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Thermal and conductivity properties of poly(ethylene glycol)-based cyclopolymers†

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Cyclopolymers bearing a hexaethylene glycol-based malonate crown ether, have been synthesized and characterized from the point of view of their thermal properties and of their use, in thin films, either on their own or as blends with poly(ethylene glycol), in lithium ion battery applications.

Introduction

Lithium electrolytes play an essential role in advanced battery applications.[1] Solid polymer electrolytes are composed of poly(ethylene oxide) (PEO) as a blend with the lithium salt of a large anion. If ion transport was originally thought to occur *via* 'ion hopping' along the PEO chains, it was later shown that ionic mobility in the above system takes place primarily in the amorphous region of the electrolyte.[2] The currently accepted model for ion transport involves a cooperative ion-polymer motion activity. Recent variations in polymer electrolyte composition and structure include both variations of the counterions associated with the lithium salt, and the study of macrocyclic compounds, both of the crown ether and cryptand type,[3] included as a blend with PEO. In a report, acrylic-like polymers, with crown ethers covalently bound, *via* a flexible ethylene glycol spacer of varying length, have been tested as materials for lithium ion battery applications.[4]

We were interested in examining the properties of novel type of materials in which rigid, pre-organized, channel-like structures could favor a high degree of intrachain mobility and recognition affinity between the crown ether structure and the lithium cation. Towards this objective, we have considered the use of 'malonate' crown ethers, characterized by a poly(ethylene glycol) portion modified by the insertion of a malonate ester functionality.[5] ‡ The modification of the malonate unit is then easily achieved by mild organic functionalization of the acidic CH_2 carbon atom, for different purposes.[6]

Cyclopolymerization procedures are very useful for achieving a high degree of structural control within the polymer backbone of a certain macromolecular structure,[7] and have been used recently as a protocol for obtaining stereoregular polymers, or to impart peculiar materials properties.[8] Mathias and co-workers have also demonstrated that the polymerization of a variety of malonate-derived difunctional acrylic-like monomers yields a polymer backbone comprised exclusively of six-membered rings.[7c] In our design approach, the *spiro* quaternary carbon center obtained after double alkylation reaction on the malonate moiety should hold, after polymerization, the crown ether portions in a stacked fashion, so favoring packed channel-like structures (see Fig. 1).

We report here the synthesis of novel cyclo-copolymers bearing a substantial content of their structure as poly(ethylene glycol), their thermal and, when doped with Li^+ ion salts, their electrical properties either on their own or as blends with PEO.[9]

Experimental

All commercially-available compounds were purchased from Aldrich and used as received. THF (CaH_2) and CH_2Cl_2 (CaH_2) were dried before use. Compound **1** and polymer **4**[9] were synthesized as previously reported. Flash chromatography was carried out using silica gel (Merck 60, 0.040–0.063 mm). ^1H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on Bruker 200 or AMX300 spectrometers with the solvent residual proton signal as a standard. Infrared spectra were recorded on

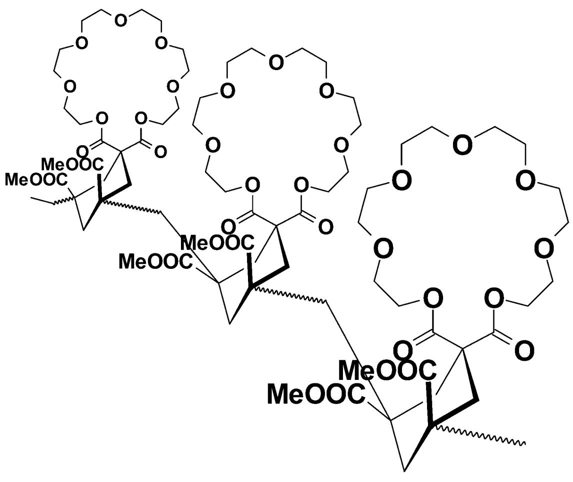

Fig. 1 One of the possible conformations of cyclopolymer **4**.

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† Electronic supplementary information (ESI) available: ^1H NMR spectra and gel permeation chromatography traces of polymers **4**, **5a** and **6** after purification by precipitation in the non-solvent. See http://www.rsc.org/suppdata/jm/b4/b402677b/

‡ There is no close resemblance between the size selectivity towards the binding of metal ion shown by these series of compounds and that shown by the 15-crown-5, 18-crown-6 and 21-crown-7 series; one general trend is that their binding constants towards alkaline metal cations were found to be generally lower than the latter series.

