A new Bifunctional Coupling Agent: Synthesis and Model Reactions

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SUMMARY: The preparation of a new bifunctional coupling agent with one oxazoline group and one oxazinone group has been described. Model reactions with dodecanoic acid, benzoic acid, *n*-dodecyl alcohol and *n*-dodecylamine in melt evidenced that both carboxylic acids react selectively with the oxazoline group whereas the oxazinone group is exclusively attacked by the amino and the hydroxy compound, respectively. In blends of amino group terminated polyethers with a carboxy group containing polyethylene the new coupling agent has proven very effective.

Introduction

Coupling reactions play an important role in polymer chemistry. They have been applied in chain extension of various polymers with reactive terminal groups, in synthesis of block copolymers and in reactive blending. In that field of polymer research cyclic iminoethers and iminoesters have proven very suitable. They react fast with nucleophiles by ring opening addition without any by-products.

Commonly, bifunctional compounds with reactive groups of the same type have been used. Among them, bisoxazolines able to react with carboxy groups have to be mentioned. Chain extension of carboxy group containing polyesters with bisoxazolines was described by Inata and Matsumura[1], Loontjens et al.[2], and Cardi et al.[3] We practized oxazoline modification of liquid crystalline poly(ethylene therephthalate-co-oxybenzoate)s under the conditions of reactive processing.[4, 5, 6] With aliphatic hydroxy or amino groups, the reactivity of oxazolines is distinctly lower. Therefore, bisoxazolones and bisoxazinones were rather used for polymers containing these groups.[7, 8]

In reactive polymer blending the utilization of bisiminoethers and esters is limited on systems whose components possess groups of the same type. In those systems coupling reactions take place in the phase boundary but also within the single phases. Under some circumstances it might even be possible that the reactions occur in one of the components preferably. It was our intention to overcome this problem by a coupling agent containing two different reactive

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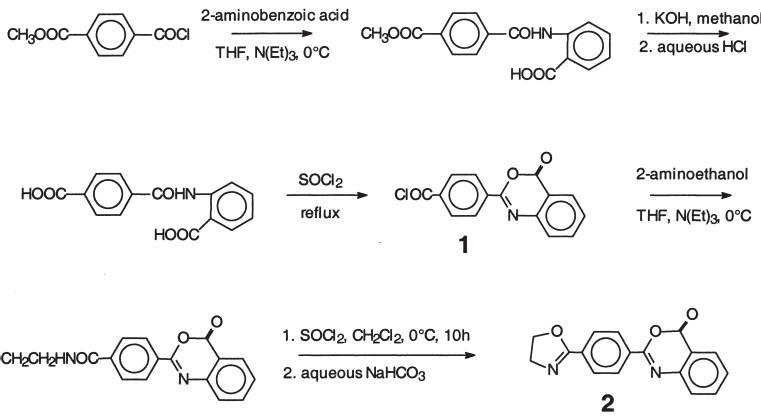
groups which are able to react with both phases selectively. The application of such a coupling agent would insure that linking reactions only occur in the phase boundary. The aim of this article is to describe the synthesis, model reactions and utilization of a bifunctional coupling agent with one oxazoline group and one oxazinone group.

Results and Discussion

Synthesis of the bifunctional coupling agent

The synthesis of 2-(4-(4H-3,1-benzoxazin-4-on-2-yl)phenyl)-1,3-oxazoline **2** was carried out according to *Scheme 1*. Starting from monomethylester chloride of terephthalic acid a step-wise conversion with 2-aminobenzoic acid and 2-aminoethanol, respectively, and subsequent cyclization was realized (see experimental part).



Scheme 1: Synthesis of the bifunctional coupling agent **2**

Model Reactions of 1 with low molecular compounds

In order to get information about the selectivity of the reactions of **2** with various nucleophiles, such as benzoic acid, dodecanoic acid, *n*-dodecylamine, and *n*-dodecyl alcohol, model reactions were performed in melt. The resulting structures were characterized by ^{1}H NMR spectroscopic investigations. As an example, the ^{1}H NMR spectra of **2** and its reaction products with *n*-dodecylamine and dodecanoic acid are presented in Figure 1. The spectra clearly show that the reactions proceeded highly selective. From the signals at 4.02 and 4.47 ppm in Figure 1b one can conclude that the oxazoline group did not react with *n*-dodecylamine whereas characteristic NH-signals at 8.84 and 12.61 ppm indicate the reaction

of the oxazinone group. In case of the reaction of **2** with dodecanoic acid (Figure 1c) only the conversion of the oxazoline group to the respective ester amide group could be evidenced.

