

# Highly Conducting Lithium Polyelectrolytes Based on Maleic Anhydride–Styrene Copolymers

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Comblike polyelectrolytes comprising immobilized carboxylic anions and poly(oxyethylene) (OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub> side chains of various length were obtained from the reaction of appropriate lithium alcoholates with maleic anhydride–styrene alternating copolymers. These materials may be fabricated as films of ambient temperature conductivity in the range of 10<sup>−9</sup>–10<sup>−6</sup> S·cm<sup>−1</sup>, depending on the side-chain length. The conductivity values increase by 2–3 orders of magnitude after the addition of strong polar plasticizers such as dimethyl sulfoxide and propylene carbonate. A further increase in conductivity was observed after the complexation of carboxylic anions by BF<sub>3</sub>. On the basis of <sup>13</sup>C NMR studies and <sup>7</sup>Li NMR relaxation times of lithium carboxylates, it was found that the anion complexing agent reduces ion pairing in polyelectrolytes more effectively than cation-solvating solvents. The possible conduction mechanism in the solid and gel polyelectrolytes is discussed.

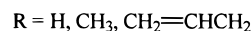
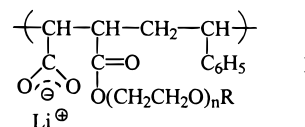
## Introduction

Since the early 1970s proton conducting polyelectrolytes have been intensively studied with respect to their application as solid electrolytes in fuel cells.<sup>1</sup> There are a number of commercially available membranes based on polymeric perfluorosulfonic acids, which saturated with water can reach conductivity levels of 10<sup>−2</sup>–10<sup>−1</sup> S·cm<sup>−1</sup> at the cell's operating temperature.<sup>2</sup> Many attempts were also undertaken to obtain highly conducting solid polyelectrolytes in the form of lithium salts for making safe lithium rechargeable batteries, which are one of the most promising candidates for the future power source system.<sup>2–15</sup> In these systems the role of the solvent solvating lithium cations was played by polyether macromolecules, particularly high molecular weight poly(ethylene oxide) or oxyethylene units incorporated into the polyelectrolyte structure. However, none of these electrolytes showed sufficient ionic conductivity to allow a reasonable current density in a solid-state battery. Conductivity of about 10<sup>−3</sup> S·cm<sup>−1</sup> is regarded now as a minimum practical value, while typical conductivity values of lithium polyelectrolytes are of the order of 10<sup>−7</sup>–10<sup>−11</sup> S·cm<sup>−1</sup>. The tight ion pairing and rigidity of macromolecules induced by the presence of an ionizable group attached to the polymer backbone are probably the main reasons for the low mobility of charge carriers in solid polyelectrolytes.

It can be expected that the conductivity of these polyelectrolytes would considerably increase after the addition of polar plasticizers capable of complexing lithium cations,<sup>13,14</sup> but this phenomenon was not systematically studied until now. It is known, however, that mixtures of polymers, polar organic solvents, and lithium salts are successfully applied as so-called gel electrolytes in plastic lithium–ion rechargeable batteries, which are currently of great interest commercially.<sup>16,17</sup> In such systems cations and anions are both mobile, although only cations take part in electrode reactions. Anions accumulate at the anode and become depleted at the cathode since they can be neither formed nor discharged at the electrodes, which limits the performance of electrochemical cells.

Gel electrolytes based on polymeric lithium salts should act as single cation conductors such as superionic glasses or crystalline solid conductors, preserving high flexibility of the polymer electrolytes.

In this paper we describe the conducting properties of solid and solvent-plasticized polyelectrolytes bearing immobilized carboxylic anions of the following structure:



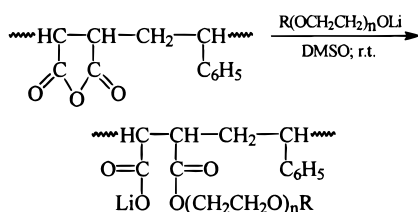
In some experiments the polyelectrolyte was additionally cross-linked by free-radical polymerization of the C=C bonds present in the side-chain terminal group (R = CH<sub>2</sub>CH=CH<sub>2</sub>) in order to improve the mechanical properties of the gels obtained. In studies of solid systems, attention was drawn to determining the effect of the oxyethylene side-chain length on the polyelectrolyte conductivity and flexibility. Dimethyl sulfoxide (DMSO) and propylene carbonate were used as solvents solvating the cation, and BF<sub>3</sub> as the agent complexing carboxylic anions. The thermal transitions of polyelectrolytes were studied by differential scanning calorimetry (DSC) and ionic conductivities were calculated on the basis of impedance spectroscopy data. The <sup>13</sup>C and <sup>7</sup>Li NMR studies were performed to obtain information about the complexing agent effect on the interaction between lithium cations and carboxylic anions.

## Experimental Section

**Materials.** Maleic anhydride, styrene, DMSO, propylene carbonate, and methyl alcohol were purified by double distillation over drying agents. The commercially available poly(ethylene oxide) glycols and monomethyl ethers of poly(ethylene oxide) glycols (Aldrich) were dried over molecular sieves in a

nitrogen atmosphere. The poly(ethylene oxide) glycols terminated by an allyl group were obtained by anionic polymerization of ethylene oxide in allyl alcohol according to the general method described elsewhere.<sup>18</sup> The average degree of polymerization was determined from the end-group analysis by means of <sup>1</sup>H NMR spectroscopy. Benzoyl peroxide was purified by crystallization. Boron trifluoride etherate (Aldrich), *n*-butyllithium in hexane (15 wt % Aldrich) and the photoinitiator Irgacure 184 (CIBA) were used as received.

**Electrolyte Preparation.** An alternating maleic anhydride and styrene copolymer of  $M_n = 3.2 \times 10^5$  was used as the initial polymeric product for the synthesis of electrolytes. The copolymer was obtained by free radical copolymerization carried out at 60 °C in toluene. A solution of the copolymer (0.5 g) in 15 cm<sup>3</sup> of DMSO was added dropwise to an equimolar amount of poly(ethylene glycol) alcoholate obtained from corresponding glycols and *n*-butyllithium (~25 mmol in 15 cm<sup>3</sup> of DMSO).



