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Synthesis and Catalysis of B_{12}–Core–Shell Hyperbranched Polymer

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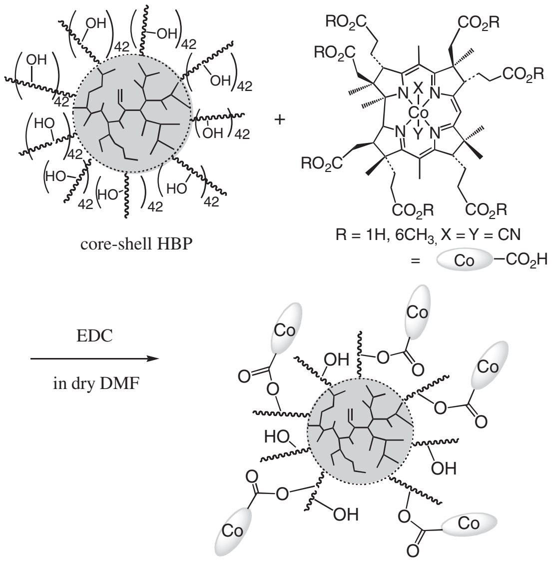
A vitamin B_{12} derivative was immobilized on a core–shell hyperbranched polymer, and the hybrid polymer was characterized by GPC, UV–vis, IR as well as TEM analyses. The hybrid polymer exhibits catalysis for the dehalogenation of phenethyl bromide to form ethylbenzene and 2,3-diphenylbutane by irradiation with UV light at room temperature.

The immobilization of catalysts onto various supports, such as metals, clays, zeolites, and polymers has been performed by many researchers in order to develop a good catalytic system.[1] Cobalt complexes, i.e., vitamin B_{12} derivatives, are good catalysts for several molecular transformation reactions,[2] and efforts for the immobilization of these vitamin B_{12} derivatives on various supports have been reported by several groups.[3]

Most of these studies used a solid-phase support, and the prepared hybrid materials exhibited both advantages and disadvantages as a support due to the heterogeneous nature of the reaction conditions. The use of a soluble polymer may be applicable as an alternative to conventional solid-phase supports to alleviate such disadvantages. Dendric polymers, particularly perfect dendrimers and hyperbranched polymers (HBPs), offer a wide range of new possibilities. Since dendrimers have to be prepared in tedious multistep syntheses which are difficult for large-scale syntheses, the HBPs offer a promising alternative among these soluble polymers.[4]

The HBP is rapidly and conveniently prepared by a one-pot procedure, and due to its globular (spherical) shape, the HBP is soluble in various solvents. Furthermore, many functional groups are present on the polymer surface due to its dendric topology. Therefore, the HBP is expected to be a practical support for the catalyst.[5] In this study, the synthesis and characterization of new hybrid catalysts composed of a vitamin B_{12} derivative and a core–shell HBP are reported. As a large number of functional groups are present in the HBP, propagation of the shell polymer on the HBP was effectively generated to form the unique core–shell topological HBP.

The core unit of the core–shell HBP was prepared by the living radical polymerization of 2-(*N*,*N*-diethyldithiocarbamoyl)ethyl methacrylate under UV irradiation,[6] and subsequent grafting from this HBP with 2-hydroxyethyl methacrylate produced the core–shell HBP.[7,8] Immobilization of the vitamin B_{12} derivative on the core–shell HBP was achieved by esterification of the hydroxy groups of the core–shell HBP with the vitamin B_{12} derivative bearing a carboxylic group[5] as shown in Scheme 1. The B_{12}–core–shell HBP was characterized by GPC, UV–vis, IR, and TEM (see the Supporting Information[12]). The hybrid polymer showed the typical UV–vis spectrum of B_{12} with absorption maxima at 372, 505, 546, and 587 nm in CH_2Cl_2 as shown in Figure S4.[2,5] The hybrid polymer well dissolved in other solvents, such as $CHCl_3$, CH_3CN, acetone, THF, DMF, 1,4-dioxane, and MeOH. The amount of the immobilized B_{12} (modified yields of hydroxy groups of core–shell HBP with B_{12}) was determined by UV–vis[12] and was controlled by the added equivalents of B_{12} under the synthetic conditions as shown in Figure S7. The modified yields of the hydroxy groups of the polymer were in good relationship to the added B_{12}. But the value reached a maximum at nearly 20%. It is assumed that B_{12} was immobilized on the surface of the polymer due to steric hindrance of the B_{12}. Therefore, the modified yield reached a maximum at a certain value. From the TEM image, the spherical shape of the polymer was clearly observed, and the topology of the polymer is similar to that of the dendrimer as shown in Figure S6. The size of the polymer is estimated to be 3–5 nm.

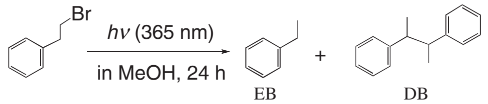


Modification ratio of -OH group of core–shell HBP with B_{12} : 1~20 %

Scheme 1.

