Macromolecules
Article
pubs.acs.org/Macromolecules

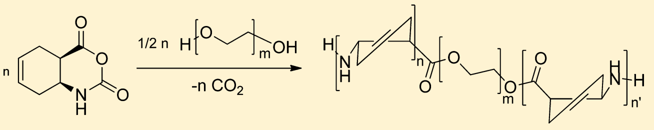
Access to Amphiphilic *Cis*-Configurated Polyamide-3 Using Alcohols as Initiators

Olga Maiatska, Alexander Belkin, and Helmut Ritter*

Institute of Organic Chemistry and Macromolecular Chemistry, Heinrich Heine University of Duesseldorf, Universitaetsstrasse 1, 40225 Duesseldorf, Germany

Supporting Information

ABSTRACT: The synthesis of polyamide-3 from 4a,5,8,8a-tetrahydro-1*H*-benzo[*d*][1,3]oxazine-2,4-dione (*β*-NCA, **1**) using methanol, dye (Disperse Red 13), and poly(ethylene glycol) as initiator is described. The ring-opening polymerization under release of CO_2 produces polyamides-3 with definite terminal groups, high purity, and relatively narrow dispersity. This route was used for preparation of block copolymers from as an example.



INTRODUCTION

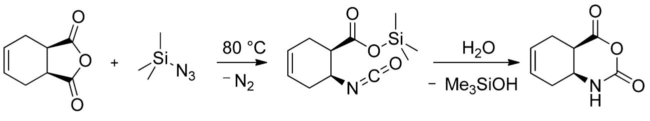
For many decades, aliphatic polyamides have been of great practical and scientific importance.[1] Especially polyamide-6 (Perlon) or polyamide-66 (Nylon) are the main products. They are produced worldwide in megatons via ring-opening polymerization or via polycondensation, respectively. However, polyamide-2 belongs generally to the group of proteins. The synthesis can be conducted enzymatically via ring-opening polymerization of *N*-carboxyanhydride of natural *α*-amino acids step by step under irreversible release of CO_2. This type of polycondensation was the subject of many papers and was first described by Curtius et al.[2−4] and Wessely et al.[5−12] In contrast to that, the knowledge about preparation and properties of polyamid-3 is relatively poor.[13] Thus, it can be stated that the required *N*-carboxyanhydrides of *β*-amino acids belong to the group of "forgotten monomers". Basically, polyamide-3 is a polycondensate of 3-amino acids. It turned out that the preparation polyamide-3 succeeds via ring-opening polymerization of *β*-amino acid *N*-carboxyanhydrides (*β*-NCA's) under release of CO_2 per monomer unit which is in analogy to the preparation of polyamide-2 from *α*-amino acid *N*-carboxyanhydrides (*α*-NCA's).[14−16] The synthesis of *β*-NCA's can be conducted from cyclic anhydrides with trimethylsilyl azide via rearrangement and final cyclization. This method was first described in the early 1970s.[17,18] The ring-opening polymerization of *β*-NCAs to yield polyamide-3 can be catalyzed with various amines, e.g., triethylamine, pyridine, or 4-bromoaniline.[13]

However, up to now, the use of alcohols as initiators for the design of targeted end-groups of polyamide-3 has not been described in the literature. According to our interest to rediscover "forgotten monomers", we were motivated to use methanol and an OH group containing dye (Disperse Red 13) as model compounds and also poly(ethylene glycol) to obtain amphiphilic block copolymers.

RESULTS AND DISCUSSION

In the present work, the required monomer 4a,5,8,8a-tetrahydro-1*H*-benzo[*d*][1,3]oxazine-2,4-dione (*β*-NCA, **1**) was prepared according to literature from *cis*-1,2,3,6-tetrahydrophthalic anhydride and trimethylsilyl azide (Scheme 1).[13]

Scheme 1. Synthesis of *cis*-*β*-NCA (1)



