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마이오 이노시톨을 이용한 고분자 리간드의 합성 및 형태 분석

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Synthesis and Conformational Analysis of Novel Polymeric Ligands based on *myo*-Inositol

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요 약. 마이오 이노시톨을 이용한 새로운 고분자 리간드를 합성하였다. 형태적으로 안정한 이노시톨 고분자를 얻기 위해 고리화 고분자반응을 시도하였으며, 고리화의 메커니즘 및 고리 구조가 입증되었다. 또한, 분광학적 비교 방법을 이용해 합성된 고분자들의 형태가 밝혀졌다. 마이오 이노시톨 카보네이트를 이용해 형태적으로 고정된 고분자 리간드를 성공적으로 합성하였다.

주제어: 마이오 이노시톨, 형태적으로 안정한 고분자, 금속배위 리간드, 싸이클로헥산 고분자의 형태분석

ABSTRACT. Synthesis of novel polymeric ligands based on *myo*-inositol was performed. Cyclopolymerization, whose mechanism and the cyclic structure were proved, was first attempted to build a conformationally rigid inositol polymer. Comparative spectroscopic methods were introduced to verify the conformation of the prepared cyclohexane polymers. A conformationally rigid polymeric ligand was successfully prepared using *myo*-inositol carbonate.

Keywords: *myo*-Inositol, Conformationally Rigid Polymer, Metal-binding Ligand, Conformational Analysis of Cyclohexane Polymers

INTRODUCTION

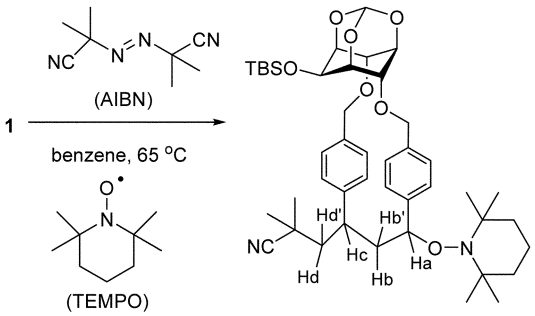
The search for new polymeric ligands capable of binding certain metal ions has continued over the last decade.[1,2] The performance of such fuctional polymers is governed by a large number of functional groups present in these macromolecules. The functional groups are responsible for the desired interaction with a substrate, whereas the polymer backbone provides a structural and mechanical stability. It is well known that nature uses only a small variety of functional groups such as carboxylates, amines, amides, alcohols and thiols. Biological macromolecules, however, achieve high performance and unparalled selectivity by orienting these functional groups *via* non-covalent interactions.[3] This concept of oriented functionalities has not been cited to any great extent for synthetic polymers, largely because there is no simple way of controlling the conformation of synthetic macromolecules in bulk or solution. If the functional groups are situated on a rigid scaffold within the monomer unit, their relative orientation is fixed, and hence increased performance, together with higher selectiv-

ity, can be achieved. We were, therefore, interested in developing a novel polymer with an organized backbone and oriented functional groups. Inositol (cyclohexane-1,2,3,4,5,6-hexaol) scaffolds were considered to be suitable to deliver such features.[4-6] It was known that as few as three neutral O atoms in a cyclohexane can form well-defined and fairly stable complexes with cations, provided that the O atoms are located in suitable steric arrangements.[4a,4b] The steric requirements of the cyclohexane polyols to form complexes with cations are, however, rather strict and the three O atoms on a cyclohexane ring have to be located axially at the 1, 3 and 5 positions.[7] This arrangement (syn-triaxial) is not common in nature and the only example is *cis*-inositol. There are many cyclohexane derivatives containing three equatorial hydroxyl groups at the 1, 3 and 5 positions including *myo*-inositol, but complexation with cations does not generally provide sufficient energy to preferentially adopt one chair conformation. Many works have been focused on the preparation of structurally rigid inositol platforms that have the syn-triaxial arrangement,[4c-e] but none of these compounds is readily available, especially in large scales. We hereby introduce synthetic approaches to prepare conformationally rigid polymers, having all-axial triols, based on the readily available *myo*-inositol.

