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Novel Initiators for Oxazoline Polymerization: Generation of Polydiacetylene-Polyoxazoline Networks

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Summary: A series of bolaform polyoxazolines (POZO) with 1,3-diacetylene cores ($(POZO)_m$-$(CH_2)_n$-C≡C-C≡C-$(CH_2)_n$-$(POZO)_m$) were synthesized by the living polymerization of 2-methyl-1,3-oxazolines initiated by triflate esters derived from bis(ω-hydroxyalkyl)-1,3-diacetylenes. The chain length of the alkylspacers within the diacetylene core as well as the length of the attached polyoxazoline chains was varied between n = 1 and 4; m = 5, 10 and 15. The thermally induced 1,4-addition process yielding polydiacetylenes (PDA) was studied leading to highly conjugated POZO-PDA hybrid materials.

Introduction

The thermal and photochemical polymerization of substituted diacetylenes yields polydiacetylenes (PDA) via a 1,4-addition process [1]. These highly conjugated polymers have a quasi one dimensional structure with a long effective coordination length. Effective polymerization is only possible when strict steric requirements with respect to the packing of the diacetylenes are fulfilled [2]. In order to achieve a topochemical 1,4-polymerization the distance d between neighboring acetylenes should not be less than 5 Angstrom and the tilting angle γ between the main axis and the diacetylene chains around 45°. Thus a high level of molecular preorganization is required to effect polymerization giving way to the interlocking of supramolecular assemblies. The polymerization in highly organized polymeric layer systems such as Langmuir Blodgett films, vesicles and self assembled monolayers has been effected [3-5]. Recently the polymerization of 1,3-diacetylenes in disclike mesogenic molecules and gels has been reported 6) verifying the high ability to lock in supramolecular structures in slightly less ordered systems. Among the many interesting properties of the resulting materials are photochromicity and third order nonlinear optical effects envisioning a broad applicability in optical devices and biological sensors [7-9].

Südhölter et. al. [10,11] and others [12] have intensely studied the influence of steric parameters of symmetrically and nonsymmetrically substituted short chain 1,3-diacetylenes on the 1,4-addition process and found an enormous influence of

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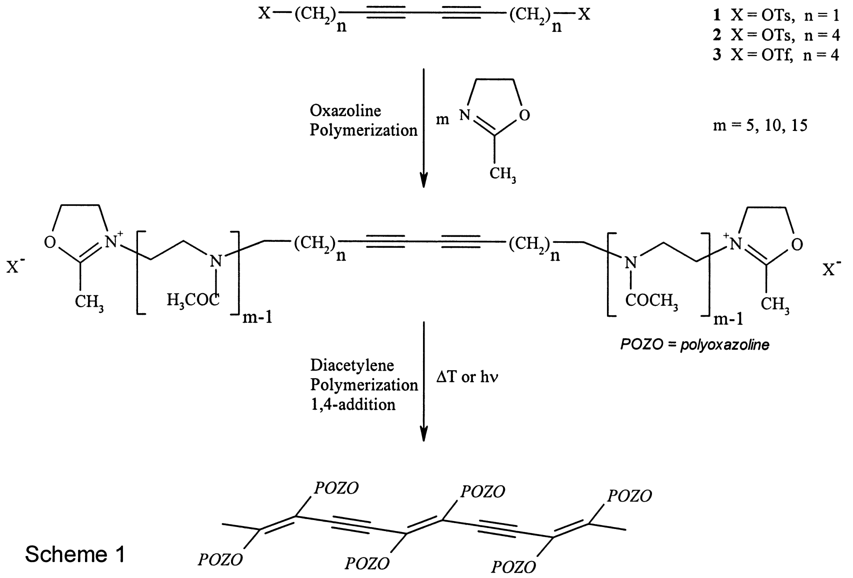
noncovalent interaction such as π-π-stacking, hydrogen bonds and van der Waals interactions. The influence of the aliphatic chains flanking the 1,3-diyne moiety proved less pronounced on the polymerization efficiency.



Scheme 1

We have synthesized bolaform 1,3-diacetylenes with attached short hydrophilic polyoxazoline (POZO) sidechains (Scheme 1). Similar to polyethyleneglycols polyoxazolines exert the steric stabilization effect [13] effective at molecular weights between 1000 and 4000 Dalton. This effect leads to a repulsive interaction of hydrophilic polymer chains at short distances opening way to long-term stabilization of colloidal particles [14] and flat surfaces towards aggregation and biological recognition [15]. A basic explanation of this repulsion can be given by entropic restraints and subsequent compression imposed on the freely moving polymer chains during aggregation.

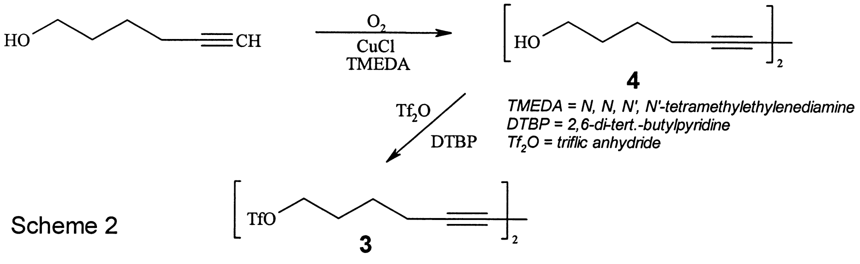
Our combination of 1,3-diacetylenes with polyoxazolines opens the possibility for a closer look on the steric requirements of the 1,4-addition process as well as the generation of hybrid polymers consisting of a conjugated PDA-network with flanking polyoxazoline polymers.

