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Template-Induced, Stereoselective Cyclizations in the Cyclopolymerization of TADDOL-Dimethacrylate**

Günter Wulff,* Anja Matussek, Christian Hanf, Stefan Gladow, Christian Lehmann, and Richard Goddard

In the context of the synthesis of main-chain chiral copolymers, Kakuchi et al.[1] cyclo-copolymerized[2] 2,3-*O*-isopropylidine-D-threitol-1,4-(dimethacrylate), derived from D-tartaric acid, with styrene. After removal of the 2,3-*O*-isopropylidine-D-threitol template, the resulting copolymers containing methylmethacrylate and styrene units showed relatively small optical rotations, in contrast to copolymers prepared from D-mannitol derivatives previously obtained by us.[2] In order to obtain increased asymmetric induction, we used (*R*,*R*)-TADDOL, introduced by Seebach et al.,[3] instead of the threitol derivative, and prepared for the first time the dimethacrylate **M** (see Scheme 1).[4, 5] Surprisingly, copolymerization with styrene followed by removal of the template resulted in a copolymer with a significantly smaller optical activity. This can only be explained if the methacrylate units are arranged as *meso* diads to one another. Homopolymerization should lead to an isotactic arrangement in the chain, and this was indeed the case. After anionic polymerization, removal of the template, and esterification, the polymethacrylate obtained was completely isotactic, but it exhibited a small but distinct optical rotation, which decreased with increasing molecular weight.

Independent of our work, Sogah, Okamoto, and co-workers[6, 7] also prepared the monomer **M** and homopolymerized it by radical, anionic, and group-transfer polymerization. They obtained a homopolymer with a large optical rotation, from which they assumed that it exists as an atropisomeric single-handed helix, as found for tritylmethacrylate. After removal

[*] Prof. Dr. G. Wulff, Dr. A. Matussek, Dr. C. Hanf, Dr. S. Gladow
Institut für Organische Chemie und Makromolekulare Chemie
Heinrich-Heine-Universität Düsseldorf
Universitätsstrasse 1, 40225 Düsseldorf (Germany)
Fax: (+49) 211-8114788
E-mail: wulffg@uni-duesseldorf.de
Dr. C. Lehmann, Dr. R. Goddard
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, 45470 Mülheim/Ruhr (Germany)

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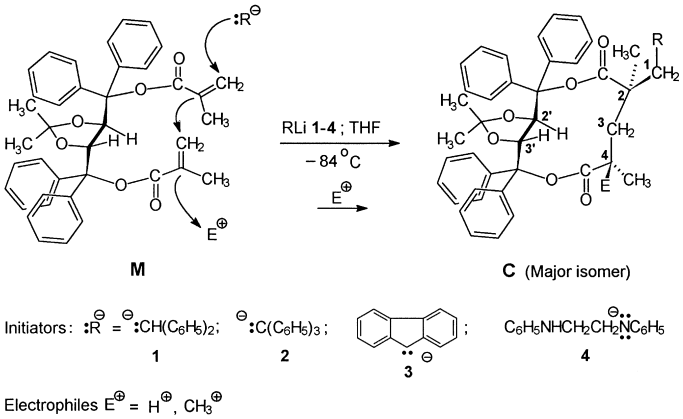
of the template and conversion to the methyl ester, they similarly obtained a highly isotactic polymethacrylate (PMMA).

We now wanted to investigate more precisely the mechanism of this cyclopolymerization—in particular the first steps—to obtain further details about the polymerization and the structure of the helical polymers, as well as the PMMAs. We therefore attempted to bring about just the first step of the polymerization—the cyclization—using the monomer **M** and various anionic initiators (Scheme 1). By using a



Scheme 1. Anionic cyclization of TADDOL-dimethacrylate **M** with various initiators.

sufficiently large excess of the initiator, a monocyclization was indeed successfully achieved.[8] Subsequently, this anionic intermediate was then allowed to react with MeOH or with CH_3I, whereby the H- or CH_3-terminated cyclic compound was obtained in yields of 60–70%. The termination with CH_3^+ has the advantage that only one new stereogenic center is created, and thus only two diastereomers can be formed. Termination with H^+ results in two stereogenic centers, so that in total four diastereomers are possible. The disadvantage here is that the second step proceeds less stereoselectively, and thus under these conditions one always obtains a mixture. If, however,—as intended in our case—the products so obtained are deprotonated again in order to serve as optically active initiators for anionic polymerization or as chiral building blocks,[9] this is not a considerable disadvantage, since this stereogenic center is removed again in the anion.