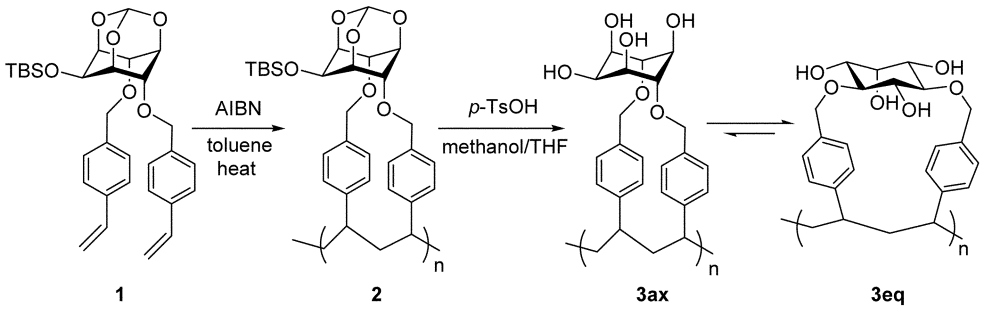
RESULT AND DISCUSSION

Cyclopolymerization of the difuctional monomer **1** was previously pursued to obtain a conformationally locked inositol polymer **2**.[8] The rigid inositol unit, introduced by the orthoformate group, acts as a template for bringing two polymerizable groups into close proximity to enable cyclopolymerization. Another key structural feature offered by this monomer **1** includes the orthoformate group which, after the cyclopolymerization reaction, can be easily deprotected to yield (ideally) an all-axial triol repeat unit. The cyclopolymerizable groups were, therefore, anticipated to work as both polymerizable and ring locking groups.

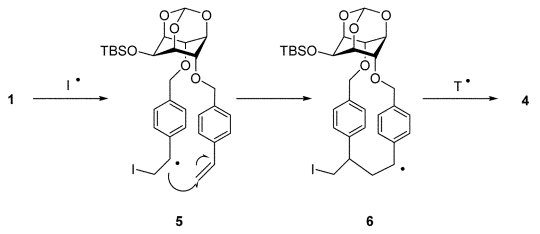
Heating a toluene solution of the monomer **1** at 65 °C in the presence of 2-3 wt.% of AIBN as a radical initiator afforded an organic soluble polymer, which is formulated as a linear cyclopolymer **2** (*Scheme* 1). The evidence for the cyclopolymer **2** came from the trapping of the first formed cyclic intermediate **4** (*Scheme* 2).[8] The TEMPO radical trapping technique was used to isolate the reactive



Scheme 2. TEMPO trapping of the first formed cyclic intermediate.



Scheme 1. Cyclopolymerization and following deprotection to give the hydroxylated inositol polymer **3**, whose structure has two alternative conformations.



Scheme 3. Proposed mechanism for trapping of the reactive intermediate in a radical induced cyclization reaction.

radical intermediate generated during cyclopolymerization.

