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Preparation of Hydroxytelechelic Poly(butadiene) via Ring-Opening Metathesis Polymerization Employing a Well-Defined Metathesis Catalyst[†]

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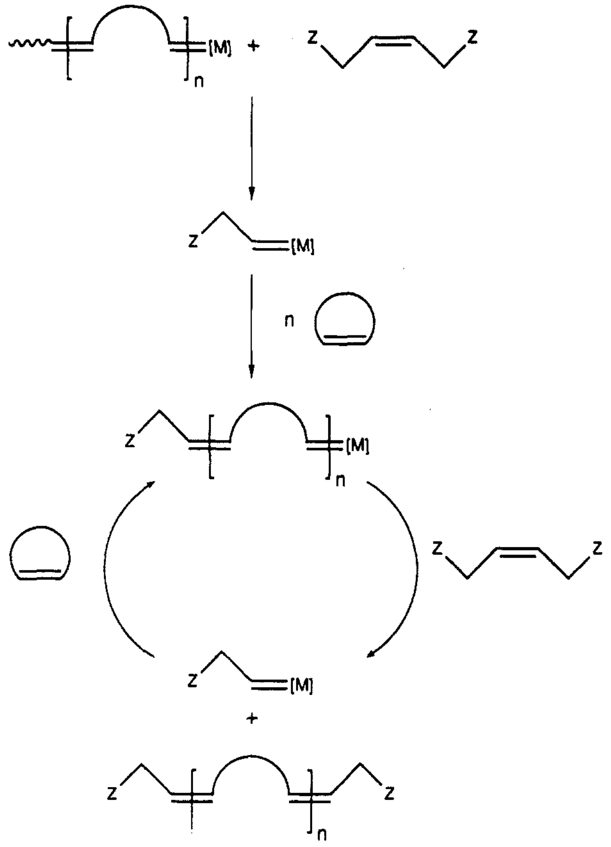
Telechelic polymers, macromolecules with one or more reactive end-groups, are useful materials for chain extension processes, block copolymer synthesis, reaction injection molding, and network formation.[1,2] For most applications a functionality (number of functional groups per chain) of 2 or greater is required. In particular, commercially produced hydroxytelechelic poly(butadiene) (HTPBD) has found a variety of industrial applications.[3-5] Commercially available HTPBD obtained by the radical polymerization of 1,3-butadiene in the presence of hydrogen peroxide is a mixture of 1,4 and 1,2 repeat units containing at least three types of hydroxy end-groups.[6-9] Although the functionality of HTPBD obtained from this radical polymerization is typically greater than 2,[7,10] termination by disproportionation can lead to monofunctional polymers which are detrimental to the production of high molecular weight polymers in a subsequent step-growth polymerization. As with most radical polymerizations, the ease of HTPBD preparation by this method is balanced by the lack of regiospecificity and end-group specificity. The ability to systematically tailor the structure of HTPBD (both the regiochemistry and functionality) would allow a fundamental understanding of structure–property relationships in the polymer and derived copolymers. Living anionic polymerization techniques offer a potential solution, and progress has been made in this area.[1,2] In this paper we show that ring-opening metathesis polymerization (ROMP)[11] using a discrete metal alkylidene catalyst offers another alternative polymerization technique that is applicable to the synthesis of well-defined HTPBD.

Acyclic olefins act as chain-transfer agents to regulate the molecular weight of polymers produced by ROMP.[11] When α,ω-difunctional olefins are employed as chain-transfer agents, difunctional telechelic polymers can be synthesized.[12-19] However, ill-defined classical metathesis catalysts have been employed in all cases reported to date. It is not possible either to modulate the activity of the catalyst systematically, to define the structure of the initiating alkylidene, or to control the mode of termination of these multicomponent catalysts. In addition, the Lewis acid cocatalysts typically found in these systems (e.g., AlR_3, SnR_4, or $AlClR_2$) can react with functional groups of the chain-transfer agent or with the monomer itself,[20] leading to unwanted byproducts and catalyst deactivation. These problems can potentially be circumvented by the use of well-defined, Lewis-acid-free metal alkylidene complexes whose structure and activity can be easily modified.[21-24] Furthermore, these catalysts can produce living polymer chains where there is no termination of the active catalyst center in the absence of an end-capping reagent. In the chain-transfer reaction with a symmetric α,ω-difunctional olefin, the propagating alkylidene is terminated with a functional group, and the new functionally substituted alkylidene reacts with a monomer to initiate a new chain. This process preserves the number of active catalyst centers and leads to symmetric telechelic polymers with a functionality that approaches 2.0 (Scheme I). The only polymer end-groups that do not contain residues from the chain-transfer agent are those from the initiating alkylidene and the end-capping reagent. In principle, these end-groups could be chosen to match the end-group from the chain-transfer agent. The following data are results on the preparation of HTPBD using a protected allylic diol as the chain-transfer reagent and a single-component metathesis catalyst with a well-defined initiating alkylidene.

