Table I
Equilibrium Values for Conversion of Mo(CPr)(O^{t}Bu)$_3$ (1a) into Mo{[C(CH$_2$)$_6$C]$_x$CPr}(O^{t}Bu)$_3$ (1b)[a]

equiv C_8H_{12}	% 1a	% 1b
1	40 (33[b])	60 (67[b])
2	23 (18[b])	77 (82[b])
3	15[b]	85[b]
4	11	89
8	5	95
10	5[b]	95[b]
12	4	96
20	2	98

[a] Cyclooctyne in 0.75 mL of C_6D_6 was added rapidly to a stirred solution of 10 mg of **1a** and *p*-dichlorobenzene (internal standard) in 1.5 mL of C_6D_6. The ratio of **1a** to **1b** was determined by integration after 24 h. In several analogous experiments the equilibrium values did not change after heating the samples at 100 °C for 10 min. [b] These values were obtained in a separate set of analogous experiments.

Table II
GPC Studies on Polyethylene Prepared by Hydrogenation of 1b[a]

equiv C_8H_{12}	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ (theory)
250	26 000	4300	6.1	27 000
350	33 000	7500	4.4	37 900
500	60 000	8600	7.0	54 100

[a] 1a was hydrogenated at 60 psig of H_2 overnight in toluene employing $Rh(PPh_3)_3Cl$ as the catalyst. The resulting polyethylene was analyzed at 145 °C in 1,2,4-trichlorobenzene on a Waters 150C instrument equipped with three Styragel columns. A single relatively symmetric peak was observed in each case with a polydispersity from 4.4 to 7.0 and molecular weight as listed. The columns were calibrated with polystyrene standards in the usual way. The usual conversion factor of 4.1 was employed in order to obtain the molecular weight.

I). We also know that if a sample of **1b** prepared from 15 equiv of cyclooctyne is mixed with an equal amount of **1a**, the amount of **1a** slowly decreases and an equilibrium mixture consisting of ~8% **1a** and 92% **1b** is established. The most plausible explanation of these findings is that cyclooctyne or some cyclic oligomer comes out of **1b** and reacts with **1a** until equilibrium is established between **1b** and **1a**. Examination of an ^1H NMR spectrum of **1b** (x = 15) at 120 °C showed no sign of cyclooctyne (≤2% estimated—there was some irreversible decomposition of the sample) or 1,9-cyclohexadecadiyne (the cyclic dimer of cyclooctyne). Therefore the equilibrium shown in eq 2 must lie far to the right. 1,9-Cyclohexadecadiyne *could* be responsible for the equilibration of **1a** and **1b** since upon adding it to **1a** **1b** is formed on the time scale of the equilibration of **1a** and **1b**.

$$\text{Mo\{[C(CH}_2\text{)}_6\text{C]}_x\text{CPr\}(O}^t\text{Bu)}_3 \underset{-(C_8H_{12})_n}{\overset{+(C_8H_{12})_n}{\rightleftharpoons}} \text{Mo\{[C(CH}_2\text{)}_6\text{C]}_y\text{CPr\}(O}^t\text{Bu)}_3 \quad (2)$$

If **1a** is added to 250, 350, and 500 equiv of cyclooctyne in toluene, then all monomer is consumed in seconds to give an insoluble gelatinous precipitate. Since all efforts to analyze this relatively insoluble polymer by standard GPC methods failed, it was hydrogenated under 60 psig of hydrogen at 60 °C to give a polymer whose T_g and melting point were close to those of polyethylene.[5] This polymer was analyzed by GPC in 1,2,4-trichlorobenzene at 145 °C. The results are shown in Table II. The most important finding is that $\bar{M}_n$ depends directly on the number of equivalents of cyclooctyne employed. Therefore we can say that the polymerization most likely is living, as all the evidence so far suggests. The relatively high polydispersities and low values of $\bar{M}_n$ (vs. theory for a perfect system) could be the result of the hydrogenation procedure, about which we know virtually nothing.[5] We will be searching for unambiguous methods of cleaving off the polymer chain (e.g., by reactions analogous to that shown in eq 1) and converting it under mild conditions into a soluble, easily characterized polymer.

