lactone **14**. We also thank Professor S. Takano and Dr. K. Ogasawara, Tohoku University, for their kind gift of the spectral data of the lactones **9** and **15**.

**Supplementary Material Available:** Optical rotations and spectral and analytical data for **1**–**13** (4 pages). Ordering information is given on any current masthead page.

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# The Ring Opening Metathesis Polymerization of 7-Oxabicyclo[2.2.1]hept-5-ene Derivatives: A New Acyclic Polymeric Ionophore

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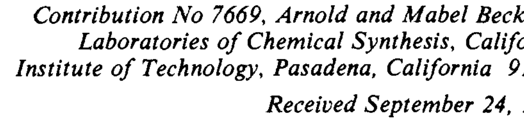
Ring opening metathesis polymerization (ROMP) methods have been shown to be quite effective for the polymerization of strained cyclic, olefinic hydrocarbons.[1] Recently, the utility of this polymerization technique was considerably expanded by the development of well-characterized alkylidene catalysts[2] which are able to produce living monodispersed polymers.[3] In addition, these living polymers can be specifically end-capped with a variety of carbonyl compounds.[4] The extension of ROMP methods, however, to monomers other than hydrocarbons has been significantly more challenging. Metathesis polymerizations of monomers containing pendant functionalities have met with only limited success,[5] and successful metathesis polymerizations of strained heterocyclic monomers are even more rare.[6] These limitations are primarily the result of side reactions between the heteroatoms in the monomers and the typically oxophilic alkylidene ROMP catalysts.[7] In an effort to further the development of the polymerization of heterocyclic monomers, we report herein the first successful ring opening metathesis polymerization of a series of monomers based on the 7-oxabicyclo[2.2.1]hept-5-ene (7-oxanorbornene) ring structure[8] (eq 1). The poly(ethenylidene-*co*-2,5-tetrahydrofuran) (poly(7-oxanorbornene)) materials resulting from the selective metathesis polymerization of the 7-oxanorbornene monomers are of keen interest due to their potential ionophoric properties. CPK molecular model studies indicate that these poly(7-oxanorbornene) polymers have the ability to form helical structures with all of the tetrahydrofuran oxygens facing into the interior of the helix (Figure 1). This unique helical conformation may allow these polymers, when in solution, to act as useful acyclic ionophores,[9] much like their cyclic analogues, the cyclic crown ethers.[10] In addition, thin films composed of these poly(7-oxanorborne) materials may possess oxygen rich ionophoric channels that would enable them to act as ion permeable membranes.[11]



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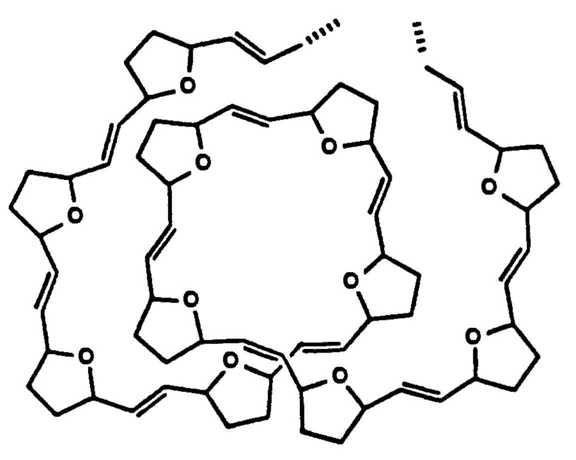

**Figure 1.** Ion binding cavity formed from a helical turn of poly(7-oxanorbornene).

**Table I.** Derivations of 7-Oxanorbornene

| compd | R | R′ | R″ | catalyst[c] |
|---|---|---|---|---|
| I | H | H | $CH_3$[a] | IX, X, XI, XII, XII |
| II | H | H | $CH_2OCH_3$[a] | IX, X, XI, XII, XIII |
| III | H | H | $CH_2OH$[a] | XI, XII, XIII |
| IV | H | $CH_2OH$ | $CH_2OH$[b] | XI, XII, XIII |
| V | H | $CH_2OTMS$ | $CH_2OTMS$[b] | XI, XII, XIII |
| VI | H | $CH_2OCH_3$ | $CH_2OCH_3$[b] | IX, X, XI, XII, XIII |
| VII | $CH_3$ | $CH_2OCH_3$ | $CH_2OCH_3$[b] | X |
| VIII | $CH_2CH_3$ | $CH_2OCH_3$ | $CH_2OCH_3$[b] | X |

[a] Endo/exo = 3/1. [b] Greater than 95% exo. [c] Catalysts: IX, $((CH_3)_3CCH_2O)_2W(CH\text{-}t\text{-}Bu)Br_2$; X, $((CF_3)_2(CH_3)CO)_2W(CH\text{-}t\text{-}Bu)(C_6H_3\text{-}2,6(CH(CH_3)_2)N)$; XI, $RuCl_3$: XII, Ru(1,5-cyclooctadiene)$Cl_3$; XIII, $OsCl_3$.

