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Linear and network polymer electrolytes based on low melting prepolymers

Robert A. Colley,[a] **Shao-Min Mai,**[a] **Colin Booth,**[a] **Peter M. Budd***[a] **and Simon Balderson**[b]
[a]*Department of Chemistry, University of Manchester, Manchester, UK M13 9PL. E-mail: Peter.Budd@man.ac.uk*
[b]*Sealed Air Cryovac, Stafford Park 9, Telford, Shropshire, UK TF3 3BZ*

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Prepolymers $E_4C_3E_4$ and $E_3C_3E_3$, where E represents an oxyethylene unit and C_3 the spacer group $–O(CH_2)_3O–$, were prepared by anionic polymerization of ethylene oxide using propane-1,3-diol as initiator. Oxymethylene-linking polymerization of the prepolymers gave high molar mass polymers with crystalline melting points [$T_m \approx -8$ °C for $P(E_4C_3E_4)$ and -16 °C for $P(E_3C_3E_3)$] and degrees of crystallinity [*ca.* 25% for $P(E_4C_3E_4)$ and 1% for $P(E_3C_3E_3)$] which could be related to the average E-sequence length. Inclusion of 2-methylenepropane-1,3-diol in the recipe for oxymethylene-linking polymerization gave crosslinkable polymers. Networks were obtained by photochemical crosslinking with benzophenone as sensitizer and network characteristics were determined by mechanical and swelling measurements. Linear and network polymer electrolytes were prepared by inclusion of lithium perchlorate at concentrations corresponding to $O:Li = 25$ and $O:Li = 70$, and conductivities were determined over the temperature range -20 to $+80$ °C.

Introduction

Ionically conducting polymer electrolytes based on poly(oxyethylene) (POE) and lithium salts have attracted much interest in recent years. Crystallisation of POE reduces the conductivity that is obtained in unplasticised systems at ambient temperatures ($\sigma < 10^{-7}$ S cm^{-1} at 25 °C), but improved conductivity has been achieved with a number of modified polymer–salt systems.[1–4]

A promising polymer for application in batteries and electrochromic devices is poly[oxymethylene-oligo(oxyethylene)] (POMOE).[5–13] This has the repeat unit $–OCH_2(OCH_2CH_2)_n–$ where *n*, a number-average value, is typically in the range 4–20. It is prepared by the reaction of polyethylene glycol (PEG) with dichloromethane (DCM) in the presence of an excess of powdered KOH. The initial step of the reaction is the formation of the chloroether [eqn. (1)].

$$–OCH_2CH_2OH + CH_2Cl_2 \longrightarrow –OCH_2CH_2OCH_2Cl \quad (1)$$

This is followed by an extremely rapid reaction of the chloroether with a second hydroxy group to form an oxymethylene (acetal) link [eqn. (2)].

$$\begin{aligned} &–OCH_2CH_2OCH_2Cl + HOCH_2CH_2– \\ &\longrightarrow –OCH_2CH_2OCH_2OCH_2CH_2– \quad (2) \end{aligned}$$

The difference in reactivities of the chloromethylene and chloroether groups is so great that high molar mass products can be obtained without the need to balance the concentrations of reagents, and DCM can be used as the solvent for the reaction.

Recently, we have extended this technique to the preparation of network electrolytes by the inclusion of diols bearing unsaturated groups.[14] The diols used were 2-methylenepropane-1,3-diol (MPD) and hexa-1,5-diene-3,4-diol. Crosslinking was carried out both thermally and photochemically. Network formation was shown to have little effect on the conductivity of the polymer electrolyte.

A reduction in the oxyethylene (E) sequence length of POMOE leads to a reduction in the crystalline melting point, T_m, and in the degree of crystallinity. Materials based on PEG400 ($n \approx 9$) have T_m in the range 15–20 °C, whereas materials based on PEG200 ($n \approx 4$) are amorphous or have T_m around -9 °C.[5] However, the efficiency of the oxymethylene-linking polymerization is lower for shorter PEGs, and whilst up to about 500 oxymethylene links can be achieved with PEG400 (giving $M = 2 \times 10^5$ g mol^{-1}), for polymers based on PEG200 a typical value is about 270 ($M = 5.4 \times 10^4$ g mol^{-1}).[14]

The concept explored in the present work was to utilise a prepolymer comprising two E sequences separated by a non-crystallizable spacer group. The objective was to obtain oxymethylene-linked polymers with molar masses comparable to those which can be achieved with PEG400, but exhibiting the reduced T_m associated with the E-sequence length of PEG200. Prepolymers were prepared by anionic polymerization of ethylene oxide, utilising propane-1,3-diol as initiator, so that initiation could occur from both ends of the alkoxide. The spacer group was thus $–OCH_2CH_2CH_2O–$.

Both linear and network polymers were studied. Crosslinkable oxymethylene-linked polymers were prepared by incorporation of 5 mol% MPD in the recipe for oxymethylene-linking polymerization and crosslinking was carried out photochemically, with benzophenone as sensitizer. Polymer electrolytes were prepared with $LiClO_4$.

