



Pergamon

Tetrahedron Letters 41 (2000) 1433–1437

TETRAHEDRON
LETTERS

Pinacol rearrangement in the polymer backbone: a new class of reactive polymers with condensed benzopinacol units in the main chain

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Received 4 November 1999; revised 1 December 1999; accepted 3 December 1999

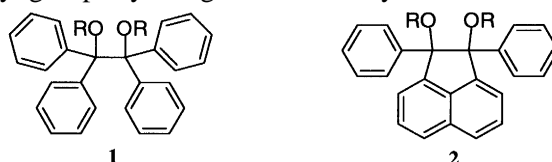
Abstract

Novel reactive polymers based on condensed benzopinacol dimethyl ether moieties in the main chain were synthesized and their acid-catalyzed pinacol rearrangement in the polymer backbone proceeded to afford poly(benzopinacolone)s quantitatively with elimination of methanol. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: polymers; rearrangements; naphthalenes.

Tetraarylpinacol derivatives have been of interest owing to their potential physical properties and reactivities based on their central carbon–carbon bonds, diols and/or aromatic rings. For instance, it has been known that tetraarylpinacols undergo thermal¹ and photolytic dissociation.² It is also well known that benzopinacol derivatives (**1**) work as ‘iniferter’ for controlled radical polymerisation.³ Focusing on diols in benzopinacol, it was found that oxidation of benzopinacol gives two molecules of benzophenone.⁴ On the other hand, Olah and co-workers have recently reported that various benzopinacol derivatives undergo pinacol rearrangement or convert to condensed aromatics, and the proportion of the products is dependent on the added acids.⁵

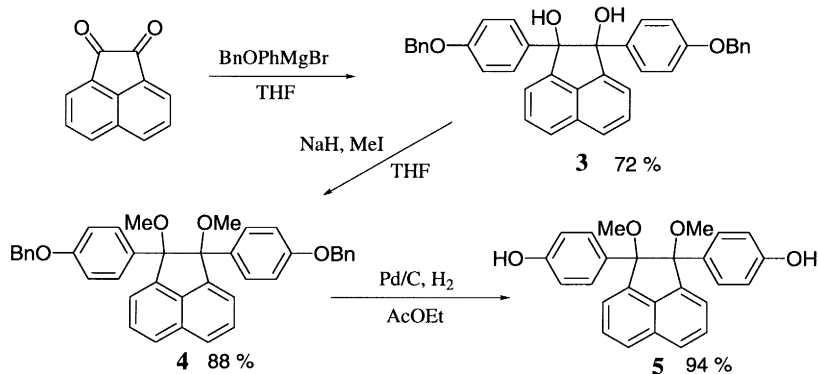
Since the parent benzopinacol is not so stable under basic conditions, an alternative condensed benzopinacol such as 1,2-diaryl-1,2-acenaphthenediol (**2**, R=H) is useful for modification due to its high stability against a strong base. In fact, in the case of condensed benzopinacol, it is possible to introduce substituents into the hydroxyl groups by using alkali metal hydride.



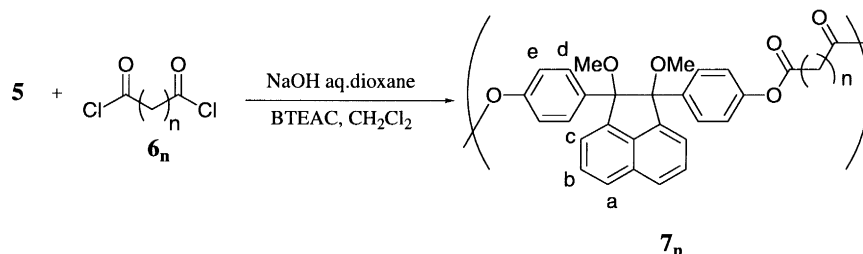
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Since condensed benzopinacols can be regarded as precursors for various functional systems, it may be possible to construct novel reactive polymers by incorporating such units into the polymer chain. In other words, various reactions can take place in the polymer backbone if condensed benzopinacol moieties are introduced into the polymer chain.⁶ To realize a novel reactive polymer system based on benzopinacol in the backbone, we designed polymers containing 1,2-diaryl-1,2-acenaphthenediol moieties in the main chain by polycondensation of a bisphenol-type monomer with bifunctional acyl chlorides. Among various reactions of benzopinacol derivatives, pinacol rearrangement is known to proceed as an intramolecular reaction.⁷ Here, we preliminarily communicate the synthesis of polymers containing condensed benzopinacol and their complete rearrangement to poly(benzopinacolone).

