Synergistic effects in cross-linked blends of ion-conducting PEO-/PPO-based unsaturated polyesters

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Received: 12 March 2021 / Revised: 7 June 2021 / Accepted: 16 June 2021 / Published online: 8 July 2021
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Abstract
Ion-conductive unsaturated polyesters (UP) were synthesised from poly(ethylene oxide) \((X_n = 9, 13, 22, 90)\) or poly(propylene oxide) \((X_n = 7, 13, 20, 34, 68)\) and maleic anhydride. Subsequently, the polyesters were doped with LiClO_4 and cross-linked with styrene using a redox initiator. For PEO-based polyesters, the minimum resistivity is found at an O/Li⁺ molar ratio of 50/1. In contrast, more lithium is required to reach the minimum when using PPO \((O/Li^+ = 10/1)\). Unlike the PEO-based polyesters, cross-linking of the PPO types gives rise to decreasing resistivities at increasing molecular weight. This correlates well with the transverse proton relaxation time determined by single-sided NMR, which is an indicator of the chain mobility. The cross-linking reaction of these UP with styrene exactly follows the predictions based on the copolymerisation parameters and is, therefore, not dependent on the ratio of styrene to UP double bonds as previously reported. Due to the opposing effects of the molecular weight on the ion conductivity of PEO- and PPO-based UP, 1:1 blends of short-chain PPO and long-chain PEO polyesters were cross-linked with styrene. The resulting networks showed a resistivity of 4 kΩm \((\sigma = 2.5 \times 10^{-4} \text{ S m}^{-1})\), which is 5 times lower than the pure PEO and 3 times lower than the pure PPO materials.

Keywords Ion-conductive polyester · Unsaturated polyester · Impedance spectroscopy · Polymer blends · Polycondensation

Introduction
Polymer electrolytes are gaining increasing importance in the everyday life as seen by the massive use of diverse electrochemical devices such as lithium ion batteries for portable electronics and cars, [1] or electrochromic devices such as flat screens, smart windows [2] or monitoring systems. [3] These applications are based on the ability of electrolytes to serve as a medium for charge transfer. [4] The transport of ions through solid polymer electrolytes (SPE) depends on the enthalpy of solvation and the rate of dissociation of the ionic species as well as the mobility of the solvated ions within the polymer matrix. [5, 6] The solvation of low lattice-energy salts gives rise to the formation of polymer-salt complexes. [7–9] Therefore, the presence of heteroatoms (usually O, N, S), which enable the solvation through interaction of their lone pairs with “free” cations, is a prerequisite for sufficient ionic conductivity. [10–14] The dissolved cations can subsequently move through the polymer electrolyte from one complexing site to another by a hopping process. [9, 14–17] High chain flexibility increases the segmental motion and improves the ion conductivity. Therefore, ion transport is faster in the amorphous polymer phase, [18–20] and the conductivity of SPE is significantly influenced by the glass transition temperature of the polymer. [4, 10, 11, 21] In addition, the hopping process is also affected by the location and distance between the coordination centres. [22]

The most widely studied polymer for SPE with conductivities of approximately \(10^{-7}–10^{-4} \text{ S cm}^{-1}\) at ambient temperature is poly(ethylene oxide) (PEO). [20, 23, 24] PEO is a good complexing agent for lithium salts, albeit it has a rather low dielectric constant \((\varepsilon = 5)\). [25] However, PEO tends to crystallise already at intermediate molecular weights \((> 600 \text{ g mol}^{-1})\) at room temperature, which significantly decreases the conductivity and therefore limits its usage. [25–27]

One approach to suppress crystallisation and to obtain amorphous, highly conductive polymers is to modify the molecular structure. Literature focusses on changing the \(T_g\), the dielectric constant, the ion solvation, salt dissociation, or ion hopping rates [28] by using polymer blends and copolymers,
unsaturated polyesters. [40] Since cross-linking can potentially suppress the crystallisation of PEO, the question, thus, arises how increasing the molecular weight of the polyester block and to what extent substituting PEO for PPO affects the performance of these systems. Herein, we present the combination of the conductive properties of PEO-based UP with the structural properties of PPO-based UP, which appear to exhibit a synergistic effect in terms of the ionic conductivity.