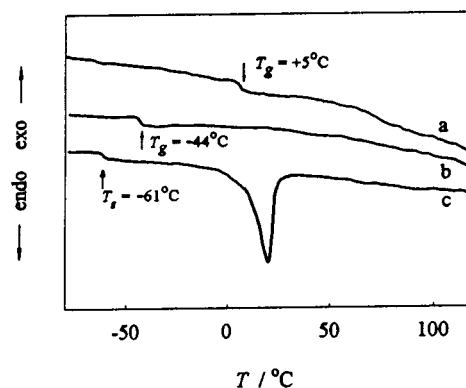
The reaction course was controlled by measuring the intensity of bands of the C=O bonds stretching vibrations at 1770 cm<sup>-1</sup> (in the anhydride groups) and at 1720 cm<sup>-1</sup> (in the ester groups) according to the procedure presented earlier.<sup>19</sup>

When poly(ethylene glycol)s of  $M_n$  up to 750 g/mol were used, after about 12 h of reaction at room temperature complete conversion of the anhydride groups was achieved. When glycols of  $M_n$  1000 and 2000 were used the degree of conversion reached ~85%, however, neither the prolongation of the reaction time nor a rise of temperature caused a further increase in the yield.

The thus obtained lithium salts solutions were processed by two methods, A and B. In method A DMSO was removed under reduced pressure from thin solution layers and the residual solvent content was determined by means of elemental analysis. Samples in which sulfur was not detected were treated as solid electrolytes. In the case of some electrolytes containing allyl groups, 1 wt % of benzoyl peroxide (with respect to the salt) was additionally introduced and a thin solution layer was heated for 1 h at 70 °C in order to obtain a gel.

In method B the electrolyte solution in DMSO was poured onto acidified water. The polymer precipitated was filtered off and purified by dissolution in methanol and precipitation in water. Finally, the acidic form of the electrolyte (0.2 g) was dissolved in 5 cm<sup>3</sup> of absolute methanol and converted into a salt by dropping in solutions of lithium, sodium, or potassium methanolate. An appropriate amount of the plasticizers and free radical initiator or photoinitiator were added to the solution. A thin layer was poured out and methanol was removed. Gels were obtained by thermal cross-linking at 70 °C for ~1 h or by UV irradiation for ~10 min at room temperature in the presence of Irgacure 184.

**Measurements.** AC impedance analysis was used to determine the bulk conductivities of electrolytes with a Solartron 1255 frequency analyzer. Measurements were performed in the frequency range from 10<sup>-2</sup> to 10<sup>5</sup> Hz applying stainless steel blocking electrodes. The electrode area was equal to 1.5 cm<sup>2</sup> and the samples thickness 1.5–1 mm. The samples were kept



**Figure 1.** DSC traces for solid lithium polyelectrolytes **I** with different numbers (*n*) of oxyethylene monomeric units in the poly(ethylene glycol) side chain: (a) *n* = 3, terminated with -OCH<sub>3</sub>; (b) *n* = 16, terminated with -OCH<sub>3</sub>; (c) *n* = 22, terminated with -OH.

for 0.5 h at each experiment temperature that was maintained within ±0.1 °C.

Calorimetric investigations were performed on Unipan 605 and Du Pont TA 2910 scanning calorimeters between -110 and 150 °C. The heating rate was 10 °C/min. The diffractograms were registered for the Bragg angles 2θ between 20 ° and 70 ° by using a Dron 2.0 powder diffractometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker 300 spectrometer.

Spin–lattice relaxation times (*T*<sub>1</sub>) at <sup>7</sup>Li resonant frequency of ω<sub>0</sub>/2π = 24.5 MHz were measured over the temperature range 180–400 K with a Bruker MSL 100 spectrometer in conjunction with a tunable cryomagnet. A typical π/2 pulse length was determined to be about 8 μs. The *T*<sub>1</sub> was determined by sampling the amplitude of free induction after the standard π – π/2 or comb π/2 pulse sequences.<sup>20</sup>

## Results and Discussion

**Thermal Analysis of Electrolytes.** DSC studies showed that the solid electrolytes of type **I** with side chains of  $M_n \leq 750$  ( $n \leq 16$ ) are amorphous (Figure 1). In lithium polyelectrolytes with polyglycols of  $M_n$  1000 ( $n \leq 22$ ) and 2000 ( $n \leq 45$ ) in the side chains, the occurrence of melting transition with maxima at 22 and 40 °C, respectively, was observed. The X-ray diffraction patterns of the acidic forms of these samples showed typical signals for the poly(ethylene oxide) crystalline phase (2θ = 24.5° and 29.5°). Thus, one can expect that melting transition is attributed to the side-chain crystallinity. At this assumption the degree of crystallinity for *n* = 22 can be estimated on the basis of the heat of transformations as ~33%, and for *n* = 45, as ~80%. No signals indicating the formation of crystalline complexes between lithium carboxylates and polyglycol chains were observed. The *T*<sub>g</sub> values of solid lithium electrolytes decrease with an increase in the length of the side-chain polyglycols from about +5 °C for electrolytes of 3 ethylene oxide monomeric units to about -61 °C for electrolytes having an average of 22 units. The sodium and potassium electrolytes studied exhibited similar *T*<sub>g</sub> values as lithium ones of the same polyglycol side chain length.

The plasticized and gel electrolytes were found to be amorphous at ambient temperature.

As can be seen from Table 1, the addition of DMSO leads to a decrease in the polyelectrolyte *T*<sub>g</sub> values. Studies carried out for electrolytes of an average oxyethylene chain length 3 and 7 containing up to 80 wt % DMSO indicate that samples of longer chain length exhibit generally lower *T*<sub>g</sub> values also in the presence of an external plasticizer.

