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Multicyclic Polythioesters Derived from Pentaerythritol Tetra(mercaptoacetate)

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Dry pentaerythritol tetra(mercaptoacetate), PETMA, was polycondensed with double molar amounts of phthaloyl chloride, isophthaloyl chloride, tetraphthaloyl chloride, adipoyl, suberoyl, sebacoyl and 1,10-decanedioyl chloride. Pyridine served as HCl-acceptor and catalyst. The concentration of PETMA was varied between 0.1 mol/L and 0.0125 mol/L. With the aromatic dicarboxylic acid, dichlorides gelation occurred in all experiments. With aliphatic dicarboxylic acid dichlorides (ADADs), soluble multicyclic polythioesters were obtained at concentrations of 0.025 or 0.0125 mol/L. These multicyclic polythioesters were characterized by viscosity measurements, ¹H-NMR spectroscopy and MALDI-TOF mass spectrometry. A few experiments with pentaerythritol tetra(mercaptoacetate) showed a lower cyclization tendency relative to PETMA. Polycondensations of PETMA with α,ω -dibromoalkanes or tri(ethylene glycol) bistosylate all ended with gelation.

Keywords: polycondensations; polythioesters; multicycles

1 Introduction

The present work is part of a broader study of “ $a_2 + b_4$ ” polycondensations based on commercial “ b_4 ” monomers. The first report on an “ $a_2 + b_4$ ” polycondensation goes back to the work of Flory (1, 2) who studied polycondensations of pentaerythritol with dicarboxylic acids in bulk. With a so-called equifunctional feed ratio (“ $a_2 + b_4$ ” = 2/1) cross-linking was observed at rather low conversion (around 58%), and it was concluded that “ $a_2 + b_4$ ” polycondensation involves a higher risk of gelation than “ $a_2 + b_3$ ” polycondensations under identical conditions. In later decades, “ $a_2 + b_4$ ” polycondensations have attracted little interest until recently when the first author of this paper (Kricheldorf) launched a systematic study in this direction (3–12). A special case, the synthesis of so-called water-wheel (or noria) was also quite recently described by Nishikubo and coworkers (13).

Polythioesters were never in the focus of international research activities, but recent publications by Steinbüchl et al. (14–18) describing enzymatic syntheses of certain polythioesters have raised the interest in this group of polyesters. The various polythioesters prepared by chemical methods were summarized in a recent review (19). The present work had the purpose of exploring, for the first time, syntheses of

multicyclic polythioesters via “ $a_2 + b_4$ ” polycondensations starting out from commercial tetramercaptanes (Scheme 1).

2 Experimental

2.1 Materials

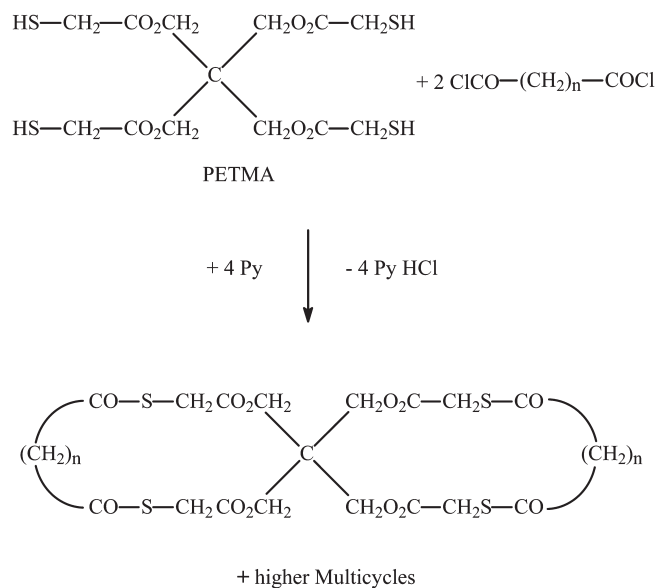
Pentaerythritol tetra(mercapto acetate), PETMA, and pentaerythritol tetra(mercapto propionate) were purchased from Aldrich Co. (Milwaukee, WI) and dried by azeotropic distillation with toluene (finally, a vacuum of 10^{-1} mbar was applied at 60°C). The aliphatic dicarboxylic acid dichlorides, ADADs, were purchased from ACROS Organics (Geel, Belgium) and distilled *in vacuo* prior to use. Phthaloyl chloride, isophthaloyl chloride and terephthaloyl chloride were purchased from Aldrich Co. and used as received. Dioxane was distilled over liquid sodium and pyridine over freshly powdered calcium hydride.