Notation

The notation used indicates an oxyethylene unit (OCH_2CH_2) by E and the spacer group arising from propanediol ($OCH_2CH_2CH_2O$) by C_3. The batch of prepolymer is indicated by a number in square brackets. Thus $E_4C_3E_4[2]$ denotes the second batch of a prepolymer of nominal composition

$$H(OCH_2CH_2)_4OCH_2CH_2CH_2O(CH_2CH_2O)_4H$$

An oxymethylene-linked polymer is indicated by the prefix P. Where a second polymerization has been carried out with the same prepolymer, this is indicated by adding (2). A crosslinkable polymer is denoted by the addition of M and the mol% of MPD relative to prepolymer. Thus, $P(E_4C_3E_4[2])$-M5 is an oxymethylene-linked crosslinkable polymer prepared from $E_4C_3E_4[2]$ with 5 mol% MPD. A network prepared from this polymer is indicated by $P(E_4C_3E_4)[2]$-M5-N. A polymer electrolyte formed by adding $LiClO_4$ is distinguished by adding a number indicating the mole ratio (O:Li) of salt in the material.

Experimental

Preparation of prepolymers

Prepolymers were prepared by anionic polymerization of ethylene oxide, using propane-1,3-diol as initiator. Vacuum line techniques were employed, high vacuum being attained by use of a rotary oil pump in conjunction with a mercury diffusion pump. All glassware was flame-dried under vacuum prior to use.

Materials. Ethylene oxide (Fluka, 99.8%) was transferred under vacuum ($<10^{-3}$ mmHg) from the cylinder into a flask containing CaH_2 powder, stirred for 8 h, then cooled under vacuum with solid CO_2 and stored in a freezer until required. Propane-1,3-diol (Fluka, $>97\%$) was fractionally distilled under reduced pressure, the fraction boiling at 88 °C (9 mmHg) being collected over freshly activated molecular sieves under dry nitrogen and stored in a refrigerator until required. Petroleum ether (100–120 °C) was stirred over CaH_2 powder for 8 h, then distilled under dry N_2 and stored over sodium wire.

Preparation of initiator. Potassium metal (BDH, *ca.* 0.33 g) was freshly cut under petroleum ether to produce a clean surface, weighed into a tube containing petroleum ether, then carefully cut into smaller pieces and added under a flow of dry N_2 to a 15 cm^3 volumetric flask containing a portion of dry, distilled propane-1,3-diol, each piece being allowed to dissolve before more was added. When all the potassium was dissolved, the contents of the flask were made up to 15 cm^3 with propane-1,3-diol. The required amount of initiator solution was injected under a flow of dry N_2 into a reaction ampoule fitted with a PTFE tap. After closing the tap, the ampoule was immersed in liquid N_2 and evacuated for 15 min (10^{-4} mmHg). An [OH]/[OK] ratio of 50 was used in all preparations.

Polymerization. The vacuum manifold was thoroughly evacuated (10^{-4} mmHg) before use. A flask containing dry ethylene oxide was attached to the vacuum line, frozen in liquid N_2, then pumped under high vacuum for 10 min. The main manifold was isolated from the pumps and the required amount of ethylene oxide transferred to a graduated flask, and then to the reaction ampoule, which already contained the initiator solution. The mixture in the ampoule was frozen with liquid N_2 and pumped under high vacuum. The ampoule was sealed then allowed to warm to room temperature with gentle agitation to ensure mixing of the contents. The ampoule was then subjected to a ramped heating regime, a typical temperature profile being: 2 days at ambient, 3 days at 30 °C, 4 days at 40 °C, 6 days at 65 °C, then 5 days at 80 °C. The prepolymers produced by this route (see Table 1) were clear liquids.

Oxymethylene-linking polymerizations

A 700 cm^3 resin kettle was equipped with a mechanical stirrer, water condenser and pressure equalising dropping funnel and immersed in a hot water bath at *ca.* 50 °C. Freshly ground KOH and dichloromethane (DCM) were added under a N_2 atmosphere, and stirred to ensure complete wetting of the solids. Prepolymer was added from the dropping funnel as quickly as possible and the mixture stirred for 4 to 6 h, or until it became too viscous to stir. The mixture was left overnight under dry N_2 to allow the reaction to reach completion. The product was then dissolved in DCM and the cloudy solution filtered through a Celite pad to remove excess KOH and KCl by-product. The clear filtrate was rotary evaporated under reduced pressure to yield the polymer, which was then vacuum dried (<0.001 mmHg, 24 h). If elemental analysis indicated that potassium residues were greater than 0.05 wt%, the polymer was re-dissolved in DCM, washed with distilled water three times to separate water-soluble inorganic impurities, then rotary evaporated and dried as before.

For the first polymerizations, quantities were employed which had proved successful with conventional PEG400 (55 g KOH, 53 g DCM, 50 g prepolymer; KOH : glycol = 8), but reaction was sluggish and only low molar mass polymer was produced. Consequently the KOH : glycol ratio was increased for subsequent polymerizations.