Scheme I



The ROMP of 1,5-cyclooctadiene (COD) leads to a polymer having a repeat unit that is identical to that of 1,4-poly(butadiene). The catalyst chosen for this study was $W(CHAr)(NPh)[OCCH_3(CF_3)_2]_2(THF)$ (Ar = *o*-methoxyphenyl) (1), due to its ease of synthesis and high metathesis activity.[22,25] The chain-transfer agent was obtained by the protection of *cis*-1,4-butenediol as the bis(*tert*-butyldimethylsilyl) (TBS) ether (2).[26] In a typical experiment, COD and 2 were mixed in a vial under an inert atmosphere and transferred by syringe into a separate vial that contained 1 (dissolved in a minimum amount of benzene). The mole ratio of 2 to COD ranged from 1.5×10^{-3} to 1.9×10^{-2}, and the mole ratio of COD to 1 was kept constant at approximately 700. All reactions were run at room temperature for 2 h and terminated by the addition of excess pivalaldehyde (eq 1). The reaction mixtures were then dissolved in benzene and precipitated into methanol. Molecular weights of the polymers were determined by GPC in methylene chloride (referenced to polystyrene standards), and these results are shown in Table I. The molecular weights of the telechelic poly(butadiene)s decreased with increasing concentration of the chain-

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[†] Contribution No. 8721.

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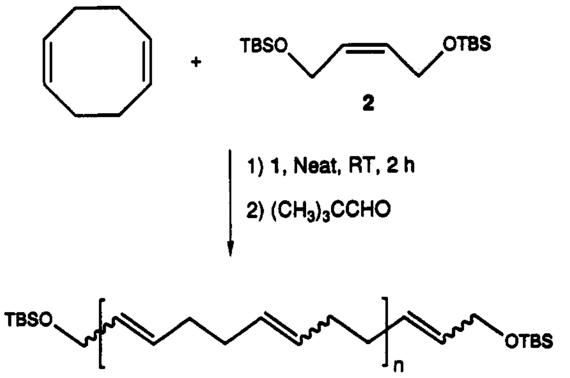


(1)

Table I
Molecular Weight and Yield Data for Poly(butadiene) Telechelomers

run	([2]/[COD]) × 10^3	[COD]/[1]	$M_n \times 10^{-3}$	PDI	yield (%)
1	0	712	47.4	2.1	92
2	1.53	710	41.7	2.0	90
3	5.49	713	37.1	2.0	71
4	9.31	708	26.9	2.1	62
5	12.7	701	21.3	2.1	51
6	18.5	713	14.1	3.0	40

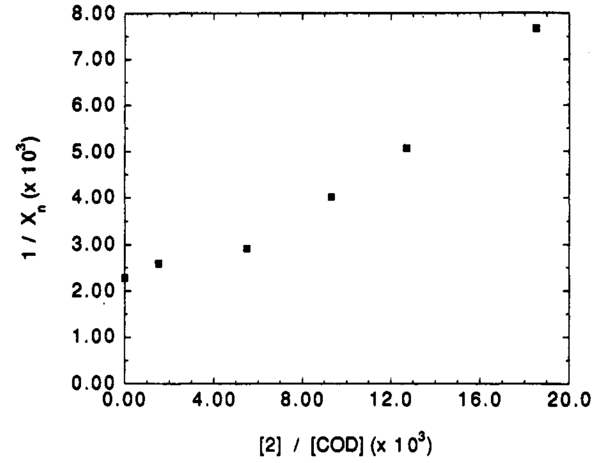


Figure 1. Effect of [2]/[COD] on the number-average degree of polymerization.

transfer agent. The relationship between the number-average degree of polymerization and the mole ratio of 2 to COD is shown in Figure 1.