2.2 Polycondensations

2.2.1 Equifunctional Feed Ratio (No. 4, Table 1)

PETMA (5.0 mmol) and suberoyl chloride (10.0 mmol) were dissolved in dry dioxane (180 mL) and pyridine (40 mmol) dissolved in dioxane (10 mL) was added dropwise. After stirring for 48 h, the reaction mixture was concentrated *in vacuo* to a volume of 100–120 mL and precipitated into water. The isolated polyester was dried at 50°C *in vacuo*.

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Sch. 1. Equifunctional polycondensation of PETMA with aliphatic dicarboxylic acid dichlorides.

2.2.2 With Excess of 1,10-Decane Dicarboxylic Acid Dichloride (No. 11, Table 1)

PETMA (5.0 mmol) and 1,10-decane dicarboxyl chloride (10.2 mmol) were polycondensed as described above, whereby gelation occurred. After 48 h, the reaction product was precipitated into vigorously stirred water. The precipitated product was filtered off after 4 h of stirring and dried at 50°C *in vacuo*. Part of this product was shaken for 10 min with a mixture of chloroform and trifluoroacetic acid (1 mL), and this suspension/solution was used for the preparation of the MT irradiation target.

2.3 Measurements

The inherent viscosities were measured in a mixture of CHCl₃ and trifluoroacetic acid, TFA, in an automated Ubbelohde

viscometer thermostated at 20°C. The 400 MHz ¹H-NMR spectra were recorded on a Bruker "Avance 400" FT spectrometer in 5 mm o.d. sample tubes. The MALDI-TOF (MT) mass spectra were recorded with a Bruker Biflex III mass spectrometer equipped with a nitrogen laser (λ = 337 nm). All mass spectra were recorded in the reflection mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform/trifluoroacetic acid solution (volume ratio 9:1) with dithranol as matrix and potassium trifluoroacetate as dopant. The calculated masses of multicycles discussed below were listed in Table 2.

3 Results and Discussion

3.1 Polycondensations with Dicarboxylic Acid Dichlorides

A first series of experiments was performed in such a way that PETMA was polycondensed with phthaloyl chloride, isophthaloyl chloride and terephthaloyl chloride using a feed ratio of 1.0:2.0. The concentration of PETMA was varied from 0.10 mol/L to 0.50, 0.25 and finally to 0.125 mol/L. All twelve experiments ended with gelation. Therefore, the next series of experiments based on four aliphatic dicarboxylic acid dichlorides (ADAs) was started at a PETMA concentration of 0.5 mol/L. Yet, in spite of the higher flexibility of the ADAs, all experiments yielded gels. Lower PETMA concentrations proved to be more successful and the polycondensations conducted with initial PETMA concentrations of 0.25 or 1.125 mol/L were compiled in Table 1. It was learned from previous syntheses of (cyclic) polyesters (20) that a slight excess of the ADA dichloride is required to achieve maximum molecular weights, and thus, also an optimization of ring formation. This excess is required, because ADA dichlorides undergo side reactions with bases (used as HCl acceptors) in contrast to the more stable aromatic dicarboxylic acid dichlorides. For this reason, the excess of ADA dichlorides was also varied in the polycondensations of this work. In the case of adipoyl

Table 1. Polycondensations of PETMA with various aliphatic dicarboxylic acid dichlorides (ADADs)

