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To cite this article: Viktoria Kreuzer, Klaus Bretterbauer, Gerhard Buchinger, Lisa Kaiser, Lukas Roiser & Clemens Schwarzinger (2022): Spectroscopic studies on the formation of different diastereomers in polyesters based on nadic acid, International Journal of Polymer Analysis and Characterization, DOI: 10.1080/1023666X.2022.2112642

To link to this article: https://doi.org/10.1080/1023666X.2022.2112642

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Published online: 26 Aug 2022.

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Spectroscopic studies on the formation of different diastereomers in polyesters based on nadic acid

Viktoria Kreuzer, Klaus Bretterbauer, Gerhard Buchinger, Lisa Kaiser, Lukas Roiser, and Clemens Schwarzinger

ABSTRACT

Nadic acid-based polyesters were prepared by polycondensation with different diols and different stoichiometry of the monomers. Due to the four stereocenters of the acid component, four diastereomers can form in the polyester. The use of different alcohols and influence on the formation of diastereomers in the polyester was investigated. Identification of the stereoisomers has been done with 1D and 2D NMR spectroscopy, which revealed an influence of the diol component on their formation. Further structural elucidation was done by MALDI mass spectrometry and size exclusion chromatography. Another big influence of the diols was found on the glass transition temperatures, which ranged from −30°C to 40°C.

ARTICLE HISTORY

Received 3 June 2022
Accepted 9 August 2022

KEYWORDS

Polyester characterization; NMR; MALDI; nadic acid; diastereomers

Introduction

In the 1930s, the first unsaturated polyesters were introduced. Due to their great advantage over saturated polyesters because of the cross-linking via the double bond, they found a wide range of applications. A favorable attribute of unsaturated polyesters is the broad temperature range available for processing. The disadvantage of these polyesters is the high shrinkage during the cross-linking reaction and the resulting poor surface quality. By choosing appropriate monomer components, the structure-property relationship can be varied, and adjustments can be made to suit the individual requirements of the material.

Due to the double bond in unsaturated polyesters and the associated reactivity of the systems, side reactions during synthesis can occur. A reaction published by Ordelt et al. in 1962 explains the addition of the diol to the double bond. Due to the conjugated system in, for example, fumaric acid and maleic anhydride, these monomers can undergo this side reaction. To suppress this, the conjugation must be interrupted. One way of doing so is using nadic anhydride, the Diels-Alder product of maleic anhydride and cyclopentadiene, as acid component (Scheme 1).

The Diels-Alder reaction of a diene and a dienophile is a well investigated reaction which was first reported by O. Diels and K. Alder in 1928. The Diels-Alder reaction of maleic anhydride (1) with cyclopentadiene (2) (Scheme 1) was first reported by Levchenko et al. and Maruyama et al. in 1981. Since then, many studies have been carried out to investigate the influences on the reaction as well as to elucidate the distribution between exo (3a) and endo (3b) products. Another
important aspect of this reaction is its thermal reversibility, called retro Diels-Alder reaction, which might lead to undesired decomposition of the products during further polymer synthesis.

Polymer characterization offers a wide range of instrumental possibilities, each of which provides different information about the polymer. To obtain the most accurate information possible, those data must be compared and interpreted as a whole. Nuclear Magnetic Resonance spectroscopy (NMR) plays a major role in polymer characterization, especially in the determination of end groups of small and medium molar mass polymers. For very large polymers, however, the end group to repeat unit ratio becomes too small and the corresponding signals are no longer distinguishable from the noise. Furthermore, the residual content of the monomers in the polymer itself can be determined.\textsuperscript{[9]} Additionally, NMR can differentiate between diastereomers, in particular the distinction between \textit{cis} and \textit{trans} products in polyesters is reported,\textsuperscript{[10]} as well as the identification of esterified nadic acid diastereomers.\textsuperscript{[11]} A downside of NMR is its inability to differentiate between cyclic polymers, which are regularly formed in polycondensation reactions,\textsuperscript{[12]} and linear molecules and due to the lack of end groups no proper quantification can be done.

Most of the information missed by NMR can be obtained from mass spectrometry, in the case of polymer analysis most frequently from Matrix-Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI ToF MS), such as determination of the individual polymer chain structure, cyclic oligomers, and, under ideal circumstances, even molar mass distribution.\textsuperscript{[13–16]}

In this paper, nadic acid was used as monomer in combination with various diols to investigate their influence on physical properties such as glass transition temperature, but most importantly on molar mass distribution and formation of the various diastereomers of nadic acid esters.