**Experimental**

**Materials**

Poly(ethylene glycol) \( (M_w = 400 \text{ g·mol}^{-1}, \text{Carl Roth GmbH & Co. KG}) \); PEO \( (M_w = 600 \text{ g·mol}^{-1}, \text{Merck}) \); PPO \( (M_w = 1000 \text{ g·mol}^{-1}, \text{Calbiochem}) \); poly(propylene glycol) \( (M_w = 2000 \text{ g·mol}^{-1}, \text{Merck}) \); PEO-PPO-PEO \( (M_w = 4000 \text{ g·mol}^{-1}, \text{Sigma-Aldrich Chemistry}) \); poly(ethylene carbonate) \( (M_w = 425 \text{ g·mol}^{-1}, \text{Sigma-Aldrich}) \); polycarbonate \( (M_w = 725 \text{ g·mol}^{-1}, \text{Sigma-Aldrich}) \); poly(trimethylene carbonate) \( (M_w = 1200 \text{ g·mol}^{-1}, \text{Sigma-Aldrich}) \); maleic anhydride \( (\text{Alfa Aesar}) \); and anhydrous LiClO\(_4\) \( (\text{Alfa Aesar}) \).

**Synthesis of unsaturated polyesters**

The unsaturated polyesters were prepared from poly(ethylene glycol) (PEO) or poly(propylene glycol) (PPO) with maleic anhydride in the presence of \( p \)-toluenesulfonic acid monohydrate as catalyst. The reactants were used equimolarly only for determining the reaction kinetics. In other cases the molar ratio of reactants was adjusted to a theoretical degree of polymerisation of 6. Details of the sample compositions are given in Table S1 in the Supplementary information. For all experiments, the reactants were dissolved in toluene \( (c = 0.07 \text{ mol/l}) \) in a round bottom flask, and the polycondensation was performed at 140 °C under nitrogen atmosphere for 24 h using a Dean–Stark apparatus. The conversion was determined by titration with 0.1 M KOH using phenolphthalein as an indicator. For that, the solvent was evaporated, and 0.2 g polyester was dissolved in acetone and 3 drops of 0.1 M phenolphthalein solution were added. The reaction kinetics was determined in the same way by titration of 1 ml polyester solution.

**Curing of UP with styrene**

The unsaturated polyesters \( (\text{e.g. } 2.00 \text{ g for } 50\text{E}_0) \) were mixed with 1 M LiClO\(_4\) solution in acetonitrile to obtain the desired O to \( \text{Li}^+ \) ratios \( (\text{e.g. } 0.720 \text{ ml, } 0.730 \text{ mmol, for } 50\text{E}_0) \) with a
ratio of 50/1). After obtaining a homogeneous solution, acetonitrile was removed by lyophilisation.

The mixture containing unsaturated polyester and LiClO₄ were mixed with the desired amount of styrene (e.g. 600 mg, 5.70 mmol, for 30 wt% using 50E₉) at 60 °C. After that, methyl ethyl ketone peroxide (MEKP) (e.g. 78.0 mg, 120 μmol for 3 wt%) and cobalt(II) 2-ethylhexanoate solution (e.g. 39.0 mg, 700 μmol for 1.5 wt%) were added and cured at 60 °C overnight. All sample compositions are given in Table S2.

**Electrochemical impedance spectroscopy (EIS)**

Potentiostatic EIS measurements were performed using a PCI4/300 Gamry Potentiostat (C3 Prozess und Analysetechnik GmbH). Standard electroporation cuvettes (a = 4 mm) with two aluminium oxide electrodes (19×8 mm) were filled with the liquid Li-doped polyester resin, and the mixture was fully cured at 60 °C. The cured polyester was analysed by impedance measurements recorded in a frequency (f) range of 0.01 Hz–10 MHz with an ac voltage of 141 mV at room temperature. The electrolyte resistance is calculated by fitting an equivalent circuit model for systems containing blocking electrodes (Fig. 1).

**Differential scanning calorimetry**

DSC measurements were performed on a 206 Phoenix (Netzsch) in aluminium crucibles operating in a temperature range from −80 to 150 °C under nitrogen atmosphere. The dynamic measurements were carried out using an empty aluminium crucible as reference. All samples were first heated from room temperature to 150 °C and cooled down to −80 °C. In a second run, the sample was reheated in steps of 10 K/min to 150 °C and cooled down to −22 °C. The procedure was then repeated with a heating rate of 3 K/min.

**Results and discussion**

The unsaturated polyesters are prepared by acid-catalysed polycondensation of polyetherdiols with maleic anhydride (MSA) (Fig. 2). The theoretical degree of polymerisation was adjusted to 6 by using a calculated excess of the diol. All types of polyesters were doped with lithium perchlorate to achieve ion conductivity and then cross-linked (cured) by radical copolymerisation with styrene using methyl ethyl ketone peroxide (MEKP) and cobalt(II) 2-ethylhexanoate (Co-Oct) as redox initiator to increase the mechanical stability [40].