Experimental

Solvents and reagents used were purified and dried by distillation over appropriate drying agents. For requirements and details see references [16] and [17]. Instruments used in these investigations were a Bruker Avance 400 for NMR measurements and a Shimadzu DSC for thermal analyses. Heating rates were 10°C/min. Preparation of the PDA-polyoxazoline networks was performed by casting a film from solution and heating to the temperature above the polymerization temperature.

Synthesis of Bolaform 1,3-Diacetylenes

The living polymerization of 1,3-oxazolines enables the exact tailoring of chain length and thus a good control over the degree of polymerization by adjusting the monomer to initiator ratio. We have shown that it is possible to introduce functional moieties by use of functional trifluoromethansulfonic acid esters [17]. Thus various 1,3-diacetylenes were transformed into the corresponding trifluoromethanesulfonic acid ester serving as initiators for the subsequent cationic ring opening polymerization of 2-methyl-1,3-oxazoline. The preparation of the triflate esters **3** was accomplished via reaction of the alcohol **4** with triflic anhydride in the presence of the sterically hindered base 2,6-di-*tert*-butylpyridine. Crystalline bistosylates **1** and **2** was prepared according to literature methods [18].



TMEDA = N, N, N', N'-tetramethylethylenediamine
DTBP = 2,6-di-tert.-butylpyridine
Tf_2O = triflic anhydride

Scheme 2

Preparation of the Oxazoline Polymers

The electrophilic initiators **1** and **3** were used for the cationic ring opening polymerization of 2-methyl-1,3-oxazoline [18] generating the polymers ***5-10***. The chain length of the attached polyoxazolines were varied between 5 and 15 whereas the alkylspacers changed between n = 1 and n = 4. The polymers were characterized by various analytical methods to verify their chemical structure and composition (Table 1). Experimental molecular weights correlated well with the expected, polydispersities were generally below 1.20. The presence of the 1,3-diacetylene moiety could be proven by ^{1}H-NMR and ^{13}C-NMR spectroscopy in the low molecular weight polymers due to the presence of resonances at 66 ppm and 76 ppm respectively.

Polymerization of 1,3-Diacetylene-POZO Conjugates and Their Thermal Behavior

The synthesized polymers ***5-10*** were subjected to DSC and photo-DSC measurements. All compounds yielded a brownish polymer after heating to temperatures above the polymerization temperature for the 1,4-addition process. Additional reheating of the polymerized sample indicated the absence of the respective exothermic peak around 190 – 322 °C clearly identifying this with the 1,4-polymerization process (Fig. 1).

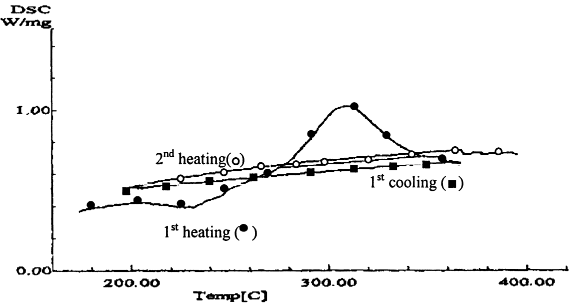


Figure 1. DSC-thermogramm of polymer *8* with a heating/cooling/reheating cycle.

In addition IR-spectra of the polymerized product showed the loss of bands at 2256 cm^{-1} favoring a 1,4-polymerization over a 1,2-polymerization of these materials. The data of thermal polymerization are indicated in Table 1. None of the compounds showed a transition indicative of photopolymerization after conducting photo-DSC measurements. The known crystal structures [20] of the bistosylates **1** and **2** with d = 5.1 Å and $\gamma = 44°$ and 45° respectively are consistent with a thermal and UV-induced 1,4-addition process. Clearly there is a strong influence of the alkyl-spacer length on the thermal polymerization process. Thus the 1,3-diynes with a short spacer length (n = 1, *polymers 5-7*) indicate significantly lower polymerization temperatures than the ones with a chain length of n = 4 (*polymers **8-10***). The influence of the attached POZO-chain is much less pronounced. Thus steric effects from the POZO-chains are less important than the ordering effects close to the 1,3-diacetylene moieties.

Table 1. Analytical and Experimental Results of Polymers ***5*** - ***10***

Initiator		**Polymer**		**GPC**		**DSC**
Nr.	n	Nr.	m	M_n	M_w/M_n	$T_{peak.}$
1	1	***5***	5	1300	1.17	208 °C
1	1	***6***	10	2100	1.17	217 °C
1	1	***7***	15	2900	1.10	227 °C
3	4	***8***	5	1100	1.05	308 °C
3	4	***9***	10	1800	1.07	313 °C
3	4	***10***	15	3100	1.05	322 °C
1	1	--	--	--	--	240 °C
2	4	--	--	--	--	198 °C

These results are in contrast to investigations by Südhölter et. al. [10] on symmetrically 1,3-diacetylenes substituted with phtalimide- and perylene moieties respectively, who observed a higher polymerization temperature with shorter alkyl spacer length and a strong influence of the aromatic side groups. Obviously there is a very delicate balance between intra- and intermolecular forces directing the 1,4-addition process.

Conclusion

The synthesis of bolaform polyoxazolines with 1,3-diacetylene cores has been accomplished. Symmetrically substituted 1,3-diacetylene triflates served as initiators for the living cationic ring opening polymerization of 2-methyl-1,3-oxazolines. All polymers can be thermally polymerized further via a 1,4-addition process yielding PDA-POZO networks. The polymerization is strongly influenced by the alkyl-spacer between the 1,3-diacetylene moiety and the POZO-polymer, and much less by the length of the POZO chain itself. Steric effects of the flanking polymer thus are less determining in the 1,4-addition process than ordering effects near the 1,3-diacetylene moiety.

Acknowledgements

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