Materials and methods

Materials

Neopentyl glycol used for polyester synthesis was provided by Perstorp AB. Methyl isobutyl ketone (MIBK, 99\%) was purchased from Alfa Aesar. Nadic anhydride (99+\%) and 1,10-decanediol were obtained from Acros Organics. 1,6-hexanediol was used from Fluka. Unstabilized tetrahydrofuran (THF) for SEC and MALDI-ToF-MS and 1,4-butanediol were purchased from Carl Roth. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DHCB) from abcr and sodium trifluoroacetate from Fluka were used for MALDI-ToF-MS sample preparation. Chlorofrom-\textit{d} for NMR spectroscopy was used from VWR Chemicals with a purity of 99.8\%. All reagents used without further purification.

Methods

Synthesis of polyesters

Polyesters were synthesized using a diol, one or two diacid(s)/anhydride(s) and MIBK as entrainer. A tin catalyst and a commonly available phosphite as stabilizer were used. In a 4-necked flask with a nitrogen inlet, a Dean-Stark apparatus and a KPG stirrer all reactants were heated to 170°C. The water formed during the polycondensation reaction was collected and used to monitor the reaction progress. MIBK was removed under vacuum at the end of the reaction.
**NMR spectroscopy**

NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. Samples for $^1$H-NMR were prepared using about 15 mg of polyester dissolved in 0.6 mL chloroform-$d$ with dimethyl formamide (DMF) as internal standard. All peaks are reported relative to tetramethyl silane. For $^{13}$C NMRs and all 2D experiments about 25 mg of each sample was dissolved in 0.6 mL chloroform-$d$ without using an internal standard. Deconvolution and integration were performed with TopSpin 4.0.6 software.

**SEC – size exclusion chromatography**

Size exclusion chromatography was used for determination of mass-average molecular weight ($M_w$), number-average molar mass ($M_n$) and polydispersity ($D$). The SEC setup consisted of a pump (PU-2086 Plus, Jasco), autosampler (728, Bischoff) UV/Vis detector (UV-975, Jasco) recording at a wavelength of 260 nm. Separation was carried out on Phenogel columns (300 × 4.6 mm, 5 μm) with porosities of 1000 Å, 500 Å and 50 Å. Calibration was performed with polystyrene standards using a quadratic regression. The data are evaluated manually, a baseline correction is performed, and the peak cut off is set to the molar mass of the smallest dimer (10.5 mL). The samples were prepared by dissolving 2–3 mg of each polymer in 1 mL THF which was also used as eluent. Flow rate was 350 μL min$^{-1}$ and injection volume 100 μL.

**DSC – differential scanning calorimetry**

3–5 mg of the polyester was weighed into aluminum pans for the determination of the glass transition and were analyzed on a Perkin Elmer DSC 8000. The measurements started at 30 °C followed by heating to 150 °C at a heating rate of 20 °C per minute. After holding that temperature for 1 min, the sample was cooled to −50 °C at 20 °C per minute and again held there for 1 min. In the second heating up to 150 °C, the glass transition temperature was determined.

**MALDI-ToF-MS – matrix-assisted laser desorption ionization – time of flight – mass spectrometry**

MALDI mass spectra were recorded on a Bruker Autoflex III smartbeam in reflectron mode. Sample preparation was done following the dried droplets protocol from THF as solvent with DHCB as matrix (10 mg mL$^{-1}$) and sodium trifluoroacetate (1 mg mL$^{-1}$) as ionization agent. Sample (10 mg mL$^{-1}$), matrix and salt solutions were mixed in a 100:10:1 ratio and an aliquote of 1 μL was spotted onto a ground steel target. Bruker Flex Analysis 3.0 software was used for peak integration and deconvolution. For quantification Na adducts were taken into account.

**Results and discussion**

Scheme 2 exemplifies the reaction of polycondensation of nadic anhydride 3 and ethylene glycol 4 under organometallic catalysis. A hindered phenol-based stabilizer was added to prevent undesired side reactions and MIBK was used as entrainer to help remove the reaction water.