**TABLE 1:  $T_g$  Data Determined from DSC for Polyelectrolytes I<sup>a</sup>**

$n^b$	conducting cation	DMSO concn (wt %)	$T_g$ °C	$n^b$	conducting cation	DMSO concn (wt %)	$T_g$ °C
3	Li	0	+5	3	Li	78	-80
7	Li	0	-23	7	Li	3	-32
16	Li	0	-44	7	Li	5	-33
16	Na	0	-45	7	Li	15	-70
16	K	0	-51	7	Li	57	-76
22	Li	0	-61	7	Li	9	-90
3	Li	15	-8	7	Na	25	-58
3	Li	25	-20	3.5 <sup>c</sup>	Li	25 <sup>d</sup>	-82
3	Li	60	-52	3.5 <sup>c</sup>	Li	25 <sup>d,e</sup>	-93

<sup>a</sup> Terminated with a  $\text{CH}_3$  group. <sup>b</sup> Number of oxyethylene monomeric units in polyelectrolyte I. <sup>c</sup> Cross-linked gel polyelectrolyte. <sup>d</sup> Propylene carbonate, 25 wt %. <sup>e</sup> After addition of equimolar amount of  $\text{BF}_3$  with respect to the carboxylic anion.

Glass transition temperatures in gel systems are not always distinctive and were not studied systematically. Singular experiments indicate that at the content of polar solvents (DMSO or DMSO and PC) in the range of 50–70 wt % the  $T_g$  values are between -70 and -90 °C, and thus they do not differ essentially from those values for non-cross-linked systems.

**Conductivity of Solid Electrolytes.** In Table 2 are presented the ionic conductivity values at 30 and 90 °C for solid electrolytes I bearing oxyethylene substituents of various length. Salts containing 7–9 oxyethylene units showed the highest conductivities (of the order of  $6 \times 10^{-7} \text{ S}\cdot\text{cm}^{-1}$ ) at 30 °C among the lithium electrolytes studied. The concentration of lithium cations in these salts is  $1.5\text{--}1.8 \text{ mol}\cdot\text{kg}^{-1}$ . It is close to the lithium salt concentrations applied usually in polymer electrolytes based on polyethers (usually  $1.8\text{--}2.2 \text{ mol}\cdot\text{kg}^{-1}$ ).

An increase in the side-chain length to 16–22 oxyethylene units causes a small decrease in ambient temperature conductivity. However, at 90 °C the conductivity of electrolytes containing 7–22 ethylene oxide monomeric units differs only slightly and exceeds  $10^{-5} \text{ S}\cdot\text{cm}^{-1}$ .

As can be seen from Figures 2 and 3, the conductivity–temperature plots for these electrolytes tend to be non-Arrhenius. The experimental data can be better analyzed by the empirical Vogel–Tamman–Fulcher (VTF) equation of the form

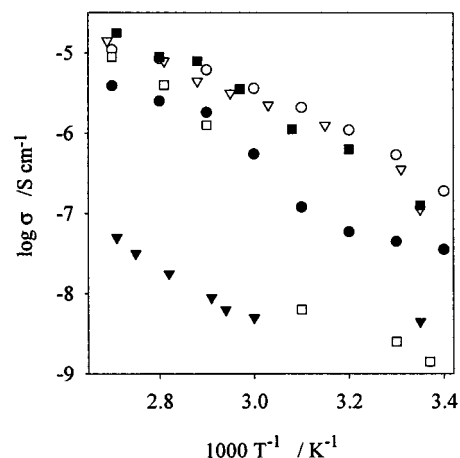
$$\sigma = AT^{-0.5} \exp[-E/(T - T_0)]$$

In this equation  $E$  is the pseudoactivation energy for ionic conductivity,  $A$  is a preexponential factor proportional to the number of charge carriers, and  $T_0$  is quasiequilibrium glass transition. Examples of the fitted parameters are given in Table

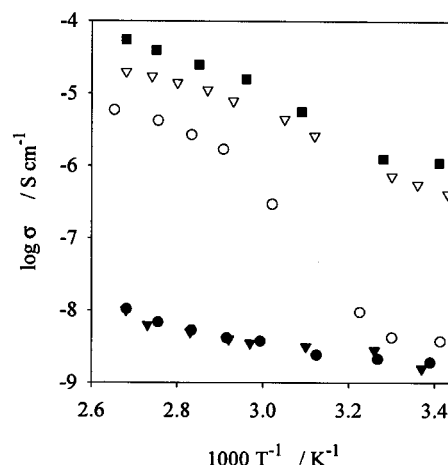
**TABLE 2: Ionic Conductivity of Solid Polyelectrolytes I**

cation	cation (Mt) concn (mol/kg of electrolyte)	$n^c$	end group	$\sigma^a$ ( $\text{S}\cdot\text{cm}^{-1}$ )		$\sigma/\text{mol of Mt}^b$ ( $\text{S}\cdot\text{kg}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1}$ )	
				30 °C	90 °C	30 °C	90 °C
Li	3.17	2	OH	$5.0 \times 10^{-9}$	$5.0 \times 10^{-7}$	$1.6 \times 10^{-9}$	$1.6 \times 10^{-8}$
	2.68	3	$\text{OCH}_3$	$4.5 \times 10^{-8}$	$3.9 \times 10^{-6}$	$1.7 \times 10^{-8}$	$1.5 \times 10^{-6}$
	1.83	7	$\text{OCH}_3$	$5.3 \times 10^{-7}$	$1.1 \times 10^{-5}$	$2.9 \times 10^{-7}$	$6.0 \times 10^{-6}$
	1.51	9	$\text{OCH}_2\text{CH}=\text{CH}_2$	$6.5 \times 10^{-7}$	$1.3 \times 10^{-5}$	$4.3 \times 10^{-7}$	$8.6 \times 10^{-6}$
	1.04	16	$\text{OCH}_3$	$3.2 \times 10^{-7}$	$1.4 \times 10^{-5}$	$3.1 \times 10^{-7}$	$1.3 \times 10^{-5}$
	0.83	22	OH	$2.2 \times 10^{-7}$	$1.8 \times 10^{-5}$	$2.6 \times 10^{-7}$	$2.2 \times 10^{-5}$
	0.46	45	OH	$2.8 \times 10^{-9}$	$8.9 \times 10^{-6}$	$6.1 \times 10^{-9}$	$1.9 \times 10^{-5}$
Na	2.91	2	$\text{OCH}_3$	$3.2 \times 10^{-9}$	$6.3 \times 10^{-9}$	$1.1 \times 10^{-9}$	$2.2 \times 10^{-9}$
	1.77	7	$\text{OCH}_3$	$7.1 \times 10^{-7}$	$1.7 \times 10^{-5}$	$4.0 \times 10^{-7}$	$9.6 \times 10^{-6}$
	1.03	16	OH	$1.8 \times 10^{-6}$	$4.0 \times 10^{-5}$	$1.7 \times 10^{-6}$	$3.9 \times 10^{-5}$
K	2.56	3	OH	$1.8 \times 10^{-9}$	$6.9 \times 10^{-9}$	$7.0 \times 10^{-10}$	$2.7 \times 10^{-9}$
	1.85	6	OH	$5.6 \times 10^{-9}$	$4.3 \times 10^{-6}$	$3.0 \times 10^{-9}$	$2.3 \times 10^{-5}$

<sup>a</sup>  $n$  = number of oxyethylene monomeric units in poly(ethylene glycol) side chain. <sup>b</sup> Bulk. <sup>c</sup> Calculated per 1 mol of  $\text{Li}^+$  cations.