Crosslinkable polymers were prepared by including 5 mol% 2-methylenepropane-1,3-diol (MPD) in the formulation.

All polymers were stabilised as follows: the polymer was re-dissolved in DCM, 200 ppm stabiliser (2,6-di-*tert*-butyl-4-methylphenol, Stavox CX, Shell Ltd.) added, then the solution rotary evaporated and dried as before.

Photochemical crosslinking

For photochemical crosslinking, benzophenone (Fisons) was used as sensitizer. Polymer (2.0 g) and benzophenone (0.5 wt%) were dissolved in dry distilled acetonitrile (10 cm^3). The solutions were poured into polytetrafluoroethylene (PTFE) dishes, the solvent slowly evaporated under dry N_2 to form thin films (thickness *ca.* 1 mm) and the films dried under vacuum. Samples were kept in the dark until exposure to UV to prevent premature crosslinking. Dried films were exposed to UV radiation from a Spectroline R-51/F lamp (short wave UV, 140 W) at a distance of 15–20 cm for 24 h. Films were flipped once during exposure to promote an even cure.

To clean films of residual initiator and any other impurities, they were immersed in methanol and allowed to swell for several hours. The swollen films were rinsed with clean methanol and allowed to dry under atmospheric conditions, then under vacuum (<0.01 mmHg, 40 °C) for 48 h. Elastic, non-tacky films were obtained.

Sloop[15] has previously used benzophenone, at much higher concentrations than those used here, for photochemical crosslinking by hydrogen abstraction of linear poly(oxyethylene) and POMOE containing no double bonds. However, polymers prepared without MPD did not crosslink under the conditions employed here.

Characterization of networks by mechanical properties

A strip of known cross-sectional area was clamped at its upper end and suspended vertically in a constant temperature (±1 °C) enclosure. The sample was preconditioned by applying a large load for 5 h at 30 °C, then allowing it to recover overnight before stress–strain measurements were made at 25 °C. The undeformed length between marks was determined before weights were clamped to the lower ends of the strips and the strain (λ, ratio of deformed to undeformed length) was measured over a range of applied stress for increasing load. A steady reading was obtained after *ca.* 20 min. Some samples were investigated with both increasing and decreasing load to verify that equilibrium was achieved under the conditions employed.

The shear modulus G was determined from plots of nominal stress (σ, ratio of tensile force to undeformed cross-sectional area) against strain function (λ–λ^{-2}), using eqn. (3).

$$\sigma = G(\lambda - \lambda^{-2}) \tag{3}$$

The kinetic theory of elasticity of an ideal affine network[16] was used to calculate the crosslink density c_c and the molar mass of network chains M_c using eqn. (4),

$$c_c = \frac{G}{RT} \text{ and } M_c = \frac{\rho}{c_c} \tag{4}$$

where ρ is the density of the network (taken to be that of amorphous poly(oxyethylene), $\rho = 1.12$ g cm^{-3}).[17]

Characterization of networks by swelling

A weighed strip of network polymer was immersed in water for 3 days at 25 °C, then removed, surface dried and reweighed. Approximate volume fractions of water in the swollen gel were calculated from the density of water and the density of liquid poly(oxyethylene) (1.12 g cm^{-3})[17] at 25 °C.

The concentration of network chains c_c was determined from the extent of swelling using eqn. (5),[16]

$$c_c = -\frac{\ln \phi_1 + \phi_2 + \chi\phi_2^2}{V_1\phi_2^{1/3}} \quad (5)$$

where ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer, repectively, and V_1 is the molar volume of the solvent (*ca.* 18 cm^3 mol^{-1}). The polymer–solvent interaction parameter χ was taken as 0.45, a value appropriate to the semi-dilute regime. Malcolm and Rowlinson[18] have shown that the value of χ for poly(oxyethylene) and water depends strongly on ϕ_2, increasing from 0.4 at $\phi_2 = 0.24$ to 1.24 at $\phi_2 = 0.9$.

Preparation of electrolytes

Materials. Polymers were dried under vacuum (<0.001 mmHg, 48 h) before placing in a dry box. Lithium perchlorate (Fluka, >99%) was dried with care under high vacuum and stored in the dry box. Acetonitrile was distilled under N_2 onto freshly activated molecular sieve 4A and stored under N_2 in the dry box.

Procedure. Polymer and $LiClO_4$ were weighed accurately (±0.0001 g) in the dry box, mixed with dry distilled acetonitrile and left overnight for the solids to dissolve, before shaking thoroughly to ensure even mixing of the components. The solutions were poured into PTFE dishes and placed under a flow of N_2 to allow the solvent to evaporate slowly (2–3 days). The polymer electrolyte films were dried under high vacuum (<0.001 mmHg, 40 °C, 48 h) and returned to the dry box for storage.

Network electrolytes. For network electrolytes, the salt was added prior to photochemical crosslinking, as described above, under a N_2 atmosphere. Network electrolytes were not washed with methanol after crosslinking, as this would have removed the salt.

