On the Propensity of a Diels–Alder (DA) Ladder Polymer To Undergo Retro-DA Degradation

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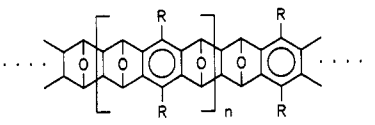
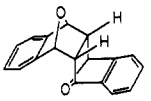
Introduction

Conventional ladder polymers[1] upon thermal treatment undergo nonconcerted bond cleavage processes at sites randomly distributed over the two strands of bonds. The molecular weights remain constant until, coincidentally, two opposing bonds are cleaved.[2] Recently, the synthesis of soluble and characterizable Diels–Alder (DA) ladder polymers has been reported.[3] Since DA cyclization/recyclization is an equilibrium process,[4] this new generation of ladder polymers may exhibit an additional mode of decomposition, the retro-DA cleavage.[5,6] By this reaction two bonds of the same six-membered ring are cleaved in a concerted manner. Such a process would have a detrimental effect on the properties of DA ladder polymers in that each single retro-DA step breaks apart the backbone into two independent fragments and, thus, decreases the molecular weight. We therefore investigated this issue using 1 as one of the best investigated DA ladder polymers.

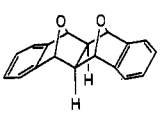


1

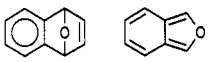
R = n-hexyl



anti-2



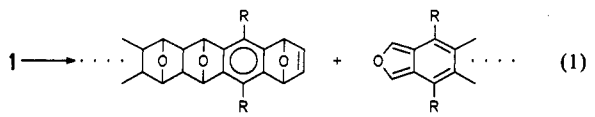
syn-2



3 4

Results and Discussion

Polymer 1 in principle can undergo retro-DA cleavage between two adjacent oxygen bridges (eq 1). This part of



(1)

the backbone can be considered a DA adduct of an isobenzofuran and a dienophile (here a 7-oxanorbornadiene derivative). Many such adducts, similar to those of furans and dienophiles, are known to undergo retro-DA reactions even at low to moderate temperatures.[7] The structure of compound 2 closely resembles that part of 1 and can easily be prepared and separated into its two stereoisomers, *syn*-2 and *anti*-2.[8] It was therefore selected for an initial model study. Retro-DA cleavage of both isomers should yield identical products, namely, 1,4-dihydronaphthalene *endo*-1,4-oxide (3) and isobenzofuran (4). In an equilibrium situation, these products ought to recyclize to 2, in an approximate ratio of *anti*-2:*syn*-2 = 2:1. This ratio is known since compound 2 is actually prepared from 3 and 4.[8] It varies only slightly with reaction temperature and time. Thus, thermal treatment of any of the two isomers should lead to the formation of this mixture of isomers if no side reaction occurs. This was checked by NMR experiments carried out in sealed tubes at 180 °C (solvent, toluene-d_8; internal standard, 1,2,3,4-tetraphenylbenzene). 180 °C is the highest reasonable temperature since thermogravimetric measurements (heating rate, 5 K/min; under nitrogen) show that polymer 1 starts to lose mass at approximately 200 °C, a process presumably associated with loss of water and parts of the alkyl chains.[9] Even after a period of 4 h at 180 °C, the absolute concentration of each isomer remained constant (^{1}H NMR integration). No trace of any other compound could be detected even when the spectra were expanded to the extent that the ^{13}C satellites were observable. Thus, in the temperature range considered, neither *syn*- nor *anti*-2 undergoes a retro-DA reaction or any kind of decomposition.

Table I
Dependence of the Molecular Weight ($\bar{M}_{peak}$) and Polydispersity ($\bar{M}_w/\bar{M}_n$) of DA Ladder Polymer 1 on Reaction Time and Molar Ratio 1:3 (Reaction Temperature 180 °C)

reaction time (min)	$\bar{M}_{peak}$ ($\bar{M}_w/\bar{M}_n$)			
	1:3 = 1:0	1:3 = 1:1	1:3 = 1:5	1:3 = 1:10
15	16 500 (1.7)	16 100 (1.7)	16 700 (1.7)	16 400 (1.5)
30	16 500 (1.8)	16 400 (1.7)	16 200 (1.6)	16 400 (1.6)
60	16 900 (1.9)	16 600 (1.7)	16 400 (1.7)	16 400 (1.6)
120	16 400 (2.0)	16 600 (1.7)	16 500 (1.7)	16 400 (1.6)

After this promising result, the dependence of the molecular weight and the polydispersity index (PDI) of polymer 1 on thermal treatment at 180 °C, in the presence of varying amounts of 3 and for varying periods of time, was investigated.[10] The sample of 1 used in this series of expriments had $\bar{M}_{peak}$ = 16.250 and PDI = 1.7. If retro-DA cleavage occurs, 3 should react with the newly formed isobenzofuranoid end groups and, thus, act as a terminating agent. The results are summarized in Table I. First, the molecular weight distribution of 1, if 3 is not present, broadens slightly which is attributed to some further polymerization. Obviously, reactive end groups are still present.[11] Second, the molecular weights of 1 in the presence of different amounts of 3, within experimental error, are constant. Two effects are responsible for this: (a) further polymerization is suppressed by the reaction of 3 with reactive end groups, and (b) no retro-DA cleavage takes place. The apparent trend to narrower distributions with increasing amounts of 3 is an artifact.[12] Thus, within the temperature range which can be investigated reasonably, polymer 1 does not have any propensity to undergo retro-DA degradation.

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References and Notes

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(9) We are presently investigating the potential use of 1 as a precursor for polyacene.
(10) The molecular weights and PDI values were obtained by using SEC in THF at room temperature calibrated with PS (UV detection). All samples were taken from raw materials (no reprecipitation) and were measured in one run using an automized injector.
(11) An investigation into the nature of the end groups is in preparation.
(12) With increasing amounts of **3**, its elution curves become so intense that their onsets merged slightly with the curve of 1, thus shifting the PDI's artificially to somewhat lower values.