![Scheme 2](image)

**Scheme 2.** Polycondensation of nadic anhydride (3), ethylene glycol (4) with a catalyst, stabilizer and MIBK as entrainer.
For polycondensation with two components various diols were used and the ratio of diol and anhydride was varied. Table 1 shows the different educts used, the anhydride to diol ratios and their influence on molar mass distributions as well as glass transition temperature. The glass transition temperature is also listed in Table 1. A comparison of the values shows a trend, that the glass transition temperature decreases with the chain length of the diol when comparing EG2, BD, HD and DD (all having a 1:1 stoichiometry).

Size exclusion chromatography

The SEC results of all polyesters are summarized in Table 1. A comparison of polyesters EG1, EG2 and EG3, which differ in the nadic anhydride to ethylene glycol ratio, can be seen in Figure 1. The grey-dashed line indicates the lower molar mass limit that was used to calculate $M_n$ and $M_w$ of the polymer chains excluding unreacted monomers. Whereas the influence of educt ratio on the glass transition temperature is only marginal, a quite obvious effect can be seen in the weight average molecular weights and the polydispersities. The stochiometric EG2 does have the narrowest distribution, the one with excess anhydride the broadest, while all three do have basically the same shape of SEC curve.

Table 1. Polycondensations with various diols and the stoichiometry of components, molecular weights, polydispersity and glass transition temperature ($T_g$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diol ratio</th>
<th>$M_n$/g mol$^{-1}$</th>
<th>$M_w$/g mol$^{-1}$</th>
<th>$D$</th>
<th>$T_g$/$^\circ$/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG1</td>
<td>Ethylene glycol</td>
<td>0.8:1</td>
<td>1530</td>
<td>7880</td>
<td>5.1</td>
</tr>
<tr>
<td>EG2</td>
<td>Ethylene glycol</td>
<td>1:1</td>
<td>1520</td>
<td>4900</td>
<td>3.2</td>
</tr>
<tr>
<td>EG3</td>
<td>Ethylene glycol</td>
<td>1.06:1</td>
<td>1670</td>
<td>15350</td>
<td>9.2</td>
</tr>
<tr>
<td>NPG</td>
<td>Neopentyl glycol</td>
<td>1:1</td>
<td>2440</td>
<td>31190</td>
<td>12.8</td>
</tr>
<tr>
<td>BD</td>
<td>1,4-Butanediol</td>
<td>1:1</td>
<td>1310</td>
<td>3590</td>
<td>2.7</td>
</tr>
<tr>
<td>HD</td>
<td>1,6-Hexanediol</td>
<td>1:1</td>
<td>2200</td>
<td>16650</td>
<td>7.5</td>
</tr>
<tr>
<td>DD</td>
<td>1,10-Decandiol</td>
<td>1:1</td>
<td>1670</td>
<td>10570</td>
<td>6.3</td>
</tr>
</tbody>
</table>

*aAnhydride to diol ratio.*

**Figure 1.** SEC chromatogram of EG1, EG2 and EG3.
Figure 2 shows the chromatograms of the polyesters with linear diols in a 1:1 ratio, enabling an easy comparison of the influence of aliphatic chain length of the various diols. In contrast to the other polyesters, EG2 has the lowest $M_n$ and $M_w$, as well as the lowest polydispersity. Reason for this is most likely the lower reactivity of ethylene glycol, since the reactivity increases with increasing chain length of the diol.[17] In contrast to the linear diols, neopentyl glycol shows a shoulder in the high molecular weight region, indicating a rather heterogeneous formation of the polymer chains and thus a very high $M_w$ and polydispersity.

**NMR spectroscopy**

Nadic anhydride, mostly present in *endo* form before polycondensation (purity 99+% with traces of *exo* form, forms four different diastereomers which are displayed in Scheme 3 with ethylene glycol as diol exemplary. Diastereomer A represents a stereochemistry of (1R, 2R, 3S, 4S), diastereomer B displays a stereochemistry of (1R, 2S, 3R, 4S) and diastereomer C of (1R, 2S, 3S, 4S). Diastereomer D has a stereochemistry of (1R, 2R, 3R, 4S).

