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CONCENTRATION DEPENDENCE OF IONIC RELAXATION IN LITHIUM DOPED POLYMER ELECTROLYTES

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Abstract

A detailed impedance spectroscopy study at ambient temperature was carried out on polymer electrolytes based on low molecular weight poly(ethylene oxide) 400, poly(propylene oxide) 400 and a random copolymer of molecular weight 600, to which were added $LiN(CF_3SO_2)_2$ (LiTFSI) salt. The ionic conductivity exhibits a maximum at intermediate salt concentrations and is significantly higher for poly(ethylene oxide) and the copolymer. A dielectric relaxation was found in a frequency region above the one, where the ion conductivity dominates the dielectric response, and below the region of the relaxations of the polymer host. The relaxation strength scales with ion concentration, as appropriate for an ion pair relaxation in systems above the glass transition. The frequency of this relaxation, multiplied by the relaxation strength, has been found to be proportional to the ion conductivity, and the relaxation has therefore been assigned to short-range ion pair motion in the polymer. It exhibits characteristics similar to conductivity relaxations in inorganic solid ion conductors, and is considered to be due to the same species that give rise to the ion conductivity.

1. Introduction

Polymer electrolytes are commonly doped with an alkaline salt in order to achieve high ion conductivity, which in general is due to both anions and cations [1-3]. They are of major interest for a range of applications, for example in battery technology [1,4] and electrochromic devices [5,6] where the metallic cation is the electroactive species. The ionic conductivity of a polymer electrolyte is highly dependent on the concentration of the added salt but it is not clear if the conduction process involves all the ions of the salt [7], since they may be bound to the polymer chains or form neutral ion pair dipoles [8]. An improved ionic conductivity can be obtained by using short chain length polymers, which are transparent liquids at room temperature. With the addition of a suitable salt they become viscous liquids with good ionic conductivity. This kind of optically transparent electrolyte is of special interest for electrochromic (EC) devices [6,9].

A large number of EC device types employing a bewildering variety of electrolytes have been developed, as reviewed by Granqvist et al. [5,10,11]. In the 1990's, Stevens et al. developed a number of polymer electrolytes based on mixtures of polypropylene oxide (PPO) or polyethylene oxide (PEO), with poly(methyl methacrylate) (PMMA) and Li triflate (LiCF$_3$SO$_3$) [6,9]. Addition of PMMA increases the viscosity and adhesiveness and gives improved mechanical properties, while propylene carbonate is sometimes added as a plasticizer. More recently, a renewed interest in the development and systematic studies of polymer electrolytes for EC devices has been noted [12-14].

In this paper we report a detailed room temperature impedance spectroscopy study of the conductivity relaxation in PEO and PPO of molecular weight 400 as well as a random copolymer (P(EPO)) of molecular weight 600, all containing LiN(CF$_3$SO$_2$)$_2$ (LiTFSI). The objective is not to present detailed equivalent circuit fits to the data, but rather to distinguish between dielectric and conductive models for the impedance response [15,16] associated with the ionic charge carriers. To this end we carry out a thorough analysis of a dielectric

loss peak at frequencies slightly above the onset of the ionic conductivity response. This relaxation occurs only in the salt-containing polymers and has previously been assigned to ion pair dipoles [17,18]. In section 2 below the experimental procedures are described, while section 3 presents our results, followed by a discussion in section 4. We argue that a conductive response model is appropriate for the description of the dielectric response due to ionic motion.

2. Experimental

The samples were prepared from PEO and PPO of average molecular weight 400 (Aldrich; Polysciences), and from a random copolymer poly(ethylene (x) propylene (x) oxide) (P(EPO)), with x=50% and of average molecular weight 600. The latter polymer is described in ref. [9]. All polymers were dried in vacuum (10^{-2} Pa) at 328 K for 24 h. We then added lithium TFSI ($LiN(CF_3SO_2)_2$) to the polymer. The salt was dried at a temperature of 393 K, and at the same pressure as the polymer. The handling of the samples was done in a glove box filled with dry argon gas (< 1 ppm water). The solutions were stirred at 328 K in a sealed flask for 12 h, without the use of any additional solvent. The concentration of salt in the polymers is given as 1/n, where n is the ratio of ether oxygen to lithium. Samples with n ranging from 8 to 1024 were produced.