1

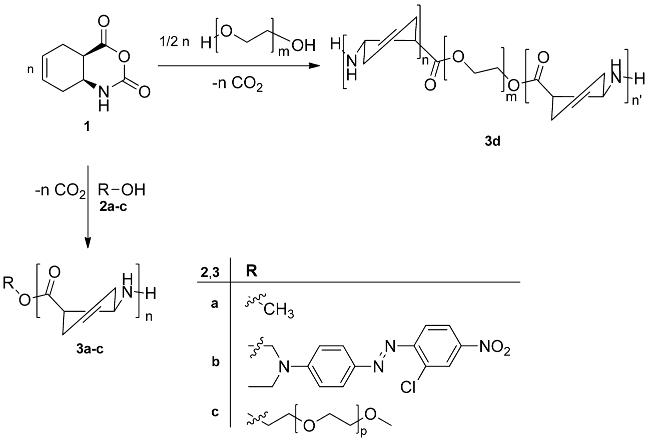
The structure of **1** was confirmed by ^1H NMR spectroscopy and characteristically by the FT-IR spectrum which exhibits strong absorption bands of the carbonyl groups at 1784, 1746, and 1724 cm^{-1}. Since tetrahydrophthalic anhydride is prepared in a technical scale from butadiene and maleic anhydride via a typical Diels−Alder ($2\pi + 4\pi$) cycloaddition, the two carbonyl groups are necessarily positioned in the 1,2-*cis*-configuration. This means that, after Curtius rearrangement, the *cis*-configuration is also retained. Accordingly, the bicyclic compound **1** must be *cis*-configurated.[19]

The alcohol-initiated ring-opening polymerization of **1** was accomplished by using of methanol (**2a**), Disperse Red 13 (**2b**), and methoxypolyethylene glycol 350 (**2c**) (Scheme 2). Since the initiation step with alcohol is relatively slow compared to propagation reactions with the terminal amines, an excess of alcohol could be used quasi as solvents and initiator. In the case of the solid dye **2b**, toluene was used as solvent. During the reaction, a release of bubbling carbon dioxide can be observed. As mentioned above, this important

Received: February 11, 2015
Revised: March 30, 2015

DOI: 10.1021/acs.macromol.5b00272
Macromolecules XXXX, XXX, XXX−XXX

Scheme 2. Ring-Opening Polymerization of β-NCA (1) Starting from OH-Containing Derivatives



point was not described in the former literature.[13] Additionally, as indicated in Scheme 2, the *cis*-configuration of the incorporated monomer units is characteristic of the main chain. This aspect was also not yet considered in former investigations.[13]

Molecular weights of the **3a–d** were determined by use of GPC. The thermal properties were evaluated using differential scanning calorimetry (DSC) measurements. Polymers **3a–3d** show a glass transition between 125 and 153 °C, depending on the end-groups of polyamides. Block copolymers **3c** and **3d** contain PEG residues and exhibit lower glass transition compared to the **3a** and **3b** (Table 1).

Table 1. Characterization of Polymers 3a–3d

sample	alcohol/monomer molar ratio	M_w[a] [g mol^{-1}]	D[b]	T_g[c] [°C]
3a	40/1	2300	1.2	145
3b	1/1	6700	1.5	153
3c	1/1	5800	1.2	123
3d	1/2	8600	1.2	133

[a] Determined by GPC (DMF) with polystyrene standards. [b] $D = M_w/M_n$. [c] Determined by DSC.

Compared to the **3a**, the polymers **3b–3d** show a higher number- and weight-average molar mass. The reason for the relatively low molecular weight of **3a** therefore is excess amount of methanol (Table 1).

The chemical structures of **3a–3d** were verified by ^{1}H NMR and FT-IR spectroscopy (Supporting Information). A strong C=O vibration at about 1640 cm^{-1} (amide I), 1730 cm^{-1} (ester), and 1550 cm^{-1} (amide II) corresponds to the proposed structure.

The MALDI-TOF mass spectrum of **3a** (Figure 1) also clearly confirmed the formation of polyamide-3, showing the mass difference of the repeating unit of 123 g mol $^{-1}$. The highest assignable degree of polymerization of **3a** is $n = 25$ polymer which correspond to a molar mass of $[M + Na]^+ = 3131$ m/z. Also, the formation of polymer **3b** could be confirmed by MALDI-TOF mass spectrometry (Supporting Information).

