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 ($\text{O/Li}^+ = 10/1$). 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 $4 \text{ k}\Omega \text{ m}$ ($\sigma = 2.5 \cdot 10^{-4} \text{ S}\cdot\text{m}^{-1}$), 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} – $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ 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 ($\epsilon = 5$). [25] However, PEO tends to crystallise already at intermediate molecular weights ($> 600 \text{ g}\cdot\text{mol}^{-1}$) 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,

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[5] combs [29] and ladders. [22, 30] Of these, the use of copolymers in combination with poly(propylene oxide) seems to be a promising approach to reduce crystallisation. [22] However, the conductivities of pure PPO are significantly lower than those of PEO, because of its lower dielectric constant and the hindered complexation of Li^+ ions by methyl groups. [5, 31, 32]

Angel et al. first investigated block copolymers containing PEO_{25} and PPO_{31} doped with lithium iodide. The incorporation of PPO inhibits the crystallisation of PEO and leads to highly conductive polymer electrolytes. [1, 33] Furthermore, Khan et al. found that the conductivity more than doubles for blends of PEO ($M_w = 600,000$) with PPO ($M_w = 1025$) containing LiClO_4 , from $1.4 \cdot 10^{-6}$ to $3.55 \cdot 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ in comparison to pure PEO. [34] Also, for PEO_{20} - PPO_{70} - PEO_{20} triblock copolymers studied by Wang et al., the conductivity increases up to $8.9 \cdot 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at a O/Li^+ ratio of 8/1 at 30°C . [35]

A further approach to suppress crystallisation is the use of cross-linked polyethylene glycols. Cross-linking [36] can be accomplished either directly via isocyanates, [22, 32, 37] hyperbranched polymers [38], or by using unsaturated polyesters as precursors. [39] The latter offers the advantage that polycondensation tolerates the presence of water and oxygen and cross-linked polyesters are resistant to alkaline hydrolysis. In addition, polyesters are not as toxic as polyurethanes and, therefore, are more suitable for the use in structural health monitoring of infrastructural buildings. [40]

The use of carbonyl-coordinating polymers in the form of carbonates such as poly(ethylene carbonate) [41] or poly(trimethylene carbonate) [42] or polyesters such as poly(caprolactones) [43–45] or poly(lactic acids) has additional advantages due to the interaction between the Li^+ ions and the carbonyl function. High dielectric constants of these polymers lead to effective charge separation of the salts, which further results in high concentration of charge carriers [20, 30]. Although, the weaker coordination of Li^+ compared to polyethers leads to the formation of more ion pairs, which lowers the overall conductivity, the lithium ions are less immobilised. This causes faster ion transport (high Li^+ transport number) [41, 46]. The balance of ion coordination, segmental mobility, and ion pairing plays a key role in current research [13, 46] and can be tuned for example by the use of copolymers, [36, 42, 43, 47, 48] blends [49], or inorganic fillers [50–54]. Johansson et al. synthesised polyester/polycarbonate SPEs for high-temperature applications via UV radiation with good ionic conductivity $\sim 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ and long cycle periods [55].

There are some reports in literature on cross-linked networks based on unsaturated polyesters of PEO/PPO as well as blends of commercial UP with PEO and/or PPO, but mainly with the focus on the morphology, miscibility, and thermal properties. [56–60] In our previous paper, we studied the curing kinetics and impedance behavior of PEO-based