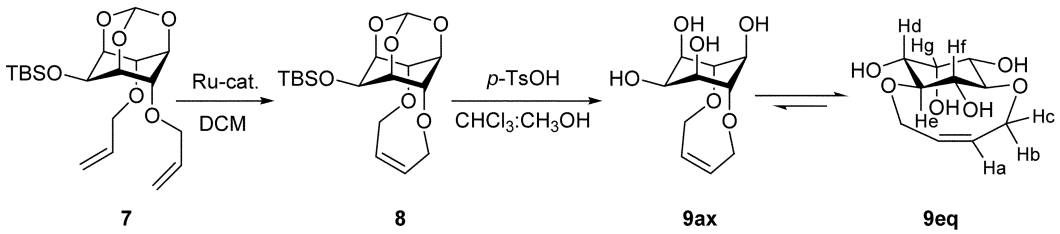
The mechanism of trapping cyclic intermediate is suggested in *Scheme* 3 and involves 'trapping' carbon-based radicals with suitable nitroxide reagents. Thermal decomposition of the AIBN initiator would give the cyanoisopropyl radical (I·) which would add selectively to the less substituted end of the vinyl group as depicted by **5**. If cyclization is fast enough, the radical formed should then add to the next vinyl group intramolecularly to give **6**. Finally, the radical trapping agent (T·) can react with the resulting secondary radical to afford the trapped product **4**. The structure determination of the cyclic product **4** was carried out by ^{1}H NMR TOCSY and NOE experiments.[8] Selective 1-D TOCSY experiments assisted in determining the connectivity sequence of atoms. Mutual NOE effects were also observed between two methine protons (Ha and Hc), further indicating that both are part of the same cyclic structure.

The cyclopolymer **2** was then deprotected in the presence of toluene-*p*-sulfonic acid to give the hydroxylated polymer **3** (*Scheme* 1). The deprotected polymer **3** was expected to exhibit interesting hydrophilic and metal binding properties if all five hydroxyl groups remained axial (**3**ax). However, the alternative conformation (**3**eq) would also be feasible (*Scheme* 1).

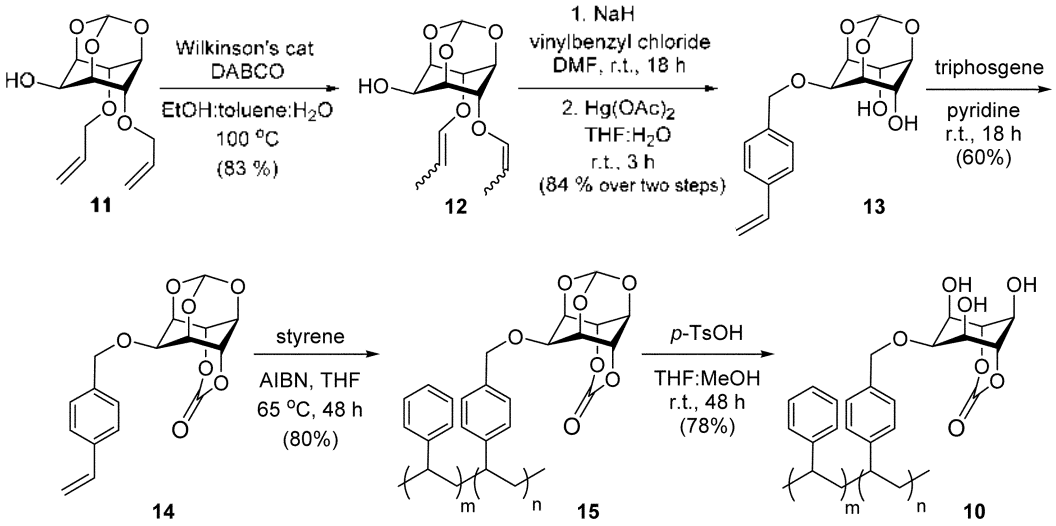
Conformational studies using a model small molecule were performed to gain an insight into the conformation, as the polymer **3** showed very broad ^{1}H and ^{13}C NMR spectra. The diallyl inositol derivative **7** was obtained in a similar manner to **1**. The ring closing metathesis (RCM) of **7** using ruthenium catalyst afforded the cyclized product **8**, which was finally deprotected to give the hydroxylated product **9** (*Scheme* 4).[9,10]

