (DMSO-d_6 versus TFA-d_1) used. From the integral ratio of the oxazoline signals of H^1 + H^3 and the signal of H^6, an oxazoline conversion of approx. 50% could be determined. Caused by the higher processing temperature of PA6, the reactions of the oxazoline group and the oxazinone group proceed more or less simultaneously, although the latter is still slightly preferred. Comparing the results of PA6 and PA12, one can conclude that the two-step character of the coupling reaction is much more pronounced in the case of PA12. Other side reactions, which one could assume because of the water formation during the cyclization reactions in PA6, could not be detected, provided the reaction times do not exceed 2 min.

A controlled stepwise conversion of **1** and **2,** which is less influenced by the temperature, can be performed using polyamides that are mainly amino group terminated. Two polyamide samples of this kind ($\mathbf{PA6_{NH2}}$ and $\mathbf{PA12_{NH2}}$) were converted in a Haake extruder. The reaction conditions were the same as for the conversion of $\mathbf{PA12_{eq}}$ and $\mathbf{PA6_{eq}}$, respectively.

Figure 5 shows the ^{1}H-NMR spectra of the respective polyamides. $\mathbf{PA12_{NH2}}$ is a polyamide sample, the molecular weight of which was controlled by adding a certain amount of *n*-dodecylamine. Correspondingly,

a strong signal of the CH_2-NH_2 terminal group (H^1) appears in the spectrum of the virgin compound (Fig. 5a). After conversion with coupling agent **2**, this signal strongly diminishes (Fig. 5b), whereas the signals of the unreacted oxazoline groups are distinctly visible. From the spectrum one can conclude that the conversion proceeded smoothly without any side reactions and resulted in an oxazoline terminated polyamide.

Similar results were obtained for the conversion of $\mathbf{PA6_{NH2}}$ with coupling agent **1** (Fig. 5c). Also here the degree of oxazoline group termination is high. However, because of the higher processing temperature, cyclization as already seen for $\mathbf{PA6_{eq}}$ occurred (H^6, H^7, H^8). Additionally, some traces of the oxazoline reaction with the small amount of carboxylic groups in the sample could be evidenced (H^9).

In both cases, polyamides with oxazoline end groups were obtained that can be activated by adding carboxylic groups to the system.

CONCLUSION

Both coupling agents **1** and **2** proved to be versatile modifiers for AB-type polyamides. Because of their two different reactive groups, both the amino and the carboxylic terminal groups of polyamides are addressed simultaneously by the coupling agents. The reactions of the oxazoline and the oxazinone groups with carboxylic and amino groups, respectively, proceeded independently from each other with high selectivity. This led, in the case of polyamides possessing both kinds of terminal groups in equimolar ratio, to a strong increase in molecular weights. Amino group terminated polyamides reacted only with the oxazinone side of the coupling agents and resulted in oxazoline group terminated polyamides. Such telechelic polyamides can be used for preparation of block copolymers or as fast-reacting components in polymer blends.

Although the coupling behavior of PA6 and PA12 proved similar, some differences attributed to their different melting points could be found. In the case of PA6 with an equilibrium melting point of 231°C and a processing temperature of 250 to 260°C, an additional cyclization reaction under evolution of water resulting in the formation of a quinoxaline structure was observed. Moreover, because of the high processing temperature the reactivity of the oxazoline and the oxazinone group came closer together and therefore it was impossible to control the chain growth by temperature as done earlier in the case of model compounds.[17]

PA12 with an equilibrium melting point of 187°C can be processed at significantly lower temperatures than PA6. As shown by NMR spectroscopy, the reaction of PA12 with coupling agent **2** at 210°C resulted first in an oxazoline termination of the polymer. At longer reaction times or higher temperatures at about 230°C, chain extension by the reaction of the oxazoline group with the carboxylic group occurred in significant yields. This offers interesting applications in which the viscosity of the material can be tuned according to the processing demands.

Generally, the introduced coupling agents with different reactive groups enlarge the possibilities of tailoring polymer properties and structures by melt processing and offer better control of chain extension reactions in polycondensates, including blends. This will be the subject of further publications.

References

1. Inata, H.; Matsumura, S. J Appl Polym Sci 1986, 32, 4581.
2. Loontjens, T.; Belt, W.; Stanssens, D.; Weerts, P. Polym Bull 1993, 30, 13.
3. Kylma, J.; Tuominen, J.; Helminen, A.; Seppala, J. Polymer 2001, 42, 3333.
4. Nery, L.; Lefebvre, H.; Fradet, A. Macromol Chem Phys 2004, 205, 448.
5. Wörner, C.; Müller, P.; Mülhaupt, R. J Appl Polym Sci 1997, 66, 633.
6. Chalamet, Y.; Taha, M. J Polym Sci Part A Polym Chem 1997, 35, 3697.
7. Acevedo, M.; Fradet, A.; Judas, D. EP 581641 (1994) CA 1994, 120, 165299.
8. Inata, H.; Matsumura, S. J Appl Polym Sci 1987, 34, 2609.
9. Douhi, A.; Fradet, A. Polym Bull (Berl) 1996, 36, 455.
10. Douhi, A.; Fradet, A. J Polym Sci Part A Polym Chem 1995, 33, 691.
11. Leistner, D.; Stephan, M.; Häussler, L.; Vogel, R.; Rätzsch, M. Angew Makromol Chem 1993, 206, 141.
12. Torres, N.; Robin, J. J.; Boutevin, B. J Appl Polym Sci 2001, 79, 1816.
13. Loontjens, T.; Pauwels, K.; Derks, F.; Meilen, M.; Sham, C. K.; Serne, M. J Appl Polym Sci 1997, 65, 1813.
14. Jakisch, L.; Böhme, F. DE 19812409 (1998) CA 1999, 130, 312216.
15. Jakisch, L.; Böhme, F. DE 100 34 154 (2000), WO 02/04441 (2001) CA 2002, 136, 102787.
16. Jakisch, L.; Komber, H.; Häußler, L.; Böhme, F. Macromol Symp 2000, 149, 237.
17. Jakisch, L.; Komber, H.; Böhme, F. J Polym Sci Polym Chem 2003, 41, 655.
18. Errede, A. US 3 408 326 CA 1969 1968, 70, 58558.

Contract grant sponsor: Degussa AG.