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an FT-IR PE Paragon 1000 spectrophotometer using potassium bromide with a diffuse reflectance accessory. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyzer. Size-exclusion chromatography was carried out on a Perkin-Elmer chromatograph (Series 2000) equipped with a DRI detector. Low polydispersity polystyrene standards (Fluka) were used for the calibration curve and the mobile phase was tetrahydrofuran (1 mL min^{-1}, 40 °C). A bank of four columns with porosities of 500, 1000, 10 000 Å and mixed was used.

Monomer and polymer preparation. Compound 2

Compound **2** was prepared similarly to a published procedure for an ethylene glycol derivative.[10] A solution of triethylene glycol monomethyl ether (2 g, 1.95 mL, 12.2 mmol) and triethylamine (3.37 g, 4.6 mL, 33.3 mmol) in $CHCl_3$ (30 mL) were cooled to 0 °C. Acryloyl chloride (1.01 g, 0.9 mL, 11.1 mmol) in $CHCl_3$ (20 mL) was added to the solution dropwise over a 30 min period. After 12 h of stirring at room temperature, the reaction mixture was washed with brine, then the aqueous phase washed with fresh chloroform and the combined organic phases dried (Na_2SO_4). The product was purified by flash column chromatography (cyclohexane/AcOEt: 80/20) to yield **2** as a clear oil (1.2 g, 50%). IR (cm^{-1}): 1735 ($\nu_{C=O}$), 1640, 1250, 1225. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.38 (dd, 1H; $H_2C{=}CH$–), 6.12 (dd, 1H; $H_2C{=}C$–), 5.80 (d, 1H; $H_2C{=}C$–), 4.30 (m, 2H; –$COOCH_2CH_2O$–), 3.8–3.5 (m, 10H; –OCH_2CH2O–), 3.38 (s, 3H; –OCH_3). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 165.8, 130.7, 128.0, 71.6, 70.3, 68.8, 63.4, 58.7.

Free radical polymerization

The monomer and the initiator (AIBN), dissolved in the solvent at the concentration and relative proportions outlined in Table 1, were degassed with argon for 30 min and then heated at 65 °C in a thermo-controlled bath for 48 h. Upon cooling at room temperature, the reaction mixture was examined by TLC to monitor the complete disappearance of the starting monomer, the solvent removed *in vacuo*, the remaining solid dissolved in the minimum amount of CH_2Cl_2, and the solution added dropwise to a solution of the non-solvent (20 times its co-solvent volume).

Polymer 5a. From monomer **1** (265 mg, 0.48 mmol) and monomer **2** (26 mg, 0.12 mmol) in dry THF (2.4 mL) with AIBN (1.97 mg, 0.012 mmol, 2% mol *vs.* total monomer concentration). Purified by precipitation in cyclohexane (175 mg, 83%). IR (cm^{-1}): 1730, 1450, 1350, 1250, 1130. Anal. calc. for $C_{22}H_{34}O_{11.4}$: C, 54.94; H, 7.01. Found: C, 54.96; H, 6.91%.

Polymer 5b. From monomer **1** (265 mg, 0.48 mmol) and monomer **2** (70 mg, 0.32 mmol) in dry THF (3.2 mL) with AIBN (2.63 mg, 0.016 mmol, 2 mol% *vs.* total monomer concentration). IR (cm^{-1}): 1730, 1450, 1350, 1250, 1130. ^{1}H NMR ($CDCl_3$): δ 4.5–4.0 (broad s; –$COOCH_2CH_2O$–), 3.9–3.5 (broad s; –$COOCH_3$ and –OCH_2CH_2O–), 3.4 (broad s; –OCH_3), 1.8–2.2 (broad s; aliphatic –CH_2–).