The catalytic activity of a hybrid catalyst, the B_{12}–core–shell HBP, was investigated for comparison to that of the monomeric B_{12} (heptamethyl cobyrinate perchlorate). TiO_2 was used as a reducing reagent for the B_{12} moiety of the hybrid catalyst to form the reactive Co^I species.[9] When phenethyl bromide was used as a substrate, ethylbenzene (EB) and 2,3-diphenylbutane (DB) were obtained as products by irradiation with UV light (365 nm). Especially, the coupling product, DB, was obtained in a high yield when compared to that of the monomeric B_{12} under the same reaction conditions. In addition, the yields of DB were independent of the modified yield of B_{12} and ranged from 16 to 2%. The yield then decreased to 8% with the modified 0.5% yield. In the case of the monomeric B_{12}, the yield of DB was

Table 1. Catalytic activity of various B_{12} catalysts[a]



Catalyst (B_{12} Modification ratio)	Conversion[b] /%	Product (Yield[b]/%)		Selectivity[c] /%
		EB	DB	
B_{12}–core–shell HBP				
16%	99	55	23	29
7%	96	56	25	31
2%	98	46	19	29
0.5%	92	76	8	9
B_{12} linear polymer				
19%	99	71	22	24
2%	99	78	11	12
B_{12}[d]	95	86	4	4

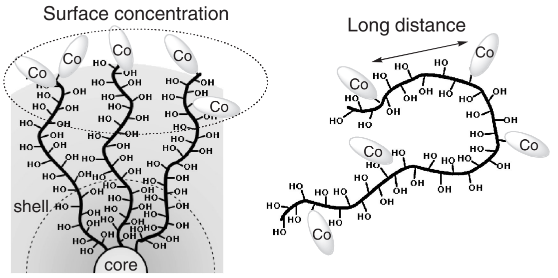
[a] 2.0×10^{-5} M/B_{12}, [$PhCH_2CH_2Br$] = 2.0 mM, TiO_2 19 mg, solvent MeOH 25 mL under N_2. Each experiments were carried out 2 or 3 times. [b] Conversions were estimated by the recovery of the substrate. Yields were based on the initial concentration of the substrate. No other product was detected by GC-MS and GC. [c] Selectivity (%) = [yield of DB/(yield of DB) + (yield of EB)] × 100. [d] Heptamethyl cobyrinate perchlorate was used.

very low (Table 1, B_{12}).[10] These results indicate that B_{12} was concentrated on the surface of the core–shell HBP, and this catalyst morphology presumably enhanced the coupling reaction. In fact, as the number of B_{12} immobilized on each shell unit was estimated, at least one mole of B_{12} should be immobilized in one unit shell for the B_{12} modified yield over 2%. Therefore, coupling of the substrate was preferred in the hybrid polymer. In contrast, below a 2% B_{12} modified yield, only 0.2 mol of B_{12} was immobilized in one unit shell.

Based on these results, we proposed the following reaction mechanism. Supernucleophilic Co^{I} species generated by electron transfer from TiO_2 located on the surface of the polymer reacts with phenethyl bromide to form the corresponding alkylated complex. Cleavage of the cobalt–carbon bond afforded the phenethyl radical. The primary radical rearranged into a secondary radical. Coupling of this radical may produce a DB before diffusing out from the surface of the polymer.

To confirm this hypothesis, we synthesized the B_{12}–linear polymer (poly(2-hydroxyethyl methacrylate), $M_w = 2000$) without the core moiety.[11] This linear polymer corresponds to the shell unit of the core–shell HBP. In the case of the B_{12}-linear polymer, the yield of the coupling product decreased to 11% as the modified yield of B_{12} decreased to 2% in contrast to that of HBP as shown in Table 1. The B_{12} is probably separated from each other in the linear polymer, thus the yield of the coupling product becomes lower. Based on this result, the core of the polymer plays an important role in this catalysis, mainly concentrating the immobilized B_{12} as shown in Figure 1.

In conclusion, the vitamin B_{12} derivative was immobilized on the core–shell HBP. The hybrid polymers were highly soluble in various organic solvents and showed a unique catalysis for the coupling reaction of phenethyl bromide.



B_{12}-core-shell HBP

B_{12}-linear polymer

Figure 1. Schematic representation of B_{12}–core–shell-HBP and B_{12}–linear polymer with 2% B_{12}-modified yield.

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6 $M_w = 14000$ by GPC measurement, $M_w/M_n = 2.9$. Details were reported in the Supporting Information.[12]

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8 $M_w = 59000$ by GPC measurement, $M_w/M_n = 4.5$. The length of shell unit was estimated by content of *N,N*-diethyldithiocarbamoyl group. Details were reported in the Supporting Information.[12]

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10 When the concentration of the monomeric B_{12} catalyst was increased to 2 mM (100-fold higher concentration), the yield of DB reached 20%.

11 B_{12} was modified on the linear polymer in the same way.[12] The obtained B_{12} linear polymer well dissolved in MeOH.

12 Supporting Information is electronically available on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.