

Properties of Solid Solutions of Poly(ethylene oxide)/Epoxidized Natural Rubber Blends and LiClO₄

C. H. Chan,¹ H. W. Kammer²

¹Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia

²Department of Chemistry, Martin-Luther University of Halle, D-0699 Halle, Germany

Received 14 June 2007; accepted 30 March 2008

DOI 10.1002/app.28555

Published online 9 July 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Solid solutions of blends of poly(ethylene oxide) (PEO) and epoxidized natural rubber (ENR) comprising 12 wt % of LiClO₄ were studied. Two glass transition temperatures, corresponding to the T_g s of the constituents, confirm immiscibility of the polymers over the entire composition range. It turns out that the T_g s of both polymers slightly increase after addition of salt to the blends. This shift is approximately constant over the whole range of blend composition. Accordingly, T_g measurements reveal that the salt dissolves to approximately equal relative amounts in the two phases. The degree of crystallinity of PEO in blends with ENR descends only to a minor extent with ENR content. However, addition of salt leads first to decreasing crystallinity and second this decrease becomes more pronounced with the addition of ENR. It shows that under these experimental conditions the salt content in PEO increases as compared to ENR. As one expects, the rate of isothermal crystal-

lization does not change in blends as long as PEO is in excess. The situation changes again when salt is added. The rate decreases in a certain range of crystallization temperatures when ENR is added, demonstrating that salt is favorably dissolved in PEO. Conductivity was measured in polymers comprising different salt concentrations. A power-law dependence of conductivity on salt concentration was found. It results that the mobility of charge carriers in PEO exceeds that of ENR by five orders of magnitude. Therefore, the conductivity in blends is primarily governed by PEO as long as PEO is in excess. Conductivity measurements reveal again that salt is preferably dissolved in PEO. The distribution coefficient is estimated. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 424–432, 2008

Key words: solid solutions; polymer blends; ionic conductivity

INTRODUCTION

Solid polymer electrolytes, exhibiting ionic conductivity, are solid solutions of salts in polymers. Interrelations between ions and polymer chains play an important role in mobility of charge carriers. Hence, ion mobility in those systems is strongly correlated to segmental motions.

The first study on solid electrolytes dates back to 1973.¹ Later on it was shown that complexation of salt cations results in significant ionic conductivity.² The most frequently studied polymer in that context is poly(ethylene oxide) (PEO) because a large variety of salts is soluble in PEO.

Not only homopolymers have been used in forming of polyelectrolytes but also polymer blends,^{3,4} graft⁵ and block copolymers,⁶ as well as interpenetrating networks.⁷ For example, solid solutions of

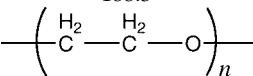
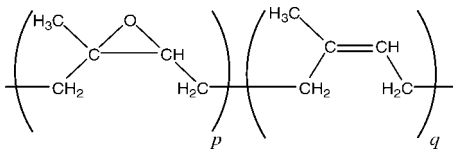
lithium perchlorate in blends of poly(vinyl acetate) and poly(vinylidene fluoride) have been proven to be promising candidates for solid polymer electrolytes.⁴

The aim for inserting polymer blends as polymer matrix material in polymer electrolytes was the hope for improving both mechanical properties as well as the ionic conductivity of the principal polymer, the PEO, used in solid electrolytes. Miscibility and morphology of semicrystalline/semicrystalline^{8,9} and semicrystalline/amorphous¹⁰ polymer blends have been extensively studied in recent years. These studies may be helpful in better understanding of interactions between salt molecules and polymer chains. Most polymers are immiscible with PEO, that is, the polymer blend forms a heterogeneous system. Hence, one may observe minor influence of the second constituent on the properties of PEO that are governing electric conductivity. Nevertheless, it seems to be worthwhile to study influence of salt on thermal and electric properties of immiscible blends comprising PEO as one component. We select epoxidized natural rubber (ENR) as the second component. This selection is related to the hope that dispersion of ENR in PEO leads to enhanced physical strength and ionic conductivity of the alloy.

Correspondence to: C. H. Chan (cchan@salam.uitm.edu.my).

Contract grant sponsor: Institute of Research, Development and Commercialization, Universiti Teknologi MARA; contract grant numbers: 600-IRDC/ST 5/3/687, 600-IRDC/ST 5/3/1039.

TABLE I
Characteristics of the Blend Constituents

Polymer	PEO	ENR (50 mol % epoxy content)
M_w^a (g mol ⁻¹)		700,000
M_n^a (g mol ⁻¹)		200,000
M_v^b (g mol ⁻¹)	300,000	
T_m^c (°C)	66	–
T_g^d (°C)	–54	–19
T_d^e (°C)	440	412
ΔH_{ref} (J g ⁻¹)	188.3 ^f	–
Molecular structure		
Supplier	Aldrich Chemical Co. (St. Louis, MO)	Rubber Research Institute, (Sungai Buloh, Malaysia)

^a Molecular masses as estimated in this work by gel permeation chromatography. Polystyrene with low polydispersity was used as standard.

