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Synthesis of 1,2-bis(2-oxazolinyl-2)ethane and its application as chain extender for poly(ethylene terephthalate)

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Summary

The reaction of ethanolamine (EA) with nitriles is a general route to prepare oxazolines. However, in case of vicinal nitrile groups, cyclic imidines are formed. It is shown, that succinonitrile gives with EA mainly 1-(hydroxyethyl)-2,5-bis-(hydroxyethylimine) azacyclopentane (= triol). The corresponding 1,2 bis-(2-oxazolinyl-2) ethane (BOXE) is formed by heating the triol. BOXE can be used as chain extender of poly(ethylene terephthalate) (PET). If PET is heated with BOXE at 270 °C the viscosity increases first. However, on prolonged heating the viscosity decreases again, which can not be ascribed to the normal degradation processes. Therefore, a mechanism is proposed in which the chain scission takes place in the newly formed bridge.

Introduction

Oxazolines are already known for a long time (1). In the last two decades, there is a renewed interest for these products. One reason is, that new synthetic methods were found which give high yields, using cheap starting materials such as carboxylic acids and nitriles (2). Another reason is that oxazolines give interesting homo- and copolymers via the living cationic ringopening polymerization. T.Saegusa investigated the oxazoline polymerization in great detail and showed the versatility of these monomers (3).
Others have shown that oxazolines can react with a lot of co-monomers which have a labile proton, such as carboxylic acids (4), thiols (5), phenols (6), with electron deficient double bonds such as maleimides (7) and acrylic acid (8), with heterocyclic compounds such as anhydrides (9), lactones (10) and with isocyanates (11).
An interesting feature of bisoxazolines is, that they can act as chain extender for polyesters (12). It is supposed, that the bisoxazoline reacts with the carboxylic groups of two polyester macromolecules. We are in particular interested in the synthesis and use of bisoxazolines based on succinonitrile (SN) as precursor.

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Experimental

Synthesis of 1,2-bis(2-oxazolinyl-2)ethane

In a glass flask 169 g SN (DSM chemicals) (2 mol) is dissolved in 488 g EA (Aldrich) (8 mol) and heated to 120 °C. After 6 hours the emission of ammonia ceases and the excess of EA is distilled off under reduced pressure (20-30 mm Hg). The residue is heated to 160-170 °C at reduced pressure (20-30 mm Hg) in a nitrogen stream for several hours (see table 1) to remove the liberated EA. The BOXE is isolated by distillation at 170-180 °C by 5-10 mm Hg.

Synthesis of N,N′-bis(2-acetoxyethyl) succinamide

20 g of BOXE is dissolved in 200 ml toluene and 72 g acetic acid. The mixture is refluxed for two hours. Next, toluene and the excess of acetic acid is distilled off under reduced pressure (50 mm Hg). The product was recrystallized from hot toluene and dried in a vacuum stove at 60 °C.

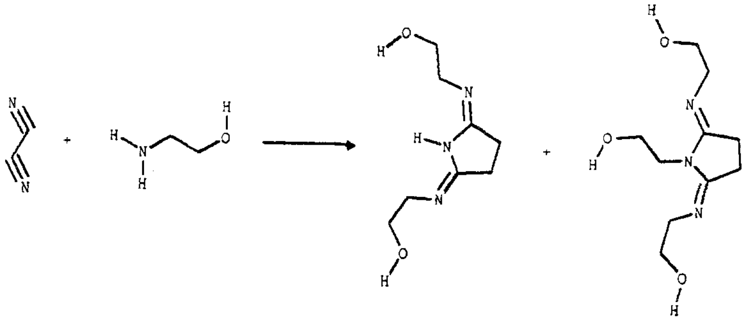
Dynamic mechanical measurements

0.1 g BOXE is dissolved in 2 g $CHCl_3$ and intimately mixed with 20 g dried PET. The $CHCl_3$ is removed by evaporation at room temperature. Small plates are pressed at room temperature and subsequently measured on the Rheometrics RMS 800. A parallel plate system (upper plate 25 mm, lower 50 mm) was used. The samples are melted and thermally equilibrated between the plates at 270 °C. After ca. 2.5 minutes the first frequency sweep is started and repeated after specified intervals.