Expt. no.	Dichloride of	Excess of ADAD (mol%)	Molar conc. of PETMA	Yield (%)	η_{inh}^a (dL/g)
1	Adipic a.	0	0.025	67	0.115
2	Adipic a.	2	0.025	Gel	—
3	Adipic a.	4	0.025	Gel	—
4	Suberic a.	0	0.025	53	0.105
5	Suberic a.	2	0.025	63	0.120
6	Suberic a.	4	0.025	73	0.115
7	Suberic a.	8	0.025	28	0.115
8	Sebacic a.	0	0.025	40	0.160
9	Sebacic a.	0	0.0125	83	0.115
10	1,10-Decane dicarboxylic a.	0	0.025	Gel	—
11	1,10-Decane dicarboxylic a.	2	0.025	Gel	—
12	1,10-Decane dicarboxylic a.	0	0.0125	51	0.120

^aMeasured at 20°C with *c* = 2 g/L in CHCl₃/trifluoroacetic acid (mol. ratio 4:1).

Table 2. Calculated masses (incl. K⁺-doping) of multicyclic polythioesters derived from PETMA and ADAD's

n	Sebacoyl chloride			1,10-Decanedioyl dichloride		
	B _n CN	B _{n-1} CN	B _{n+1} CN	B _n CN	B _{n-1} CN	B _{n+1} CN
1	804	638	974	860	666	1058
2	1569	1403	1739	1681	1487	1880
3	2334	2168	2504	2502	2308	2701
4	3099	2933	3269	3323	3129	3522
5	3864	3698	4034	4145	3950	4343
6	4629	4463	4799	4966	4771	5164

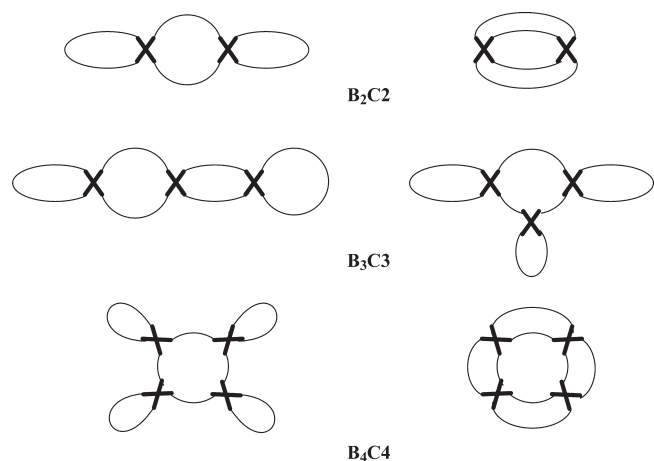
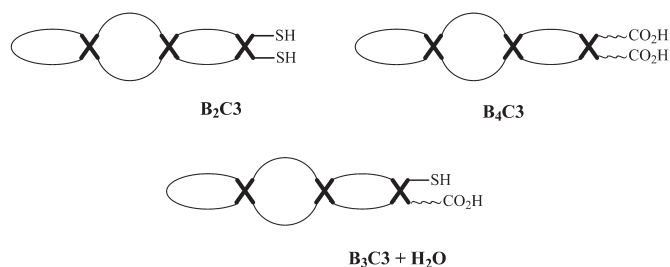
chloride (Nos. 1–3, Table 1), a soluble product was only obtained with an exact equimolar feed ratio, whereas a slight excess of adipoyl chloride resulted in gelation of the reaction mixture. The MT mass spectrum of the soluble product No. 1, indicated that the perfect multicycles of formula B_nCN (n = N, (Scheme 2) were the main products, but multicycles lacking one adipoyl unit B_{n-1}CN (Scheme 3) were also present. Therefore, it may be concluded that an excess of adipoyl chloride yielded a higher conversion with the consequence of partial crosslinking.