Analysis of the ^{1}H NMR spectrum of the model compound **9** indicated that the preferred ring conformation was **9eq**.[9] With this result in hand, the conformation of the deprotected polymer **3** was verified. The ^{1}H NMR signals of the inositol ring protons of the RCM product **8** occurred at 4.4-4.0 ppm and resembled closely the analogous signals in the polymer **2** (δ 4.5-4.1), indicating that the ring conformation was maintained, as expected, in the polymer. The ^{1}H NMR chemical shifts of the ring protons of the deprotected metathesis product **9** were shifted upfield (δ3.6-2.9) compared with those in the model **8**. Similarly the inositol ring protons of the deprotected polymer **3** were shifted upfield (δ 3.5-3.0), from which it is concluded that the inositol ring in **3** has the conformation **3**eq. It was thought that such a large ring system generated by the cyclopolymer was not rigid enough to hold the conformation of the deprotected polymer **3** to get its desired axial conformation (**3**ax). The metal chelating properties would, therefore, not be achieved using this polymer **3** (or **3**eq).

Alternatively, we have prepared the inositol polymer based on *myo*-inositol carbonate **10** (*Scheme* 5).[11]



Scheme 4. Synthesis of the model compounds **8** and **9** by RCM of the diallyl inositol **7** and following deprotection, respectively.



Scheme 5. Synthesis of *myo*-inositol 4,6-carbonate-based polymer.

Here, the carbonate group was introduced as a short bridge between O-4 and O-6 of *myo*-inositol and was expected to hold the conformation of the cyclohexane to have three axial hydroxyl groups.

The 4,6-diallylated *myo*-inositol derivative **11** was first prepared, followed by the isomerization of the diallyl groups to enol ethers using Wilkinson's catalyst[12] to give **12**. Introduction of the styrenyl moiety as a polymerizable group to the free alcohol, followed by hydrolysis of the enol ethers using mercury(II) acetate produced the diol **13** in 84% yield over two steps. Further treatment with triphosgene in the presence of pyridine afforded the carbonate **14** in a moderate yield (60%). *Myo*-inositol carbonate monomer **14** was then copolymerized with styrene by a radical polymerization to afford the inositol copolymer **15** in 80% yield. Homopolymerization of the monomer **14** gave only an insoluble product. Finally, removal of the orthoformate group in polymer **15** was accomplished in the presence of *p*-TsOH to give the desired hydroxylated inositol polymer **10**. The ^{13}C NMR spectrum of **10** showed the absence of the characteristic signal corresponding to the orthoformate carbon (δ=102), whilst preserving the carbonate signal (δ=145). IR spectrum also confirmed the presence of the carbonate group (C=O peak at 1750 cm^{-1}). At last, the conformation of the deprotected polymer **10** was determined by the ^1H NMR spectrum: the signals of the cyclohexane ring protons appear at the region between δ 4.5 and 4.0, strongly indicating that the axial conformation was maintained (*vide supra*). It was, therefore, concluded that the inositol carbonate-based polymer **10** had the desired conformation, having all-triaxial hydroxyls, for metal binding.

EXPERIMENTAL

Melting points were determined using Büchi 510 melting point apparatus and uncorrected. IR spectra were recorded on a Nicolet MAGNA 560-FTIR spectrometer. ^1H NMR spectra were recorded on a Bruker Advance DPX-300 and DPX-500 spectrometer with TMS as an internal standard. Mass spectra were obtained on a JEOL JMS-AX505WA instrument. The solvents were purified according to the conventional methods.

Polymerization of 2-silyloxy-4,6-di(vinylbenzyloxy) inositol orthoformate to give polymer 2: The inositol monomer **1** (5.0 g, 9.3 mmol) and AIBN (150 mg, 3 wt%) were dissolved in distilled toluene (93 mL). The solution was freeze-thaw degassed using liquid nitrogen (4 cycles), and was allowed to warm to r.t. before the solution was