Nuclear magnetic resonance spectroscopy

^{13}C NMR spectra of prepolymers and polymers were obtained using a Varian Associates Unity 500 spectrometer operating at 125 MHz. *Ca.* 0.6 g sample was dissolved in 3 cm^3 $CDCl_3$ and spectra recorded at ambient temperature with proton decoupling. Chemical shifts were measured with reference to the main chain poly(oxyethylene) peak at 70.33 ppm.

Gel permeation chromatography

Gel permeation chromatography (GPC) of the prepolymers was carried out at 25 °C using four μ-Styragel columns in series (nominal pore sizes in range 500–10^6 Å) with tetrahydrofuran (THF) as solvent at a flow rate of 1 cm^3 min^{-1}. A Waters 410 differential refractometer was employed as detector.

GPC of the polymers was carried out using three μ-Styragel columns in series (nominal pore sizes 500, 10^4 and 10^6 Å) with dimethylacetamide (DMA) as solvent at a flow rate of 1 cm^3 min^{-1}. The column temperature was 60 °C. A Knauer HT differential refractometer was employed as detector.

Both systems were calibrated with commercial linear poly(oxyethylene) standards.

Differential scanning calorimetry

A Perkin-Elmer DSC-4 instrument was used. The sample was dried under vacuum then 7–14 mg was weighed (±0.01 mg) in a glove box, under dry N_2, into an aluminium sample pan and sealed. The pan was quenched in the calorimeter from room temperature to −100 °C, then heated at 10 °C min^{-1} to +100 °C, to give an 'as stored' DSC curve. The molten sample was then quenched to −100 °C and re-heated at 10 °C min^{-1} to +100 °C, to give a 'quenched' DSC curve. In this work, 'quenched' and 'as stored' curves were very similar to each other.

Melting and glass transition temperatures were obtained from the DSC curves as the temperature of the melting peak and the mid-point of the inflection, respectively. Calibration of the power and temperature scales was with pure indium. The correction for thermal lag at the heating rate employed was *ca.* −2 °C, as determined by experiments on standards at various heating rates.

Conductivity

Conductivities of polymer and network electrolytes were determined over a range of temperatures (–20 to 80 °C) by ac impedance spectroscopy, using a Schlumberger Model SI 1260 impedance/gain phase analyser, operating over a frequency range of 5 to 15 MHz. A dried film under a dry N_2 atmosphere was sandwiched between two gold-plated brass electrodes and held in place by springs within a cylindrical glass cell. The assembled cell, maintained under a slight positive pressure of dry N_2, was placed in a temperature controlled oven (Büchi Model TO-51). The cell temperature was raised to 80 °C and allowed to equilibrate for 30 min before making the first measurement. The temperature was lowered to −20 °C in steps of about 10 °C, allowing 20 min for equilibration at each step before taking measurements. Temperature was monitored by a thermocouple to ±0.1 °C. Film thickness was monitored by a Schlumberger SM3 linearly-variable differential transducer (±0.0001 cm, pre-calibrated with feeler gauges) fixed in parallel with the electrodes. A complex impedance plot was produced at each temperature, and the bulk resistance R determined as the point where the extrapolations of the semicircle and the inclined spike cut the real impedance axis. The conductivity σ was calculated as $\sigma = l/RA$, where l is the sample thickness and A the electrode surface area.

Results and discussion

Prepolymers

Three batches of nominal composition $E_4C_3E_4$ and one batch of $E_3C_3E_3$ were prepared. Average molar masses determined by GPC are given in Table 1. A ^{13}C NMR spectrum for $E_4C_3E_4$ is shown in Fig. 1 and assignments are indicated in the Figure. Values of the mole ratio of oxyethylene units to propanediol, E:C_3, and average E-sequence length, n, as

Table 1 Molecular characteristics of prepolymers

Prepolymer	M_{pk}/g mol^{-1} (GPC)	$\bar{M}_w/\bar{M}_n$ (GPC)	E:C_3 (NMR)	Average n (NMR)	% unreacted C_3 ends (NMR)
$E_4C_3E_4$[1]	410	1.07	8.3	4.15	15
$E_4C_3E_4$[2]	460	1.07	8.3	4.15	14
$E_4C_3E_4$[3]	500	1.10	9.2	4.50	6
$E_3C_3E_3$	400	1.09	7.1	3.55	22

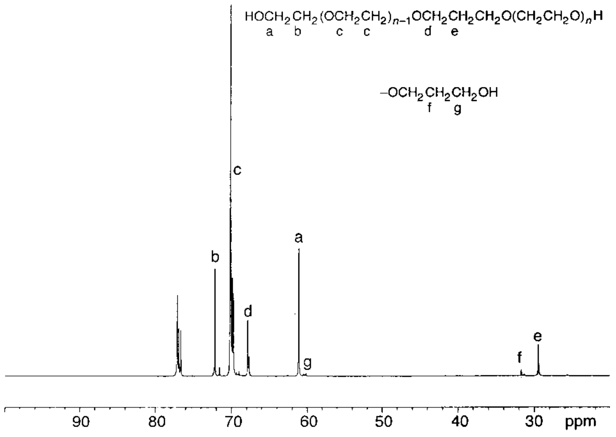

Fig. 1 ^{13}C NMR spectrum of prepolymer $E_4C_3E_4[1]$.