Polymer 6. From monomer **1** (200 mg, 0.37 mmol) and *N*-phenylmaleimide **3** (64 mg, 0.37 mmol) in toluene (3 mL) with AIBN (2.43 mg, 0.0148 mmol, 2 mol% *vs.* total monomer concentration). Purified by precipitation in cyclohexane (189 mg, 74%). IR (cm^{-1}): 2920, 1715, 1500, 1250. ^{1}H NMR ($CDCl_3$): δ 7.4–7.2 (broad m; Ph–H), 4.2–4.0 (broad m), 3.9–3.2 (broad m), 3.0–1.2 (broad s). Anal. calc. for $C_{35}H_{45}O_{15}N$: C, 58.48; H, 6.30; N, 1.95. Found: C, 58.48; H, 6.13; N, 1.80%.

Differential scanning calorimetry measurements

The polymer samples used for the characterization and conductivity experiments were the ones obtained in THF (entries 1 and 3 in Table 1). Modulated (MDSC^{TM}) Differential Scanning Calorimetry measurements were performed with an MDSC 2910, equipped with a 2000 Thermal Analyst (TA Instruments Inc., USA). The MDSC was fitted out with an auto-fill liquid nitrogen cooling accessory (LNCA). A nitrogen gas flow of 30 mL min^{-1} was used as the purge gas. The measurements were performed at a heating rate of 5 °C min^{-1}, in the temperature range −100 °C to 100 °C, by imposing a temperature modulation with a period of 40 s and an amplitude of 0.5 °C. All samples were kept in a desiccator and crimped in standard aluminium pans just before measurements.

Thin film preparation

Films with thickness in the range 10–20 μm were prepared by means of a Spincoater® P6700 (Specialty Coating Systems, USA). They were deposited on co-planar interdigited-comb electrodes (IDE, surface area *ca.* 440 mm^2, pitch 0.2 mm) in order to perform the dielectric measurements (see below). The IDEs were attached under vacuum at the spin-coater chuck (2.54 mm diameter). Stoichiometric amounts of the synthesized polymers, PEO and $LiN(CF_3SO_2)_2$ (Sigma) were dissolved in CH_2Cl_2 and quantities of solution of the order of 10^{-6} dm^3 were dropped onto the IDEs by means of a micro-syringe under N_2 atmosphere. The rotating speed ranged between 2000 and 4000 rpm.

Dielectric analysis

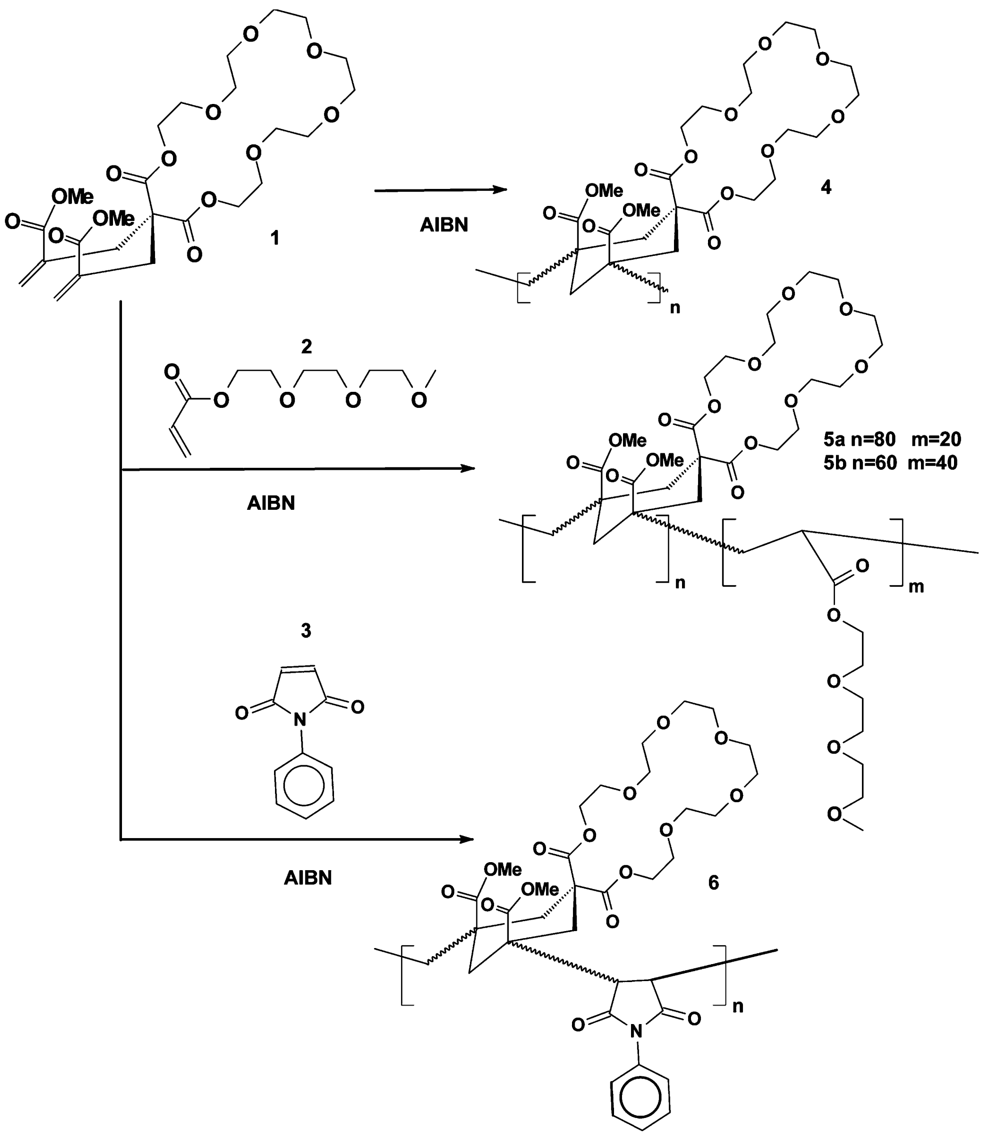
Dielectric measurements were performed by means of a DEA2970 analyzer (TA Instruments, USA), in the frequency range from 1 to 10^5 Hz, and in the temperature range from room temperature to 200 °C. A N_2 flow of 500 mL min^{-1} was used to purge the analysis chamber (volume $\approx$ 2 dm^3). The film thickness was continuously monitored during the measurements by means of a Linear Variable Differential Transformer (LVDT) with a 1 μm resolution.