heated at 65 °C for 48 h. The solution was concentrated *in vacuo* to give an oil. The oil was dissolved in THF (10 mL) and the solution was added dropwise to vigorously stirred methanol (100 mL). The colorless precipitate was collected and reprecipitated into methanol (100 mL) from THF (10 mL). The precipitate was collected and dried in vacuo to give the polymer **2** as a free flowing colorless powder (4.5 g, 90%); (Found: C, 69.2; H, 7.5. $C_{31}H_{46}O_6Si$ requires C, 69.4; H, 7.5%); ν_{max} (KBr)/cm^{-1} 2930, 2857, 1619, 1515, 1003 and 843; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 6.8-6.0 (8H, br signal, 8×ArH), 5.5 (1H, br signal, orthoformate), 4.8-4.6 (4H, br signal, 2×OCH_2Ar), 4.5-4.1 (6H, br signal, 6×ring C*H*), 1.8-0.8 (15H, br signal, 2×C*H* and 2×CH_2 from polymer backbone, and $SiC(CH_3)_3$) and 0.3-0.0 (6H, br signal, $Si(CH_3)_2$); GPC ($CHCl_3$, RI)/Da M_n 18.3×10^3, M_w 49.1×10^3 and M_w/M_n 2.7.

Deprotection of polymer 2 to give the hydroxylated polymer 3: A solution of the inositol polymer **2** (1.0 g) and *p*-toluenesulfonic acid (0.1 g, 10 wt.%) in a mixture of THF (20 mL) and methanol (10 mL) was heated at 45 °C for 24 h. The large amount of precipitate that had formed was broken up with a spatula and the solution was heated for further 24 h at 45 °C. The solution was allowed to settle and the excess solvent was decanted off. The solid was filtered through a glass frit and washed with THF (2 mL). The solid was collected and dried to give the hydroxylated polymer **3** as an off-white solid (0.74 g, 96%); ν_{max} (KBr)/cm^{-1} 3400-3000 (O-H), 2921, 1512, 1422, 1103 and 1055; ^{1}H NMR (300 MHz, DMSO-d_6, δ) 7.6-5.9 (8H, br signal, 8×Ar*H*), 4.7-4.4 (4H, br signal, 4×O*H*), 4.3-4.1 (4H, br signal, 2×OCH_2Ar), 3.5-3.0 (6H, br signal, 6×ring C*H*) and 2.3-0.5 (6H, br signal, 2×C*H* and 2×CH_2 from polymer backbone).

TEMPO trapping experiment: Preparation of 4: The inositol monomer **1** (78 mg, 0.15 mmol), AIBN (22 mg, 0.14 mmol) and TEMPO (9 mg, 0.05 mmol) were dissolved in distilled benzene (5 mL). The red-orange solution was freeze-thaw degassed using liquid nitrogen (4 cycles) and was allowed to warm to r.t. under argon before the solution was heated for 12 h at 65 °C. The solvent was evaporated to give a liquid, which was purified by column chromatography (3:1 hexane:EtOAc and 2:1 hexane:ether). The unreacted inositol monomer **1** (70 mg, 90%) was first eluted, followed by the TEMPO adduct **4** as a colorless oil (2.5 mg, 5%); R_f 0.42 (3:1 hexane:EtOAc); ν_{max} ($CHCl_3$)/cm^{-1} 3683, 3619, 3462, 3028, 2894, 2399 (CN), 1601, 1522, 1476, 1422, 1247 and 1045; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 6.70 (2H, br d, J = 7.5, Ar*H*), 6.63-6.57 (6H, m, Ar*H*), 5.60 (1H, s, orthoformate), 4.63 (1H, br s, ring C*H*), 4.50-4.47 (2H, multiplet containing dd, J=11.4 and 2.5, C*H*aAr and ring C*H*), 4.42 (2H, ABq, J=10.0, OCH_2Ar), 4.38 (2H, m, ring C*H*), 4.33 (2H, ABq, J=10.0, OCH_2Ar), 4.26-4.22 (2H, m, ring C*H*), 2.73 (2H, multiplet containing dt, J=13.3 and 2.5, CH_cAr and CH_b), 2.28 (1H, ddd, J=13.3, 11.4 and 11.4, CH_b), 1.93 (1H, dd, J=14.0 and 5.0, CH_d), 1.83 (1H, dd, J=14.0 and 9.0, $CH_{d'}$), 1.55 (6H, br s, $C(CH_3)_2$), 1.54-1.13 (12H, multiplet containing br s, CH_2 and CH_3), 1.03 (9H, s, $C(CH_3)_3$), 1.02, 0.46 (6H, each br s, CH_3) and 0.23 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ) 142.2, 141.5, 135.6, 135.0, 129.7, 126.7, 126.2, 126.0, 103.2, 87.5, 73.7, 73.4, 73.3, 70.4, 69.7, 66.9, 62.0, 49.5, 43.6, 41.8, 40.4, 32.1, 28.4, 27.0, 26.2, 18.7, 17.2 and -4.6; *m/z* (FAB) 761 [$(M+H)^+$, 20%] 604 (15%) and 287 (100%); [Found: $(M+H)^+$ 761.4515. $C_{41}H_{65}N_2O_7Si$ requires *M*, 761.4561].