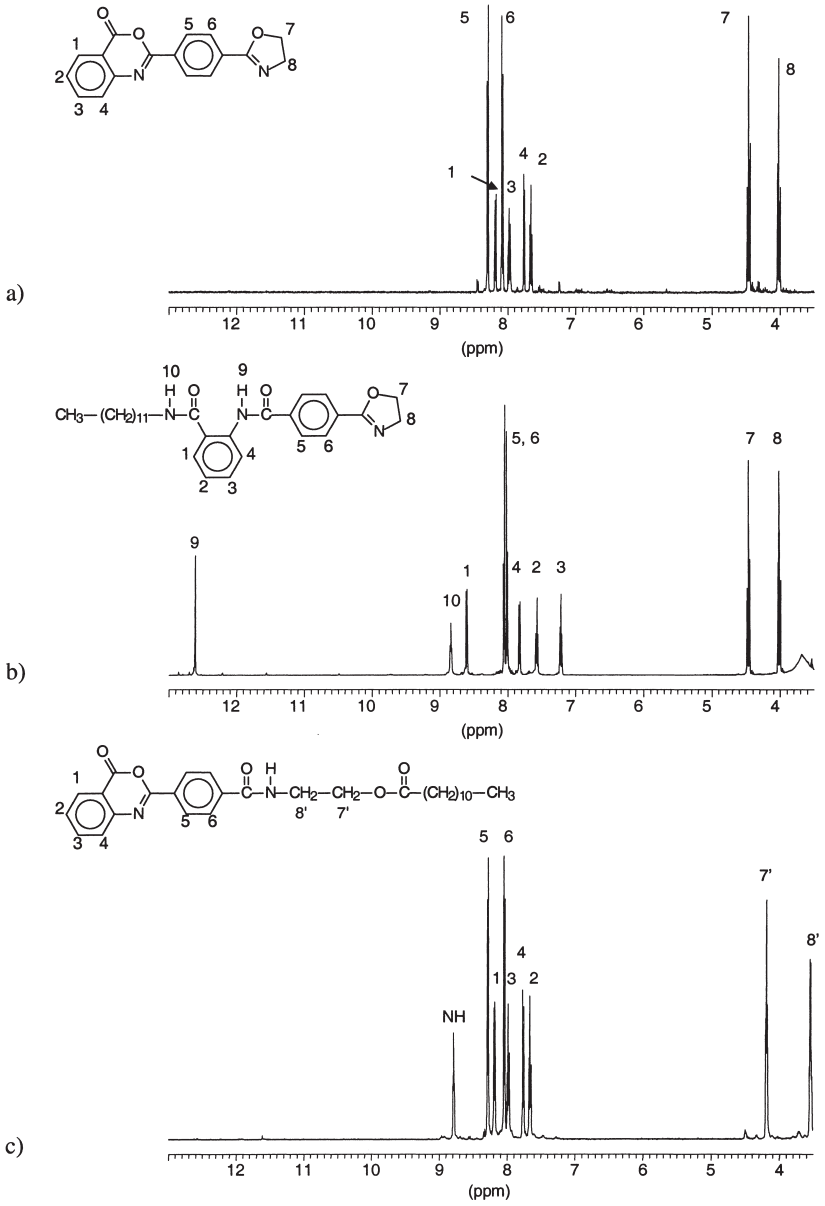
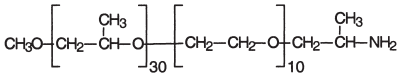


Fig. 1: ^{1}H NMR spectra of a) **2** and his reaction products with b) *n*-dodecylamine, and c) dodecanoic acid

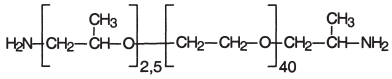
Similar results were obtained with benzoic acid. Summarizing all results, we can conclude that at 200 °C benzoic acid and dodecanoic acid react with the oxazoline group almost completely within 20 min with high selectivity. In contrast with this, *n*-dodecylamine and *n*-dodecyl alcohol attack exclusively the oxazinone group. The reaction of the oxazinone group with *n*-dodecylamine started at significantly lower temperatures (< 150 °C) than the reaction of the oxazoline group with carboxylic acids (> 170 °C). This fact offers the possibility to control coupling reactions in amino and carboxy group containing systems by step-wise conversions at different temperatures. At higher temperatures the reaction of the oxazoline groups with *n*-dodecylamine cannot be prevented completely when *n*-dodecylamine is in excess. The reaction with *n*-dodecyl alcohol demands higher temperatures. After 20 min at 240 °C the conversion of the oxazinone group is not complete. More detailed investigations including reactions with further nucleophilic compounds are in progress.