**Figure 2.** Ionic conductivity vs reciprocal temperature for lithium polyelectrolytes I [samples with different numbers ( $n$ ) of oxyethylene monomeric units in the poly(ethylene glycol) side chain]. (●)  $n = 3$ , terminated with  $-\text{OCH}_3$ ; (○)  $n = 7$ , terminated with  $-\text{OCH}_3$ ; (▼)  $n = 2$ , terminated with  $-\text{OH}$ ; (▽)  $n = 16$ , terminated with  $-\text{OCH}_3$ ; (■)  $n = 22$ , terminated with  $-\text{OH}$ ; (□)  $n = 45$ , terminated with  $-\text{OH}$ .



**Figure 3.** Ionic conductivity vs reciprocal temperature for sodium and potassium polyelectrolytes I [samples with different numbers ( $n$ ) of oxyethylene monomeric units in the poly(ethylene glycol) side chain]. (●)  $n = 3$ , terminated with  $-\text{OH}$ , potassium polyelectrolyte; (○)  $n = 6$ , terminated with  $-\text{OH}$ , potassium polyelectrolyte; (▼)  $n = 2$ , terminated with  $-\text{OCH}_3$ , sodium polyelectrolyte; (▽)  $n = 7$ , terminated with  $-\text{OCH}_3$ , sodium polyelectrolyte; (■)  $n = 16$ , terminated with  $-\text{OH}$ , sodium polyelectrolyte.

3. One can observe that the best fits of the VTF equation give rise to  $T_0$  values close to the experimental glass transition temperature that is typical for electrolytes of low charge carrier

**TABLE 3: VTF and Arrhenius Fitting Parameters for Solid Polyelectrolytes I**

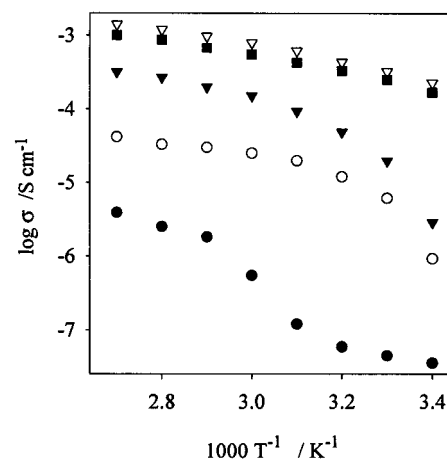
conducting cation	$n^a$	Arrhenius fitting		VTF fitting		
		$E_a$ (kJ·mol <sup>-1</sup> )	$\ln \sigma_0$	$A$	$E$ (K)	$T_0$ (K)
Li	2	39.4	-4.44			
	3	19.8	-8.13			
	7			$8.0 \times 10^{-3}$	465	235
	16			$1.0 \times 10^{-3}$	196	224
Na	22			$1.9 \times 10^{-2}$	622	216
	2	17.8	-12.9			
	7			$2.0 \times 10^{-2}$	641	210
K	22			$1.6 \times 10^{-1}$	980	177
	3	19.2	-12.4			
	6			$1.1 \times 10^{-2}$	676	230

<sup>a</sup> Number of oxyethylene units in poly(ethylene glycol) side chain.<sup>b</sup> Fitting to the Vogel–Tamman–Fulcher equation (see text).

concentration.<sup>21</sup> Low concentration of charge carrier is indicated also by the values of parameter  $A$ , which are 2 orders of magnitude smaller than those of classical electrolytes, in which anions are mainly responsible for conduction. The reason for this may be the low dissociation constant of carboxylates (lower than that of lithium salt solutions in polar organic solvents). Moreover, in the case of polyelectrolytes the charge cannot be transferred by ion aggregates (ion pairs, triplets), which causes a lower concentration of charge carriers than in classic solid polyether electrolytes, in which ion aggregates contribute remarkably to the overall charge concentration.<sup>22</sup> As will be shown further in the paper, the  $A$  parameter increases by 2 orders of magnitude after the addition of a plasticizer (Table 5), which causes an increase in the electrolyte dielectric constant, and thus an increase in the dissociation degree. The VTF behavior lets us suppose that cation transports in the systems studied are coupled with segmental relaxations of polymers. In these cases one can expect that side chains having a sufficient amount of oxyethylene units may promote cation mobility by creating and cleaving coordination bonds. However, this does not exclude the possibility of cation transportation by thermally activated hopping between ionic clusters that is suggested for systems of high lithium cation concentration.<sup>21</sup> This latter mechanism is very probable in the case of polyelectrolytes containing short segments of ethylene oxide monomeric units ( $n = 2, 3$ ). In the case of lithium salts of electrolytes with 3 oxyethylene units, the ambient temperature conductivity is about  $5 \times 10^{-8} \text{ S·cm}^{-1}$  and initially slightly increases with a rise of temperature. A clear increase in conductivity of this system is observed in the 50–70 °C temperature range (Figures 2 and 3). Similar changes were observed in other amorphous systems, and also during studies on the relaxation times, and it is assumed that this is connected with “freezing” of certain chain motions at temperatures slightly higher than those experimentally determined by the DSC method.

An electrolyte containing 2 oxyethylene units exhibits ambient temperature conductivity of about  $5 \times 10^{-9} \text{ S·cm}^{-1}$ , which starts to clearly increase only above 70 °C. Still lower ambient temperature conductivities are exhibited by a polyelectrolyte containing a side chain of approximately 45 ethylene oxide monomeric units. However, its conductivity increases significantly above the crystalline phase melting point (~40 °C) and at 90 °C is close to  $10^{-5} \text{ S·cm}^{-1}$  (Figure 2).