**Table II.** Cis Double Bond Content, Ring Diad Tacticity, Molecular Weight, and PDI's of Poly VI Synthesized by Various Catalysts

| catalyst | solvent | % cis[a] | syn/iso[b] | $M_w$-($\times10^{-3}$)[c] | $M_N$-($\times10^{-3}$)[c] | PDI |
|---|---|---|---|---|---|---|
| IX | $C_6H_6$ | 42 | | 5.80 | 3.20 | 1.81 |
| X | $C_6H_5CH_3$ | 93 | 55/45 | 29.5 | 19.4 | 1.52 |
| XI | $C_6H_6$/EtOH; 5/1 | 7 | 28/72 | 338 | 172 | 1.97 |
| XI | EtOH | 34 | | 1120 | 973 | 1.15 |
| XII | $C_6H_6$/EtOH | 18 | 50/50 | 133 | 77.6 | 1.71 |
| XII | $CH_3OH$ | 30 | | 965 | 792 | 1.22 |

[a] Determined by $^{13}C$ NMR. [b] Determined by $^{13}C$ NMR of saturated poly VI. [c] Determined by GPC relative to PS.

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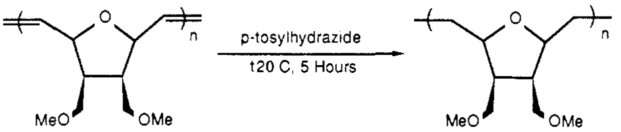
Table I summarizes several of the 7-oxanorbornene derivatives successfully polymerized.[12] The choice of catalyst employed is critical. Highly Lewis acidic transition-metal compounds such as $WCl_6$ or $WOCl_4$ preferentially coordinate to and cationically open the 1,4-bridging epoxide moiety.[13] Tungsten alkylidene catalysts IX and X are also more selective toward olefin metathesis but are still subject to deactivating side reactions. These side reactions are more pronounced by using catalyst IX, as evidenced by the production of only low molecular weight oligomers (Table II). The successful polymerization of monomers containing reactive pendant functionalities (such as alcohols or carbonyl groups) is best achieved by the use of catalysts based on group VIII metals such as ruthenium and osmium.[14] Choice of the appropriate catalyst can potentially offer significant synthetic control over polymer characteristics such as the cis/trans ratios of the metathesized double bonds and the ring diad tacticity[15] (Table II).

Structural characterization of the isomeric constitution of these highly soluble poly(7-oxanorbornene) polymers can be accomplished by use of $^1H$ and $^{13}C$ NMR data. The cis/trans double bond ratio in these unsaturated polymers can be determined directly from the $^1H$ and $^{13}C$ NMR spectra[16] (Table II). Assignment of the ring diad tacticity, however, first requires the hydrogenation of the main chain double bonds (eq 2) to generate



(2)

the fully saturated polymer.[17] The $^{13}C$ NMR spectrum of saturated poly VI shows two sets of resonances which can be unambiguously assigned to the isotactic and syndiotactic diads.[18]

Preliminary liquid/liquid and solid/liquid ion extraction experiments indicate that these poly(7-oxanorbornene) polymers do indeed coordinate various cations. Poly VI will coordinate $Na^+$, $K^+$, and $Cs^+$ (but not $Li^+$) salts as observed through solid/liquid extractions.[19] Of greater interest, however, is the observation that the flexible binding cavities formed by poly VI will preferentially complex large polyaromatic cationic dyes such as methylene blue and rhodamine 6G.[20] Poly VI demonstrates high selectivity by complexing only dyes comprised of large organic cations and small anions ($Cl^-$). Dyes comprised of $Na^+$ and large aromatic anions are not complexed. This selectivity is exactly opposite to that observed for ion complexation by using 18-crown-6. Further ion complexation studies which will relate the isomeric constitution of a particular polymer to its ion binding efficiency are currently in progress.

In addition to binding ions in solution, these poly(7-oxanorbornene) polymers act as ion permeable membranes.[11] Demonstration of ion transport through these ionophoric materials is obtained by placing solid membranes cast from the poly(7-oxanorbornene) polymers between two ion concentration cells and measuring, by means of two SCE electrodes, the membrane potential resulting from diffusion of ions through the ionophoric membranes.[21] From the measured membrane potentials, cation transport numbers for $K^+$, $Na^+$, and $Li^+$ (all $Cl^-$ salts) were calculated to be 0.84, 0.73, and 0.73, respectively. Current efforts are focusing on systematic structural modifications of the basic poly(7-oxanorbornene) skeletons, in order to enhance both their ion transport and ion selectivity properties.