Results and discussion

Polymer and monomer synthesis

Monomer **1** (Scheme 1) could be prepared in large quantities (up to 3 g) following a procedure we recently reported.[9] Monomer **2** was obtained, after purification by column chromatography, in fair yields by esterification reaction of commercially-available triethylene glycol monomethyl ether, according to a procedure already reported in the literature for similar compounds.[11]

The cyclopolymerization and cyclo-copolymerization of monomer **1** by AIBN-induced free radical polymerization produced in all cases linear polymers soluble in a variety of organic solvents. The polymers were purified by precipitation in cyclohexane as the non-solvent, and characterized by NMR and IR spectroscopies, and Gel Permeation Chromatography (GPC). The ^{1}H NMR of polymer **4**, when compared with monomer **1**, showed complete disappearance of the signals associated with the olefinic protons, indicating both complete cyclization and efficient polymerization processes (see ESI†). IR spectroscopy also indicated the complete disappearance of the band at 1630 cm^{-1}, which was present in the monomer **1** and attributed to the unsaturated double bond olefinic functionalities. We have also copolymerized monomer **1** with increasing amounts of monomer **2**: by possessing a highly mobile ethylene glycol chain, our hope was that to introduce a tunable glass transition temperature in the copolymer, and



Scheme 1 Synthesis of polymers **4**–**6**.

therefore study the conductivity behavior as a function of the glass transition temperature. Both copolymers **5a** and **5b**, synthesized with, respectively, 20 and 40 mol% of comonomer **2** in the feed ratio, could be obtained as linear copolymers, soluble in a variety of organic solvents. Whereas copolymer **5a** could be easily precipitated in cyclohexane, copolymer **5b** formed a gummy suspension difficult to separate and purify, and therefore was not characterized further. The ^{1}H NMR spectrum of polymer **5a** showed the resonances associated with the terminal methyl ether as a broad signal, to confirm effective incorporation of the comonomer **2**.

Copolymerization with *N*-phenylmaleimide **3** was also carried out: maleic anhydride and maleimide derivatives are known to undergo free radical-induced alternating copolymerization with acrylic and styrenic derivatives. Furthermore, other malonate-derived acrylic-like difunctional monomers have been shown to undergo a similar radically-induced alternating process with maleic anhydride.[8c] Indeed, the polymer was obtained in high yields after purification by precipitation in cyclohexane. Incorporation of the maleimide comonomer is clearly evident in the ^{1}H NMR of the polymer: the relative integration of the aromatics area with the area related to the α-protons on the crown ether structure gave a fair correspondence to the proposed 1:1 stoichiometry.