Synthesis of the model compound 8 by ring closing metathesis: A solution of ruthenium bis(tricyclohexylphosphine) benzylcarbene dichloride (122 mg, 148 mmol, 5 mol%) in dichloromethane (60 mL) was added to a solution of 4,6-di(allyloxy)-2-silyloxy-*myo*-inositol **7** (1.14 g, 2.96 mmol) in dichloromethane (230 mL) at r.t. *via* cannula and the solution was stirred for 1 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (3:1 hexane:EtOAc) to give the cycloalkene **8** as a white solid (84 mg, 8%); m.p. 188-190 °C (from EtOAc); R_f 0.27 (3:1 hexane:EtOAc); ν_{max} (KBr)/cm^{-1} 2956, 2858, 1472, 1401, 1259, 1165, 1003 and 852; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 5.79 (2H, br s, vinyl C*H*), 5.53 (1H, s, orthoformate), 4.45 (1H, m, ring C*H*), 4.28 (1H, m, ring C*H*), 4.25-4.20 (4H, m, ring C*H* or

OCH_2), 4.18-4.03 (4H, m, OCH_2 or ring C*H*), 0.87 (9H, s, $C(CH_3)_3$) and 0.07 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ) 127.7, 103.1, 74.4, 73.1, 69.1, 67.7, 61.7, 26.0, 18.5 and -4.6; *m/z* (CI) 357 [$(M-H)^-$, 100%], 356 [M^-, 70%]; [Found: $(M-H)^-$ 357.1728. $C_{17}H_{29}O_6Si$ requires *M*, 357.1733].

Deprotection of the cyclized orthoformate 8 to give the model compound 9: A solution of the cycloalkene **8** (20 mg, 0.056 mmol) and *p*-toluenesulfonic acid (6 mg, 30 wt%) in a mixture of chloroform (2 mL) and methanol (1 mL) was stirred at r.t. for 24 h. The heterogeneous solution was filtered and the solid was washed with chloroform (5×2 mL) and methanol (5×1 mL). The solid was collected and dried under reduced pressure to give the tetraol **9** (2 mg, 20%) as a white solid; m.p. 281-283 °C (from methanol); ν_{max} (KBr)/cm^{-1} 3500-3100 broad (O-H), 2961, 2931, 2872, 1457, 1363, 1250, 1156, 1108, 1058, 995 and 893; ^1H NMR (500 MHz, DMSO-d_6, δ) 5.75 (2H, br s, CH_a), 4.64 (1H, br s, O*H*), 4.58 (3H, m, O*H*), 4.12 (4H, ABq, *J*= 14.0, H_b and H_c), 3.60 (1H, br s, H_g), 3.31 (2H, dd, *J*=9.0 and 9.0, H_e), 3.20 (2H, multiplet containing dd, *J*=9.0 and 3.0, H_d) and 2.92 (1H, ddd, *J*=6.0, 9.0 and 9.0, H_f); ^{13}C NMR (125.7 MHz, DMSO-d_6, δ) 129.7, 81.1, 74.3, 74.0 and 71.0; *m/z* (EI) 233 [$(M-H)^-$, 5%] and 173 (100%); [Found: $(M+H)^-$ 233.1004. $C_{10}H_{17}O_6$ requires *M*, 233.1019].