Here only the CH_3-terminated monocycles will be described in detail. Diphenylmethyllithium (**1**), triphenylmethyllithium (**2**), fluorenyllithium (**3**), and *N*,*N*′-diphenylethylenediamine-*N*-lithium (DPEDA-Li) (**4**) were used as initiators. The composition of the reaction products were analyzed by ^{1}H NMR spectroscopy; the protons on C-2′ and C-3′ of the TADDOL group, in particular, differ significantly in the diastereomers. As expected, two diastereomers were obtained, which depending on the initiator (diphenylmethyl < trityl < fluorenyl < DPEDA) were formed with diastereoselectivities *de* of between 16.6 and 96.4% (Table 1).

Table 1. Percentage composition of the stereoisomers obtained from the monocyclization of **M** with various initiators.

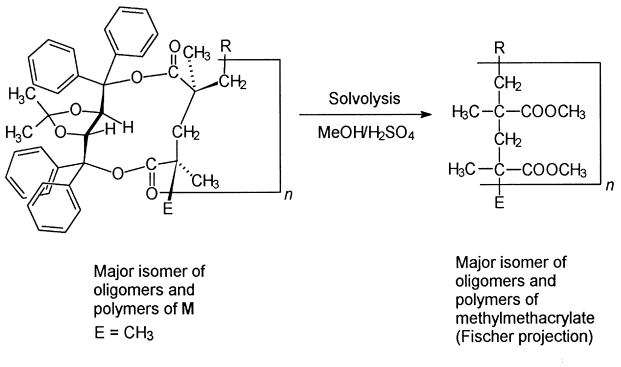
Initiator	Ring system	Product ratio on termination with CH_3I [%][a]		*de* [%]
1	**C1**	58.3	41.7	16.6
2	**C2**	74.9	25.1	49.8
3	**C3**	91.7	8.3	83.4
4	**C4**[b]	98.2	1.8	96.4

[a] The diastereomers produced were identified by NMR analysis. If not otherwise stated, on the left is the amount of the (2*S*) isomer and on the right the (2*R*) isomer. [b] In this case according to the CIP rules, on the left is the (2*R*) isomer and on the right is the (2*S*) isomer; the absolute configurations are, however, the same as those for the other substances given in same columns.

In order to show that in each case C-2 epimers are indeed involved, the isomeric compounds **C2** (major isomer) and **C2′** (minor isomer) cyclized with the trityl derivative **2** were obtained analytically pure by chromatographic separation, and the template was removed by methanolysis.[10] The resulting methacrylate dimers $\mathbf{C_h2}$ (major isomer, Scheme 2) and $\mathbf{C_h2'}$ (minor isomer) prove unequivocally to be enantiomers, by virtue of their equal but complementary optical rotations and their CD spectra. The absolute configuration was then determined by an X-ray structure analysis of **C2**,[11] which shows it to be the (2*S*) compound. Accordingly, **C2′** is the (2*R*) compound.

The first step of the cyclopolymerization to form the 11-membered ring thus proceeds highly stereoselectively for the fluorenyl and DPEDA initiators. Correspondingly, one obtains in these cases one diastereomer in high yields which can be isolated completely pure by crystallization. Subsequent hydrolysis readily affords the pure enantiomer $\mathbf{C_h3}$ and $\mathbf{C_h4}$, respectively (see Scheme 2).

The stereochemical direction of the subsequent polymerization steps can be best investigated by using trityl as initiator, since both epimers are formed in the first step. Whereas it is comparably simple to obtain the monocycles from **M** by using an excess of initiator, the second polymerization step to the dimer with two cycles must be extremely carefully controlled, since the anion of the dimer, and even more so that of the trimer, have higher reaction rates than that of the monocycle. By optimization of the conditions, a mixture



C : *n*=1 ; **B** : *n*=2 ; **T** : *n*=3 ; $\mathbf{P}_n$: *n*=12–90 $\quad$ $\mathbf{C_h}$: *n*=1 ; $\mathbf{B_h}$: *n*=2 ; $\mathbf{T_h}$: *n*=3 ; $\mathbf{P_{nh}}$: *n*=12–90

Scheme 2. Removal of TADDOL from the cyclized compound with formation of oligomers and polymers of methylmethacrylate.

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can be obtained after termination with CH_3I that comprises 16% from monocycles **C2**, 15% from dimers with two cycles **B2**, 1% from trimers with three cycles **T2**, and 60% from oligomers $\mathbf{P_n}$**2** with $n > 10$. The dimers **B2** possess three new stereogenic centers and can therefore form eight diastereoisomers. In fact, one observes only four, in the ratio of 77:15:7:<1 in the NMR spectrum, whereas for the trimer **T2** only one single isomer is detectable.