Different information can be detected by $^1$H NMR and is described in the following exemplarily for EG1. First, the free monomer content can be determined by integrating and comparing signals with an internal standard, but also the ratio of the diastereomers of the nadic component can be identified. Due to the possible retro-Diels-Alder reaction of nadic anhydride during synthesis, fumaric acid, the product of this reaction, is also incorporated into the polyester. By
integrating the signal at 8.65 ppm, the amount of fumaric acid in the polyester can be determined. Figure 3 shows the NMRs of EG1, EG2 and EG3, which are formed from nadic anhydride and ethylene glycol. The difference between these polyesters results from the stoichiometry: EG1 is a polyester with diol excess, EG2 with a stoichiometry of 1:1 and EG3 is an acid terminated polyester. In the spectrum of EG2 and EG3 – with excess acid – the free nadic acid can be seen in the spectrum in the range of 3.60–3.47 ppm and in between 1.80 and 1.73 ppm. The other $^1$H-peaks from the free acid overlap with the peaks of the polyester. The differences between EG1 compared to EG2 and EG3 are clearly seen in the lack of free acid, this suggests a complete conversion of the acid component. With a ratio of 1:1, the free acid can still be detected. A longer reaction time could lead to the excess acid reacting off. The protons of the polyester can be assigned to individual ranges. Whereas the signal of the double bond can be found in the range of 5.9–6.4 ppm, the protons of the glycol can be assigned to the range of 4.5–3.6 ppm. The CH-groups can be seen in the range of 3.5–2.5 ppm due to their shielding. The H-atoms of the bridge atom can be detected in the range of 2.1–1.3 ppm.

$^{13}$C-NMR, HMBC (heteronuclear multiple bond correlation), HSQC (heteronuclear single quantum coherence), and a homonuclear COSY (Correlated Spectroscopy) experiments were used to assign each peak to its respective diastereomer.

For further evaluation, an overview of the individual C-atoms and their assignment to each region via an APT (Attached Proton Test) $^{13}$C-NMR of EG1 is shown in Figure 4. Different shifts of the individual diastereomers can also be observed in $^{13}$C-NMR. The carbonyl carbons 8 and 9 of the ester are assigned to the region of 170–175 ppm, and the double bond atoms 5 and 6 are in the range of 132–137 ppm. CH$_2$-carbons of ethylene glycol (10 and 11) are located between 60 and 70 ppm. A distinction between nadic acid and fumaric acid units can be made by different shielding of the latter signals. Ethylene glycol signals next to fumaric acid (F) are in a higher ppm range. Sp$^3$ hybridized C-atoms 1,2,3,4 and 7 are found in the range of 45–49 ppm and the CH$_2$-group 7 can be distinguished in an APT spectrum because of its signal going in the negative direction.

In the region of the double bonds from 6.00 to 6.50 ppm in $^1$H-NMR, a splitting of the single stereoisomers can be seen. Due to the coupling of the protons 5 and 6 of the double bond, with two different hydrogen atoms, namely 1 and 4, splitting into a doublet of doublets of each signal should be seen as a quartet.

Figure 3. $^1$H-NMR of EG1, EG2 and EG3 in CDCl$_3$ with assignments to the polyester with nadic acid and fumaric acid and monoester (*) as well as the monomer (**).
Figure 4. $^{13}$C-NMR APT of EG1 in CDCl$_3$ (77.2 ppm) with the assignment of nadic and fumaric acid-based polyester units.

Figure 5. COSY-NMR of EG1 in the region of 5.5–6.5 ppm with the correlation of two protons of diastereomers C and D.
given. In diastereomer A as well as B the respective protons 5 and 6 within each stereoisomer show chemical similarity and thus no splitting is seen and they appear as singlet. Figure 5 shows the COSY-NMR in the double bond region and thus the coupling of adjacent protons. Marked in red are the signals 6.00–6.03 ppm and 6.23–6.26 ppm coupling with one another, hence they can be assigned to diastereomers C and D because of their splitting. These two cannot be distinguished further via NMR. For the other two signals in the range of 6.15–6.25 ppm no further coupling is indicated in COSY-NMR and they thus can be assigned to diastereomers A and B. The distinction between diastereomers A and B follows at a later stage but will be marked correctly in the further elucidation. The ratio in which the individual diastereomers occur in the polymer can only be determined statistically. Due to the thermodynamically favored endo-isomer of the nadic anhydride, a correlation between the composition of the diastereomers can be concluded.