8,9-Bispropenyloxy-2,4,10-trioxatricyclo[3.3.1.$I^{3,7}$]-decane-6-ol (12): The diallyl ether **11** (16.8 g, 62.2 mmol) and DABCO (7.0 g, 62.2 mmol) were added in a mixture of ethanol-toluene-water (7:3:1, 100 mL), followed by heating to 80 °C for 0.5 h to obtain a clear solution. The solution was cooled to r.t. and the tris(triphenylphosphine) rhodium(I) chloride (2.87 g, 3.1 mmol) was added, and the solution was left to stir overnight at 100 °C. The TLC analysis showed complete conversion to the isomerized form. The solution was passed through a short plug of Celite, washed with ethyl acetate and dried *in vacuo*. The isomerized product was purified by column chromatography (3:1 hexane:EtOAc) as a pale yellow oil (14 g, 83%); R_f 0.35(3:1 hexane:EtOAc); ν_{max} ($CHCl_3$)/cm^{-1} 3480 (O-H), 3050, 2967, 1672, 1170, 1000 and 900; ^1H NMR (300 MHz, $CDCl_3$, δ) limited data due to the presence of *ca.* 1:1 mixture of geometric isomers: 6.02 (1H, multiplet containing doublet, *J*=13.5, OC*H*=CH of trans), 5.93 (1H, multiplet containing doublet, *J*=8.0, OC*H*=CH of cis), 5.43 (1H, s, orthoformate C*H*), 1.49 (6H, m, 2×CH_3); *m/z* (FAB) 99 (100%), 115 (85%) and 289 (5%); [Found: $[(M+H)^-$ 271.1186. $C_{13}H_{19}O_6$ requires *M*, 271.1181].

9-(4-Vinylbenzyloxy)-2,4,10-trioxatricyclo[3.3.1.$I^{3,7}$]-decane-6,8-carbonate (14): To a solution of the diol **13** (3.0 g, 9.8 mmol) in dry pyridine (60 mL), triphosgene (8.7 g, 29.4 mmol) was carefully added at r.t. under N_2. The reaction mixture was stirred at r.t. for 18 h before it was quenched by the addition of sat.-NH_4Cl solution (20 mL). The aqueous layer was separated and was extracted with ethyl acetate (3×50 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$ and evaporated. The milky oil was purified by column chromatography (1:1 hexane:EtOAc) to give the carbonate **14** as a white solid (1.93 g, 60%); m.p. 155-158 °C; R_f 0.43 (1:1 hexane:EtOAc); ν_{max} (KBr)/cm^{-1} 3010, 2931, 1750 (carbonate C=O), 1601, 1394, 1180, 1105, 995 and 970; ^1H NMR (500 MHz, $CDCl_3$, δ) 7.44-7.34 (4H, m, Ar*H*), 6.73 (1H, dd, *J*=17.5 and 11, CH_2=C*H*Ar), 5.78 (1H, d, *J*=17.5, CH_2=CHAr), 5.60 (1H, br s, orthoformate C*H*), 5.28 (1H, d, *J*=11, CH_2=CHAr), 5.05 (2H, ABq, *J*=9.5, OCH_2Ar), 4.65 (2H, m, ring C*H*), 4.60-4.24 (4H, m, ring C*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ) 145 (carbonate *C*), 138.3, 138.0, 136.6, 136.5, 114.7, 102.0 (orthoformate *C*), 72.3 (CH, ring *C*), 70.0 (CH_2, OCH_2Ar), 69.7 (CH, ring *C*), 66.6 (CH, ring *C*) and 60.0 (CH, ring *C*); *m/z* (FAB) 136 (80%), 154 (100%) and 333 (15%); [Found: $[(M+H)^-$ 333.0968. $C_{17}H_{17}O_7$ requires *M*, 333.0974].

