C−H Polyaddition of Dimethoxyarenes to Unconjugated Dienes by Rare Earth Catalysts

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S *Supporting Information*

ABSTRACT: The C−H polyaddition of dimethoxyarenes such as 1,4-dimethoxybenzene and 4,4′-dimethoxybiphenyl to unconjugated dienes such as norbornadiene and 1,4-divinylbenzene has been achieved for the first time by using cationic half-sandwich rare earth alkyl catalysts. This protocol afforded novel polymer materials consisting of dimethoxyarene moieties and nonpolar hydrocarbon structure motifs (cyclic, linear, and aromatic) in perfectly alternating sequences that are otherwise difficult to make. The reaction proceeded via C=C double bond insertion into a C−H bond ortho to each of the two methoxy groups in a step-growth polymerization fashion.

Organic macromolecules consisting of multicomponents distinctly different in structure and property in an alternating sequence are of great interest as functional materials.[1] Generally, the polycondensation of prefunctionalized or preorganized organic molecules in a step-growth fashion is the most powerful method for the synthesis of alternating copolymers.[2] However, the polycondensation approach usually yields an equimolar amount of unwanted byproducts. In contrast, the C−H polyaddition of an organic compound to an unconjugated diene (either cyclic or acyclic) could, in principle, serve as an atom-economical route for the synthesis of the corresponding perfectly alternating copolymer through C−C formation without release of a byproduct (see Scheme 1).

Scheme 1. Synthesis of Perfectly Alternating Copolymers through C−H Polyaddition to Dienes

Alternating A-B copolymer
100% atom efficiency
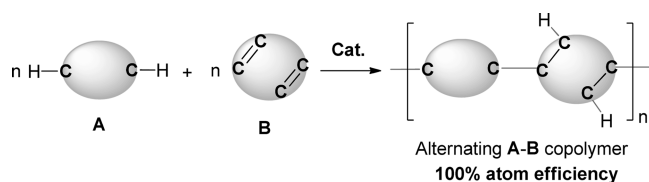
However, the application of such a C−H bond activation protocol to the synthesis of macromolecules has remained almost unexplored to date.[3] Previously, Weber and co-workers reported the C−H polyaddition of aromatic ketones to some silylated α,ω-dienes[3] by a ruthenium catalyst originally developed by Murai and co-workers for the C−H addition of aromatic compounds to alkenes.[4] In contrast to the wide substrate scope reported for the original single C−H addition reactions, the substrates

suitable for the C−H polyaddition transformation seemed rather limited.[3d] Obviously, C−H polyaddition is much more difficult than the analogous single C−H addition. In fact, although a great number of transition metal catalysts have been reported for the C−H activation and functionalization of various organic substrates,[5] the Murai (ruthenium-catalyzed) reaction is perhaps the only precedent that was reported to be applicable to C−H polyaddition. Exploring the potential of other catalyst systems and other substrates for the C−H polyaddition reactions is therefore of great interest and importance.

Half-sandwich rare earth alkyl complexes have recently emerged as a new class of highly efficient catalysts for the polymerization and copolymerization of a wide range of olefins.[6] These catalysts can also efficiently catalyze the regio- and stereospecific C−H addition of some functional aromatic compounds such as pyridines,[7a,c] anisoles,[7b] and N,N-dimethylanilines[7d] to a wide range of olefins and allenes with substrate scope and selectivity in contrast or complementary to those of late transition metal catalysts. For example, because of the strong oxophilicity of the rare earth metal ions, even an ether moiety could serve as a directing group, thus enabling the ortho-selective C−H addition of anisoles to various 1-alkenes, which is difficult to achieve with other catalysts.[7b,8] These results encouraged us to examine whether the rare earth catalysts could work for the C−H polyaddition of dimethoxyarenes such as 1,4-dimethoxybenzene[9] to unconjugated dienes via the activation of a C−H bond ortho to each methoxy group.

