

Synthesis and lithium transport in ionically conducting crown ether polymers

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The synthesis and characterization of a series of crown ether 'comb-branch' polymers is reported wherein [12]- and [14]-ring lithium binding units have been linked to a polyacrylate or polymethacrylate backbone via a simple ester link or a C₆ or oxydiethylene chain. Preliminary data on glass transition temperature, T_g , and conductivity reveal a relative insensitivity of T_g to added lithium in the [14] series and higher conductivities in the [12]-O₄ series.

(Keywords: lithium; doping; ionic conduction; polymethacrylate; crown ether)

Introduction

The dissolution of lithium salts in polymers containing ethylene oxide units results in ionically conducting materials in which charge transport occurs in the amorphous phase due to the mobility of both the anion and the cation^{1,2}. In the archetypal system — poly(ethylene oxide) (PEO) — addition of lithium ions causes a considerable structural reorganization. Effectively, the lithium ions cross-link the PEO chains and the increased order is associated with an elevated glass transition temperature, T_g , which reduces the polymer mobility and hence the ionic mobility, resulting in reduced conductivity levels. In crown ether polymers, the ring offers an attractive alternative lithium binding moiety. A 16-crown-5 ring has been linked recently to a flexible polyphosphazene backbone and doped with sodium³.

In binding the lithium ion, [14]-crown-4 is known to form relatively strong 1:1 complexes in which the lithium ion sits in the plane of the ring⁴. Both cation solvation and anion separation are likely to be more effective than the corresponding 1:1 complex in a [12]-crown-4 system where the lithium sits above the ring plane^{5,6}. The mobility of a lithium ion (either in solution or in an amorphous phase) is likely to be higher with proximate [12]-crown-4 rings than in the [14]-crown-4 system, as the higher stability of lithium complexes in the latter series is associated with slower rates of decomplexation and a higher free energy of activation for lithium dissociation.

In order to probe the relative importance of the degree of lithium solvation (in systems where lithium binding is accompanied by minimal ligand reorganization) and the mobility of both the lithium ion and the associated anion, we have begun to study the lithium binding and transport properties of a series of [12]-, [13]- and [14]-crown-4 functionalized 'comb-branch' polymers.

Additional design features include an oxyethylene or alkyl chain to separate the main chain from the lithium binding unit thereby reducing T_g . For the oxyethylene chain, the β -oxygen may play an active role in lithium binding, thereby aiding lithium migration. Ligation of lithium by such a β -oxygen has been observed in various monomeric [14]-crown-4-derivatives⁷.

Experimental, results and discussion

The synthesis of the 2-benzyloxymethyl derivatives of the [12]-, [13]- and [14]-crown-4 ligands was effected following the method of Miyazaki *et al.*⁸ involving condensation of the appropriate linear ditosylate with racemic 5-phenyl-4-oxa-pentan-1,2-diol (*Figure 1*). Debenzylation was accomplished by catalytic hydrogenation (Pd(OH)₂-C/H₂/EtOH, p-TolSO₃H) and the resultant primary alcohol **1** was reacted directly with methacryloyl or acryloyl chloride (Et₃N, THF, 0°C, 90%) to give the corresponding monomers **2–5**. Chain extension involved either alkylation of the thallose alkoxide derived from **1** (TIOEt, PhMe) with the bromo-tetrahydropyranyl derivative **6** (MeCN, 80%) or with the benzyl protected iodide, **7**. Deprotection (involving aqueous acetic acid or hydrogenation (Pd(OH)₂-C, H₂, EtOH)) afforded the extended alcohols which were subsequently esterified to their acrylate or methacrylate esters, **8–11**. Polymerization of monomers **2–5** and **8–11** was effected using standard methods of radical initiation (AIBN, butan-2-one) and the resultant polymers typically had molecular weights in the range 10⁴–4 × 10⁴ (e.g. for **5**, $M_n = 28\,000$, $M_w = 39\,000$, $M_w/M_n = 1.39$). Representative T_g values for polymers and lithium-doped mixtures are given in *Table 1*. The lithium-doped materials were obtained by mixing anhydrous acetone solutions of lithium trifluoromethanesulfonate with the polymer, followed by solvent evaporation (80°C, 0.01 mmHg). Unlike many PEO-based polymer-salt mixtures, the addition of