The sample identifiers are explained in Table 1. For unsaturated polyesters that are not cross-linked with styrene, the identifier simply refers to the amount of the repeat units; e.g. E₉ refers to a polyester made from PEO with 9 EO repeat units and MSA. For the cross-linked samples containing LiClO₄, the identifier is, e.g. 50E₉, where the first number specifies the numerical ratio of the repeat units to Li⁺, in this case 50:1. An additional italic letter characterises a blend, e.g. 17BE₄₅P₇ being a blend of E₄₅ and P₇ with an O/Li⁺ ratio of 17. A detailed sample composition is given in Table S1 for the polycondensation reaction and Table S2 for the curing parameters.

The polycondensation of the pure PEO or PPO with maleic anhydride to give E₉ and P₇ (Fig. 1A, B) was monitored over time using the acid number (Supplementary Figs. S1, S2), and the results were fitted using a second-order kinetics (Supplementary Figs. S3, S4). The first phase in the reaction is the nucleophilic opening of the cyclic anhydride by the diol component and occurs so fast compared to the subsequent acid-catalysed esterification (second phase) that it is usually not directly observed. The second phase nicely obeys the second-order kinetics up to a conversion of 89% for E₉ and 84% for P₇ at 4500 min. Table S3 lists the second-order rate constants. As previously reported, the reaction rate decreases for both PEO and PPO with increasing molecular weight (Fig. 3) due to the increased viscosity of the reaction mixture and the lower mobility of the higher molecular weight reactants [61]. Generally, the rate constants for PPO are approximately
2–3 times lower than those for PEO at comparable molecular weights. One reason could be that the PPO chain bears at one end a secondary hydroxyl group, which is sterically more hindered than the primary ones of PEO.

The unsaturated polyesters are then doped with LiClO₄ to cause ion conductivity and, with regard to future applications as sensor materials, cross-linked with styrene in order to increase the mechanical stability [40]. The styrene polymerisation was found to go to completeness, as IR spectroscopy did not show any signs of residual monomer evidenced by the absence of the characteristic styrene bands at ν = 778, 912, and 1296 cm⁻¹. Differential scanning calorimetry (DSC) measurements confirm this finding as no post-curing was found at higher temperatures (Supplementary Fig. 5).

The lithium concentration has an enormous influence on the electrical properties of polymer electrolytes and is usually reported as molar ratio of ether repeat units to Li⁺ ions (e.g., O/Li⁺). In analogy to low-molecular salt solutions, the resistivity of polymer electrolytes decreases with increasing Li⁺ content (increase of O/Li⁺) and passes a minimum beyond which the resistivity increases again. The occurrence of a minimum was assigned to a higher ion aggregation and an increased viscosity at higher salt concentrations. [5] This, in turn, reduces both the number of free ions and the ionic mobility simultaneously. The location of the maximum depends on the dielectric constant of the polymer and the temperature. A higher dielectric constant shifts the occurrence of ion pairing to higher salt concentrations, similar to higher temperatures which reduce the solution viscosity. [4] For lithium perchlorate–doped pure PEO, the minimum was found to be O/Li⁺ = 50 [23] and this was also found for the PEO-based UP which is consistent with previously reported literature [39, 40, 62].

Similar to PEO, the resistivity of cross-linked PPO systems decreases with increasing Li⁺ content and passes a minimum, which was reported to be 25:1 for isocyanate cross-linked systems when using LiClO₄ as dopant. [31–33, 63] In contrast to PEO, PPO is a weaker solvent for lithium salts due to a smaller dielectric constant caused by the methyl group protruding from the ether PPO backbone. The presence of a methyl group results in a larger diameter of helical secondary

![Fig. 2 Polycondensation reaction of maleic anhydride (MSA) and PEO, PPO](image)

![Fig. 3 Rate constants for the polycondensation of maleic anhydride with PEO (squares) E₉₋₉₁ and PPO (triangles) P₇₋₃₄ as function of the molecular weight](image)

| Table 1 | Sample composition of cured unsaturated polyesters with related O/Li⁺ ratio |
|---------|---------------------------------------------------------------|
| Abbreviation | Explanation |   |
| B       | Blend |   |
| First number O/Li⁺ ratio |   |   |
| Subscript number (s) Repeat units in ether blocks |   |   |

![Image](image)
structure wrapping around the lithium ions. [25, 64] As a result, more ions are needed to overcrowd the helix in comparison to PEO and hamper the movement [5]. For styrene-cured PPO polyesters, the minimum was found at a molar ratio O/Li\(^+\) = 10 (Fig. 4).