Herein, we report the C−H polyaddition of 1,4-dimethoxybenzene (DMB) and 4,4′-dimethoxybiphenyl (DMBP) to unconjugated dienes such as norbornadiene (NBD) and 1,4-divinylbenzene (DVB) catalyzed by half-sandwich rare earth catalysts. This is the first example of the application of a rare earth catalyst for C−H polyaddition and also the first example of copolymerization of dimethoxyarenes with unconjugated dienes by any catalyst. The copolymerization of these two distinctly different types of components took place efficiently in a step-growth fashion, affording a new family of macromolecules with 2,5- (or 2,5′-) dialkylated 1,4- (or 1,4′-) dimethoxyarene moieties and other hydrocarbon structure motifs in a perfectly alternating sequence.

On the basis of the screening of various half-sandwich rare earth catalysts (see Table S1), we chose the C_5Me_5-ligated scandium complex **1-Sc** (Chart 1)[10] together with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ to examine the copolymerization of
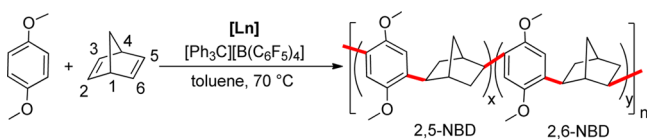
Chart 1. Half-Sandwich Rare Earth Dialkyl Complexes

1-Ln
Ln = Sc, Y

2-Ln
Ln = Sc, Y
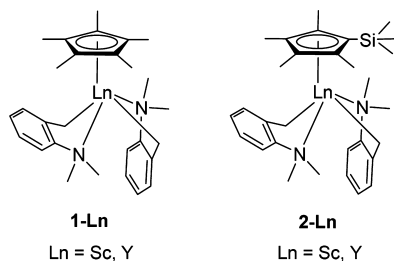
1,4-dimethoxybenzene (DMB) with an equimolar amount of norbornadiene (NBD) in toluene at 70 °C. Representative results are summarized in Table 1. In the case of the monomer

Table 1. Copolymerization of 1,4-Dimethoxybenzene (DMB) with Norbornadiene (NBD)[a]

entry	[Ln]	$[M]/[Ln]^b$	time (h)	yield[c] (%)	M_n^d (×10³)	M_w/M_n^d	T_g^e (°C)
1	1-Sc	40	1	89	1.90	2.18	144
2	1-Sc	40	2	95	4.07	2.11	166
3	1-Sc	40	4	100	7.21	2.04	194
4	1-Sc	40	8	100	9.33	2.03	193
5	1-Sc	40	12	100	9.72	1.98	193
6	1-Sc	40	24	100	9.80	2.00	199
7	1-Sc	40	48	100	10.01	1.97	198
8	1-Sc	100	24	100	7.49	2.18	200
9	1-Sc	500	24	100	3.94	2.26	176
10	1-Sc	500	72	100	7.74	2.10	196
11	2-Sc	40	24	64	1.63	1.59	127
12	1-Y	40	24	0			

[a]Reaction conditions: [Ln], 0.025 mmol; $[Ph_3C][B(C_6F_5)_4]$, 0.025 mmol; [M], 0.5 mol/L; 70 °C. [b]Molar ratio of monomer feed/catalyst. [c]Isolated yield. The ratio of 2,5-NBD/2,6-NBD is ~1.2, as estimated by ^{13}C NMR. [d]Determined by GPC against polystyrene standard at 145 °C in *o*-dichlorobenzene. [e]Measured by DSC.