To our knowledge this is the first report of ring-opening polymerization of cyclooctyne. We will be exploring the details of this reaction and will be searching for other catalysts that yield well-behaved living polymers.

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Registry No. Mo(CPr)(O*t*Bu)$_3$, 91780-93-7; Mo([C(CH$_2$)$_6$C]$_x$CPr)(O*t*Bu)$_3$, 106989-28-0.

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(4) The reaction appears to be extremely clean. Other resonances ascribable to the carbon atoms of the backbone are found at 18.78, 28.44, and 29.10 ppm. At this concentration of monomer other resonances can be observed for carbon atoms relatively close to the metal. The oligomer can be cleaved from the metal with phenylacetylene and fully characterized. Details will be reported in the full paper.
(5) We assume for the present that the catalyst is no longer active after the hydrogenation procedure. However, we do not know if the metal is still attached to the polymer (and therefore whether the GPC analysis is accurate or not) if the hydrogenation procedure leaves the polymer chain length unchanged.
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Stereocomplex Formation between Enantiomeric Poly(lactides)

It has been reported that a polymer–polymer complex can be formed upon mixing two polymers with different chemical compositions if a favorable interaction prevails between the different polymer chains as with complementary nucleic acids and proteins. The well-known interpolymer complexes include (1) a polyelectrolyte complex between polyanion and polycation,[1] (2) a hydrogen-bonding complex between a poly(carboxylic acid) and a polyether or polyol,[2] and (3) a charge-transfer complex between polymeric donor and acceptor.[3] However, only a few pairs

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are known in which complex formation occurs between polymers with identical chemical composition but different steric structures. The reported pairs leading to such stereopolymeric complex formation are (1) syndiotactic and isotactic poly(methyl methacrylate (PMMA),[4] (2) isotactic polymers of (*R*)- and (*S*)-*tert*-butylthiiranes,[5] (3) isotactic polymers of (*R*)-(+)- and (*S*)-(−)-α-methylbenzyl methacrylates,[6] (4) optically active polymers of (*R*)- and (*S*)-α-methyl-α-ethyl-β-propiolactone,[7] and (5) optically active polymers of γ-benzyl L- and D-glutamate.[8-10]

In this Communication we will describe for the first time stereocomplex formation from optically active poly(L-(−)-*S*-lactide) and poly(D-(+)-*R*-lactide), which represent the simplest class of polyesters. Lactic acid has two stereoisomers, the L-(+)- and D-(−)- compounds, both of which are naturally occurring. Lactic acid may give rise to two dilactones, L-(−)-lactide and D-(+)-lactide, without change at the asymmetric carbon. The D,L mixture is also commonly found. Catalytic ring-opening polymerization of lactides yields polylactides of high molecular weight; their properties and structures have already been studied by many research groups.[11-13] D,L-lactide provides an amorphous and optically inactive polymer, while the polymer from L- or D-lactide is crystalline and optically active.

L-Lactic acid of 98% optical purity was purchased as a 90 wt % aqueous solution from CCA Biochem bv, The Netherlands. Methyl D-lactate of 97% optical purity was supplied by Daicel Chemical Industries, Ltd, Japan, and hydrolyzed to D-lactic acid. Both poly(L-lactide) and poly(D-lactide) were prepared by the method described by Sorenson and Campbell.[14] Briefly, low molecular weight poly(lactic acid) was prepared by condensation polymerization of the free acid and then thermally decomposed to yield the lactide. Ring-opening polymerization of the lactide was performed in bulk at 140 °C using stannous octoate and lauryl alcohol as polymerization catalyst and initiator, respectively.[15] The polymerization conditions were the same for L- and D-lactide. The resulting polymer was used without fractionation, following purification by the reprecipitated method. The viscosity-average molecular weight of the polymer employed in this work was 7.0×10^4 for both polymers. The optical rotation, $[\alpha]_D$ in chloroform at 25 °C was −151° for poly(L-lactide) and +151° for poly(D-lactide), in good agreement with the reported value.[11]

The polymer complex formation was carried out in the following manner. First, each of the polymers was dissolved separately in methylene chloride to a polymer concentration of 1.0 g·dL^{-1}, and the solutions were then mixed together at room temperature in different volume ratios. The mixed solution was poured into excess methanol to give precipitates having different ratios of poly(L-lactide) to poly(D-lactide). After the precipitates were dried under reduced pressure, the fibrous precipitates were subjected to measurements of wide-angle X-ray diffraction and differential scanning calorimetry (DSC).