To remove the TBS end-groups from the polymer, a THF solution of a low molecular weight TBS end-capped polymer was reacted with excess tetra-*n*-butylammonium fluoride at room temperature for 12 h. The polymer was precipitated into methanol, redissolved in benzene, and filtered twice through silica gel. The ^1H NMR spectrum of the purified HTPBD polymer is shown in Figure 2. Only signals from the polymer backbone and end-groups are present. The pseudotriplets at 4.14 and 4.04 ppm are assigned to the methylene protons adjacent to the oxygen (both cis and trans isomers) of the end-group. Addition of trifluoroacetic anhydride results in the downfield shift of these signals by 0.75 ppm and collapse of the pseudotriplets into doublets. End-groups from the initiating alkylidene are identified by the presence of singlets at 3.81 and 3.83 ppm. These signals were assigned to the aromatic methoxy group from the initiating alkylidene (both cis and trans isomers) and are seen in the spectra of both the protected and deprotected polymers.[27] The end groups from the end-capping reagent, pivalaldehyde, are not observed. Hydroxyl functionalities of 1.7–1.9 were calculated for the low molecular weight polymers.[28]

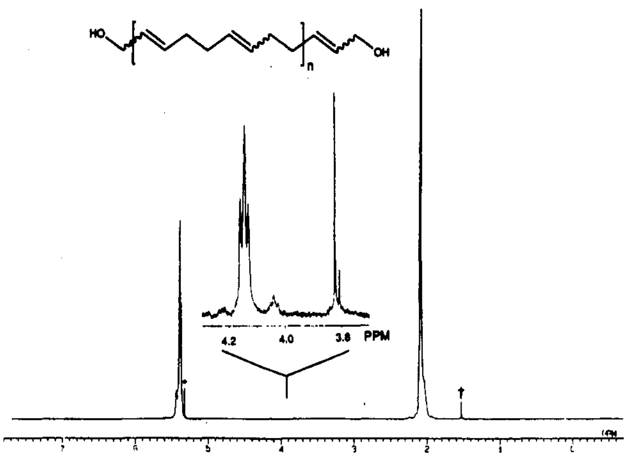
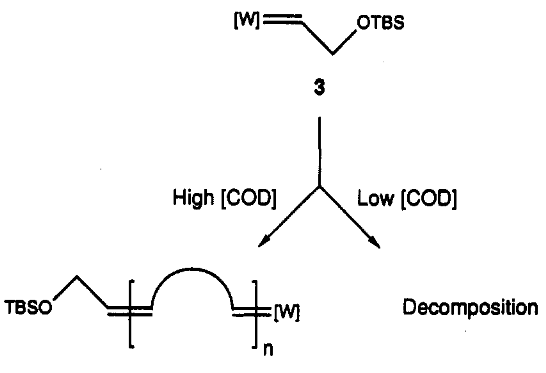


Figure 2. 400-MHz ^1H NMR spectrum of HTPBD in CD_2Cl_2: (*) solvent; (†) H_2O impurity.

Scheme II



The presence of end-group fragments only from the initiating alkylidene and the chain-transfer agent (2) but not from the end-capping reagent indicates that the catalyst decomposes during the course of the reaction. This likely results from the instability of the alkylidene moiety, 3, generated from the reaction of the propagating alkylidene with 2 (Scheme II). It is speculated that in the presence of high COD concentrations this alkylidene will reinitiate the polymerization, but as the concentration of COD decreases during the polymerization an alternative decomposition pathway involving the β oxygen becomes competitive. Consistent with this observation is the decrease in the yield of polymerization with increasing concentration of 2 (Table I) and the insensitivity of the yield to increased reaction time. Also, this hypothesis is consistent with the inability of 1 to effect the isomerization of 2 from cis to trans and with the decomposition of 1 in the presence of 2. The instability of β-oxygen-substituted alkylidenes is not surprising since the metathesis of allylic ethers has generally met with little success.[29] To alleviate this problem, the homoallylic derivative of 2 (1,6-bis(*tert*-butyldimethylsiloxy)-*cis*-3-hexene) was synthesized. In preliminary experiments it was found to be an effective chain-transfer agent, and near quantitative yields of telechelic polymer were obtained. In addition, the cis–trans isomerization of this extended chain-transfer agent was effected by 1.

In conclusion, the use of a well-defined metathesis catalyst for the preparation of HTPBD has been demonstrated. The HTPBD obtained has entirely 1,4 repeat units and only one type of hydroxy end-group. Also, the functionality of the HTPBD is close to 2.0. This system demonstrates the utility of this approach, and more efficient chain-transfer agents that will lead to stable alkylidenes, increase polymer yields, and provide other functionalities are being investigated.

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