to catalyst ratio [M]/[Ln] = 40, a full conversion of both monomers was achieved in ~4 h. The molecular weight of the resulting polymer product reached 7.21 kg/mol with M_w/M_n = 2.04 (Table 1, entry 3). The norbornenyl and *para*-dimethoxyphenyl chain-end groups in this polymer product (and those obtained in shorter periods of time) could be observed by ^1H NMR spectroscopy (see Figure S6). When the reaction time was further prolonged, the molecular weight of the resulting polymers gradually increased, reaching 10.01 kg/mol in 48 h (Table 1, entry 7). The molecular weight distribution of the polymer products remained around 2 irrespective of polymerization time. All of these features are in agreement with a step-growth polymerization mechanism. Higher monomer feeds are also applicable to this copolymerization. In the case of [M]/[Ln] = 100 and 500, quantitative conversion was achieved within 24 h. When the reaction time was extended from 24 to 72 h in the case of [M]/[Ln] = 500, the molecular weight of the resultant polymers increased from 3.94 to 7.74 kg/mol (Table 1, entries 9 and 10),

demonstrating the high efficiency and excellent stability (lifetime) of the present catalyst system. The resulting copolymers showed high glass transition temperatures (T_g) (190−200 °C) in most cases.

The analogous scandium complex bearing a more sterically demanding $C_5Me_4SiMe_3$ ligand (2-Sc, Chart 1) showed relatively lower activity than 1-Sc for the present copolymerization reaction (Table 1, entry 11), probably because of steric hindrance. The yttrium complexes 1-Y and 2-Y showed no catalytic activity under the same conditions, in agreement with their low activity for olefin polymerization[6] and the C−H addition of anisole to norbornene.[7b]

Because little comparable information is available in the literature, the polymer products were characterized in detail by ^1H, ^{13}C, DEPT-^{13}C, HSQC, and HMBC NMR analyses to establish their microstructures (see Supporting Information). It was revealed that all of these polymer products are alternating DMB−NBD copolymers in which a DMB component is bonded to two NBD units exclusively at the 2,5-positions (a pair of para carbon atoms ortho to the methoxy groups) (see Figure 1).
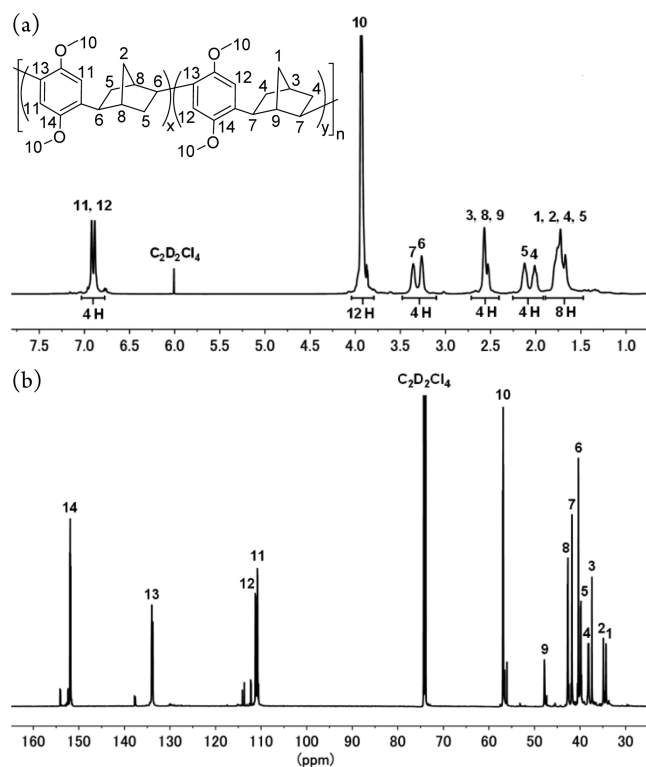

Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectra of a DMB−NBD copolymer ($C_2D_2Cl_4$, 120 °C) obtained in Table 1, entry 6.

The bicyclic NBD units are connected to two DMB moieties in both 2,5- and 2,6-manners with a ratio of 1.2 to 1, as estimated by integration of the ^{13}C NMR signals at δ 34.9 and 34.3 ppm (see Figure 1b).