Coupling reactions in polymer mixtures

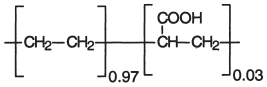
The suitability of **2** as a selective coupling agent was checked in mixtures of the amino functionalized polyethers **PEPO 1** and **PEPO 2** and the poly(ethylene-*co*-acrylic acid) **PEAA**.



PEPO 1 (Jeffamine® M 2070)



PEPO 2 (Jeffamine® ED 2001)



PEAA

A 50/50 w/w blend of **PEAA** and the amino group monoterminated polyether **PEPO 1** was prepared by melt mixing at 200 °C. The coupling agent **2** was added in molar ratio with respect to the amount of the amino groups. After 20 min a rubber like transparent material was obtained. The ^{1}H NMR spectrum (Figure 2) shows that the reaction resulted in a graft copolymer **PEAA-co-PEPO 1** with residual carboxylic groups. Both functional groups of the coupling agent **2** were converted completely. The characteristic signals for the reaction of the

oxazoline and oxazinone group appear in the same region as in the spectra of the respective model compounds (see Figure 1).

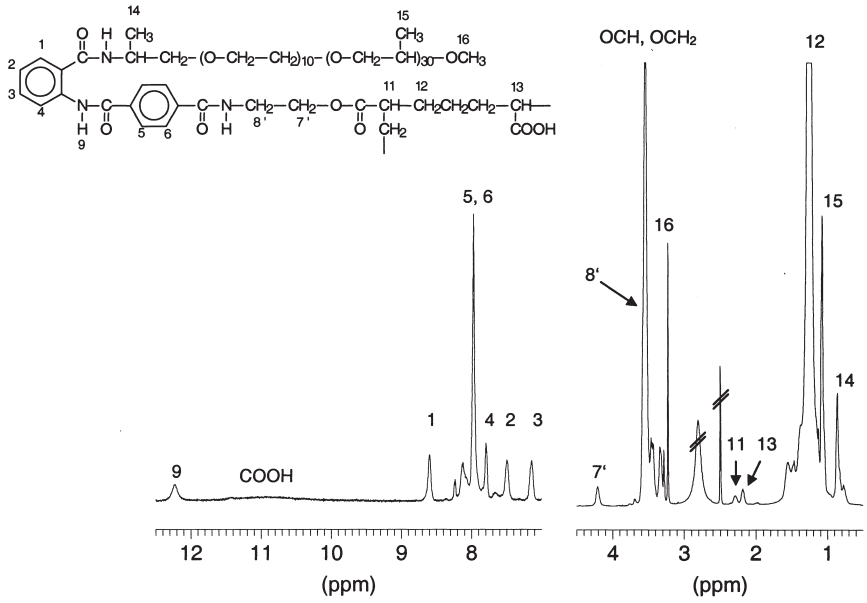


Fig. 2: ^{1}H NMR spectrum of **PEAA-*co*-PEPO 1** at 120 °C in DMSO-d_6

In Figure 3 the torque/time curve of the conversion of **PEPO 2** and **PEAA** (30/70 w/w) with the coupling agent **2** in a melt kneader at 200 °C is shown. Due to the bifunctionality of **PEPO 2** an insoluble cross-linked product was obtained. Figure 3 shows that within the first 15 min without coupling agent no significant change in torque occurs. Immediately after addition of **2** in equimolar ratio with respect to the amount of the amino groups a very strong increase of the torque accompanied by an increase of the melt temperatures can be observed.

The coupling reaction strongly influences the thermal behaviour of the mixture. In Figure 4 the DSC cooling scans of the single components and the reaction product are compared. The crystallization peaks of the pure polyether and **PEAA** occur at 11 °C and 73 °C, respectively. After the reaction, the crystallization peak of the polyether component in the mixture disappears. Obviously, the chemical linkages between both components diminish the mobility of the polyether chains so, that crystallization is completely suppressed.

Both, the model reactions and the coupling reactions in polymer mixtures showed that the bifunctional coupling agent under discussion is a versatile modifier whose functional groups

possess a high selectivity with respect to the reaction with carboxy, amino and hydroxy groups.