determined by ^{13}C NMR, are included in Table 1. ^{13}C NMR spectroscopy indicated that not all propanediol end units had reacted, peaks f and g in Fig. 1 being attributed to nuclei of propanediol units with unreacted ends. The percentages of unreacted propanediol ends are given in Table 1. The presence of some unreacted C_3 ends may be attributed to slow addition of the first E unit, as compared to succeeding E additions.[19]

Glass transition temperatures, T_g, crystalline melting points, T_m, and enthalpies of fusion, $\Delta_{fus}H$, as determined by DSC, are listed for two of the prepolymers in Table 2. The sensitivity of T_m to E-sequence length is illustrated by the significant decrease in T_m observed on reducing the average E-sequence length from 4.15 ($E_4C_3E_4[2]$) to 3.55 ($E_3C_3E_3$). Values of T_m for samples of prepolymers were comparable to those expected for PEG or POMOE of the same E-sequence length, as can be seen in Fig. 2.

Polymers

Ratios of KOH : glycol used in oxymethylene-linking polymerizations, and peak molar masses of the polymers obtained, are given in Table 3. For comparison, data are also given for samples of POMOE based on PEG400, PEG300 and PEG200 (denoted P400, P300 and P200, respectively) and for a crosslinkable polymer based on PEG200 with 5 mol% MPD (P200-M5). At high KOH : glycol ratios, degrees of polymerization could be obtained for the $E_nC_3E_n$ prepolymers which compared well with those achieved in this work with conventional PEG of similar molar mass. $P(E_4C_3E_4)$ compares with PEG400-based polymers and $P(E_3C_3E_3)$ compares with a polymer prepared using PEG300.

A ^{13}C NMR spectrum for a polymer of $E_4C_3E_4$ is shown in Fig. 3 and assignments are indicated in the Figure. The spectrum differs from that of the prepolymer (Fig. 1) in that there are no peaks associated with unreacted propanediol ends. The peak due to oxymethylene carbons contains a shoulder which may be attributed to oxymethylene units linked directly to propanediol ends. Crosslinkable polymers exhibited similar ^{13}C NMR spectra, with additional peaks due to MPD units.[14] Values of mol% MPD units, determined by NMR, are given in Table 3. The efficiency of incorporation of MPD units was $\geqslant$80%.

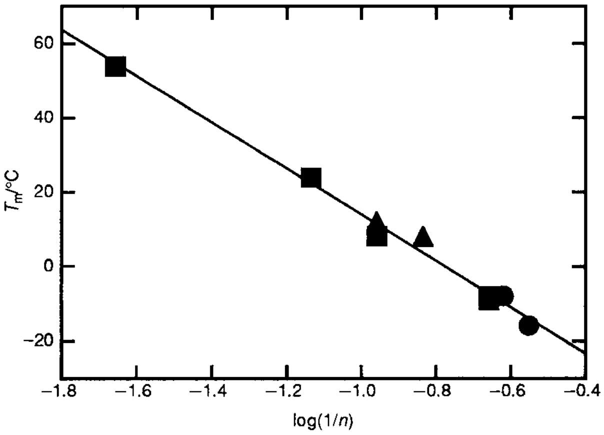

Fig. 2 Dependence of crystalline melting point, T_m, on average E-sequence length, n, for (●) $E_nC_3E_n$ prepolymers and polymers, (■) conventional PEG and (▲) POMOE prepared from conventional PEG.

DSC curves for quenched samples of representative polymers are shown in Fig. 4. Values of T_g, T_m, and $\Delta_{fus}H$ determined by DSC are given in Table 2. Glass transition temperatures are comparable to those of conventional POMOE. The DSC curves of polymers based on $E_4C_3E_4$ exhibited values of T_m in the range −5 to −8 °C and $\Delta_{fus}H$ in the range 34–40 J g^{-1}, similar to the prepolymer. For comparison, results are also included for P200, which has an E-sequence length comparable to that of $E_4C_3E_4$. P200 as prepared did not exhibit a melting peak, but after annealing the sample at −20 °C for 3 h results were obtained similar to those for polymers based on $E_4C_3E_4$.

The DSC curve of a polymer of $E_3C_3E_3$ gave a value of T_m of −16 °C, similar to the precursor, and a very small melting endotherm. The T_m values for the polymers can be correlated with the E-sequence length (Fig. 2), as has been observed previously for oxymethylene-linked polymers.[8] Compared to perfectly crystalline poly(oxyethylene) ($\Delta_{fus}H^\circ = 160$ J g^{-1} at −20 °C),[20] the degree of crystallinity of $P(E_4C_3E_4)$ was about 25%, whilst that of $P(E_3C_3E_3)$ was little more than 1%. As

Table 2 Glass transition temperatures, T_g, crystalline melting points, T_m, and enthalpies of fusion, $\Delta_{fus}H$, determined by DSC for samples of prepolymers, polymers and networks