Figure 1 shows the DSC curves for homopolymers of L-lactide and D-lactide, together with those for blend polymers of various mixing ratios. It is clearly seen that both homopolymers give a single endothermic peak around 180 °C, in good agreement with the previously found melting temperature,[15] whereas a new peak appears in the vicinity of 230 °C for the blended polymers. When the blend ratio is 50/50, the peak at 180 °C virtually disappears while the peak at 230 °C becomes sharper. This remarkable rise in melting temperature caused by polymer mixing in solution strongly suggests that blending of

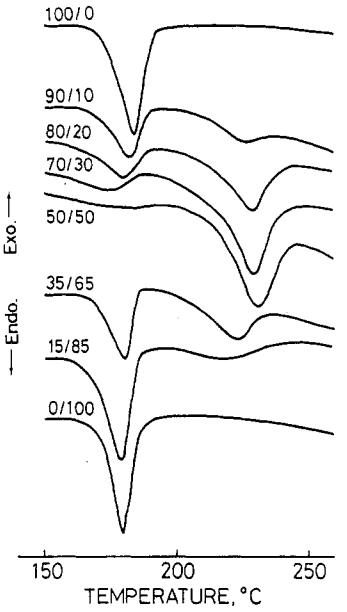


Figure 1. DSC thermograms of blend polymers from poly(L-lactide) and poly(D-lactide). The ratios on the curves denote the blend ratios of poly(L-lactide) to poly(D-lactide).

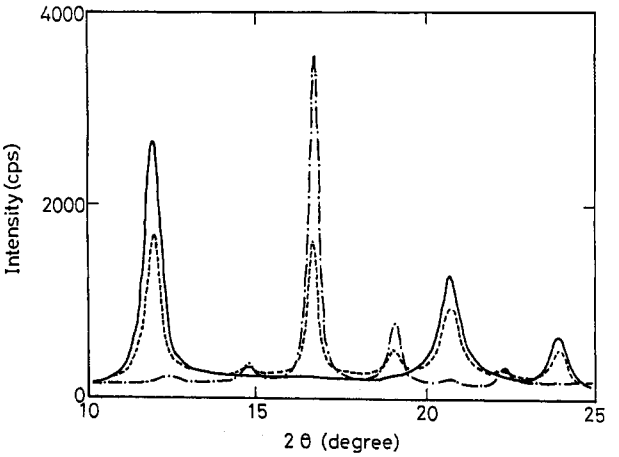
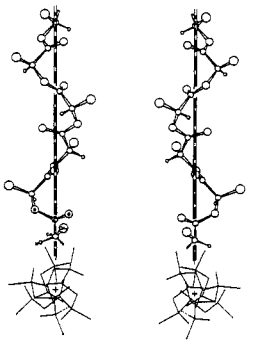


Figure 2. X-ray diffraction profiles for the D-lactide homopolymer and the blend polymers: (−·−) D-lactide homopolymers; (—) 50/50 blend; (− − −) 25/75 poly(L-lactide)/poly(D-lactide).

poly(L-lactide) and poly(D-lactide) gives rise to formation of a stereocomplex with a new crystalline structure quite different from that of each homopolymer.

Wide-angle X-ray diffraction also shows a different pattern, as can be seen in Figure 2. The diffraction profile for the homopolymer of L-lactide is not shown in Figure 2, because it is identical with the pattern of poly(D-lactide). As can be seen, the diffraction peaks appear at 2θ around 15°, 16°, 18.5°, and 22.5° for the homopolymer, whereas the 50/50 blend polymer has the diffraction peaks appearing at 2θ equal to 12°, 21°, and 24°. The diffraction peaks of the 25/75 (poly(L-lactide)/poly(D-lactide)) blend polymer involve all the peaks corresponding to the homopolymers and the 50/50 blend polymer. This X-ray diffraction study also supports the formation of a polymer complex with a crystalline structure entirely different from that of homopolymers.