It should be remembered that with an increase of the side-chain length in the polyelectrolyte the cation concentration decreases. When the conductivity value is recalculated per 1 mol of cations (Table 2), it can be noticed that at 30 °C the mobility of lithium cations in polyelectrolytes containing 7–22 oxyethylene units differs only slightly, with a maximum for the

**Figure 4.** Ionic conductivity vs reciprocal temperature for DMSO-plasticized polyelectrolytes **I** of 3 oxyethylene monomeric units in the side chain of polyglycol terminated with  $-\text{OCH}_3$ : (●) 0 wt % DMSO; (○) 15 wt % DMSO; (▼) 25 wt % DMSO; (▽) 60 wt % DMSO; (■) 78 wt % DMSO.

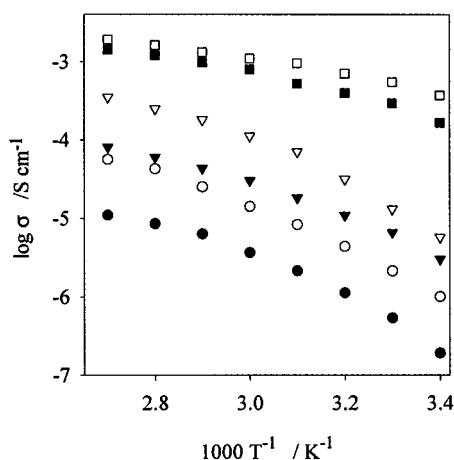
system with 9 monomeric units. At 90 °C the highest mobility is exhibited by lithium ions in polyelectrolytes of long chains (22 or 45 monomeric units). In the case of these electrolytes, at room temperature only part of the ethereal units participates in the cation transport, and with a rise of temperature the probability of charge migration along the side chain increases.

It is interesting that sodium and potassium salts of short side chains exhibit lower conductivity than lithium ones (Figure 3), despite the fact that the dissociation energies are usually smaller for larger cations. This may suggest that hopping between clusters is governed by the size of cation rather than by its polar interaction with carboxylic anions.

However, we found that in the case of electrolytes of longer side chains ( $n = 7, 16$ ) sodium salts show higher conductivity than lithium derivatives. This is in agreement with the observations of other authors,<sup>7–9</sup> who found that larger cations can move faster in solid polymer electrolytes (in some polyelectrolytes the conduction of  $\text{Cs}^+$  salts was found to be 3 orders of magnitude higher than that of lithium ones). In view of our results it seems that this rule is true only in a system where charge transport is coupled to the polymer chain segmental motion. Large cations of lower surface charge density can change the coordination centers faster due to the weaker interactions with nucleophilic species.

**Conductivity of Plasticized and Gel Polyelectrolytes.** Studies carried out for lithium salts of polyelectrolytes containing 3 and 7 oxyethylene units showed that the introduction of DMSO significantly improves their ionic conductivity (Figures 4 and 5). Films containing about 60 wt % DMSO are rubberlike and ensure good dimensional stability over the whole temperature range studied. Their ambient temperature ionic conductivity is higher than  $10^{-4} \text{ S·cm}^{-1}$  and practically does not depend on the type of matrix (Table 4). In these systems 7–9 molecules of the solvent fall on average per one lithium cation and probably the participation of oxyethylene chains in charge transport is small. The polyelectrolyte acts mainly as a source of charge carriers and frame that provides the systems with mechanical stability resulting from chain entanglements. Thus, this type of material can be treated as gel electrolytes. At lower DMSO concentrations (3–15 wt %), higher conductivity is obtained for systems containing a polyelectrolyte of longer oxyethylene chains. In these systems only 0.2–1.3 DMSO molecules fall per one lithium cation and the participation of





**Figure 5.** Ionic conductivity vs reciprocal temperature for DMSO-plasticized polyelectrolytes **I** of 7 oxyethylene monomeric units in the side chain of polyglycol terminated with  $-\text{OCH}_3$ : (●) 0 wt % DMSO; (○) 3 wt % DMSO; (▼) 5 wt % DMSO; (▽) 15 wt % DMSO; (■) 57 wt % of DMSO; (□) 79 wt % DMSO.

**TABLE 4: Ionic Conductivity of Plasticized Lithium Polyelectrolytes I**

$n^a$	DMSO content (wt %)	Li content <sup>b</sup> (wt %)	Li content (mol of Li/kg of solvent)	DMSO/Li mole ratio	$\sigma$ ( $\text{S}\cdot\text{cm}^{-1}$ )	
					30 °C	50 °C
3	0	1.88			$4.5 \times 10^{-8}$	$1.2 \times 10^{-7}$
	15	1.60	15.23	0.84	$6.1 \times 10^{-6}$	$2.0 \times 10^{-5}$
	25	1.41	8.06	1.59	$2.0 \times 10^{-5}$	$9.4 \times 10^{-5}$
	60	0.75	1.79	6.86	$3.2 \times 10^{-4}$	$6.1 \times 10^{-4}$
	78	0.41	0.75	16.37	$2.5 \times 10^{-4}$	$4.3 \times 10^{-4}$
7	0	1.28			$5.3 \times 10^{-7}$	$2.1 \times 10^{-6}$
	3	1.24	59.00	0.22	$2.1 \times 10^{-6}$	$8.3 \times 10^{-6}$
	5	1.22	34.67	0.37	$6.5 \times 10^{-6}$	$1.8 \times 10^{-5}$
	16	1.06	9.58	1.34	$1.3 \times 10^{-5}$	$7.0 \times 10^{-5}$
	57	0.55	1.38	9.29	$2.9 \times 10^{-4}$	$5.2 \times 10^{-4}$
	79	0.27	0.48	26.71	$5.5 \times 10^{-4}$	$9.4 \times 10^{-4}$

<sup>a</sup> Number of oxyethylene units in poly(ethylene glycol) side chain.

<sup>b</sup> Content in the whole polyelectrolyte.