The bisphenol-type monomer **5** was prepared according to Scheme 1. Acenaphthenequinone was treated with two equivalents of a Grignard reagent derived from *p*-bromophenylbenzyl ether to afford the benzopinacol derivative **3**. Diol **3** was methylated by methyl iodide under basic conditions and elimination of the benzyl groups was carried out using hydrogen catalyzed by palladium–carbon to give **5** in 94% yield. Since the second nucleophilic attack of the Grignard reagent to the diketone moiety in acenaphthenequinone occurs from the opposite side of the first aromatic ring, the obtained monomer **5** has ‘*anti*’ orientation.



Polyesters **7₄–7₈** were obtained by the interfacial polycondensation of the obtained monomer **5** with alkyl diacyl chlorides **6_n** in the presence of quaternary ammonium salts as a phase-transfer catalyst (Scheme 2, Table 1). The polycondensation proceeded after mixing the monomers at room temperature within several minutes to afford white fibrous flakes of polyester (**7₄–7₈**). The polymers **7₄–7₈** were successfully obtained from both dispersions and the homogeneous solutions of reagents in good yields. Gel permeation chromatographical (GPC, HLC-8020) analyses indicated that the obtained polymers have the number-average molecular weight (M_n) of approximately 10 000 and the molecular weight distribution (M_w/M_n) of 1.36–1.44.



The structure of polymers **7_n** was supported by their NMR (JEOL Lambda-500) and IR (JASCO FT/IR-5300) spectra. Fig. 1A illustrates the representative ¹H NMR spectrum of polymer **7₄**. The signals

Table 1
Polycondensation of monomer **5** with diacyl chlorides^a

Run no.	n	Yield ^b / %	M_n^c	M_w/M_n^c
1	4	88	13 000	1.44
2	6	89	9 500	1.41
3	8	77	12 100	1.36

^a Conditions: [**5**] 1 M NaOH aq/dioxane solution, [diacyl chloride] 0.4 M dichloromethane solution, polymerization time 2 h, at 25 °C.

^b Isolated yield by reprecipitation.

^c Estimated by GPC based on polystyrene standards(eluent : THF).

assigned to the naphthalene protons are observed at 7.37, 7.57 and 7.86 ppm, by doublet, triplet and doublet, respectively. As shown in Fig. 2A, the IR spectrum of **7**₄ has an absorption signal at 1753 cm⁻¹ which is assignable to C=O group.

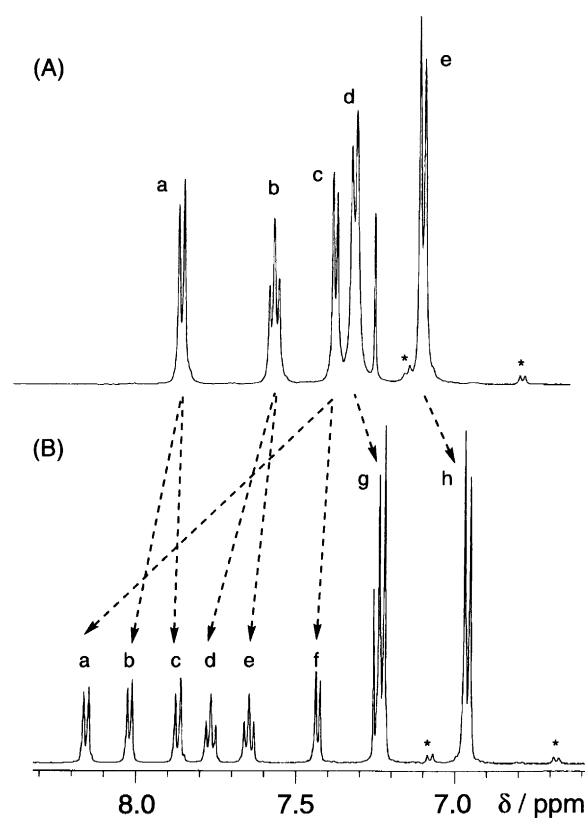


Fig. 1. Partial ¹H NMR spectra of polymers **7**₄ and **10**₄. Asterisks (*) mark bands of end groups

As a model compound for pinacol rearrangement in the polymer backbone, **8** was treated with trifluoroacetic acid (TFA) in benzene. Although the hydroxyl groups (pinacol) in **8** were methylated, the reaction proceeded to give **9** quantitatively after 30 min accompanied with elimination of methanol (Scheme 3).