Type	Sample	T_g/°C	T_m/°C	$\Delta_{fus}H$/J g^{-1}
Prepolymer	$E_4C_3E_4[2]$	−74	−8	36
Prepolymer	$E_3C_3E_3$	−76	−16	29
Polymer	$P(E_4C_3E_4[1])$	−66	−8	39
Polymer	$P(E_4C_3E_4[2])$	−66	−7	38
Polymer	$P(E_4C_3E_4[3])$	−66	−5	41
Polymer	$P(E_4C_3E_4[3])(2)$	−68	−8	34
Polymer	P200[a]	−67	None	None
Polymer	P200[b]	−66	−9	33
Polymer	$P(E_3C_3E_3)$	−67	−16	2
Crosslinkable polymer	$P(E_4C_3E_4[2])$-M5	−64	−7	39
Crosslinkable polymer	$P(E_3C_3E_3)$-M5	−67	−17	Almost zero
Network	$P(E_4C_3E_4[2])$-M5-N	−65	−8	35
Network	$P(E_3C_3E_3)$-M5-N	−66	−16	<1

[a] Sample as prepared. [b] Sample annealed by maintaining at −20 °C for 3 h before quenching to −100 °C. Estimated uncertainties are: T_g and T_m, ±3 °C and $\Delta_{fus}H$, ±5 J g^{-1}.

Table 3 Loading of KOH in oxymethylene-linking polymerizations and molecular characteristics of products

Polymer	KOH : glycol	M_{pk}/g mol^{-1} (GPC)	E : C_3 (NMR)	mol% MPD (NMR)
$P(E_4C_3E_4[1])$	8	65 000	—	—
$P(E_4C_3E_4[2])$	27	130 000	9	—
$P(E_4C_3E_4[3])$	22	78 000	10	—
$P(E_4C_3E_4[3])(2)$	41	80 000	—	—
$P(E_3C_3E_3)$	28	95 000	7	—
P400	8	100 000—200 000	—	—
P300	16	70 000	—	—
P200	8.8–10.7	38 000–54 000	—	—
$P(E_4C_3E_4[2])$-M5	27	110 000	—	4.0
$P(E_3C_3E_3)$-M5	28	62 000	—	4.9
P200-M5	8	45 000	—	4.8

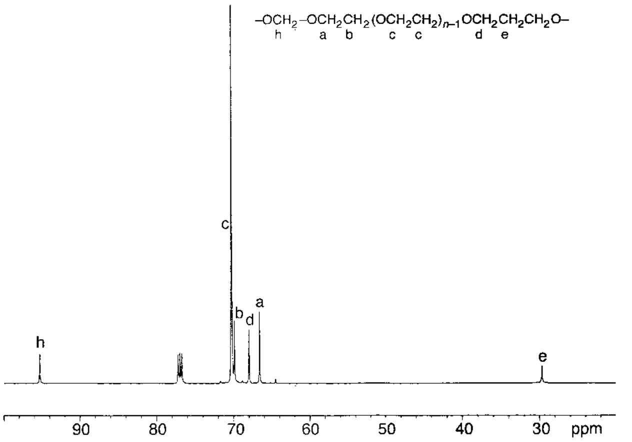

Fig. 3 ^{13}C NMR spectrum of polymer $P(E_4C_3E_4[2])$.

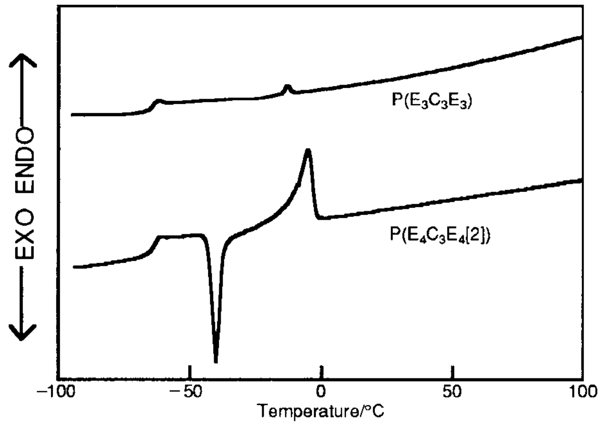

Fig. 4 DSC curves for quenched samples of oxymethylene-linked polymers $P(E_3C_3E_3)$ and $P(E_4C_3E_4[2])$.

shown below, the crystallinity of the compounded polymer electrolytes was in most cases essentially zero. Consequently, the crystallinity of the salt-free polymer was not investigated further.

Networks

Networks were characterised by mechanical properties, swelling behaviour and DSC. Plots of nominal stress, σ, against strain function $(\lambda-\lambda^{-2})$ are shown in Fig. 5, from which values of shear modulus, G, were obtained, which are listed in Table 4. The value of polymer volume fraction, ϕ_2, in the water-swollen network is given for $P(E_3C_3E_3)$-M5-N in Table 4.