Elemental analyses revealed, both in the case of polymer **4**, **5a** and **6** a close correspondence between the feed and observed

Table 1 Cyclopolymerization of monomers **1** and **2** under free radical conditions.[a]

Entry	Monomer	Polymer	Solvent/[M][b]	M_n[c]	M_w[c]	PD[c]	Yield (%)
1	**1**	**4**	THF/0.25	10 700	17 800	1.7	92
2	**1**	**4**	Toluene/0.25	20 900	25 900	1.3	54
3	**1/2**	**5a**	THF/0.25	6300	12 600	2.0	83
4	**1/3**	**6**	Toluene/0.25	6900	28 000	4.0	74

[a] Polymerizations were run for 30 h with a total monomer concentration indicated as [M]. Polymers were purified by precipitation in cyclohexane. [b] All polymerizations were run with 2 mol% (*vs.* total monomer concentration) of AIBN as a radical initiator. [c] As determined by GPC relative to polystyrene standards after purification. PD = polydispersity.

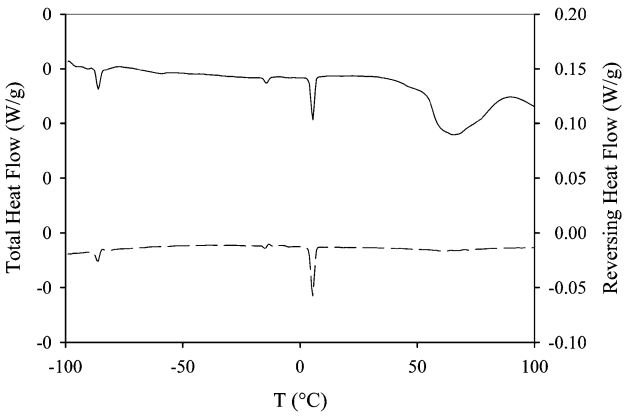


Fig. 2 MDSC thermogram of polymer **4**.

ratio of comonomers in the polymer samples (see Experimental part). Characterization of the polymers by GPC is reported in Table 1. Polymerization of monomer **1** in THF (entry 1, Table 1) and in toluene (entry 2) revealed two very different molecular weight distributions: in the former case, average M_w and M_n values for **1** in THF are considerably lower than toluene, as to be expected from a solvent with a relatively higher chain transfer to solvent constant. As shown in entry 2, an unusually low PDI was also recorded, but has to be attributed to a fragmentation of the polymer composition obtained by precipitation in cyclohexane.[9] Incorporation of monomer **2** or the *N*-phenylmaleimide comonomer instead gave a broader molecular weight distribution profile, together with a somewhat lowered average degree of polymerization (entries 3 and 4, Table 1).

Thermal characterization of polymers 4 and 5a

Figs. 2 and 3 show the MDSC thermograms of polymers **4** and **5a**, respectively. In both cases, the continuous line represents the total heat flow that is the signal given by a standard DSC, whereas the dashed line is the reversing heat flow, which is due to the thermal phenomena reversible in the time scale of the temperature modulation.[11] The total heat flow curves of both the polymers show three thermal effects: the first endothermic peak at *ca.* −90 °C is likely related to residual CH_2Cl_2 melting; a second peak at *ca.* 5 °C is associated with the melting of residual cyclohexane, which was used for allowing the sample to precipitate; finally, the broad endotherm above *ca.* 50 °C is due to solvent volatilization.

The reversing signals, as expected, show only the peaks related to the melting of solvents. In the examined temperature range we did not observe any evidence of glass transitions or melting of the polymer backbone. It is interesting to note that these polymers, and chiefly **5a**, do not display the typical melting peaks of the PEO-based phases in the range 60–100 °C,[12] although they contain a large amount of ethylene glycol groupings.