Compared to similar isocyanate cross-linked PPO networks (\(\sigma = 10^{-7}\) S cm\(^{-1}\)), the conductivity of cross-linked PPO polyesters is ten times higher at \(\sigma = 10^{-6}\) S cm\(^{-1}\) and, thus, in the conductivity range reported for pure PPO (10\(^{-5}\) to 10\(^{-6}\) S cm\(^{-1}\)) [31, 32].

With regard to the molecular weight, the resistivity of PEO-based ion-conducting polyesters at O/Li\(^+\) = 50 (50Ex) was found to increase with molecular weight (Fig. 5, squares). The increase in resistance is moderate for a small number of repeat units 50E9–22. The exception is 50E13 which represents the minimum. The significant increase in resistivity of the cross-linked UP 50E45 is, thus, assigned to crystallisation of the higher molecular weight polyesters, which hampers the movement of ions. In line with this, the cross-linked 50E9, 50E13, and 50E22 have macroscopically the appearance of rubber erasers, while 50E45 and 50E91 feel like compact powders. This observation is consistent with previously studied non-cross-linked, lithium-doped PEO polymer electrolytes, for which the resistivity decreases with increasing number of repeat units up to 18. [19] Beyond that, the resistivity increases because of higher crystallinity and finally levels off at 91 repeat units. [11, 19]

In contrast, the resistivity of lithium-doped PPO-based UP (10P7–69) was found to decrease with increasing molecular weight from 15.43 k\(^\Omega\) m for 10P7 down to 194.3 \(\Omega\) m for 10P69 (Fig. 5, triangles). On the molecular level, the movement of the ions along the chain (intrachain hopping) is faster than the transition from one chain to another (interchain hopping). [1, 15, 65] Increasing the molecular weight of the ether block should, therefore, allow the ions to span greater distances along the same chain rather than having to undergo time-consuming interchain hopping. However, this effect is normally counteracted by the increased viscosity at high molecular weights, which hinders ion movement. Although all unsaturated polyesters (P7–69) are liquid, their viscosity increases with increasing molecular weight (Supplementary Fig. 6) and, thus, the opposite behaviour was expected. To get more insight into the 10P\(_y\) system, single-sided nuclear magnetic resonance was used to measure the amplitude-weighted average of the transverse proton relaxation time \(\langle T_2 \rangle\), which correlates with the chain mobility. In brief, the transverse relaxation of exited protons can be approximated by a sum of exponential functions (Eq. 1) and from this, \(\langle T_2 \rangle\) is calculated by integrating the normalised echo sum over time (Eq. 2). [66–68]

\[
s(t) = \sum A_i e^{-\frac{t}{\tau_i}} \tag{1}
\]

\[
\int_0^\infty \frac{s(t)}{s(0)} dt = \sum \omega_i T_{2,i} = \langle T_2 \rangle \tag{2}
\]

with \(\omega_i = \frac{A_i}{A_0}\) = relative amplitudes of the components.

In general, lower \(\langle T_2 \rangle\) values indicate lower average chain mobility and vice versa. However, the effective transversal relaxation time is not an absolute measure for the chain mobility and comparisons can only be made within a group of samples. For example, the soft rubber–like PEO-based polyesters 50E22 exhibit \(\langle T_2 \rangle\) times of approximately 2.5 ms, similar to the hard, rubber-like PPO-based polyester 10P34 at approximately 3 ms (Fig. 6A and B).

For PEO-based polyesters, \(\langle T_2 \rangle\) decreases with increasing molecular weight, indicating a decrease in the chain mobility (Fig. 6A, squares). At the same time, the resistivity increases (Fig. 6A, bars), which is in accordance with the general
theory. [5] In contrast, for the styrene-cured PPO-based polyesters 10Py, \( \langle T_2 \rangle \) increases with increasing molecular weight indicating higher chain mobility despite the increased viscosity of the uncured polyesters (Fig. 6B, squares). This effect is additionally supported by a change in the glass transition temperature. DSC measurements showed the glass transition temperature to decrease linearly with increasing molecular weight of the PPO block (Supplementary Fig. 7) indicating the onset of cooperative segmental motion to shift to lower temperatures.