**TABLE 5: VTF Parameters for Plasticized and Non-Cross-Linked Gel Polyelectrolytes I**

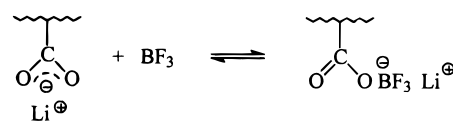
$n^a$	DMSO content (wt %)	$A$	$E$ (K)	$T_0$ (K)
3	0			
	15	$9.6 \times 10^{-3}$	396	205
	25	$1.6 \times 10^{-1}$	454	222
	60	$7.7 \times 10^{-1}$	641	172
	78	$7.6 \times 10^{-1}$	755	158
7	0	$8.1 \times 10^{-3}$	465	235
	3	$1.2 \times 10^{-1}$	633	228
	5	$1.1 \times 10^{-1}$	650	210
	16	$3.5 \times 10^{-1}$	525	231
	57	$4.3 \times 10^{-1}$	428	208
	79	$5.5 \times 10^{-1}$	495	182

<sup>a</sup> Number of oxyethylene units in poly(ethylene glycol) side chain.

oxygen atoms from side chains in the coordination of cations cannot be excluded. At low DMSO content the length of the side chain has an essential effect on the  $T_g$  value (Table 1) and thus the mobility of all particles. (Such systems are called plasticized electrolytes.) The temperature dependence of conductivity can be described by the VTF-type equations for a majority of the plasticized and gel systems studied (Table 5). Essential deviations are observed in the case of a system containing a polyelectrolyte bearing 3 oxyethylene units and 15 wt % DMSO. The  $T_g$  value for this system is  $-8$  °C and probably at room temperature some segmental motions are still

“frozen in” ( $T_g \geq 1.15T_g \geq 32$  °C). At DMSO contents greater than 60%, no distinct increase in conductivity is observed and the electrolytes obtained tend to flow. The concentration of chains in these systems is probably already too small to form dimensionally stable gels as a result of physical processes. In Table 6 are presented conductivity values for irreversible gels obtained by covalent cross-linking of some lithium polyelectrolytes in the presence of DMSO and/or propylene carbonate, which is the most widely used solvent in classical gel electrolytes containing salts with mobile anions. We found that, in systems in which the side chains had on average 3.5 oxyethylene units, it is possible to obtain dimensionally stable membranes containing up to 80 wt % solvent. In the case of using only PC as the solvent, the maximum ambient temperature conductivities are about  $10^{-5} \text{ S}\cdot\text{cm}^{-1}$ ; i.e., approximately 2 orders of magnitude lower than that observed in many electrolytes formed by dissolving conventional lithium salts. The immobilization of anions in polyelectrolytes cannot be the only reason for such a great difference in conductivity, since in a solution of lithium salts in PC the anion transport number does not usually exceed 85%.<sup>23</sup> Strong ion pairing between the lithium cation and carboxylic anions attached to the polymer backbone, which reduces the cation mobility, is probably an additional factor decreasing the conductivity of gels containing the electrolytes studied. The mobility of cations considerably increases in the presence of DMSO, and as can be seen from Table 6, a number of systems comprising mixtures of both solvents exhibit ambient temperature conductivity on the order of  $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ . DMSO is characterized by a higher donor number (DN) than PC ( $\text{DN}_{\text{DMSO}} = 29.8$ ;  $\text{DN}_{\text{PC}} = 15.1$ )<sup>24</sup> and a slightly lower viscosity (at 25 °C  $\eta_{\text{DMSO}} = 1.99$  cP,  $\eta_{\text{PC}} = 2.53$  cP), and probably this first solvent will better solvate lithium cations and ensure them higher mobility. However, both solvents are characterized by similar acceptor number (AN) values ( $\text{AN}_{\text{DMSO}} = 19.3$ ,  $\text{AN}_{\text{PC}} = 18.3$ ),<sup>24</sup> which permits to suggest that their ability to solvate carboxylic anions is similar.

To more efficiently separate lithium cations and carboxylic anions, we introduced additionally a strong Lewis acid such as  $\text{BF}_3$  to the system. IR studies showed that under the influence of  $\text{BF}_3$  a considerable increase in the frequency of signals of the carboxylic anion C–O bonds stretching vibration occurs from 1600 to 1720  $\text{cm}^{-1}$ . This probably results from the formation of a coordination bond between the oxygen atom and boron atom and disturbance of the carboxylic anion hybrid structure, in which carbon is joined to each oxygen by a “one-and-a-half” bond.



As can be seen from Table 6, the complexation of anions by  $\text{BF}_3$  favors greater cation mobility and in the presence of DMSO and PC it is possible to obtain membranes of ambient temperature conductivity  $\sim 5 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ .

Elongation of the side chain to  $n = 9$  oxyethylene units did not cause an increase in the gel conductivity. When comparing the data for systems comprising DMSO as the only solvent presented in Tables 4 and 6, it can be concluded that cross-linking resulting from the formation of chemical bonds does not lead to a decrease in conductivity. The amount of DMSO introduced is a key parameter, and the type of matrix used is not essential for ion transport, similarly to gel electrolytes based on lithium salts with mobile anions.