A possible mechanism for the present copolymerization of DMB and NBD is shown in Scheme 2. As reported previously, the reaction of the dialkyl complex 1-Sc with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ could easily give the cationic scandium monoalkyl species **A**.[10,11] The coordination of an ether group of DMB to the Sc atom in **A** would afford **B**. The σ-metathesis (or acid−base reaction) between the scandium alkyl species and a C−H bond ortho to the Sc-coordinated methoxy group in **B** could yield the anisyl species **C**, which upon insertion of NBD should give the scandium norbornyl species **D**.

Scheme 2. Possible Mechanism for Scandium-Catalyzed Step-Growth Copolymerization of 1,4-Dimethoxybenzene (DMB) with Norbornadiene (NBD)
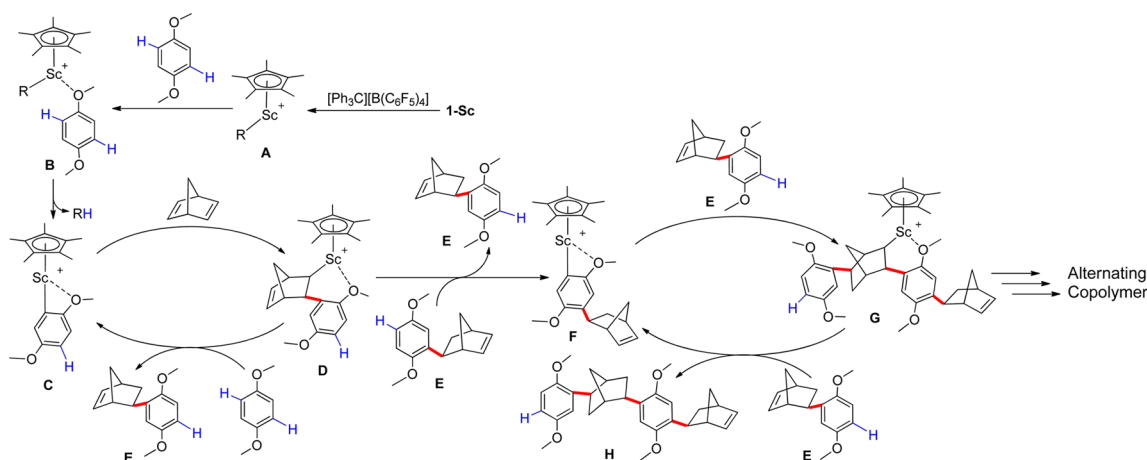
The reaction of **D** with another molecule of DMB through deprotonation of an ortho C−H bond by the Sc−norbornyl species would release the DMB−NBD dimerization product **E** and regenerate **C**. The analogous deprotonation of **E** by **D** would afford a new anisyl species **F**, which after insertion of the norbornene unit of **E** (in a 2,5-fashion) should give **G**. Deprotonation of another molecule of **E** by **G** would yield the DMB−NBD−DMB−NBD tetramer **H** and regenerate **F**. The insertion of NBD in a 2,6-bonding fashion could take place similarly. The analogous reactions between **G** and **H** and among the resulting oligomers and new scandium norbornyl species could afford the corresponding alternating DMB−NBD copolymers. It should also be noted that addition of a scandium norbnornyl species such as **D** or **G** to a norbornene unit (or continuous insertion of NBD) is much less favored than the C−H activation (deprotonation) of a DMB unit in the present catalyst system because of steric hindrance.[12] This thus enables the step-growth polymerization to occur efficiently and selectively.