Values of crosslink density, c_c, determined from G, are given in Table 4. For $P(E_3C_3E_3)$-M5-N an identical value was obtained from swelling measurements. Values of molar mass of network chains, M_c, are also listed in Table 4, together with the molar mass between crosslinks, $M_=$, calculated on the basis of the number of double bonds incorporated (determined by NMR), assuming that all take part in crosslinking. For $P(E_3C_3E_3)$-M5-N there is good agreement between M_c and $M_=$, but for $P(E_4C_3E_4[2])$-M5-N it appears that more crosslinking occurred than expected from the unsaturation content. This suggests that there was some crosslinking by hydrogen abstraction in the latter case.

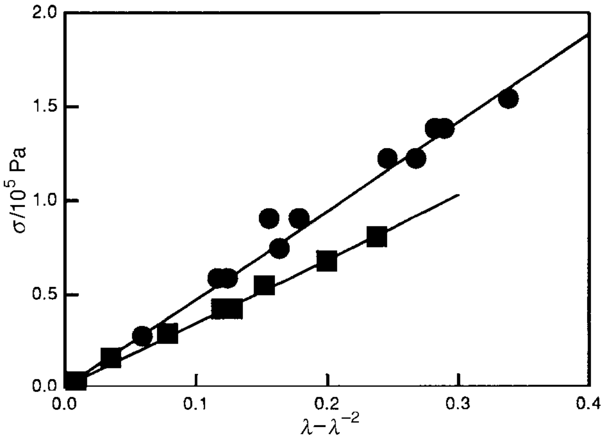

Fig. 5 Plot of nominal stress *versus* strain function for networks (●) $P(E_4C_3E_4[2])$-M5-N and (■) $P(E_3C_3E_3)$-M5-N.

Values of T_g, T_m, and $\Delta_{fus}H$ determined by DSC are given in Table 2. Networks have very similar thermal characteristics to the precursor polymers. The degree of crosslinking was not so high as to raise T_g or to suppress the crystallinity of the polymer.

Polymer electrolytes

Linear polymer electrolytes were prepared from $P(E_4C_3E_4[3])$ and $P(E_3C_3E_3)$, and network electrolytes from $P(E_4C_3E_4[2])$-M5 and $P(E_3C_3E_3)$-M5, with $LiClO_4$ concentrations corresponding to O : Li = 25 and O : Li = 70 [*ca.* 0.91 mol (kg polymer)$^{-1}$ and 0.32 mol (kg polymer)$^{-1}$, respectively]. DSC curves for quenched samples are shown in Fig. 6, where they can be compared with the corresponding curves for polymer without salt. Values of T_g, T_m, and $\Delta_{fus}H$ determined by DSC are given in Table 5. For comparison, data are also given for polymer electrolytes based on oxymethylene-linked PEG200. Electrolytes with O : Li = 25 were amorphous, and those at the lower salt concentration exhibited reduced crystallinity as compared to the saltless polymer. An increase in T_g with increasing salt concentration was observed, as is commonly found for other polymer–salt mixtures.[1–4,10,12,21–23]

Results of conductivity measurements as a function of temperature are presented as Arrhenius plots in Fig. 7a for samples with O : Li = 25 and in Fig. 7b for samples with O : Li =

Table 4 Network characteristics

Network	G/MPa (mechanical)	ϕ_2 (swelling)	c_c/mol dm^{-3} (mechanical)	(swelling)	M_c/g mol^{-1}	$M_{=}$/g mol^{-1} (NMR)
P($E_4C_3E_4$[2])-M5-N	0.46	—	0.19	—	5900	11 000
P($E_3C_3E_3$)-M5-N	0.32	0.11	0.13	0.13	8500	8000

Estimated uncertainties are ±20%.

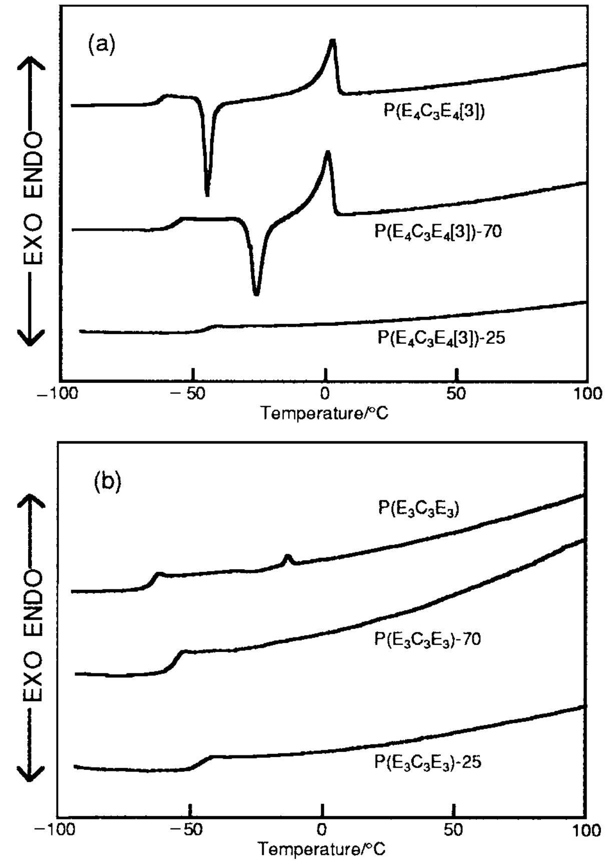

Fig. 6 DSC curves for quenched samples of oxymethylene-linked polymers and electrolytes based on (a) $E_4C_3E_4$[3] and (b) $E_3C_3E_3$.