Impedance spectroscopy was performed with a HP 4291A RF Impedance/Material Analyser, in the frequency (ω) range from 1 MHz to 1.8 GHz, using an applied voltage of 0.1 V. The measurements were carried out using a Novocontrol BDS 2100 sample cell at a constant temperature of 295.5 K. The cell consists of two 0.5 cm diameter stainless steel electrodes, with a ring-shaped Teflon spacer in between. The spacer keeps the electrodes 0.58 mm apart and holds them parallel. The assembly of the cell and the manipulation of the sample was done in a dry argon atmosphere. Each measurement was repeated a number of times in order to check the reproducibility and eliminate spurious signals, for example from samples containing gas enclosures. Systematic errors were minimized by standard calibration using open and closed circuit configurations.

The data were collected with 16 points per frequency decade. The measured data were examined in the permittivity (ε) representation. It is related to the measured capacitance (C) by

$$\varepsilon(\omega) = C(\omega)\, d\, /\, \varepsilon_{vac}\, A, \qquad\qquad (1)$$

where d is the sample thickness, A its cross-sectional area and ε_{vac} is the permittivity of vacuum.

3. Results

The dielectric permittivity, $\varepsilon(\omega)=\varepsilon'(\omega)+i\varepsilon''(\omega)$, of the pure polymers is shown in fig. 1. The real part of the permittivity was found to be almost constant at low frequencies and decreases at high frequencies. A dielectric loss peak can be seen in ε'' at about 100 MHz for PPO, and above 1 GHz for the other two polymers. This relaxation is due to segmental motions of the polymer chain. It should be noted that the measurements were carried out at temperatures much higher than the glass transition temperature and the "critical point" where the different polymer chain relaxations merge. The increase of ε'' towards low frequencies may indicate an ionic conductivity contribution due to impurities. The relaxation frequencies of PEO and PPO are consistent with the values reported in recent works [19-21]. The spectra could be fitted to a circuit model consisting of a parallel connection of an ionic resistance (R_{ion}), a high-frequency capacitance (C_{inf}) and a dielectric Havriliak-Negami (DHN) element [22]. The DHN element models the polymer chain relaxation by the following expression for the capacitance:

$$C_{HN}(\omega) = \frac{\Delta C}{[1+(i\omega\tau)^{U}]^{\varphi}}\,, \qquad\qquad (2)$$

where τ is the relaxation time and the power-law exponents are denoted by U and φ. The best fit can hardly be distinguished from the data, as seen in fig. 1.

Figure 2 shows selected dielectric permittivity data for PEO and PPO containing LiTFSI, plotted in the complex permittivity plane. For the polymers with low salt concentrations, two contributions can be seen. At high frequencies (low ε') the response is dominated by the polymer relaxation, and at low frequencies the imaginary part of ε'' increases rapidly. In fact, it increases as $\sim\omega^{-1}$, which is the behaviour characteristic of the ionic conductivity, σ_{ion}, of the samples. However, there is also an additional relaxation that is observed only in salt containing samples. It is most easily visualized by subtracting the ionic conductivity from ε'', by using the equation

$$\varepsilon''_{corr} = \varepsilon'' - \sigma_{ion} / \omega\varepsilon_{vac}. \tag{3}$$

This corrected imaginary permittivity exhibits, in all the polymer systems, in addition to the polymer relaxation at high frequencies, a broad feature in the 1-100 MHz range, as illustrated in figure 3 for PEO and PPO. As the LiTFSI concentration increases, this so called "ion pair" relaxation increases in magnitude and overlaps more and more with the decreasing polymer relaxation. This is especially so for PPO, where the two relaxations cannot be distinguished at all for samples with n<64.

The response can be fitted to any of the two circuits in figure 4 with resulting mean-square errors of at most 0.003 and usually much lower. The circuit in figure 4a represents a dielectric response with a resistance, representing the ion conductivity, in parallel with two dielectric H-N elements representing the ion pair relaxation (DHN2) and the polymer chain relaxation (DHN1). The circuit in figure 4b, on the other hand, combines the ion conductivity and ion pair relaxation into a single process described by a conductive H-N element (CHN). The impedance (Z_{HN}) of this element is given by an equation analogous to eq. (2). It is known that it is virtually impossible to distinguish between dielectric and conductive responses by data fitting alone [16]. This is also our experience; the quality of fits is similar for the two circuits in figure 4. In the following we

will use the parameters for the ion pair relaxation obtained from fits to the circuit in figure 4a, where this contribution can be analyzed separately from the other elements.