TABLE 6: Conductivity of Cross-Linked Gel Polyelectrolytes

<i>n</i> <sup>a</sup>	synthesis mode	solvent		Li content						ionic conductivity $\sigma$ (S·cm <sup>-1</sup> )	
		DMSO (wt %)	PC (wt %)	in polymer (wt %)	overall (wt %)	mol of Li/kg of electrolyte	mol of Li/kg of solvents	DMSO/Li mole ratio	PC/Li mole ratio	25 °C	50 °C
3.5	B	0	80	1.76	0.35	0.50	0.63		15.56	$1.5 \times 10^{-5}$	$2.7 \times 10^{-5}$
	A	18	0	1.58	1.29	1.84	10.31	1.24		$1.1 \times 10^{-5}$	$6.6 \times 10^{-5}$
	B	25	25	1.76	0.97	1.38	2.26	1.85	1.77	$7.8 \times 10^{-5}$	$1.6 \times 10^{-4}$
	B <sup>b</sup>	25	25	1.37	0.66	0.94	1.96	3.27	2.50	$5.3 \times 10^{-4}$	$1.2 \times 10^{-3}$
	B	45 <sup>c</sup>		1.58	0.71	1.01	2.76	0.86 <sup>c</sup>		$4.4 \times 10^{-7}$	$1.8 \times 10^{-6}$
	B	50	20	1.76	0.53	0.76	1.08	8.47	2.60	$2.1 \times 10^{-4}$	$7.6 \times 10^{-4}$
	B	8	70	1.58	0.35	0.50	0.63	2.07	13.97	$9.6 \times 10^{-5}$	$1.8 \times 10^{-4}$
6	A	24		1.32	1.00	1.43	5.97	2.14		$4.8 \times 10^{-5}$	$7.8 \times 10^{-5}$
7	A	25		1.27	0.96	1.37	5.47	2.34		$3.7 \times 10^{-5}$	$1.2 \times 10^{-4}$
	A	50		1.27	0.61	0.87	1.74	7.36		$8.6 \times 10^{-5}$	$2.7 \times 10^{-4}$
	A	22	53	1.27	0.31	0.44	0.58	6.48	11.90	$1.1 \times 10^{-4}$	$5.2 \times 10^{-4}$
9	A	27		1.06	0.77	1.10	4.10	3.13		$2.7 \times 10^{-5}$	$1.1 \times 10^{-4}$

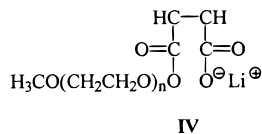
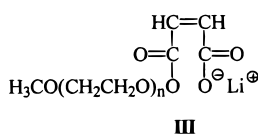
<sup>a</sup> Number of oxyethylene monomeric units in side chain. <sup>b</sup> After addition of an equimolar amount of BF<sub>3</sub> with respect to the carboxylic anions. <sup>c</sup> PEGDME (*M*<sub>n</sub> = 420 g·mol<sup>-1</sup>) instead of DMSO.

TABLE 7: Chemical Shifts of <sup>13</sup>C Nuclei in Carbonyl Groups of Lithium Salts of Maleic Acid and Succinic Acid Monoesters<sup>a</sup>

acid	ester group	additive	additive/Li <sup>+</sup> mole ratio	$\delta$ for -CO <sub>2</sub> <sup>-</sup> Li <sup>+</sup>	$\delta$ for -OC(O)-
MA	CH <sub>3</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub>	DMSO	1	172.17	166.50
				171.68	166.46
	CH <sub>3</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub>	DMSO	1	171.74	166.53
				171.57	166.51
				171.32	166.27
		PC	1	168.35	166.44
				171.64	166.45
SA	CH <sub>3</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>7</sub>	BF <sub>3</sub>	1	167.21	165.15
				171.27	166.11
	CH <sub>3</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub>	DMSO	67	179.69	174.34
				175.80	173.28
	CH <sub>3</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>7</sub>	DMSO	5	179.06	174.08
				176.71	172.73
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub>	DMSO	5	174.39	172.32

<sup>a</sup> Solvent: CDCl<sub>3</sub>.

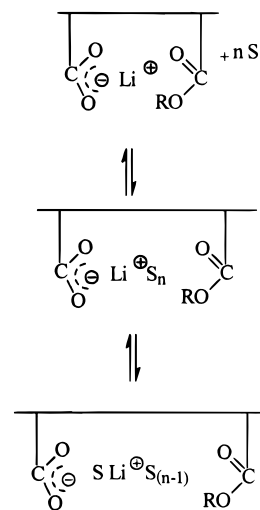
**NMR Studies.** To compare the effect of DMSO, PC, and BF<sub>3</sub> on the interactions of lithium cations with carboxylic anions, studies have been carried out on the <sup>13</sup>C NMR chemical shifts in lithium salts of half-esters of maleic (III) and succinic (IV) acids half-esters, the structure of which is similar to that of the monomeric units in the electrolytes studied.



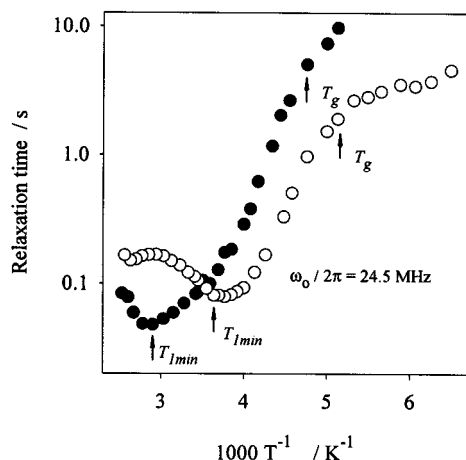
It was found that the signals of <sup>13</sup>C nuclei in a carboxylate anion are shifted toward higher field (lower values of  $\delta$ ) with an increase in the DMSO concentration in the system. The differences in chemical shifts in the spectra of the CDCl<sub>3</sub> and diluted DMSO-*d*<sub>6</sub> solutions (at the detection limit of the carbonyl groups—at a DMSO/Li<sup>+</sup> mole ratio  $\approx$ 67) are above 3 ppm. Changes in the location of other signals are much smaller and irregular (for comparison, in Table 7 the  $\delta$  values for <sup>13</sup>C nuclei in the carboxylic anion and carbonyl ester group are presented). Thus, it can be assumed that the changes in the signal positions of the <sup>13</sup>C nuclei in the carboxylic anion are of a specific character and are caused mainly by solvent coordination with the cation and thus a reduction in ion interaction. Studies carried out in the absence of polar solvents show that the chemical shift characteristic of carboxylic anion decreases systematically with an increase in the length of substituent in the ester group. Internal solvation of lithium cations by the side-chain functional

groups, the probability of which increases with an increase in the number of donor-type groups, is probably the reason for this.

The coordination of the solvent (S) around Li<sup>+</sup> may lead to the formation of contact or solvent-separated ion pairs.



In the contact pair the solvent probably dislodges the ester group or oxyethylene groups from the lithium coordination sphere (similarly as in classical gel electrolytes) but retains the intimate association of Li<sup>+</sup> with carboxylic anions, which are a strong hard nucleophile. The formation of such a pair causes an



**Figure 6.** Experimental  $^7\text{Li}$  NMR spin lattice relaxation time as a function of inverse temperature for gel electrolytes: (●) sample containing 45 wt %  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_9\text{OCH}_3$  as plasticizer; (○) sample containing 25 wt % DMSO + 25 wt % PC and  $\text{BF}_3$  in an equimolar amount with respect to the carboxylic anions.

increase in the side-chain mobility but does not cause an essential change in the conductivity mechanism, which in the case of contact pairs consists of intercluster hopping.