To examine the diene substrate scope for the present C−H polyaddition reaction, we then carried out the reaction of DMB with 1,4-divinylbenzene (DVB) by using 1-Sc/[Ph$_3$C][B(C$_6$F$_5$)$_4$] under the same conditions. Unfortunately, only a trace amount of polymer precipitate was observed (Table 2, entry 1). We reasoned that the poor performance of 1-Sc for the copolymerization of DMB and DVB might possibly be due to some extent of continuous insertion of DVB,[13,14] which could interfere with the step growth polymerization. We then examined the yttrium catalysts, which are known to show much lower activity for continuous olefin insertion (coordination polymerization) compared to that of the scandium analogues.[6,7b,13,15] To our delight, in the presence of 5 mol % 1-Y/[Ph$_3$C][B(C$_6$F$_5$)$_4$], the copolymerization of DMB with DVB took place smoothly to give the corresponding copolymer product with M_n = 1.04 kg/mol in 43% yield in 12 h (Table 2, entry 2). The more sterically demanding C$_5$Me$_4$SiMe$_3$-ligated yttrium complex 2-Y showed even higher activity for this reaction, quantitatively yielding the copolymer product with M_n = 3.18 kg/mol and M_w/M_n = 2.38 in 12 h (Table 2, entry 3). When the reaction was carried out for a longer period of time (24 h), a significant amount (∼28%) of insoluble (in hot dichlorobenzene) products were obtained, and a soluble higher molecular weight copolymer product (5.72 kg/mol) could be obtained (Table 2, entry 6). The NMR analyses established that the polymer products formed in the present reaction are perfectly alternating DMB−DVB copolymers in

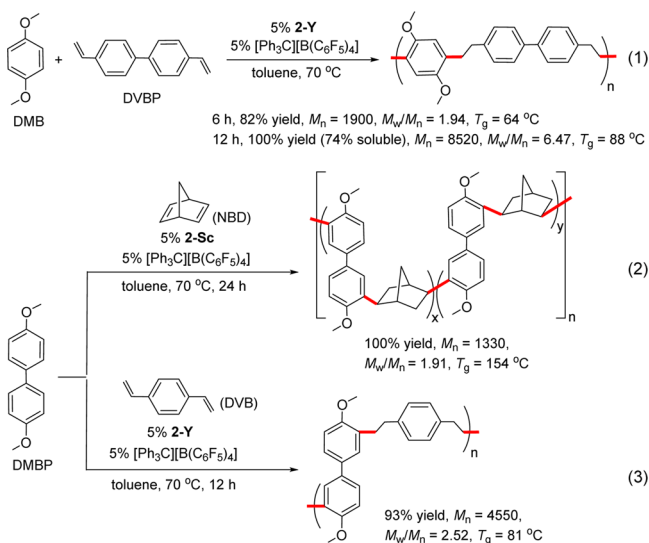**Table 2. Copolymerization of 1,4-Dimethoxybenzene (DMB) with 1,4-Divinylbenzene (DVB)[a]**
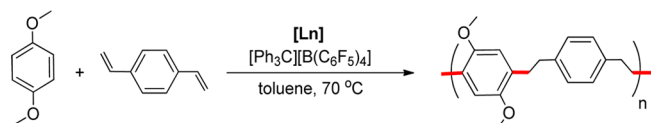
entry	[Ln][a]	time (h)	yield[b] (%)	$M_n{}^c$ (×10³)	$M_w/M_n{}^c$	$T_g{}^d$ (°C)
1	1-Sc	12	trace			
2	1-Y	12	43	1.04	1.40	29
3	2-Y	12	100	3.18	2.38	43
4	2-Y	4	45	1.12	1.48	40
5	2-Y	8	96	2.46	2.19	42
6	2-Y	24	100[e]	5.72[f]	3.13[f]	51[f]

[a]Reaction conditions: [Ln], 0.05 mmol; [Ph$_3$C][B(C$_6$F$_5$)$_4$], 0.05 mmol; 1,4-dimethoxybenzene, 1 mmol; 1,4-divinylbenzene, 1 mmol; toluene, 2 mL; 70 °C. [b]Isolated yield. [c]Determined by GPC against polystyrene standards at 145 °C in o-dichlorobenzene. [d]Measured by DSC. [e]A portion (∼28%) of the crude polymer product was insoluble in hot dichlorobenzene. [f]Measured with the soluble portion of the polymer product.

which the DMB units are connected to the two p-vinyl groups of the DVB units exclusively at the 2,5-positions, as in the case of the DMB−NBD copolymers. It is also worth noting that the present DMB−DVB copolymer products could formally be viewed as perfectly alternating "DMB−ethylene−benzene−ethylene" copolymers; such a structure sequence would be very difficult to make by direct copolymerization of ethylene with other components.