However, there seems to be no simple correlation between \( \langle T_2 \rangle \) and the resistivity, as other material properties, such as the texture, may affect \( \langle T_2 \rangle \). This can be seen by comparing 10P34 and 10P69 (Fig. 6B): the increase in \( \langle T_2 \rangle \) is much less pronounced than the decrease in resistivity. The reason could be that 10P7, 13, 20, 34 are rubber-like, while 10P69 has the consistency of a waxy paste.

The question arises if the increase in chain mobility and with it the decrease in resistance of the 10Py samples is caused by incomplete cross-linking. It was previously reported that UP chains are typically connected by three styrene units, while 3–7% of the UP double bonds remain unreacted. Additional homopolymerisation of styrene was only found to occur, if the molar ratio of styrene to UP double bonds exceeds 9. [69, 70] A prevalence of styrene homopolymerisation would lead to both longer poly(styrene) segments between the UP chains and a blend of poly(styrene) and the UP. In the present 10Py series, the mass ratio of styrene to the unsaturated polyester is kept constant. Thus, the molar ratio of styrene to UP double bonds (i.e. the MSA units) increases linearly (Supplementary Fig. S8) from 1.74 for the 10P7 sample to 14.1 for 10P69 (Table 2).

Successful cross-linking can be monitored by the C-H out of plane normal vibrations of the phenyl groups directly attached to the polyester chain at 763 cm\(^{-1}\), which marks the cross-linking point at the transition from UP to poly(styrene).

The curing reaction can additionally be followed by the C=C stretching vibration of the unsaturated polyester at 1646 cm\(^{-1}\). In addition, the vibration at 700 cm\(^{-1}\) representing the poly(styrene) chain in both the homopolymer and longer segments between the UP chains needs to be considered.

When comparing 10P7 (styrene/MSA = 1.74) with 10P13, 20, 34, it is noticeable that very low styrene/MSA ratios give rise to very few cross-linking points (Fig. 7, squares) and leave a larger number of unreacted double bonds in the polyester backbone (Fig. 7, circles). At the same time, the poly(styrene) vibration is less pronounced. Since literature postulates an average of 3 styrene units forming the cross-link, every other UP double bond should statistically remain in 10P7. With increasing styrene/MSA ratio, the number of unreacted double bonds decreases, while the number of cross-linking points and the poly(styrene) vibration increase. This is in accordance with the mechanism of radical copolymerisation. However, 10P69 exhibits an excessive signal of poly (styrene), whereas the other two vibrations change only slightly compared to 10P34. Taking into consideration that maleic anhydride as a monomer is incorporated into the UP as fumaric diester, the copolymerisation during the curing reaction can be

| Sample  | MSA/mol  | Styrene/mol | Styrene/MSA |
|---------|----------|-------------|-------------|
| 10P7    | 3.31·10\(^{-3}\) | 5.76·10\(^{-3}\) | 1.74        |
| 10P13   | 2.08·10\(^{-3}\) | 5.76·10\(^{-3}\) | 2.78        |
| 10P21   | 1.30·10\(^{-3}\) | 5.76·10\(^{-3}\) | 4.42        |
| 10P34   | 0.80·10\(^{-3}\) | 5.76·10\(^{-3}\) | 7.18        |
| 10P69   | 0.41·10\(^{-3}\) | 5.76·10\(^{-3}\) | 14.1        |

\(^1\) Amount of maleic anhydride within 2 g of unsaturated polyester
\(^2\) Equivalent to 30 wt% for the curing reaction with 2 g of unsaturated polyester
represented by styrene (monomer 1) and diethyl fumarate (monomer 2). For this system, the copolymerisation parameters are \( r_1 = 0.318 \) and \( r_2 = 0.013 \). According to the definition of the copolymerisation parameters, values < 1 imply the preference for heteropolymerisation. However, for styrene, the value of \( r_1 = 0.318 \) indicates that styrene homopolymerisation is also possible. In contrast, the value for diethyl fumarate virtually rules out any fumarate homopolymerisation. Since the product \( r_1 \cdot r_2 \approx 0 \), the copolymerisation proceeds in a mostly alternating fashion. The amount of styrene incorporated during the cross-linking reaction with the UP can be determined by IR spectroscopy using the bands described above. Comparing these experimental values with the theoretical amounts predicted by the corresponding copolymerisation diagram provides an exact match (Fig. 8). This leads to the assumption that homopolymerisation to “free” polystyrene does not occur even for 10P_69 and even though the calculated styrene to MSA ratio is greater than 14. Softening of the 10P_6 polyester with increasing molecular weight is therefore not due to incomplete cross-linking. High \( \langle T_2 \rangle \) values, on the other hand, in combination with decreasing \( T_g \), suggest that more flexible networks with larger mesh sizes are formed.