Peaks in the range of 3.6–4.2 ppm can be assigned to the CH$_2$ groups of the diol based on their shift. After the assignment of the protons attached to the double bond (5 and 6), it is possible to assign the adjacent protons 1 and 4 via their coupling in the COSY experiment (Figure 6). Diastereomer A is blue, dashed, diastereomer B is marked green, dashed-dotted and diastereomers C and D are highlighted in red, solid.

Figure 6. COSY-NMR of EG1 in the region of 3.0–6.5 ppm assignment of double bond protons (5,6) with adjacent protons (1,4) to different diastereomers A (blue, dashed), B (green, dashed-dotted) and C/D (red, solid).
To classify the remaining CH protons 2 and 3 as well as the CH₂ group (7), the correlation in COSY is examined in more detail. For this purpose, the range of 1.1—3.7 ppm is shown in Figure 7. Once protons 1 and 4 have been assigned to their signals, the COSY NMR can be used to classify the adjacent H atoms 2, 3 and 7 based on their coupling. The overlap of the bridge protons of the individual diastereomers (7) of one of the signals is shown as a black dashed line and represents all four diastereomers. Thus, except for one proton of diastereomer A, which is identified via HSQC and HMBC, all signals can be assigned.

The two H atoms (7) at the bridge C atom are connected via a geminal coupling. Since the two H atoms have a diastereotopic character, they are anisochromic and their coupling constant can be determined. To see these couplings, a reference is made to the HSQC. However, it should be noted that some diastereomers show a larger coupling whereas others do not split at all.

For the differentiation of the individual diastereomers, the H atoms of the bridge atom are used. Using literature values of NOE experiments a prediction about the assignment can be made [11]. Due to the differences of the NOE, shown in Scheme 4, between the H atoms 7 and H atoms 2 and 3, the two diastereomers A and B can be assigned. No distinction can be made between diastereomers C and D because they are nearly symmetrical in the polyester itself. Due

**Figure 7.** COSY-NMR of EG1 in the region of 1.1—3.7 ppm assignment of double bond protons (5,6) with adjacent protons (1,4) to different diastereomers A (blue, dashed), B (green, dashed-dotted) and C/D (red, solid).
to the spatial distance between protons in diastereomer A, no NOE is expected. This contrasts with diastereomer B where the spatial proximity to both, proton 2 and proton 3 is given and it thus has two NOEs. Diastereomers C and D each have one NOE of H-atom 7 to both protons 2 and 3.

Figure 8 shows the HSQC-NMR of EG1 and the assignment to each diastereomer of the protons to the carbons. Thus, not only the assignment to the carbon signal is possible, also the previous assignment can be checked, as CH₂ groups yield negative signals whereas CH groups yield positive signals.

The HMBC-NMR of EG1 is displayed in Figure 9. This NMR shows the correlation of a C-atom with different protons over several bonds, and thus the structure elucidation and the distinction of the diastereomers can be validated.

Figure 10 shows the ¹H-NMR of EG1 with the assignment of the different diastereomers A–D.

Scheme 4. Display of the NOEs of the different diastereomers.

Figure 8. HSQC-NMR of EG1 with assignment of protons of the bridge atom (7), of the H-atom in α-position (2,3) and of the β-position (1,4) to the respective diastereomer A (blue, dashed), B (green, dashed-dotted) and C/D (red, solid).
Figure 9. HMBC-NMR of EG1 in CDCl₃.

Figure 10. ¹H-NMR of EG1 with assignment to different diastereomers.
Figure 11 shows the $^1$H NMRs of polyesters made from different diols. The chain length of the diol affects the distribution of the diastereomers. Diastereomer A can be calculated based on the stand-alone signal from the bridge atom. For the calculation of diastereomer B and the mixture of diastereomers C and D, H atom 3 is used. Due to the shift downfield of the protons with the residues in *endo* position, the peaks are clearly recognizable and can therefore be used for calculation.