In order to distinguish between conductive and dielectric response models, we will analyze the relationship of the ion pair relaxation to the ion conductivity, in order to see whether they exhibit similar features in their concentration dependences. Firstly, with increasing concentration the ion pair peak moves to higher frequency and then abruptly to lower frequency, in all the Li-polymer systems. The concentration dependence of the ion conductivity shows a similar behaviour, as shown in figure 5. Secondly the relaxation strength exhibits a characteristic scaling with Li salt concentration. Figure 6 displays the relative relaxation strength of the ion pair dipoles, obtained by dividing $\Delta \varepsilon = \Delta C d / \varepsilon_{vac} A$, with $1/n$, as a function of metal ion concentration ($1/n$). For PPO we only consider the concentration range where the ion pair and polymer relaxations can be distinguished. The normalized relaxation strength decreases approximately as a power law of concentration. For our materials approximate power-law exponents in the range -0.6 to -0.65 can be extracted. Thirdly, we investigate whether our experimental data follow the so-called BNN relation, which is valid for a large number of ion conducting glasses, namely [23-25]

$$\sigma_{ion} = F \; \varepsilon_{vac} \; \Delta \varepsilon \; \omega_{max}, \qquad\qquad (3)$$

Here ω_{max} is the relaxation peak frequency and F is a numerical factor of order unity. As seen in fig. 7, most of the values of F for the Li-polymer systems fall consistently between 0.6 and 2.

4. Discussion

We have studied the dielectric relaxations in PEO, PPO and P(EPO) as a function of LiTFSI concentration. The ionic conductivity exhibits a maximum at intermediate concentrations. As expected the relaxations due to the segmental motions of the polymer chains decrease in strength with increasing salt concentration. We also

observed another relaxation peak in the Li-containing polymers. In previous works on similar systems [17,18], this second peak has been interpreted as a relaxation due to ion pair dipoles, consisting of a positive cation and a negative anion. A similar peak was found in poly(propylene oxide)/LiClO$_4$ electrolytes by Furukawa et al. and was assigned to local fluctuation of ions in a certain domain [21,26]. The strength of the peak scales with Li concentration, as shown in fig. 6. The values of the scaling exponent are close to the expected one for an ion pair dipole with at least one ion free to move. We notice that $\Delta\varepsilon$ is proportional to the square of the cation-anion distance, and that the average ion distance should be proportional to the $-1/3$ power of the ion concentration, if at least one of the ions is mobile. This analysis supports the interpretation of the relaxation process in the MHz region as being due to ion pair dipoles.

We now address a fundamental question: Are these ion pairs the same entities that give rise to the ionic conductivity or can we distinguish between free and bound ion pairs, giving rise to the conductivity and the relaxation, respectively? As seen in figure 7, our data exhibits good agreement with the BNN-relation. The vailidity of the BNN-relation is a direct consequence of the scaling of ac conduction [27,28], implying that the ionic conduction and relaxation should be viewed as two parts of the same process. The implication of this is that there exists a smooth transition between the ionic conductivity and the ion pair relaxation as the frequency increases. Hence the ionic conductivity and the relaxation process both arise from ionic motion, but on long and short time scales, respectively. This is similar to what is observed in inorganic ion conductors and a number of other disordered materials [27]. On short time scales the ions appear to be bound as ion pair dipoles, while on longer time scales at least one in each pair is free to move and gives rise to the ionic conductivity. Hence, for our samples, we conclude that the combined response should be analyzed as a conductivity relaxation, as described by the equivalent circuit in figure 4b.

5. Conclusion

In this paper we have investigated the dependence of the ion conductivity and ion pair relaxation strength on the salt concentration, for polyethylene oxide (PEO), polypropylene oxide (PPO) and a random copolymer P(EOPO) containing the salt LiTFSI. For the electrolytes the relaxation strength per added salt dipole depends on the concentration approximately as $(1/n)^{-2/3}$. This behaviour is expected for ion pair dipoles, if at least one of the ions is free to move. For PPO the ion pair relaxation overlaps more strongly with the polymer relaxation. It seems that the ionic motion is more strongly coupled to the structural rearrangements of the polymer chains in this case. The ion conductivity, relaxation strength and relaxation frequency follow to a good approximation the BNN-relation, which indicates that it is appropriate to view the conductivity and ion pair relaxation as parts of the same basic conduction process.

Acknowledgments

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Figure captions.

Figure 1. Real (a) and imaginary (b) permittivity as a function of frequency for polyethylene oxide (PEO), polypropylene oxide (PPO) and the copolymer poly(ethylene propylene oxide) (P(EPO). Squares denote experimental data and full lines denote an equivalent circuit fit as described in the text.