Results and discussion

Perhaps the most simple and versatile method to synthesize oxazolines is by using nitriles and EA. We adapted this method of Witte and Seeliger to SN (13). They have noted already, that vicinal dinitriles, such as 1,2 phthalodinitrile, don't give the corresponding oxazolines, but bisimidines.
With SN we obtain similar products (scheme 1). With two equivalents of EA a mixture of the bisimidine diol I and the bisimidine triol II is formed. With three (or more) equivalents of EA the triol is obtained in high yield.
During the cyclisation step in the synthesis of the mono oxazoline, $NH_3$is emmited. In that case the reaction goes to completion because of the volatility of NH_3. If a similar mechanism is supposed with vicinal nitriles, then EA has to be emitted during the formation of the oxazoline from the triol. This reaction appears to be an equilibrium reaction. Thus, EA has to be removed to

Scheme 1



I II

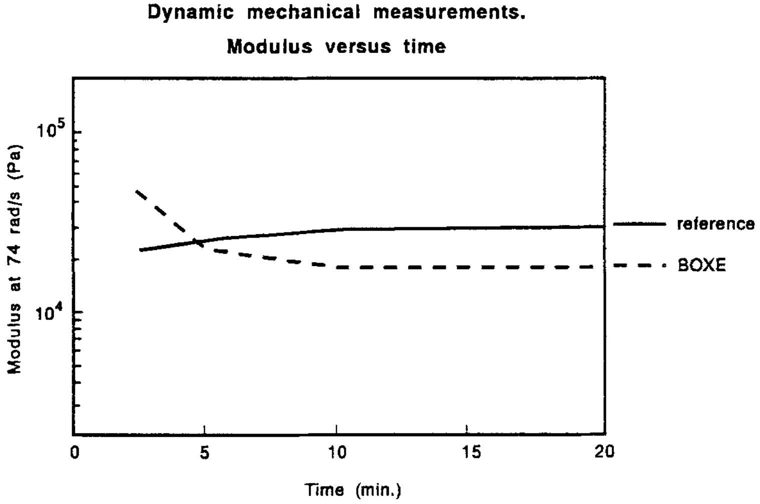
shift the process to completion. Because of the high boiling point of EA (170 °C) the reactions are performed at high temperature and under reduced pressure in a stream of nitrogen. The yield strongly increases on rising the reaction temperature. However, if the temperature is too high (>210 °C) the yield deceases again. Table 1 shows the results. The BOXE is finally isolated by distillation in a yield of 70 % with respect to SN (purity of 97 % by ^{1}H-NMR). The residue still contains BOXE, but no attemps were made to optimize the distillation step further.

Table 1. Conversion of the triol (II) into the BOXA

Experiment	Temperature	Residence time	Yield BOXE[1]
	°C	hours	%
1	130	6	50
2	150	4	70
3	170	2	60
4	170	4	85
5	170	6	90

[1] Content BOXE in the reaction mixture, measured by ^{1}H-NMR, befor distillation.

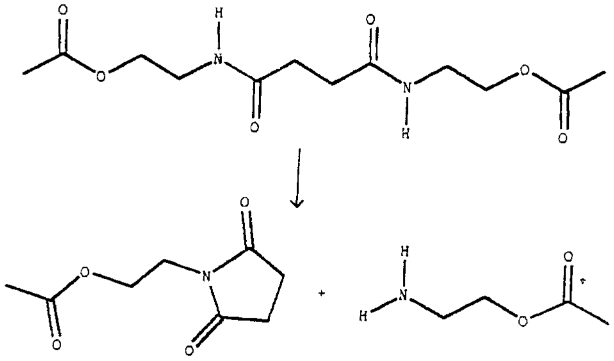
Inata et al (13) showed a strong increase of the viscosity of (PET) or poly (butylene terephtalate) (PBT) when heated at 280 °C in the presence of several bisoxazolines. It is supposed that the bisoxazoline reacts with two carboxylic end-groups of PET or PBT , giving rise to a chain extension reaction. We reproduced several of their experiments and confirmed their findings. We measured the viscosity (modulus) by DMA. (For practical reasons the first experiment can be started only after about 2-3 minutes.) With BOXE however, we find some different results (see Fig. 1). Compared with the blank, the viscosity increases also strongly in the first few minutes. However, on prolonged heating we notice a rather strong decrease of the viscosity. This decrease is stronger than with the other bisoxazolines. It is also more than one may expect from an oxidative or hydrolytical degradation process at that temperature (270 °C). In scheme 2 we postulate a reaction mechanism which might explain these results.



Dynamic mechanical measurements.
Modulus versus time

Fig. 1. Dynamic modulus at 74 rad/s versus time of PET/bisoxazoline mixtures at 270 °C.