The major component of the dimers **B2** can be obtained analytically pure by using chromatography. Crystals suitable for X-ray structure analysis can be obtained from $CHCl_3$/pentane.[12, 13] Figure 1 shows the structure, which allows important conclusions to be drawn about the structure of

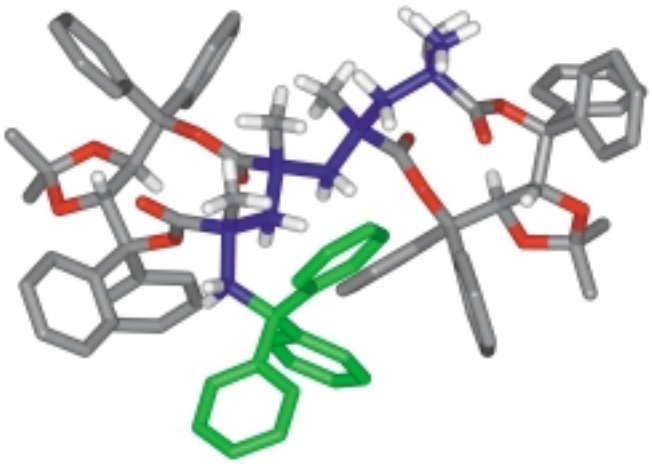

Figure 1. The X-ray crystal structure of **B2**. Initiator group (trityl): green, methylmethacrylate chain: blue.

the polymer. The stereochemistry of C-4, the second stereogenic center of the first monomer unit, has an *S* configuration. The corresponding PMMA diad, formed after removal of the template, corresponds therefore to a *meso* diad, as is present in isotactic polymers. The attack of the anion of the monocycle on a new monomer **M** thus proceeds with high stereoselectivity, as for the first monomer and also for the new stereogenic center of the second monomer (C-6). The anionic monocycle acts thus like a strongly bulky initiator and induces a new center with the same absolute configuration as in **C2**, which, however, because of the CIP rules is designated (6*R*). In the case of the fluorenyl and DPEDA initiators it should be possible to obtain the dimers **B3** and **B4**, respectively, directly in an almost diastereomerically pure form. On hydrolysis of the main isomer of **B2**, the MMA tetramer $\mathbf{B_h}$**2** was also obtained enantiomerically pure.

The trimer **T2**, which is only obtained as a single diastereomer, possesses a similarly configurated structure throughout, which on hydrolysis leads to an enantiomerically pure (2*S*, 4*S*, 6*S*, 8*R*, 10*R*) hexamer $\mathbf{T_h}$**2** of MMA, which is completely isotactic. Evidently, after the formation of the (non-methylated) anionic dimer with two cycles, a change in the steric control occurs by the helix-control mechanism, known also for the polymerization of tritylmethylacrylate,[14] which leads to an increase in the speed of the reaction and an appreciably higher stereoselectivity. For this reason also almost no oligomers $\mathbf{P_n}$ with *n* between 3 and 10 are found. Evidently, here is also a similarity to the helix-sense-selective anionic polymerization of tritylmethacrylate, in which oligomers with the incorrect configuration grow no further.[14]

By increasing the ratio of monomer to initiator, polymers $\mathbf{P_n}$ can be prepared, whose degree of polymerization *n* is extensively controlled by the monomer/initiator ratio. The specific optical rotation increases considerably with *n*. This has been attributed to a single-handed helix,[6, 7] which in this case could be either left- or right-handed. For steric reasons two neighboring monomer units can only occur in a specific relative arrangement to one another. The X-ray structure analysis of **B2** reveals that the two monomer units make an angle of 120.9° to one another, and that both units are arranged in a right-handed helical sense, thus forming a *M* helix. On increasing the length of this chain still further, all the monomer units should maintain this relation to one another, leading to a *M* helix with three monomer units per turn. Accordingly, we are looking at a 3/1 helix with a repeat distance of 13.4 Å. Thus, for the first time an atopisomeric helix of vinyl polymers has been unequivocally and completely described.

Thus, during the anionic cyclopolymerization of **M** the first step involves cyclization to give the 11-membered ring, whereby the *de* value on the first stereogenic center (C-2) lies between 17 and 96%, depending on the bulkiness of the initiator. In the second step the anion of the monocycle attacks a new monomer, during which two new stereogenic centers (C-4 and C-6) are formed. The isolated dimers show that this step proceeds with high stereoselectivity, especially when one considers that a large percentage of the dimers with the "correct" configuration reacts further. The formation of trimers, tetramers, etc., proceeds more rapidly and with higher stereoselectivity, since on the formation of a helix, the new monomer can only attack with a specific stereochemistry (helix-control mechanism). The polymer chain with **M** members can only exist in a helical, atropisomeric form, so that the polymerization is a "helix-sense-selective" polymerization, while at the same time all stereogenic centers in the chain are built up with the same absolute configuration. Correspondingly, after removal of the template one obtains uniform enantiomers of isotactic oligomers or polymers $\mathbf{P_h}$ of methylmethacrylate, which otherwise are very difficult to synthesize.[15] It should also be possible to obtain similar stereochemical control during cyclopolymerization using other monomer units bonded to TADDOL.

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