It has previously been shown that the resistance for 50E_4 increases with increasing chain length \( x \) due to greater crystallinity (cf. Fig. 5 squares) and the opposite behaviour is found for 10P_3 (cf. Fig. 5 triangles). The question thus arises if blending liquid P_7 with the E_45 and subsequent cross-linking can form networks with larger mesh size and suppress the crystallisation of the PEO, which should both cause a decrease in the resistivity of such blends.

Increasing the P_7 content in BE_45P_7 leads to a strong decrease in resistivity which passes a minimum at a mass fraction of 0.5 (Fig. 9A) after that the resistivity further increases. At the minimum, the resistivity is approximately 1/5 of the value of pure 50E_45 and approximately 1/3 of that of pure 10P_7. It should be noted that the resistance of 23BE_43P_7 falls below the lower limit predicted by the rule of mixtures already at \( w > 0.2 \) (Supplementary Fig. S9). The degree of crystallinity also decreases with increasing amount of 10P_7 and reaches 0 at \( w = 0.5 \), which means that from this point on, the materials are fully amorphous (Fig. 9B). As expected, the opposite behaviour is found for the \( \langle T_2 \rangle \) values except for the pure 50E_45, which has higher \( \langle T_2 \rangle \) values due to its powdery texture. The \( \langle T_2 \rangle \) values increase up to \( w = 0.5 \) indicating the blends become more flexible as crystallisation is increasingly suppressed. Increasing the P_7 content to more than \( w = 0.5 \) results in an increased stiffness due to the formation of a denser, less flexible network consisting of more shorter chains (Fig. 9C). This is clearly reflected in the \( \langle T_2 \rangle \) and \( T_g \) values and negatively affects the resistance of the resulting polyester network. The increasing influence of P_7 on material properties can be observed by means of the glass transition temperatures, which remain almost constant at low P_7 contents (\( T_g \) approx. \(-45 °C \) at \( w < 0.4 \), followed by a jump at approx. \( w = 0.5 \) and a subsequent exponential increase to +5 °C at \( w = 1 \) (Fig. 9D).

**Conclusions**

In contrast to PEO-based unsaturated polyesters, the resistivity of cross-linked PPO systems decreases with increasing molecular weight, i.e. the conductivity increases for the PPO-based systems and decreases for the PEO-based ones. Despite the increased viscosity of the non-cross-linked precursors, networks formed by higher molecular weight PPO are more
flexible than the lower molecular weight representatives. This is due to the larger mesh sizes and the fully amorphous nature of PPO. In addition, pronounced intrachain hopping along high molecular weight chains as opposed to time-consuming interchain hopping between the shorter chains of low molecular weight networks can be presumed. Single-sided nuclear magnetic resonance spectroscopy was found to be a valuable tool to quickly and accurately assess the chain mobility within a given set of samples of comparable consistency. This correlates with the resistivity (and inversely with the conductivity) of the samples. Due to the different effects on the conductivity of the cross-linked samples by the monomer types and chain lengths, it is possible to optimise the ionic conductivity by targeted blending and cross-linking of lithium-doped PEO- and PPO-based unsaturated polyesters. The minimum resistivity of these networks is significantly below the lower limit predicted by the rule of mixtures. This indicates the importance of cross-linking, which sparks synergistic effects in the network. Apart from synergistic conductivity effects shown by the described cross-linked PEO-PPO network, a further advantage of these systems is the rubber elasticity and high tolerance of water as previously described. [40] These properties allow for widespread applications under mechanical stresses, under atmospheric conditions, or even in aqueous environments, which is problematic for standard ion-conducting systems. [76–80]

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11581-021-04149-z.

Code availability “Not applicable” for that section.

Author contribution All authors were involved in the conceptualisation. PS carried out the lab experiments, PS wrote the original draft and OW reviewed and edited the manuscript.

Funding Open Access funding enabled and organized by Projekt DEAL. The work was funded by the Federal Ministry of Economic Affairs and Energy through the ZIM programme (Zentrales Innovationsprogram Mittelstand) under Grant No. ZF2669716KM4.
**Data availability** The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Declarations**

**Ethics approval** “Not applicable” for that section.

**Consent to participate** All authors have given their consent to participation.

**Consent for publication** All authors have given their consent to publication.

**Conflict of interest** The authors declare no competing interests.

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