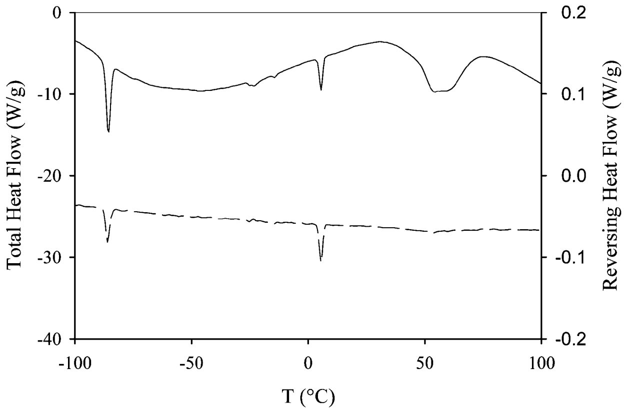


Fig. 3 MDSC thermogram of polymer **5a**.

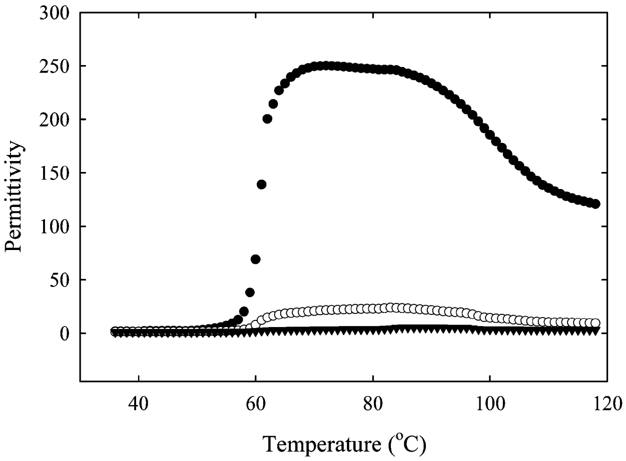


Fig. 4 Behavior *vs.* temperature of the permittivity, *ε*′, at some selected frequencies for the film **5a** + PEO 1:1 wt. (●) 1 Hz, (○) 10 Hz, (▲) 100 Hz.

Dielectric and conductivity properties of thin films

Our preliminary tests showed that both polymers **4** and **5a** did not form thick, stand-alone films by standard casting, but they did on addition of quantities of PEO of the order of 30 wt%. In the following we will report only the data obtained on thin films obtained by spin-coating, both with and without the addition of PEO to our synthesized polymers.

Fig. 4 shows the behavior *vs.* temperature of the permittivity, *ε*′, at some selected frequencies for the film **5a** + PEO 1:1 wt. We observe a strong increase near 60 °C that calls for the presence of a relevant quantity of crystalline PEO phase in the thin film. The observed increase is likely due to interfacial effects with the IDE contacts and it becomes negligible for frequencies above 100 Hz. The subsequent decrease of permittivity at temperatures of the order of 90 °C may be due to a structural rearrangement of the polymer (accompanied by small variations, of the order of 10–15%, of the film thickness) following the PEO melting.

Fig. 5 shows the behavior of the ionic conductivity *vs.* frequency at 100 °C for the sample **5a** + PEO 1:1 wt and for the

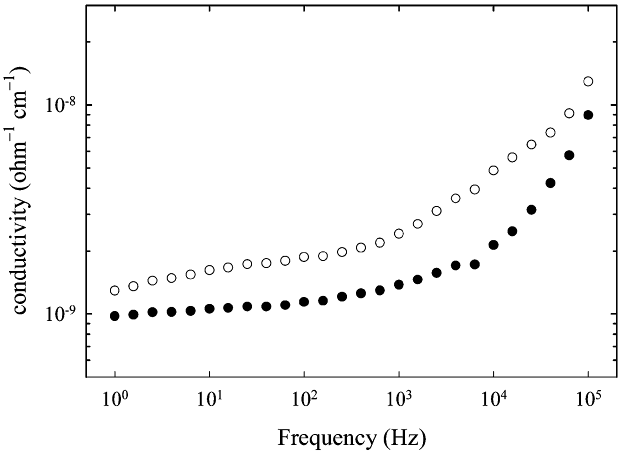


Fig. 5 Behavior of the ionic conductivity *vs.* frequency at 100 °C for the sample **5a** + PEO 1:1 wt (●) and for the same sample doped with LiTFSI (PEO:LiTFSI 8:1) (○).

