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Dendronized cyclocopolymers with a radial gradient of polarity and their use to catalyze a difficult esterification†

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Received (in Cambridge, UK) 30th June 2003, Accepted 28th August 2003
First published as an Advance Article on the web 16th September 2003

A cyclocopolymer containing pyrrolidinopyridine pendant groups was dendronized with polyester dendrons terminated with long alkyl chain ends and the microenvironment created by the dendrons was used to catalyze the difficult esterification of a tertiary alcohol with pivalic anhydride.

In the course of a general study of the transport properties of dendronized polymers with a radial gradient of polarity, we have developed the first example of a hybrid dendron-cyclocopolymer containing catalytic groups along the polymer backbone. Employing divergent growth techniques,[1,2] a cyclocopolymer bearing supernucleophilic catalytic pyrrolidinopyridine (PPY) units was dendronized with polyester-type dendrons with terminal long chain alkyl groups. The presence of tightly-packed, sterically demanding side-groups forces the random-coil to elongate, adopt a more 'rod-like' morphology[3] and exhibit shape control.[4] The catalytic sites, present as pendant groups attached to the backbone of the initial polymer, are buried within the tubular macromolecule and encapsulated by the surrounding dendrons. Elongation of the random coil by dendronization and separation of the catalytic sites by copolymerization minimizes aggregation of the PPY units and the non-cooperative effects normally associated with the coiling of the chain.

The dendronized polymer architecture affords a final polymer with a gradient of polarity from polar amine or amide groups near the backbone, to less polar aliphatic ester dendrons, to apolar alkyl chain ends. The modular design of the polymer and its facile synthesis can assist in investigating local microenvironment effects on properties such as transport or catalysis. Unlike dendrimers, which have stimulated numerous examples of catalysis,[5–14] the use of dendronized polymers in a catalytic role is unexplored.

Previous work has shown that encapsulation of a catalytic center within a dendritic nanoenvironment can dramatically affect reactivity when compared to the bulk solvent environment.[15,16] The interior volume of a highly branched dendrimer can be tuned to provide a unique nanoenvironment separate from the exterior bulk solvent. For example, increasing the polarity differential between the interior and exterior of the molecule creates a thermodynamic sink, drawing substrates into the dendrimer and expelling product back into the surrounding medium. Drawing on these concepts, and revisiting earlier work on polymer supported dialkylaminopyridine catalysts,[17–19] we have attempted to demonstrate the "concentrator" effect of nanoenvironment that may be achieved in a catalytic nanoreactor based on the dendronized polymer architectural motif (Fig. 1).

A random cyclocopolymer was prepared[20] with a repeat unit ratio of 1 : 11. Dendron growth was accomplished in a two-step acylation–deprotection process as outlined in Scheme 1. After four generations of growth, the polyol was capped with myristic anhydride to yield the alkyl terminated dendronized cyclocopolymer, **3**. Monitoring the growth by size-exclusion chromatography, IR spectroscopy and UV determination of PPY content (see ESI†) suggested that all dendronization steps were achieved in high yields as previously observed in a similar dendronization[21] and in the preparation of other dendronized structures.[22]

It was noted during UV measurements that the peak shape and absorbance maximum of PPY embedded within a G4 dendronized polymer reflect a more polar environment than the bulk solvent hexane in which it was dissolved (Fig. 2).

Thus, the absorbance spectrum of PPY embedded in the dendronized polymer dissolved in hexane exhibits a slight bathochromic shift from 253 nm to 256 nm with a bimodal peak shape similar to that of monomeric PPY dissolved in methanol. This observation is consistent with the creation of a more polar interior nanoenvironment.

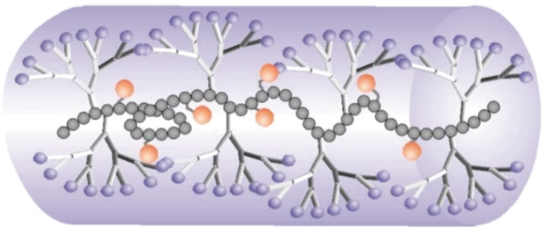
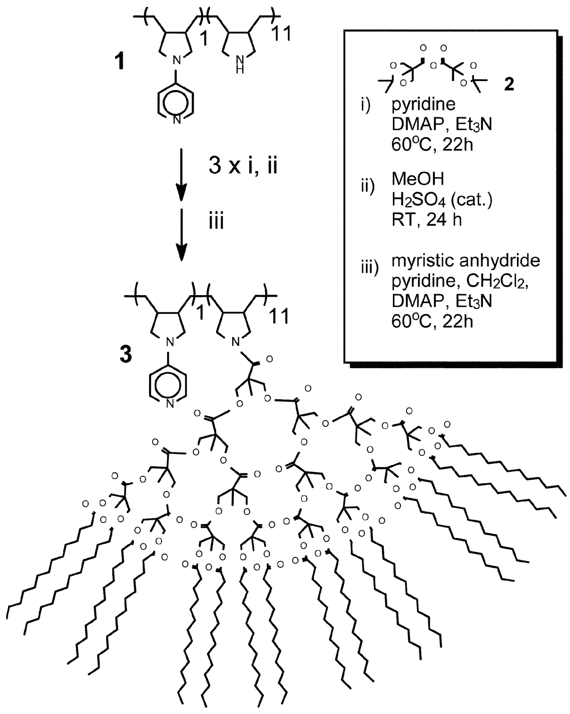


Fig. 1 Illustration of rod-like dendronized polymer bearing catalytic groups at the backbone.