unsaturated polyesters. [40] Since cross-linking can potentially suppress the crystallisation of PEO, the question, thus, arises how increasing the molecular weight of the polyether 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) ($M_w = 400 \text{ g}\cdot\text{mol}^{-1}$, Carl Roth GmbH & Co.KG; $M_w = 600 \text{ g}\cdot\text{mol}^{-1}$, Merck; $M_w = 1000 \text{ g}\cdot\text{mol}^{-1}$, Calbiochem; $M_w = 2000 \text{ g}\cdot\text{mol}^{-1}$ and $M_w = 4000 \text{ g}\cdot\text{mol}^{-1}$, Sigma-Aldrich Chemistry), poly(propylene glycol) ($M_w = 425 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 725 \text{ g}\cdot\text{mol}^{-1}$ and $M_w = 1200 \text{ g}\cdot\text{mol}^{-1}$, Sigma-Aldrich; $M_w = 2000 \text{ g}\cdot\text{mol}^{-1}$, Aldrich Chemistry; $M_w = 4000 \text{ g}\cdot\text{mol}^{-1}$, Alfa Aesar), maleic anhydride (Alfa Aesar), *p*-toluenesulfonic acid monohydrate (Carl Roth GmbH & Co. KG), methyl ethyl ketone peroxide (Promox P211 TX, 35% in aliphatic solvents, Mühlmeier GmbH & Co. KG), cobalt(II) 2-ethylhexanoate (65 % in mineral spirits, Sigma-Aldrich), styrene (MERK), and anhydrous LiClO_4 (Alfa Aesar) were used as-received.

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 (e.g. 2.00 g for 50E₉) were mixed with 1 M LiClO_4 solution in acetonitrile to obtain the desired O to Li^+ ratios (e.g. 0.720 ml, 0.730 mmol, for 50E₉ with a

ratio of 50/1). After obtaining a homogeneous solution, acetonitrile was removed by lyophilisation.

The mixture containing unsaturated polyester and LiClO_4 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.

Fig. 1 Equivalent circuit for fitting the EIS response using blocking electrodes containing two constant phase elements (CPE) and an ohmic resistor (R) [25]

Single-sided NMR

Single-sided NMR measurements were performed on a PM5 NMR-Mouse® (Magritek) by tracing the spin-spin relaxation decay (T_2) using a Carr–Purcell–Meiboom–Gill (CPMG) sequence. The cured samples were placed on a glass slide (1.3 mm thickness) on top of the sensor, and the measurements were carried out at a sensitive volume of 200 µm. The number of scans was set to 512 with a repetition delay of 1.5 s, and the number of echoes was adjusted to 3000 to provide a good signal-to-noise ratio. The acquisition time per echo was set to 5 ms, and the NMR experiments were performed at 21 °C.

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 LiClO_4 , 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 E_x and P_y (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

Fig. 2 Polycondensation reaction of maleic anhydride (MSA) and PEO, PPO

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 LiClO_4 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 $\tilde{\nu} = 778$, 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 $\text{O/Li}^+ = 50$ [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 LiClO_4 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

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

Fig. 3 Rate constants for the polycondensation of maleic anhydride with PEO ((squares) E_{9-91}) and PPO ((triangles) P_{7-34}) as function of the molecular weight

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

With regard to the molecular weight, the resistivity of PEO-based ion-conducting polyesters at $O/Li^+ = 50$ ($50E_x$) was found to increase with molecular weight (Fig. 5, squares). The increase in resistance is moderate for a small number of repeat units $50E_{9-22}$. The exception is $50E_{13}$ which represents the minimum. The significant increase in resistivity of the cross-linked UP $50E_{45}$ is, thus, assigned to crystallisation of the higher molecular weight polyesters, which hampers the movement of ions. In line with this, the cross-linked $50E_9$, $50E_{13}$, and $50E_{22}$ have macroscopically the appearance of rubber erasers, while $50E_{45}$ and $50E_{91}$ 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 ($10P_{7-69}$) was found to decrease with increasing molecular weight from $15.43 \text{ k}\Omega \text{ m}$ for $10P_7$ down to $194.3 \text{ }\Omega \text{ m}$ for $10P_{69}$ (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

Fig. 4 The resistivity of styrene-cured PPO-based UP passes a minimum at $O/Li^+ = 10$, exemplary shown for XP_{13} measured at room temperature ($X = 2, 5, 10, 15, 30, 40, 50, 60, 80$)

Fig. 5 The resistivity of lithium-doped, styrene-cured unsaturated polyesters $50E_x$ ($O/Li^+ = 50$ (squares) $X = 9, 13, 22, 45, 90$) and $10P_y$ ($O/Li^+ = 10$ (triangles) $Y = 7, 13, 20, 34, 68$) as a function of the number of repeat units in the ether block. Note: the decrease in slope beyond $50E_{45}$ is due to the interruption of the y-axis at $40 \text{ k}\Omega \text{ m}$. In a continuous scale, the trend is linear