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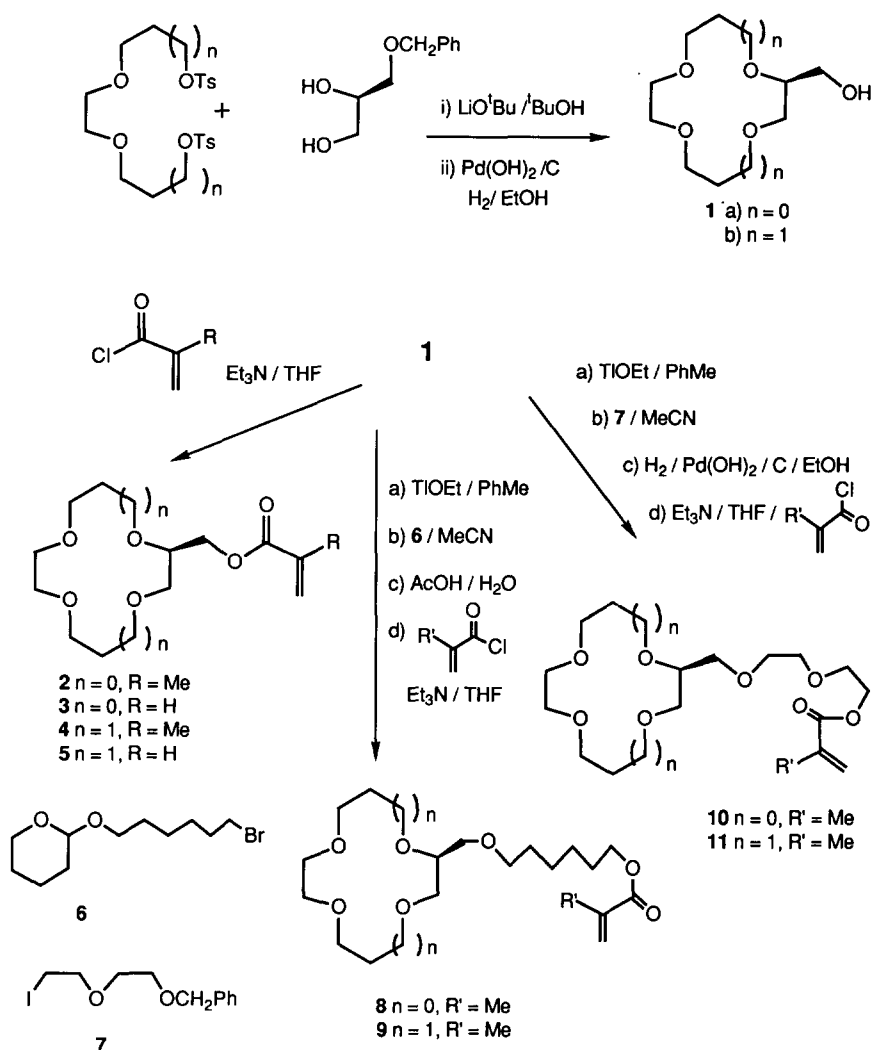

 Figure 1 Synthesis of [12] and [14]-O₄ acrylate and methacrylate monomers

Table 1 Glass transition temperatures for polymers and polymer-salt mixtures

Polymer (poly- <i>n</i>)	T_g (°C)	T_g of Li-doped mixtures (°C) [O:Li] ^a
2	0	+17 [18:1], +23 [12:1]
4	+31	+44 [18:1], +44 [12:1]
5	+3	-1 [18:1]
8	-26	-7 [18:1], -5 [12:1]
9	-20	-24 [18:1]
10	-39	-24 [18:1], -22 [12:1]
11	-55	-55 [18:1]

^a The oxygen:lithium ratio relates to the crown ether (4-0) moiety only

lithium is not accompanied by a significant increase in T_g . Such increases are usually simply attributed to effective salt dissolution and partial ionization^{9,10} accompanying an increase in order of the polymer chains. In particular, with the [14]-ring polymers there is a small change in conformation upon complexation and similar quadrangular conformations are adopted by the ligand when free and bound which may be associated with the observed lack of variation of T_g .