Table 2 Dielectric data at 50 °C and 1 kHz for formulations containing polymers **4** and **5a**[a]

Sample[a]	ε'	ε''	σ/Ω^{-1} cm^{-1}
4	1.45	0.26	2.6×10^{-11}
4 + Li (5:1)[b]	1.60	0.10	2.6×10^{-11}
5a	2.78	0.06	3.4×10^{-11}
5a + Li (5:1)[b]	3.35	0.08	4.1×10^{-11}
5a + PEO	2.68	32.95	1.22×10^{-10}
5a + PEO + Li (1:1)[c]	9.45	5020	1.31×10^{-10}
5a + PEO + Li (2:1)[c]	15.32	109.7	2.78×10^{-10}
5a + PEO + Li (4:1)[c]	2.83	32.4	6.91×10^{-11}
5a + PEO + Li (8:1)[c]	7.45	74.65	4.51×10^{-10}

[a] The ratio polymer/PEO is always 1:1 wt. [b] The amount of lithium salt is expressed as the molar ratio obtained by considering the average molecular weight of the repeat monomer unit. [c] The amount of lithium salt is expressed as the ratio between the moles of PEO and those of the salt in the sample.

same sample doped with LiTFSI (PEO:LiTFSI 8:1). A plateau giving the value of d.c. conductivity is observed at low frequencies, followed by a dispersive behavior above 1 kHz, which is probably related to the onset of slow re-orientational motions of parts of the polymer backbone. Similar behaviors are observed for all the other doped samples (see also Table 2). The conductivity of the non-doped sample is likely due to impurities introduced during the synthesis procedure (*e.g.* Na^+ ions) or to moisture. The addition of the lithium salt causes only a minor change of the overall conductivity, instead of the expected orders-of-magnitude increase which is typical of salt-doped, PEO-based systems. This means that the crown structures of the polymer **5a** do not allow fast diffusion of the lithium ions, and that the usual mechanisms of conduction assisted by segmental motions, typical of amorphous PEO–salt phases,[13] are not effective. Therefore, we can suppose that the highly regular structure of polymer **5a** is able to hinder the growth of the amorphous phases which are normally observed in PEO–salt systems near the eutectics.

Table 2 reports the values of permittivity (ε'), loss factor (ε'') and conductivity (σ) at a specific frequency and temperature for all the films we prepared. Generally speaking, we observe that the addition of an ether group in order to increase the amorphous fraction of the copolymer (sample **5a** *vs.* **4**) does not practically affect the conductivity, whereas it makes ε' change by a factor of two. On the other hand this result may be somehow expected, since the added monomer contains ethylene oxide groups, and it is well known from the literature[14] that the dielectric constant of amorphous PEO is roughly twice that of the crystalline polymer. The addition of PEO to both the polymers **4** and **5a** determines an orders-of-magnitude increase of the electric loss factor. As far as concerns the transport properties, finally, the addition of the lithium salt to the polymer blend does determine, at most, a conductivity increase by a factor of two. Further work is needed in order to prepare matrices allowing effective ion transport. In particular, we stress that our chief aim in this work was to see if highly ordered crown ether structures could allow high lithium transport. As a consequence, the addition of PEO was chiefly made to improve filmability and, only as a 'byproduct', to add another mechanism for ion motion.

In this frame, some developing strategies are: (i) changing the crown ether dimension, (ii) changing the PEO MW (short chain PEGs are recognized to work well in polymer electrolytes), and (iii) adding plasticizers (*e.g.* ethylene carbonate). Another important point in order to improve lithium transport is the study of the relationships between crystallinity of the malonate structures and ionic conductivity.

Conclusions

We have reported the synthesis and characterization of a series of new cyclo-copolymers containing unconventional crown ethers embedded in their polymer chains. Even though they incorporate a substantial portion of ethylene glycol units (51 wt% for **4** and 56 wt% for **5a**), their thermal properties are substantially different from poly(ethylene glycols) since they do not possess melting or glass transitions.

The new materials possess desirable film-forming characteristics, and it was possible to prepare films in the micrometer range by spin-coating. The conductivity of these films is not yet enough to allow high-energy delivery (*e.g.* for lithium batteries); however, the explored polymer architectures are of interest because of the possibility to 'tune' their dimensions and/or their order to allow new functional properties. Our approach is indicative of how the molecular properties of the recognition unit (*i.e.* crown ethers instead of open chain glycols) cannot be discerned from their physical properties (*e.g.* glass transition temperature). These new, robust polymers could be useful in those applications of material science requiring high thermal stability.

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