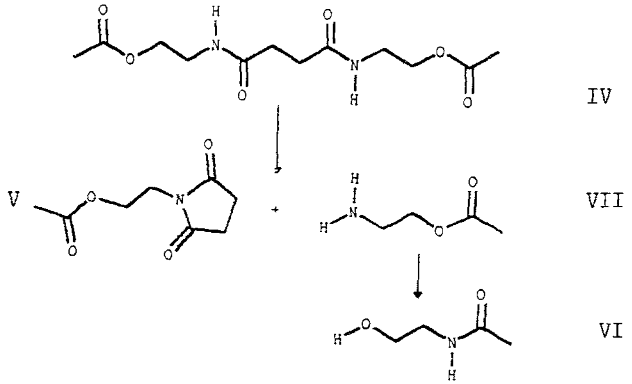
Scheme 2



III

The reaction between the BOXE and the carboxy terminated PET gives initially a bis-ester-amide (III) as depicted in scheme 2. The nitrogen of the first amide can attack the carbonyl group of the second amide group. In this case, a thermodynamically stable five membered imide ring can be formed. This reaction favours the scission of the newly formed chain extention bridge. The low concentration of carboxylic groups in PET, however, prevents the verification of this hypothesis. This prompted us to study this reaction with model compounds. N,N'-bis(2-acetoxyethyl) succinamide IV was prepared as a model for the bridge stucture. This product was heated for 5 minutes at 250 °C. The volatiles were collected and analysed with ^{1}H-NMR (Fig 2) and ^{13}C-NMR. They appear to be product V and VI (see scheme 3).

Scheme 3



These products can be rationalized by the formation of the imide V and the ester amine VII (14). At high temperature the latter will be converted into the hydroxyamide VI, a known reaction (15).

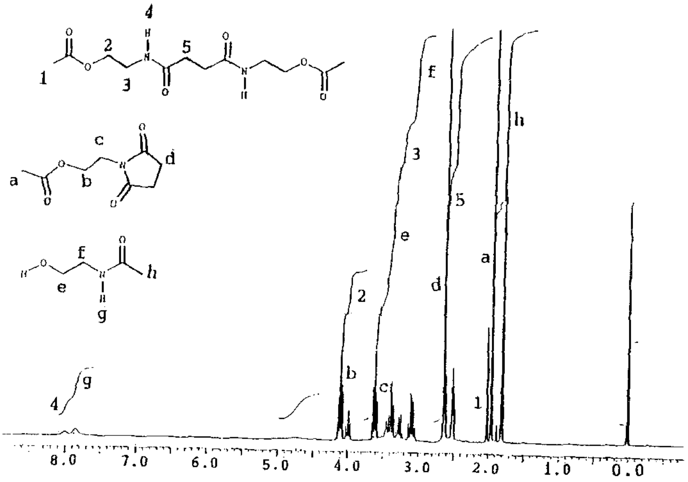


Fig. 2. ^{1}H-NMR spectra of the distillate of the reaction mixture obtained by heating N,N-bis(2-acetoxyethyl) succinamide.

These results strongly suggest that the coupling product of BOXE and two carboxylic groups of PET degradates on prolonged heating according to scheme 2. The formation of the thermodynamically stable imide group seems to be the driving force for chain scission. This reaction holds only for BOXE as chain extender because of its specific structure.
The reason for the decrease of the viscosity of PET/BOXE mixture finally below the blank is obscure. One speculation is that the original carboxylic groups are converted into an imide and a hydroxy amide. This disturbes the required stoichiometry in endgroups, necessary to obtain high molecular weight polymers. This might shift the molecular weight to a lower level.

Conclusions

The reaction between succinonitrile and an excess of ethanolamine (EA) leads to the formation of 1-(hydroxyethyl)-2,5-bis(hydroxyethylimine) azacyclopentane (triol). On heating this triol, the corresponding bisoxazoline, 1,2-bis(2-oxazolinyl-2)ethane (BOXE), is formed by splitting off one equivalent of EA.
Bisoxazolines give rise to an increase of the viscosity of poly(ethylene terphthalate) on heating the mixture at 270 °C. Probably, two chains are coupled together via the terminal carboxylic groups of the polyester. In case of BOXE however, there is a consecutive reaction. When this system is held at 270 °C, the viscosity starts to decrease after a few minutes. It is proposed, that this might be due to the degradation of the newly formed bond. Model experiments show that heating N,N′-bis(actetoxyethyl)succinamide gives a stable imide as cleavage product. These experiments makes it plausible that the same reactions occurs with the polymer.

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