Copolymerization of 9-(4-Vinylbenzyloxy)-6,8-carbonate inositol orthoformate 14 with styrene (15): The inositol monomer **14** (0.71 g, 2.1 mmol), styrene (0.25 ml, 2.1 mmol) and AIBN (0.023 g, 2.5 wt% relative to monomers) were dissolved in dry THF (42 mL; 0.1 M of monomers). The solution was freeze-thaw degassed using liquid nitrogen (4 cycles), and was allowed to warm to r.t.

before the solution was heated at 65 °C for 48 h. The solution was concentrated *in vacuo* to give an oil. This was, then, dissolved in THF (5 mL) and the solution was added dropwise into a vigorously stirred methanol (50 mL). The precipitate was collected and reprecipitated into hot hexane (50 mL) from THF (5 mL). The precipitate was collected and dried to give the copolymer **15** as a white solid (750 mg, 80%); ν_{max} (KBr)/cm^{-1} 3049, 3025, 2926, 2851, 1770 (carbonate C=O), 1600, 1456, 1446, 1385, 1166, 1002, 755 and 698; ^{1}H NMR (500 MHz, Acetone-d_6, δ) 7.2-6.2 (30H, br signal, 30×Ar*H*), 5.6 (1H, br signal, orthoformate C*H*), 4.9 (2H, br signal, OCH_2Ar), 4.6-4.2 (6H, br signal, 6×ring C*H*) and 1.9-1.0 [18H, br signal, C*H* and CH_2 from inositol unit, 5×(C*H* and CH_2 from styrene backbone)]; ^{13}C NMR (125.7 MHz, Acetone-d_6, δ) selected data 146 (C, carbonate), 102.8 (CH, orthoformate *C*); GPC (THF, RI)/Da M_n 11.0×10^3, M_w 38.9×10^3 and M_w/M_n 3.5.

Deprotection of the copolymer 15 (10): A solution of the copolymer **15** (450 mg) and *p*-toluenesulfonic acid (100 mg, 22 wt%) in THF-methanol (2:1, 3 mL) was stirred at r.t. for 48 h. After this time, the solvent was removed *in vacuo* to give a white solid. This was dissolved in THF (0.5 mL) and the solution was added dropwise into a vigorously stirred methanol (20 mL). The precipitate was collected and dried to give the deprotected polymer **10** as a white solid (322 mg, 78%); ν_{max} (KBr)/cm^{-1} 3468 (O-H), 3073, 3059, 2913, 2858, 1750 (carbonate C=O), 1603, 1490, 1449, 1347, 1261, 1159, 1039, 748 and 700; ^{1}H NMR (300 MHz, Acetone-d_6, δ) 7.2-6.2 (30H, br signal, 30×Ar*H*), 5.0-4.6 (2H, br signal, OCH_2Ar), 4.5-4.0 (6H, br signal, 6×ring C*H*), 3.8-3.2 (3H, br signal, 3×O*H*) and 2.0-1.0 [18H, br signal, C*H* and CH_2 from inositol unit, 5×(C*H* and CH_2 from styrene backbone)]; ^{13}C NMR (75.4 MHz, Acetone-d_6, δ) selected data 145 (C, carbonate).

CONCLUSION

A conformationally rigid polymeric ligand having syn-triaxial hydroxyls has been successfully synthesized using the readily available *myo*-inositol. We have also established an effective method to verify the conformation of the cyclohexane polymers by the comparative spectroscopic techniques.

Polymeric analogues of inositol should be useful as a novel metal binding ligand as polymers are generally valued as chelating agents due to their advantages of easy use and removal after chelation. We are currently investigating the metal binding properties of this polymer.

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