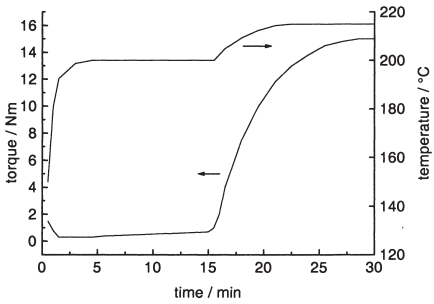


Fig. 3: Torque/time curve of the conversion of **PEPO 2**, **PEAA** and **2**

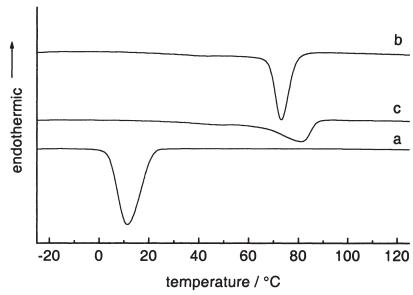


Fig. 4: DSC cooling curves a) **PEPO 2**, b) **PEAA**, and c) reactive mixture with **2**

Experimental part

All chemicals were purchased from Fluka and used without further purification. The monomethylester chloride of terephthalic acid was synthesized according to common procedures. **PEAA** was received from BASF AG and **PEPO 1** (Jeffamine® M 2070) and **PEPO 2** (Jeffamine® ED 2001) from Huntsman Co.

Synthesis of **2** (The synthesis was also described in a patent application[9].):
4-(4H-3,1-benzoxazin-4-on-2-yl)benzoyl chloride **1**:
To a solution of 19.85g (100 mmol) 4-(methoxycarbonyl)benzoyl chloride in 150 mL tetrahydrofuran 13.7 g (100 mmol) 2-aminobenzoic acid were added at 0 °C. After that 10.1 g (100 mmol) triethylamine were added at 0 °C dropwise under stirring. After 1 h stirring at room temperature tetrahydrofuran was distilled off under vacuum. The solid residue was washed with water. The product was suspended in a solution of 14.0 g (250 mmol) KOH in 400 mL water / methanol (1:1). The resulting clear solution was treated with diluted aqueous HCl. The precipitate was isolated by filtration, washed with water, and dried at 80 °C in vacuum. In a last step the obtained product was heated with 150 ml thionyl chloride under reflux for 4 h. The residue of thionyl chloride was distilled off under vacuum. After recrystallization in toluene 26,3 g 4-(4H-3,1-benzoxazin-4-on-2-yl)benzoyl chloride were obtained (m.p. = 154 °C).

2-(4-(4H-3,1-benzoxazin-4-on-2-yl)phenyl-1,3-oxazoline **2**:
Within 30 min a solution of 14.3 g (50 mmol) 4-(4H-3,1-benzoxazin-4-on-2-yl)benzoyl chloride in 100 mL tetrahydrofuran was added dropwise under stirring to a cooled solution (ice bath) of 3.05 g (50 mmol) 2-aminoethanol and 5.05 g (50 mmol) triethylamine in 150 mL tetrahydrofuran. After 1 h stirring at room temperature tetrahydrofuran was distilled off under vacuum. The solid residue was washed with tetrahydrofuran and water. After drying at 80 °C in vacuum the product was suspended in a solution of 14,9g (125 mmol) thionyl chloride in 150 ml 1,2-dichlormethane. After 10 h stirring at 0 °C the precipitate was isolated by filtration, washed with 1,2-dichlormethane, and suspended after drying for 10 min in a solution of 4,2 g (50 mmol) $NaHCO_3$ in 200 mL water. The solid residue was washed with water and dried at 80 °C in vacuum. After recrystallization in xylene 8,4 g 2-(4-(4H-3,1-benzoxazin-4-on-2-yl)phenyl-1,3-oxazoline were obtained (m.p. = 255 °C).

Model reactions of **2** were carried out in melt with a small excess of the nucleophiles under nitrogen in a small glass tube (200 °C, 20 min). The resulting products were extracted with *n*-hexane or methanol. The coupling reactions of **PEPO 1**, **PEPO 2**, and **PEAA** were performed in a glass flask with a magnetic stirrer or in a Brabender melt kneader PLE 2000 (30 ml chamber, 80 rpm, 200 °C).

500.13 MHz ^1H NMR spectra were recorded on a DRX 500 NMR spectrometer (Bruker). Dimethyl sulfoxide (DMSO)-d_6 ($\delta(^1H)$ = 2.50 ppm) was used as solvent and internal standard. Signal assignments were verified by 2D NMR measurements.
DSC measurements were performed with a Perkin Elmer DSC 7 at a scan rate of 20 K/min.

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