De Santis and Kovacs have reported that the crystalline structure of poly(L-lactide) consists of left-handed helical chains as illustrated in Figure 3.[16] Since poly(D-lactide) must have a right-handed helical crystalline structure, it is likely that the stereocomplex is formed through van der Waals forces such as dipole–dipole interactions between



poly(L-lactide) poly(D-lactide)

Figure 3. Chain models of poly(L-lactide) and poly(D-lactide).

the two different helical chains in solution where molecular motion is sufficiently great. More detailed studies on this novel stereopolymeric complex formation will be published in the near future.

Registry No. Poly(L-lactide)/poly(D-lactide) complex, 106989-12-2; poly(D-lactide) (SRU), 26917-25-9; poly(L-lactide) (SRU), 26161-42-2.

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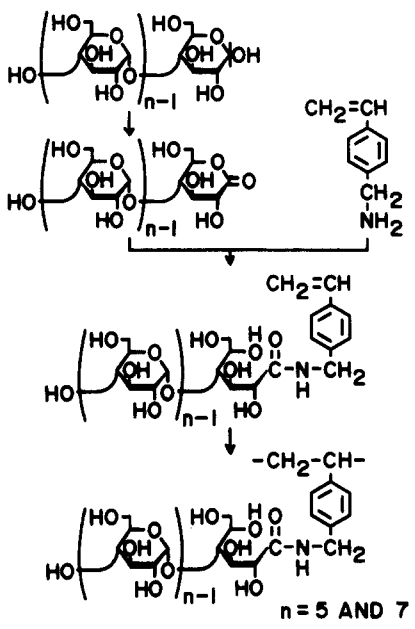
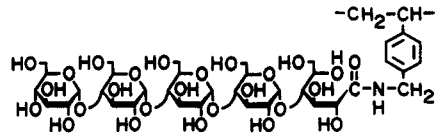
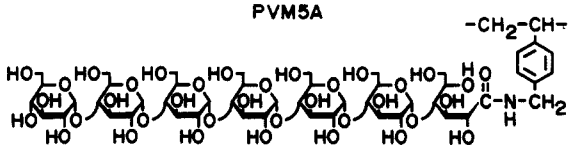
Maltopentaose- and Maltoheptaose-Carrying Styrene Macromers and Their Homopolymers

Polystyrene derivatives with maltopentaose and maltoheptaose substituents on each benzene ring, which are termed PVM5A and PVM7A, respectively, have been synthesized. These oligosaccharide-carrying polystyrenes are a new type of homopolymer with a graft of uniform length in every repeating structural unit. In each unit, the reducing end of the hydrophilic oligosaccharide is connected via an amide linkage with the hydrophobic *p*-vinylbenzylamine main chain. The synthetic route is shown in Scheme I. Each of maltopentaose ([*O*-α-D-glucopyranosyl-(1→4)]$_4$-D-glucopyranose, M5) and maltoheptaose ([*O*-α-D-glucopyranosyl-(1→4)]$_6$-D-glucopyranose, M7) was oxidized to the corresponding lactone, which was then coupled with *p*-vinylbenzylamine. The resulting well-defined water-soluble amphiphilic macromonomer, *N*-(*p*-vinylbenzyl)-[*O*-α-D-glucopyranosyl-(1→4)]$_{n-1}$-D-gluconamide (VM5A for $n = 5$ and VM7A for $n = 7$), was polymerized with a radical initiator in water. This is the first report on well-defined synthetic polymers with oligosaccharides of intermediate chain length as the pendant group.

Scheme I







Complex oligosaccharide chains of glycolipids and glycoproteins protrude from the surface of cell membranes and play an important role in biological recognition events.[1] Synthetic polymers endowed with informational oligosaccharides, even with commercially available simple ones, are of interest in connection with application for biomedical and separation materials. A few papers have been reported on di- and trisaccharide-carrying polymers.[2-8] Two synthetic methods are available for this purpose: (a) reaction of oligosaccharides onto polymeric substances[2,3] and (b) synthesis and polymerization of vinyl

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