Table 5 Glass transition temperatures, T_g, crystalline melting points, T_m, and enthalpies of fusion, $\Delta_{fus}H$, determined by DSC for quenched samples of linear and network polymer electrolytes

Type	Sample	T_g/°C	T_m/°C	$\Delta_{fus}H$/J g^{-1}
Linear	P($E_4C_3E_4$)[3])-25	−47	None	0
Linear	P($E_4C_3E_4$)[3])-70	−60	−2	34
Linear	P($E_3C_3E_3$)-25	−47	None	0
Linear	P($E_3C_3E_3$)-70	−58	−19	Almost zero
Linear	P200-25	−47	None	0
Linear	P200-70	−60	None	0
Network	P($E_4C_3E_4$[2])-M5-N25	−49	None	0
Network	P($E_4C_3E_4$[2])-M5-N70	−57	−5	10
Network	P($E_3C_3E_3$)-M5-N25	−46	None	0
Network	P($E_3C_3E_3$)-M5-N70	−58	None	0
Network	P200-M5-N25	−41	None	0
Network	P200-M5-N70	−56	None	0

Estimated uncertainties are: T_g and T_m, ±3 °C and $\Delta_{fus}H$, ±5 J g^{-1}.

70. Network electrolytes exhibited similar conductivities to their linear counterparts. Data for polymer electrolytes based on oxymethylene-linked PEG200 are included in Fig. 7 for comparison. At the higher salt concentration, conductivities for electrolytes prepared from $E_nC_3E_n$ prepolymers are higher, at a given temperature, than those based on PEG200. One might have expected $E_nC_3E_n$-based polymer electrolytes to have a similar conductivity to oxymethylene-linked PEG200 electrolytes, since there is little crystallinity in either case. The improved conductivity of the $E_nC_3E_n$-based polymer electrolytes may possibly relate to the higher molar masses of the polymers (see Table 3).

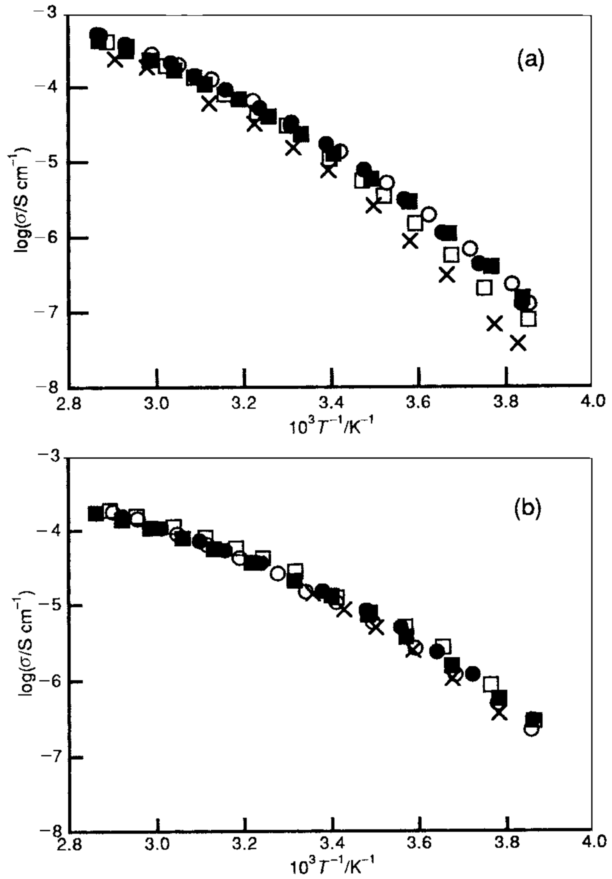

Fig. 7 Arrhenius plots (log conductivity *versus* reciprocal temperature) for linear polymer electrolytes based on (○) P($E_3C_3E_3$), (□) P($E_4C_3E_4$)[3] and (×) P200, and network electrolytes based on (●) P($E_3C_3E_3$)-M5-N and (■) P($E_4C_3E_4$[2])-M5-N, with (a) O:Li=25 and (b) O:Li=70.

Conclusions

Prepolymers incorporating a spacer group may be prepared by anionic polymerization of ethylene oxide utilising an alkanediol as initiator. Oxymethylene-linking polymerization of such a prepolymer gives a polymer with a degree of polymerization similar to that which can be achieved using conventional polyethylene glycol of similar molar mass, but exhibiting crystallization behaviour typical of a polymer with a reduced E-sequence length. Inclusion of unsaturated groups within the polymer chain enables networks to be prepared. Linear and network polymer electrolytes, formed by incorporation of a lithium salt, have conductivities comparable to or higher than those obtained with oxymethylene-linked PEG200.

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