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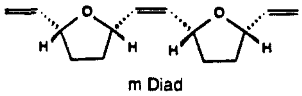
[12] A typical polymerization procedure is presented here for monomer VI. All manipulations were performed under dry, inert atmosphere. Catalyst IX (87.0 mg, 0.148 mmol) is dissolved in dry benzene (1.0 mL). To this solution is added slowly via cannula olefin VI (680 mg, 3.7 mmol, 25 equiv) dissolved in benzene (1.0 mL). After 24 h at room temperature, methanol (1.0 mL) is added to the reaction, and the resulting solution cannulated into 50 mL of pentane. The polymeric precipitate is isolated and redissolved in the minimum amount of $CCl_4$, and the insoluble catalyst residue is filtered. The polymer is again precipitated by slow addition to pentane, filtered, and dried under vacuum to yield 0.41 g (59% yield) of poly VI: $^1H$ NMR (90 MHz, $CDCl_3$) 5.72, 5.58, 4.5, 4.22, 3.45, 3.34, 2.25 ppm; IR (thin film) 2090 (s), 1475 (m), 1460 (m), 1390 (m), 1190 (s), 1100 (vs), 1018 (s), 963 (s) $cm^{-1}$.

[13] Evidence of the 1,4-epoxide ring opening is obtained by the addition of 1 equiv of VI to a solution containing $WOCl_4$. Upon mixing, the $^1H$ NMR spectrum of VI shows a complete loss of the bridgehead proton signals at 4.3 ppm, accompanied by the appearance of new olefin signals at ca. 5.3 ppm. After 15 min nonspecific decomposition to unidentified products is observed.

[14] Ho, H. T.; Ivin, K. J.; Rooney, J. J. *J. Mol. Catal.* **1982**, *15*, 245.

[15] The ring diad tacticity in these systems is defined as

r Diad
Syndiotactic



m Diad
Isotactic

[16] The allylic carbons in the $^{13}C$ NMR spectrum are the best resolved indicators of the double bond's configuration with the trans and cis signals appearing at 81.8 and 77.3 ppm, respectively.

[17] Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. *J. Mol. Catal.* **1985**, *28*, 255.

[18] The two unique ring carbons and the methylene linker carbons all appear as two sets of resonances in the $^{13}C$ NMR spectrum of saturated poly VI: the isotactic set at 32.74, 81.16, and 46.2 ppm and the syndiotactic set at 31.90, 80.83, and 45.87 ppm ($CDCl_3$). Absolute assignment of the two sets of resonances as the isotactic and syndiotactic sets required polymerization of the chiral resolved monomer 5-(methylmethoxy)-7-oxanorbornene and subsequent analysis of the resulting chiral polymer's $^{13}C$ NMR spectrum's head/tail fine structure. Details of this analysis is to be published. For a complete discussion of this method, see: Ivin, K.; Lapienis, G.; Rooney, J. *Polymer* **1980**, *21*, 436.

[19] An efficient 1,3-dinitrobenzene "yes/no" screening test was employed to determine the presence of solubilized hydroxide salts in $CCl_4$ solutions containing poly(7-oxanorbornene). The formation of the red Meisenheimer hydroxide/dinitrobenzene complex upon addition of the solid hydroxide salt to the $CCl_4$/polymer solution indicates a positive ion binding result. The appropriate control experiments were run to eliminate the possibility of any spurious complexation results not mediated by the poly(7-oxanorbornene) polymers.

[20] Typical liquid/liquid extraction experiments were performed by extracting standardized aqueous dye solutions with solutions of the poly(7-oxanorbornene) polymers dissolved in either $CCl_4$ or benzene. Dye concentrations in the aqueous phase before and after the extractions were monitored by UV absorbance measurements.

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# Activation of Dihydrogen by Organo-Iridium-Phosphido Complexes. Evidence for α-Hydrogen Abstraction by a Terminal Phosphide Ligand

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The basicity of a terminal phosphido group bound to a transition metal ($L_nM-PR_2$) is well documented.[1,2] Intermolecular transformations involving metal phosphides and electrophiles such as $CH_3I$, $I_2$,[3,4] HX,[5,6] $S_8$,[5,6] NO,[7] $Ph_2PCl$,[8] and other metal com-

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† Fellow of the Alfred P. Sloan Foundation (1984–1987).

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