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 (P_{7-69}) 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 excited 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]

$$s(t) = \sum_i A_i e^{-\frac{t}{T_{2,i}}} \quad (1)$$

$$\int_0^\infty \frac{s(t)}{s(0)} dt = \sum_i \omega_i T_{2,i} = \langle T_2 \rangle \quad (2)$$

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 $50E_{22}$ exhibit $\langle T_2 \rangle$ times of approximately 2.5 ms, similar to the hard, rubber-like PPO-based polyester $10P_{34}$ at approximately 3 ms (Fig. 6 A 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

Fig. 6 Resistivity (solid bars) determined by electrochemical impedance spectroscopy and amplitude-weighted average of the proton relaxation time $\langle T_2 \rangle$ (squares) determined by single-sided nuclear magnetic

resonance of styrene-cured 50E_x (X = 9, 13, 22, 45, 90) (A) and 10P_y (Y = 7, 13, 20, 34, 68) (B) as a function of the molecular weight

theory. [5] In contrast, for the styrene-cured PPO-based polyesters 10P_y, $\langle T_2 \rangle$ 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 10P_{7, 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 10P_y 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 10P_y 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).

[71–74] 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 10P_{13, 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

Table 2 Molar ratios of styrene to maleic anhydride (MSA) in cured samples using O/Li⁺ = 10

Sample	MSA ¹ /mol	Styrene ² /mol	Styrene/MSA
10P ₇	3.31 · 10 ⁻³	5.76 · 10 ⁻³	1.74
10P ₁₃	2.08 · 10 ⁻³	5.76 · 10 ⁻³	2.78
10P ₂₁	1.30 · 10 ⁻³	5.76 · 10 ⁻³	4.42
10P ₃₄	0.80 · 10 ⁻³	5.76 · 10 ⁻³	7.18
10P ₆₉	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

Fig. 7 Development of three characteristic IR bands used to evaluate the cross-linking reaction for the 10P_y series (Y = 7, 13, 20, 34, 68): poly(styrene) at $\tilde{\nu} = 700 \text{ cm}^{-1}$ (triangles), double bond of the unsaturated polyester at $\tilde{\nu} = 1646 \text{ cm}^{-1}$ (circles) and cross-linking point at the transition from UP to PS at $\tilde{\nu} = 763 \text{ cm}^{-1}$ (squares)

represented by styrene (monomer 1) and diethyl fumarate (monomer 2). For this system, the copolymerisation parameters are $r_1 = 0.318$ and $r_2 = 0.013$. [75] 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 10P₆₉ and even though the calculated styrene to MSA ratio is greater than 14. Softening of the 10P_x 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_x increases with increasing chain length x due to greater crystallinity (cf. Fig. 5 squares) and the opposite behaviour is found for 10P_y (cf. Fig. 5 triangles). The question thus arises if blending liquid P₇ with E₄₅ 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.

Fig. 8 Calculated copolymerisation diagram of styrene and diethyl fumarate (green) with $r_1 = 0.318$ and $r_2 = 0.013$ and copolymer composition p (triangles) determined by IR spectroscopy for 10P₇₋₆₉

Increasing the P₇ content in BE₄₅P₇ 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 50E₄₅ and approximately 1/3 of that of pure 10P₇. It should be noted that the resistance of 23BE₄₅P₇ 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 10P₇ 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 50E₄₅, 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 P₇ 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 P₇ on material properties can be observed by means of the glass transition temperatures, which remain almost constant at low P₇ 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 $+5^\circ\text{C}$ 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

Fig. 9 Development of the (squares) resistance, (circles) degree of crystallinity, (diamonds) $\langle T_2 \rangle$ values and (triangles) glass transition temperature for 50E₄₅ and 10P₇ blends cured with styrene in dependence of the 10P₇ mass fraction (w) (9–75 BE₄₅P₇)

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 Innovationsprogramm 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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