The 2-Y catalyst is also effective for the C−H polyaddition of DMB to 4,4′-divinylbiphenyl (DVBP), which afforded a soluble polymer product with M_n = 1.90 kg/mol in 82% yield in 6 h (eq 1). This DMB−DVBP copolymer product may also formally be viewed a unique, perfectly alternating "DMB−ethylene−biphenyl−ethylene" copolymer. When the reaction was carried out for 12 h, quantitative conversion was achieved, but the resulting copolymer product was only partly soluble in hot dichlorobenzene (soluble part: 74%, M_n = 8.52 kg/mol, M_w/M_n = 6.47).

Besides DMB, 4,4′-dimethoxybiphenyl (DMBP) is also applicable to the present C−H polyaddition reaction. In the presence of 5 mol % 2-Sc/[Ph$_3$C][B(C$_6$F$_5$)$_4$], the polyaddition of DMBP to NBD quantitatively gave the corresponding copolymer product with M_n = 1.33 kg/mol and M_w/M_n = 1.91

$$6 \text{ h, } 82\% \text{ yield, } M_n = 1900, \ M_w/M_n = 1.94, \ T_g = 64 \ ^\circ\text{C}$$
$$12 \text{ h, } 100\% \text{ yield (74\% soluble), } M_n = 8520, \ M_w/M_n = 6.47, \ T_g = 88 \ ^\circ\text{C}$$

$$100\% \text{ yield, } M_n = 1330, \ M_w/M_n = 1.91, \ T_g = 154 \ ^\circ\text{C}$$

$$93\% \text{ yield, } M_n = 4550, \ M_w/M_n = 2.52, \ T_g = 81 \ ^\circ\text{C}$$

in 24 h (eq 2). Similarly, the alternating copolymerization of DMBP with DVB by 2-Y afforded the polymer product with $M_n = 4.55$ kg/mol and $M_w/M_n = 2.52$ in 93% yield in 12 h (eq 3).[16] In addition to dimethoxyarenes, other dialkoxyarenes such as 1,4-dibutoxybenzene are also applicable for the present step-growth polymerization albeit with lower activity under the same reaction conditions (see Scheme S1). Moreover, aliphatic α,ω-dienes such as 1,9-decadiene could also serve as a diene substrate for the copolymerization with DMB to give the corresponding alternating copolymer, though a longer reaction time is needed (see Scheme S2).

In summary, we have achieved for the first time the C−H polyaddition of dimethoxyarenes to unconjugated dienes by using rare earth metal-based catalysts. This protocol has enabled us to efficiently and selectively synthesize a series of novel polymer materials having both polar dimethoxyarene moieties and nonpolar hydrocarbon structure motifs (cyclic, linear, and aromatic) in perfectly alternating sequences from easily available starting materials. This work demonstrates that rare earth-catalyzed C−H bond activation can serve as a unique, efficient methodology for the construction of macromolecular architectures difficult to make by other means. Studies on the copolymerization of other organic compounds via C−H polyaddition are in progress.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03859.

Detailed experimental procedures, NMR, GPC, and DSC of selected polymers (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(15) The reaction of 1,4-dimethoxybenzene with two equiv of styrene in the presence of an yttrium catalyst gave the 2,5-dialkylation product almost quantitatively (see ref 7b).

(16) A quantitative conversion could be achieved when the reaction was carried out for a longer time, which gave a significant amount of insoluble products however because of the poor solubility of the high molecular weight polymers.