At this point, the schematic formulas and terminology used for the description of multicycles based on “a₂ + b₄” polycondensation need a short explanation. In the formula B_nCN, C stands for cyclic structure and N for the degree of polymerization counting the PETMA units. B stands for bridge units meaning (in this work an ADA unit) bridging a cyclic or connecting two cycles. So-called “perfect multicycles” free of functional groups possess the general formula B_nCN with n = N and consist of n + 1 cycle in a two-dimensional presentation as illustrated in Scheme 2. Examples for three different types of multicycles are presented in Scheme 3. Multicycles having two SH groups, due to a lack of one ADA unit, obey the formula B_{n-1}CN. One additional ADA unit yields multicycles having two CO₂H endgroups (after hydrolysis of COCl endgroups) with the general formula

B_{n+1}CN and multicycles with perfect stoichiometry, but incomplete conversion may be labeled B_nCN + H₂O.

Polycondensations of PETMA with suberoyl chloride at a concentration of 0.025 mol/L yielded soluble multicycles regardless if an excess of suberoyl chloride was used or not (Nos. 4–7, Table 1). In agreement with the highest viscosity value, the MT mass spectra displayed the highest content of perfect multicycles for sample No. 5. In the case of sebacoyl chloride, two polycondensations with exact 1.0:2.0 stoichiometry were performed at two different concentrations. Soluble products with almost identical ¹H-NMR and MT mass spectra were isolated from these experiments (Nos. 8 + 9, Table 1). The ¹H-NMR spectra of PETMA (Figure 1) and of multicycles (No. 8, Table 1) indicated a high conversion. The doubled signal of the CH₂SH groups at 3.37 ppm (Figure 1) has almost completely vanished, whereas a new singlet signal CH₂S-CO groups appeared at 3.79 ppm (Figure 2, analogous ¹H-NMR spectra were also obtained for the soluble multicycles of other ADAs). The MT mass spectrum (which is also typical for the soluble products of experiments Nos. 1 and 4) demonstrates the predominant formation of B_nCN multicycles (Figure 3). Minor peaks of B_{n-1}CN multicycles indicate that a small amount of sebacoyl chloride was lost by side reactions and compensated by addition of an excess. The different yields of the products of experiments Nos. 8 and 9 result from a different extent of fractionation during precipitation.

In the case of 1,10-decane dicarboxylic chloride, the polycondensations at 0.025 molar concentration of PETMA (Nos. 10 and 11) ended with gelation and a lower PETMA concentration was needed to obtain a completely soluble reaction

**Sch. 2.** Examples (selected isomers) of perfect multicycles based on pentaerythritol-type “b₄” monomers.**Sch. 3.** Examples (selected isomers) of imperfect functional multicycles based on pentaerythritol-type “b₄” monomers.

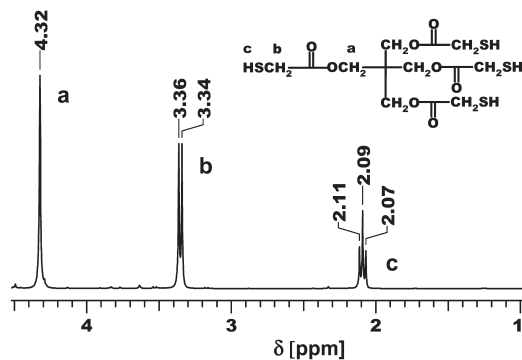


Fig. 1. 400 MHz ^1H NMR spectrum of PETMA.

product. However, MT mass spectroscopy of the gels Nos. 10 and 11 revealed that a considerable part of these reaction products consisted of perfect multicycles as illustrated in Figure 4. This result is also representative of all other gels listed in Table 1. When the results listed in Table 1 are compared to lengths of the ADA dichlorides, it seems that the cyclization tendency (defined as the ratio of cyclization rate vs. chain growth rate) passes through a maximum at

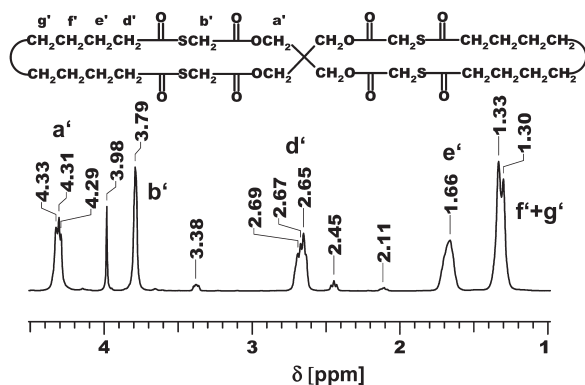


Fig. 2. 400 MHz ^1H -NMR spectrum of the multicycles obtained by polycondensation of PETMA with sebacoyl chloride (No. 8, Table 1).