Under the same conditions, pinacol rearrangement of prepolymers **7**₄–**7**₈ proceeded completely (Scheme 4, Table 2) to give the corresponding polymers with an M_n of approximately 10 000 and M_w/M_n of 1.36–1.43 without the formation of the low-molecular weight products. In all cases, no significant change in M_n and M_w/M_n was observed through the rearrangement. The structure of the

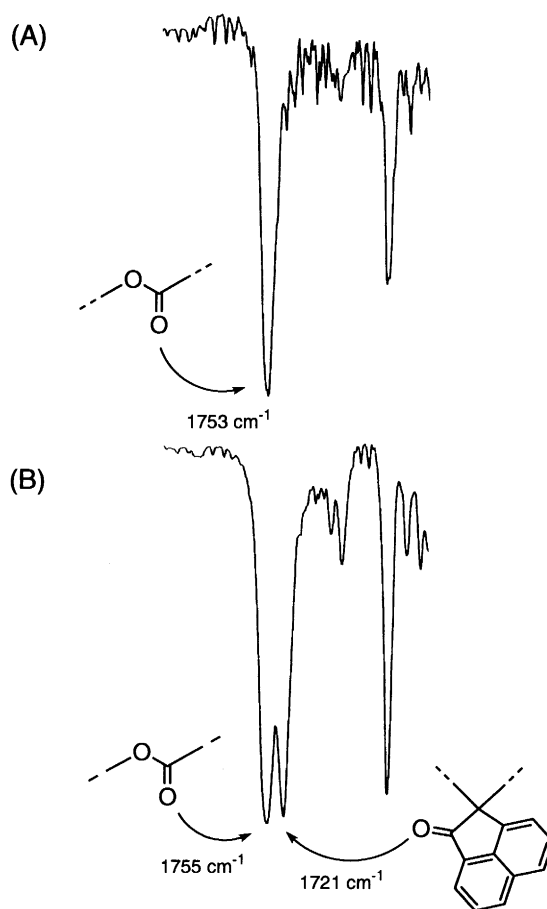
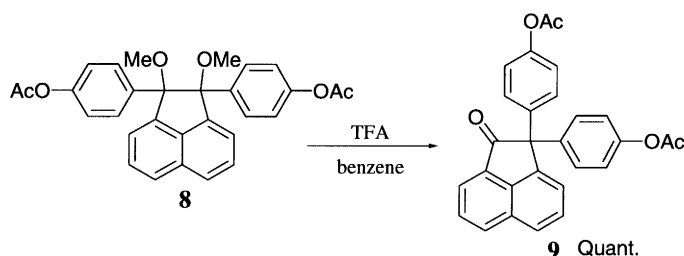


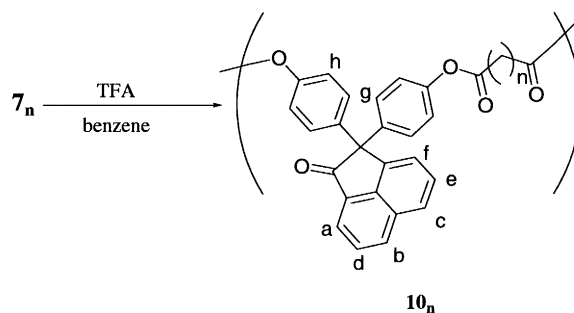
Fig. 2. Partial IR spectra of polymers **7₄** and **10₄**



Scheme 3.

obtained poly(benzopinacolone)s **10₄**–**10₈** was determined by spectroscopic methods. Fig. 1B illustrates the representative ^1H NMR spectrum of polymer **10₄**. The signals assigned to the naphthalene protons are all split because of dissymmetry, compared with its prepolymer **7₄**. In the ^{13}C NMR spectrum, the generated carbonyl carbon (pinacolone) is observed at 203.36 ppm. As shown in Fig. 2B, the IR spectrum of **10₄** has absorption signals at 1755 cm^{-1} and 1721 cm^{-1} assignable to C=O stretching not only in ester but also in benzopinacolone. These spectroscopic data clearly reveal that acid-catalyzed pinacol rearrangement in the polymer backbone proceed to give poly(benzopinacolone) quantitatively with elimination of methanol.

In summary, we have demonstrated that novel reactive polymers based on condensed benzopinacol dimethyl ether moieties in the main chain were synthesized and their reactions leading to poly(benzopinacolone) proceeded completely. Since various reactions of benzopinacol have been report-



Scheme 4.
Table 2

Pinacol rearrangement of polymers 7_n^a

Run no.	n	Yield / %	M_n^b	M_w/M_n^b
1	4	quant.	12 500	1.43
2	6	quant.	9 900	1.37
3	8	quant.	12 500	1.36

^a Conditions: [pinacol unit in 7_n] = 0.16 M benzene solution, [TFA] = 0.32 M, reaction time 30 min, at 25 °C.

^b Estimated by GPC based on polystyrene standards(eluent : THF).

ed so far, the poly(benzopinacol)s are useful not only as acid-responsive polymers but also as synthetic intermediates (reactive polymers). Further studies are currently in progress in this laboratory.

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