Figure 2. Imaginary vs. real permittivity for polyethylene oxide (a) and polypropylene oxide (b) mixed with different amounts of Li TFSI, as shown in the insets.

Figure 3. Imaginary permittivity, after subtraction of the ionic conductivity contribution, for polyethylene oxide (a) and polypropylene oxide (b) mixed with different amounts of Li TFSI, as shown in the figure.

Figure 4. Equivalent circuit models pertaining to a dielectric response (a), and a conductive response (b) of the ionic charge carriers.

Figure 5. Ion conductivity as a function of Li concentration (1/n) for polyethylene oxide (PEO), polypropylene oxide (PPO) and the copolymer poly(ethylene propylene oxide) (P(EPO) mixed with different amounts of Li TFSI, as shown in the inset. Error bars are less than the size of the points except in one case.

Figure 6. Relaxation strength due to ion pairs, normalized by division with (1/n), as a function of Li concentration, for polyethylene oxide (PEO), polypropylene oxide (PPO) and the copolymer poly(ethylene propylene oxide) (P(EPO) mixed with different amounts of Li TFSI, as shown in the inset. Lines denote fits to a power-law function. Error bars were obtained from estimated parameter uncertainties in the equivalent circuit fitting.

Figure 7. The BNN-factor, F, defined in eq. (3), is shown as a function of Li concentration (1/n), for polyethylene oxide (PEO), polypropylene oxide (PPO) and the copolymer poly(ethylene propylene oxide) (P(EPO) mixed with different amounts of Li TFSI, as shown in the inset. Error bars were obtained from estimated parameter uncertainties in the equivalent circuit fitting.
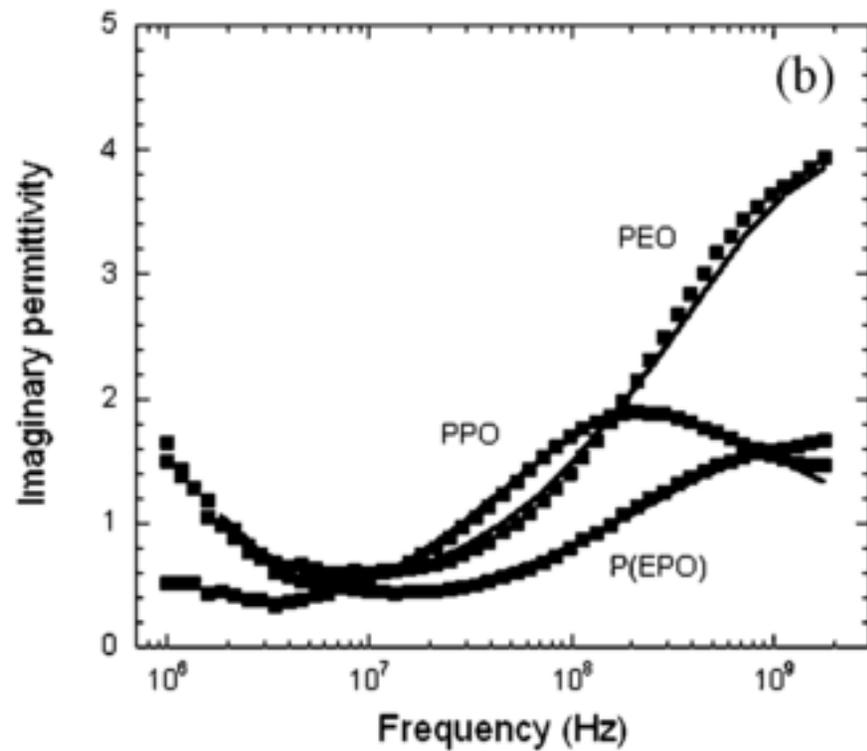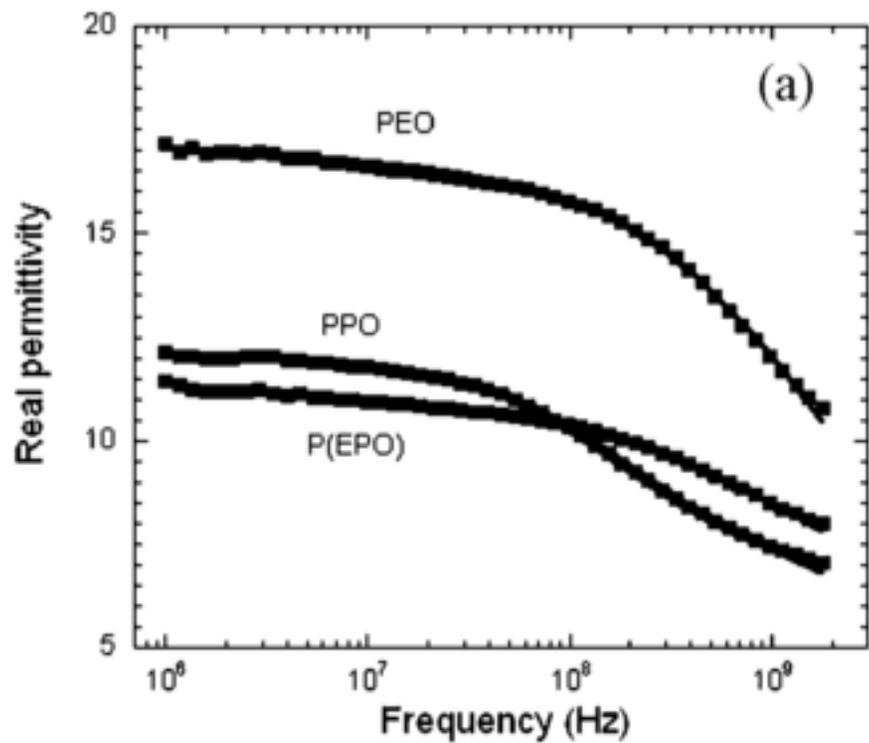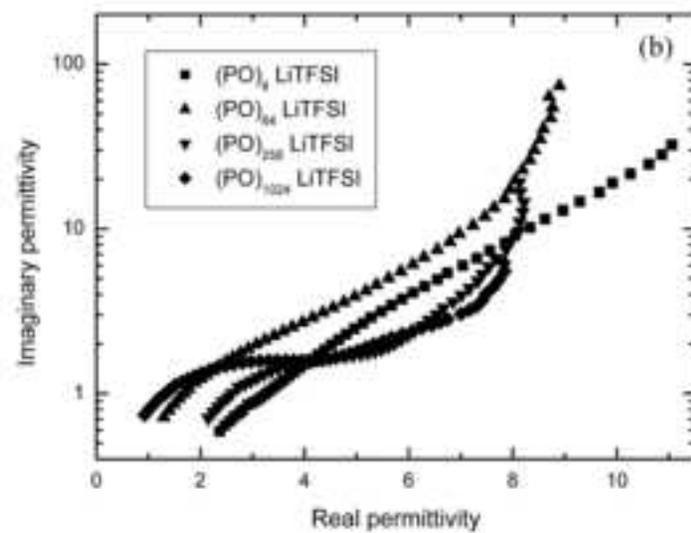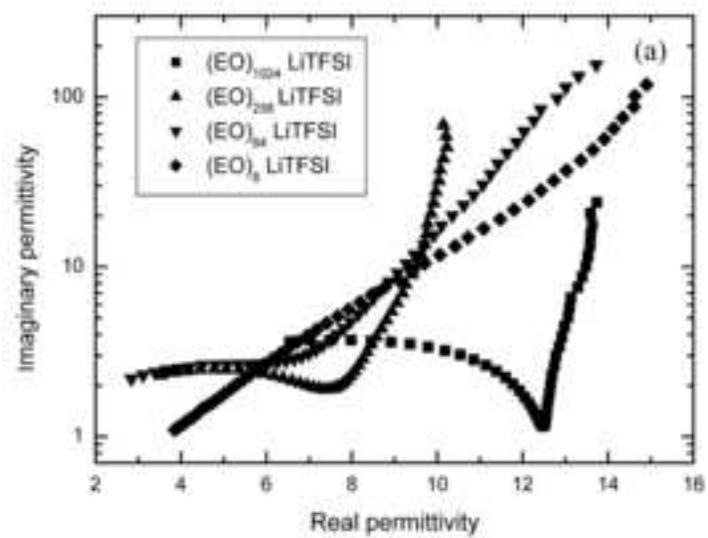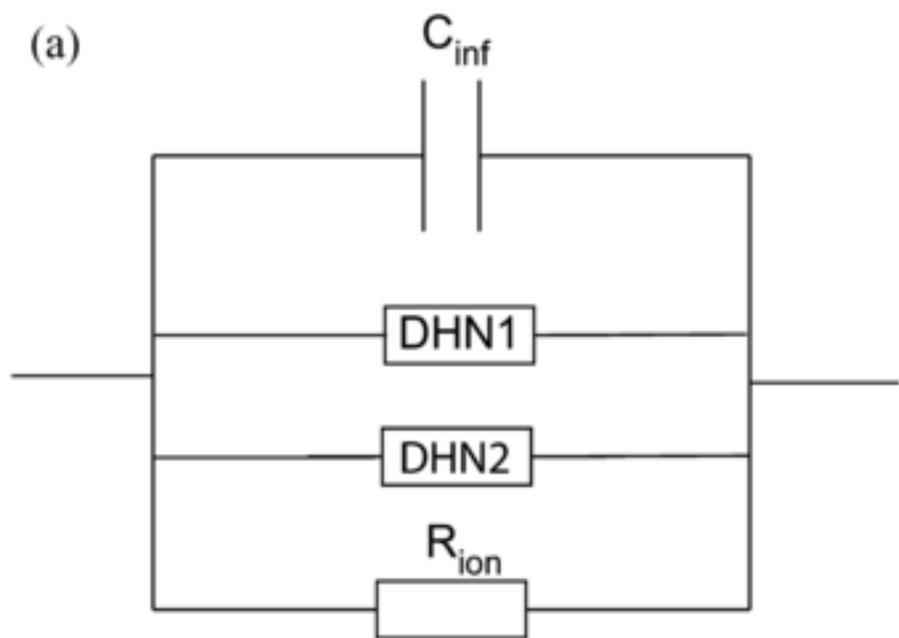
Fig. 1