The formation of pairs separated by the solvent is believed to play a crucial role in determining the ion conductivity, because these species can dissociate to yield  $\text{Li}^+$  cations, which are capable of charge transport assisted by side-chain movement or decoupled from the polymer motion depending on the solvent concentration.

The possibility of the formation of various complexes of unknown stoichiometry precludes the estimation, on the basis of an analysis of chemical shift changes, of the equilibrium between the contact and separated pairs in the systems studied. The formation of ion pairs in which carboxylic ions are complexed by  $\text{BF}_3$  causes a decrease in the chemical shift of  $^{13}\text{C}$  nuclei of the carboxylic anion by about 4.5 ppm. As mentioned, at a large DMSO excess with respect to lithium cations the shift change is 3–4 ppm. At an equimolar amount of DMSO or PC with respect to lithium cations these changes are much smaller, in the 0.1–0.5 ppm range. Therefore, it can be assumed that the coordination of the first solvent molecule leads mainly to the formation of contact pairs. The results of studies on the  $\text{Li}^+$  dynamics in monoconducting gel electrolytes, which will be described in a separate paper,<sup>25</sup> lead to a similar conclusion. For the purpose of the present discussion we show the  $^7\text{Li}$  NMR spin–lattice relaxation time ( $T_1$ ) data on two representative samples of irreversible gels with an average number of oxyethylene units  $\approx 3.5$  (Figure 6). Sample A contains 45% ethylene oxide oligomer  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$  ( $M_n = 420 \text{ g}\cdot\text{mol}^{-1}$ ) as plasticizer, and its ambient conductivity is  $\sim 5 \times 10^{-7} \text{ S}\cdot\text{cm}^{-1}$  (Table 6). In sample B of ambient temperature conductivity  $\sim 5 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$  the carboxylic anions are complexed by  $\text{BF}_3$  and the matrix is plasticized by a mixture of DMSO and PC (25 wt % each solvent with respect to the total weight of sample).

For  $^7\text{Li}$  NMR spin–lattice relaxation in polymer electrolytes it was determined<sup>26</sup> that relaxation occurs via fluctuation in the electric field gradient at the nucleus, caused by motion of the cation. A  $T_1$  minimum is normally observed when the correlation time for motions responsible for relaxation is equal to the inverse Larmor frequency of the nuclide.

As can be seen from Figure 4, a  $T_1$  minimum is observed for each sample. The  $T_1$  minimum values at 24.5 MHz are about

0.045 s for sample A and about 0.08 s for sample B. Despite a similar glass transition temperature for both samples (190–200 K), the  $T_1$  minimum for the sample containing  $\text{BF}_3$  is observed to occur at a much lower temperature than for sample A (cf. 265 versus 345 K, respectively). This observation, together with the fact that the static dipolar width for the sample containing  $\text{BF}_3$  (9.7 kHz) was found to be slightly greater than those of sample A (7.8 kHz), suggests that the shift of the  $T_1$  minimum is a reflection of the weaker  $\text{Li}^+$  cation coordination with its counterion. Similar behavior has been previously reported in comparisons between polyethers complexed with  $\text{LiClO}_4$  and  $\text{LiBF}_4$ , in which the larger line width of the  $\text{LiBF}_4$  complex was attributed to heteronuclear  $^7\text{Li}$ – $^{19}\text{F}$  dipolar interaction.<sup>27</sup>

In the absence of  $\text{BF}_3$  the  $T_1$  curves of the samples containing DMSO and PC have a similar shape as for sample A,<sup>25</sup> although broader and less well-defined minima are usually observed. However, the change of the solvent does not affect either the  $T_1$  minimum value ( $\sim 0.045$  s) or the temperature at which the minimum is observed. The lack of an essential effect of polar solvents on the relaxation times suggests that most of the lithium cations in the gel studied form contact pairs with carboxylic anions and hence are dynamically “coupled” to the motions of the polymer host.

## Conclusions

The ionic conductivity of solid comblike polyelectrolytes obtained in the reactions of lithium poly(ethylene glycol)ates with maleic anhydride and styrene copolymers depend essentially on the number of oxyethylene units incorporated to the side chain. The highest ambient temperature conductivity values are exhibited by derivatives containing 7–13 such units. They form amorphous flexible membranes of ambient temperature conductivity  $\sim 10^{-7} \text{ S}\cdot\text{cm}^{-1}$ , and that at 90 °C is  $\sim 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ . The character of conductivity changes versus temperature indicates that the motions of cations in these systems are coupled with segmental motions of side polyether-type chains. The conductivity values obtained are nearly 2 orders of magnitude lower than those achieved in completely amorphous systems containing polyether matrixes and lithium salts, in which the bulk conductivity is due primarily to anion mobility.

The conductivity of the polyelectrolytes studied clearly increases in the presence of DMSO. The results of  $^{13}\text{C}$  NMR and DSC studies indicate that this solvent solvates lithium cations, reducing their interactions with carboxylic anions and improving flexibility and segmental motion in the polyelectrolyte chains. Both effects favor faster cation transport.

Contact ion pairs of the form  $\sim \text{COO}^-\text{Li}^+$ –solvent are expected to dominate in the gel system studied. However, the presence of solvent-separated species  $\sim \text{COO}^- \rightarrow \text{solvent} \rightarrow \text{Li}^+$  is believed to play an essential role in fast charge transportation. Ion coupling can be effectively reduced by the addition of strong anion complexing agents such as  $\text{BF}_3$ , which leads to a change of the mode of  $\text{Li}^+$  relaxation and to an increase in the polyelectrolyte conductivity.

The  $\text{BF}_3$ -containing gels plasticized with DMSO and propylene carbonate can be prepared in the form of dimensionally stable membranes of ambient temperature conductivity  $\sim 5 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ . This value is very close to the threshold value, which allows the electrolytes to be considered as candidates for application in lithium batteries.

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