The chain length of the diol as well as the ratio of the individual monomers has a major influence on the distribution of the diastereomers in the polyester. Table 2 lists the composition of the diastereomers in the individual reactions. While the distribution of diastereomers in the polyester with ethylene glycol and excess anhydride shows an almost uniform formation (see entry 3 Table 2), with no distinction possible for diastereomer C and D, with increasing ethylene glycol content (EG1 and PES 2), the formation of diastereomer A is suppressed. At the same time, the value of diastereomer B and diastereomers C and D increases, but no precise statement can be made about the favoring of the individual diastereomers and the influence of stoichiometry on the different formations. Comparing the entry of BD, HD and DD in Table 2 to EG2, the formation of the different diastereomers can be inferred with respect to the influence of the chain length of the diol. With the increase of CH$_2$ groups in the diol, more of diastereomer B is formed and the formation of diastereomers C and D is further suppressed. Entry NPG, in Table 2 shows the distribution results using the branched diol neopentyl glycol. Besides the already described

![Figure 11. $^1$H-NMR of EG2, BD, HD and DD with CDCl$_3$ as solvent.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diastereomer A</th>
<th>Diastereomer B</th>
<th>Diastereomers C + D</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG1</td>
<td>1.00</td>
<td>1.45</td>
<td>3.14</td>
</tr>
<tr>
<td>EG2</td>
<td>1.00</td>
<td>1.25</td>
<td>2.42</td>
</tr>
<tr>
<td>EG3</td>
<td>1.00</td>
<td>1.00</td>
<td>2.33</td>
</tr>
<tr>
<td>NPG</td>
<td>1.00</td>
<td>1.11</td>
<td>1.02</td>
</tr>
<tr>
<td>BD</td>
<td>1.00</td>
<td>2.39</td>
<td>0.65</td>
</tr>
<tr>
<td>HD</td>
<td>1.00</td>
<td>2.73</td>
<td>0.51</td>
</tr>
<tr>
<td>DD</td>
<td>1.00</td>
<td>3.50</td>
<td>0.50</td>
</tr>
</tbody>
</table>
mechanism no explanation could be found how and why the length of the diol interacts with the formation of the diastereomers. We have only observed and thus describes this effect.

In literature two different possibilities for the formation of these four diastereomers are presented. On the one hand, a biradical mechanism is shown which can occur during a retro-DA\textsuperscript{[18]} and on the other hand a mechanism where an alkoxide anion formation is discussed.\textsuperscript{[19,20]}

MALDI-ToF-MS

By using MALDI mass spectrometry the end group determination as well as the distribution of nadic acid and its retro-Diels-Alder product fumaric acid are investigated. In the mass spectra four different end groups of the polyester systems were found. Cyclic structures [cyclic-PES], which are formed only to a certain number of repeating units, double acid terminated series [HOOC-PES-COOH], double hydroxyl terminated series [HO-PES-OH] and mixed terminated series [HO-PES-COOH] are formed. Quantification is carried out by integration of the sodium adducts, as proton adducts as well as sodium adducts of the sodium salts of carboxylic acids have not been detected in noteworthy concentrations.

Figure 12 shows the range between 780 and 1070 Da of the polyester NPG with a color-coded assignment of the series (cyclic, mixed terminated, double hydroxyl or acid terminated) with repeat units of $n = 3$–$4$ and the adducts of sodium in reflectron mode.

**Figure 12.** MALDI-ToF-MS spectra of NPG with the assignment of the series (cyclic, mixed terminated, double hydroxyl or acid terminated) with repeat units of $n = 3$–$4$ and the adducts of sodium in reflectron mode.
Conclusions

Polyesters based on nadic acid and a variety of diols have successfully been synthesized and characterized by NMR and MALDI mass spectrometry. Variation of the diol shows a major influence on thermal properties such as the glass transition temperature, which enables easy adjustment of this property by using the appropriate diol or a mixture thereof. Two out of four diastereomers formed during the polycondensation of nadic anhydride have been assigned unequivocally, whereas two could not be separated from each other. It is observed that the choice of diol has a great influence on the distribution of diastereomers in the polyester. While the formation of the four diastereomers is almost uniform when ethylene glycol is used, the formation of diastereomer B (1R, 2S, 3R, 4S) is preferred when the chain length is increased.

Acknowledgement

The authors want to thank Daniel Pernusch for programming tools enabling easy quantitative analysis of MALDI spectra and SEC chromatograms.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

The used NMR spectrometers were acquired in collaboration with the University of South Bohemia (CZ) with financial support from the European Union through the EFRE INTERREG IV ETC-AT-CZ program [project M00146, “RERI-uasb”]. This work was funded by FFG (Austrian Research Promotion Agency) under Grant 871113.
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