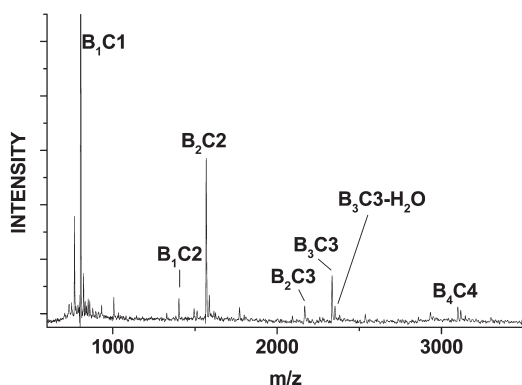


Fig. 3. MALDI-TOF mass spectrum of the multicycles obtained by polycondensation of PETMA with sebacoyl chloride (No. 8, Table 1).

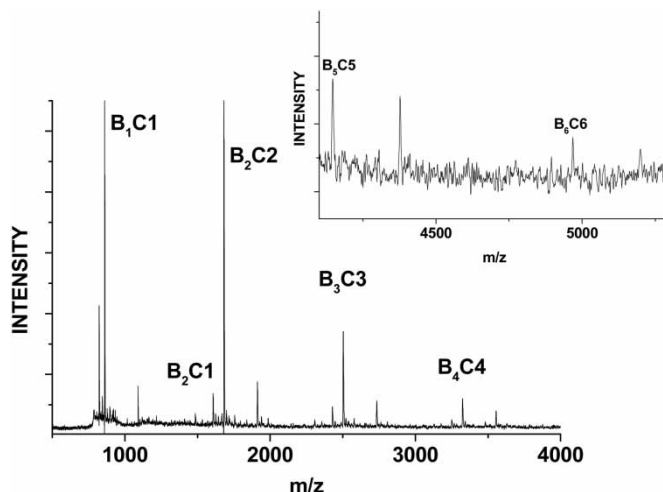


Fig. 4. MALDI-TOF mass spectrum of the multicycles extracted from the partially crosslinked polycondensates of PETMA and 1,10-decane dicarboxylic acid (No. 11, Table 1).

suberic and sebacic acid. The finding that longer alkane chains are less favorable for cyclization may be a consequence of the fact that the energetically most stable conformation of an alkane chain is the all-trans conformation which is unfavorable for cyclization.

The same argumentation also holds for the observation that syntheses of multicyclic polythioesters starting out from the tetra(3-mercaptopropionate) of pentaerythritol all failed even at a concentration of 0.125 mol/L.

Finally, it should be mentioned that SEC measurements were not feasible, because acidic solvents such as combinations of chloroform and trifluoroacetic acid are needed for complete dissolution of the multicycles.

4 Conclusions

Polycondensations of PETMA or pentaerythritol tetra(3-mercaptopropionate) with various aromatic or aliphatic dicarboxylic acid dichlorides allow the following conclusions. Syntheses of soluble multicycles at the expense of gels is easier to achieve with aliphatic than with aromatic dicarboxylic acids. The cyclization tendency (favoring formation of multicycles) passes through a maximum at suberic and sebacic acid, when ADAs of different chain lengths are compared. The tetramercaptoacetate of pentaerythritol favors formation of multicycles more than the tetra(3-mercaptopropionate). Even in the optimum case, PETMA concentrations as low as 0.025 mol/L are required to avoid gelation.

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