The relative binding ability of the monomer unit in the [12]-, [13]- and [14]-ring materials was compared

semiquantitatively using ¹³C and ⁷Li n.m.r. Incremental addition of LiCF₃SO₃ or LiClO₄ to solutions (CD₃OD) of the benzyl ethers of 1 resulted in shifts of the ligand ¹³C resonances. Stronger 1:1 binding was observed for the [14]-ring system, while shallower titration curves were obtained for the [12]- and [13]-ring systems. These results were echoed in the disubstituted series. The activation energy for lithium exchange between free and bound states with the [12] and [14] benzyl ethers was monitored by variable temperature ⁷Li n.m.r. in CD₃NO₂, a relatively weakly coordinating solvent. A coalescence phenomenon was observed in the latter case ($T_c=283$ K, $\Delta G_c=65$ kJ mol⁻¹) but not in the former, suggesting a lower energy barrier (<50 kJ mol⁻¹) for lithium exchange in the [12]-ring systems. (T_c is the coalescence temperature, and ΔG_c is the free energy barrier for this exchange process, calculated from the coalescence temperature.) Thus the [14]-ring systems may be expected to form stronger complexes with lithium — perhaps enhancing cation/anion separation — while the [12]-ring systems will offer more rapid kinetics of lithium exchange notwithstanding their weaker ion-binding ability.

The conductivity of the polymeric materials doped with lithium triflate (crown O:Li from 18:1 to 6:1) was determined over the temperature range 0–180°C using

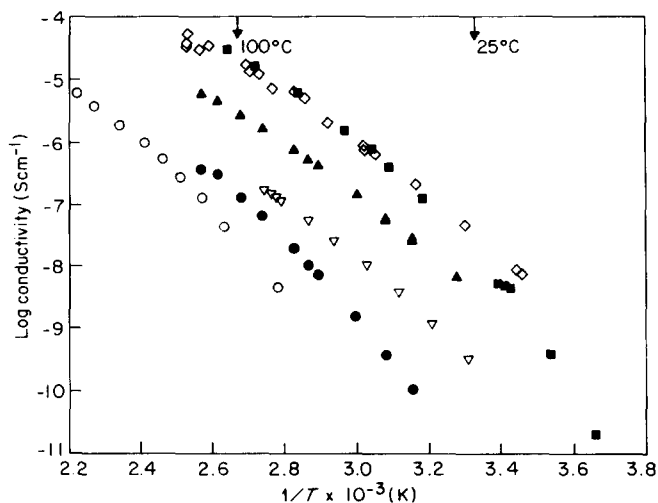


Figure 2 Variation of the logarithm of ionic conductivity with reciprocal temperature for polymer-salt mixtures: ○, 4; ■, 10; ◇, 11; ●, 2; ▲, 8; ▽, 9 (O:Li=18:1)

standard a.c. impedance spectroscopy methods, over the frequency range 1–63 kHz. Representative plots are given in Figure 2, showing that the non-extended crown ether polymers with higher T_g values show very modest conductivities. Those amorphous polymer-salt mixtures with a spacer group between the polymer backbone and the lithium-binding group have lower T_g values and higher conductivity values. Comparison of the

conductivities of the lithium-doped [12]- and [14]-extended polymers, 8–11, show that even though the [14]-ring polymers have comparable or higher T_g values, the [12]-ring polymers have the higher conductivities. Whether this primarily reflects the relative ease of Li^+ migration from one [12]-ring binding unit to another, or the enhanced tendency for [12]-rings to form 2:1 complexes^{5,6}, thereby promoting anion/cation separation, remains unclear. Further studies are underway to try to resolve this point.

Acknowledgement

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