Figure 2
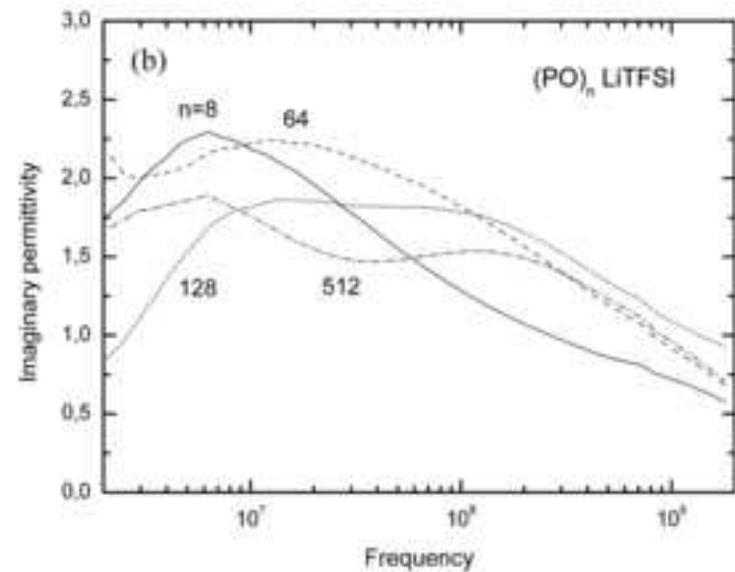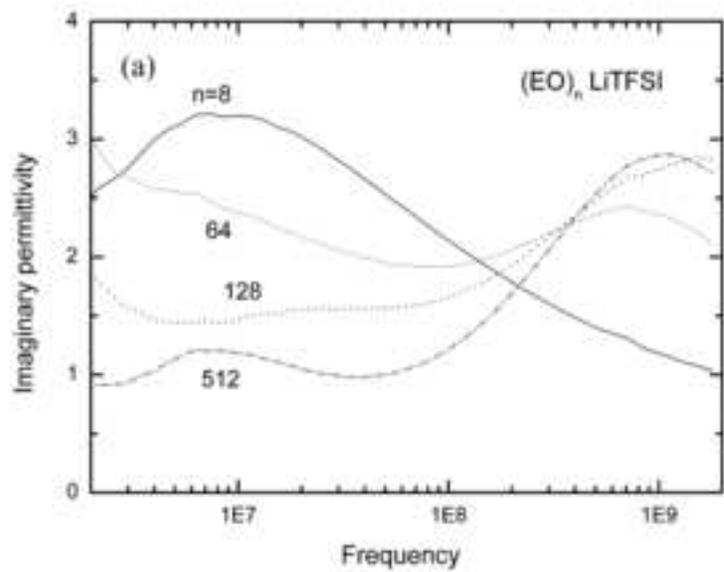
Figure 3

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