CONCLUSION

It can be concluded from the above-described results that a polyamide-3 containing *trans*-cyclohexene units in the main chain can be prepared via Diels–Alder cyclization, ring extension using a Curtius type rearrangement,[20,21] and subsequent ring-opening polymerization. The main novelty of this investigation is use of alcohols as initiator which are attached as ester end-groups. This opens the door for preparation of e.g. amphiphilic block copolymers.

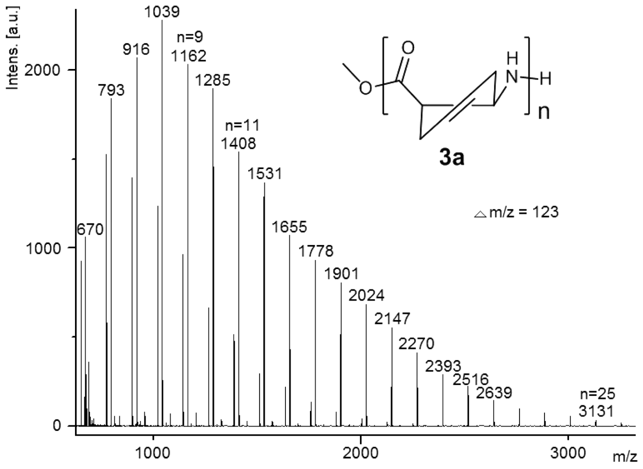


Figure 1. MALDI-TOF mass spectrum of polyamide **3a**.

ASSOCIATED CONTENT

Supporting Information

Description of the syntheses and spectroscopic data of the obtained compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*(H.R.) Tel (+49) 211 81-14760; Fax (+49) 211 8115840; e-mail h.ritter@uni-duesseldorf.de.

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Fischer, M.; Balsam, M. *Polyamide, Kunststoffe* **2001**, *10*, 284–289.

(2) Curtius, T.; Sieber, W. *Ber. Dtsch. Chem. Ges. B* **1921**, *54*, 1430–1437.

(3) Curtius, T.; Sieber, W. *Ber. Dtsch. Chem. Ges. B* **1922**, *55*, 1543–1558.

(4) Curtius, T.; Hochschwender, K.; Meier, H.; Lehmann, W.; Benckiger, A.; Schenk, M.; Nirbatz, W.; J. Gaier, W. *J. Prakt. Chem.* **1930**, *125*, 211–302.

(5) Wessely, F. *Z. Physiol. Chem.* **1925**, *146*, 72–90.

(6) Wessely, F.; Sigmund, F. *Z. Physiol. Chem.* **1926**, *159*, 102–119.

(7) Sigmund, F.; Wessely, F. *Z. Physiol. Chem.* **1926**, *157*, 91–105.

(8) Wessely, F.; John, M. *Z. Physiol. Chem.* **1927**, *170*, 38–43.

(9) Wessely, F.; Mayer, J. *Monatsh. Chem.* **1928**, *50*, 439–448.

(10) Wessely, F.; Riedel, K.; Tuppy, H. *Monatsh. Chem.* **1950**, *81*, 861–872.

(11) Wessely, F.; Swoboda, W. *Monatsh. Chem.* **1951**, *82*, 621–627.

(12) Wessely, F.; Schlgl, K.; Korgers, G. *Monatsh. Chem.* **1952**, *83*, 845–864.

(13) Kricheldorf, H. R. *Makromol. Chem.* **1973**, *170*, 89–103.

(14) Leuchs, H. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 857–861.

(15) Leuchs, H.; Manasse, W. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 3235–3249.

(16) Leuchs, H.; Geiger, W. *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 1721–1726.

(17) Kricheldorf, H. R. *Chem. Ber.* **1972**, *105*, 3958.
(18) Washburn, S. S.; Peterson, W. P.; Berman, D. A. *J. Org. Chem.* **1972**, *37*, 1738.
(19) Rauk, A.; Alewood, P. *Can. J. Chem.* **1977**, *55*, 1498−1510.
(20) Curtius, T. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 3023.
(21) Curtius, T. *J. Prakt. Chem.* **1894**, *50*, 275.