Scheme 1 Preparation of PPY embedded dendronized cyclocopolymer.

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† Electronic supplementary information (ESI) available: characterisation data. See http://www.rsc.org/suppdata/cc/b3/b307425k/

DOI: 10.1039/b307425k

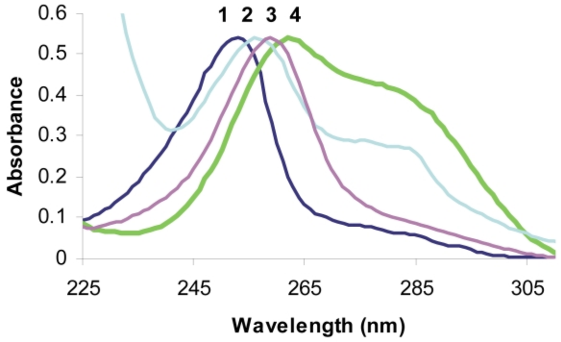
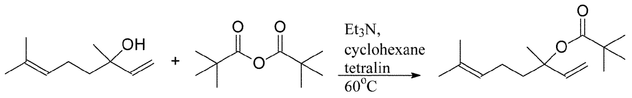


Fig. 2 UV spectra of PPY dissolved in 1 = hexane (Abs$_{max}$ 253 nm), 3 = acetonitrile (259 nm), 4 = methanol (262 nm). 2 = Compound **3** dissolved in hexane (256 nm).

The catalyst was evaluated for its ability to catalyze an esterification reaction between an alcohol and anhydride. Triethylamine was added to trap the acid by-product. Since a reaction such as that between 3-pentanol and acetic anhydride occurs readily even in the absence of a catalyst a very difficult reaction that does not proceed to a significant extent even in the presence of dimethylaminopyridine or PPY was used to test the catalyst. This involved sterically hindered tertiary alcohol linalool and pivalic anhydride (Scheme 2).‡ Using 2.5 mol% of PPY encapsulated in the dendronized polymer, a conversion of nearly 40% was achieved whereas less than 2% conversion was observed in the presence of an equivalent amount of monomeric dimethylaminopyridine, monomeric PPY, or in the non-catalyzed control (Fig. 3, Table 1). Evaporation of the reaction mixture allowed recycling of the dendronized polymer. The long reaction times required in these experiments suggest that the mol% catalyst required for this reaction should be significantly more than the 2.5 mol% we used.

The catalytic enhancement we observed can be attributed to a nanoenvironment created by the dendronized polymer. Thus, the relatively polar interior may assist in lowering the transition-state energy of the substrate complex, thereby facilitating the reaction. The contrasting polarities of the interior of the catalyst molecule and the bulk cyclohexane solvent may also induce a pre-concentration effect. For example, little product is formed even when using as much as 0.4 equiv. of monomeric PPY reagent under concentration conditions similar to those used with the polymer. Since esterification of linalool with pivalic anhydride is a process that is highly concentration dependent, the modest success of the dendronized polymer suggests that the macromolecule acts as a molecular concentrator in which substrates are being driven into the interior.



Scheme 2

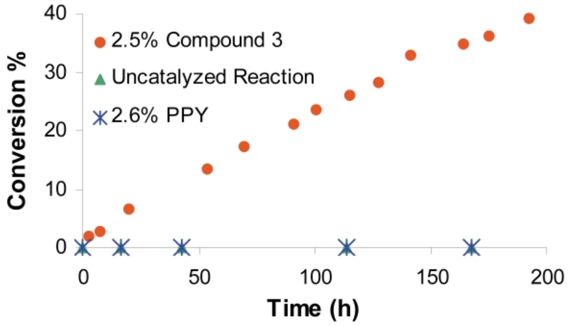


Fig. 3 Comparison of linalool esterification with pivalic anhydride in the presence of PPY, dendronized polymeric catalyst and no catalyst.

Table 1 Reaction of linalool (0.17 M) with pivalic anhydride in the presence of 2.5 mol% PPY moieties and triethylamine at 60 °C over 7 d

Catalyst	Conversion (%)
Polymer	40
DMAP	< 1
PPY	< 1
PPY in THF	< 1
—	< 1

While this is only a first example of the use of a dendronized polymer in catalysis, the results we obtained are tantalizing as numerous reactions could benefit from the free-energy driven concentration and mass transport effects observed with appropriately designed dendritic catalysts. Clearly, the properties of the dendronized polymers can be tuned by variation of dendrons and functional groups incorporated within the modular structure to create the desired microenvironment and polarity gradient. Further complexity by introduction of multi-component active sites interacting cooperatively within a single nanoreactor can be envisaged. A study of the effects derived from a variety of architectural motifs is underway.

Funding for this research was provided by the Department of Energy Biomolecular Program at LBNL (DE-AC03-76SF00098) and NSF (DMR-0317514). Fellowship support for C.O.L. from the Eastman Kodak Company is acknowledged with thanks.

Notes and references

‡ Linalool (1.0 eq., 186 μmol), pivalic anhydride (3.1 eq., 576 μmol), triethylamine (3.1 eq., 581 μmol), catalyst (0.025 eq. of PPY moiety, 4.65 μmol), and tetralin (10 μL) were combined in a sealed vial equipped with a stirbar. 500 μL of cyclohexane were added to the reaction containing the dendritic catalyst. The control reaction and the PPY and DMAP containing reactions were diluted to an equivalent volume. The mixture was stirred at 60 °C for 7 days in a sealed vial. Conversion was measured by gas chromatography using tetralin as the internal standard.

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