^b Viscosity-average molecular weight provided by the supplier.

^c Apparent melting temperature for the neat polymer during the first heating run.

^d Glass transition temperature as determined in this work.

^e Decomposition temperature by thermal gravimetry analysis as determined in this study.

^f The melting enthalpy of 100% crystalline PEO.¹¹

We report on properties of PEO in solid blend solutions and compare them with the behavior in salt-free polymer blends. We focus especially on melting and crystallization behavior of PEO as well as on conductivity. In the context of the latter, we will present some qualitative scaling arguments about the behavior of solid solutions.

EXPERIMENTAL

Materials

Characteristics of the polymers are given in Table I. In what follows, ENR denotes epoxidized natural rubber with 50 mol % of epoxy content. PEO and ENR were purified by filtration from chloroform solutions and precipitation in nonsolvent afterwards. The precipitate was filtered off and dried under vacuum.

LiClO₄ was purchased from Across Organic Company (Geel, Belgium). It melts at 236°C and decomposes at about 400°C. LiClO₄ is a very hygroscopic salt. It was used without further purification.

Preparation of the blends

Thin films of the PEO/ENR blends were prepared by casting from 2% (w/w) solutions of the two components in chloroform (Fisher Scientific, Leicestershire, UK). Compositions of the blends ranged from 100/0 to 0/100 in steps of 10 wt %.

Lithium perchlorate was added to the blend solutions. The concentration of salt in the solid solution is given by

$$\gamma = \frac{\text{Mass of salt}}{\text{Mass of polymer blend}} \quad (1)$$

Polymer films were dried for 24 h at 50°C, before further drying in a vacuum oven for 48 h at the same temperature. Afterwards, dried polymer films were kept in desiccators. Approximately 48 h before analysis of various parameters, samples were dried again in the vacuum oven at 50°C.

Differential scanning calorimetry

Perkin–Elmer DSC7 (Shelton, CT), calibrated with indium standard, has been used for the analysis of samples under nitrogen and helium atmosphere for thermal procedures (i) and (ii), respectively. Sample weights amounted to around 7 mg in differential scanning calorimetry (DSC) experiments. Samples were exposed to different thermal histories:

- i. *Isothermal crystallization*: Samples were annealed at $T_a = 80^\circ\text{C}$ for 1 min, followed by cooling with a rate of 20 K min⁻¹ to the respective crystallization temperature (T_c) and held until complete crystallization. The half-time of crystalliza-

tion ($t_{0.5}$) was determined at $T_c = \text{const.}$ The same procedure was applied for determination of the melting point. After crystallization for five half times, samples were heated up to 80°C with a rate of 20 K min^{-1} .

- ii. *Glass transition temperature:* Samples were annealed at $T_a = 80^\circ\text{C}$ for 1 min followed by cooling with a rate of 100 K min^{-1} to -90°C and held there for 1 min. Afterwards, samples were reheated up to 80°C with a rate of 20 K min^{-1} .

Optical polarizing microscopy

Morphologies of blends were studied using Leica Q Win Software (Cambridge, UK), which was attached to the Nikon microscope (Yokohama, Japan) equipped with a Linkam heating/cooling unit (Surrey, UK). Samples were subjected to the following thermal procedures:

- iii. *Radial growth rate:* Sample was annealed at $T_a = 80^\circ\text{C}$ for 1 min, followed by cooling with a rate of 20 K min^{-1} to crystallization temperature $T_c = 49^\circ\text{C}$ and held there until complete crystallization. During isothermal crystallization, micrographs were captured at suitable time intervals. Measurement of diameter of the growing spherulites was carried out afterwards by using Leica Q win software.
- iv. *Morphology:* Sample was annealed at $T_a = 80^\circ\text{C}$ for 1 min, followed by cooling with a rate of 20 K min^{-1} to $T_c = 49^\circ\text{C}$ and held until complete crystallization. Micrograph was captured at $T_c = 49^\circ\text{C}$.

Gel permeation chromatography

The molecular weight of ENR was estimated by gel permeation chromatography (GPC) at 30°C using a Waters GPC. Tetrahydrofuran was used as eluant at a flow rate of 1.0 mL min^{-1} and solvent with sample concentration of 10.0 mg mL^{-1} . Polystyrene standards with low polydispersity were used to prepare a calibration curve.

Impedance spectroscopy

Ionic conductivity (σ) at 30°C was determined from ac-impedance measurements using a Hioki 3520-01 Hi-Tester (Nagano, Japan) interfaced with a computer for data acquisition over the frequency range between 100 Hz and 1 MHz. Films of polymer electrolyte were sandwiched between two stainless steel disk electrodes, which acted as blocking electrodes for ions. Quantity σ was calculated from the bulk electrolyte resistance value (R_b) by adopting equation

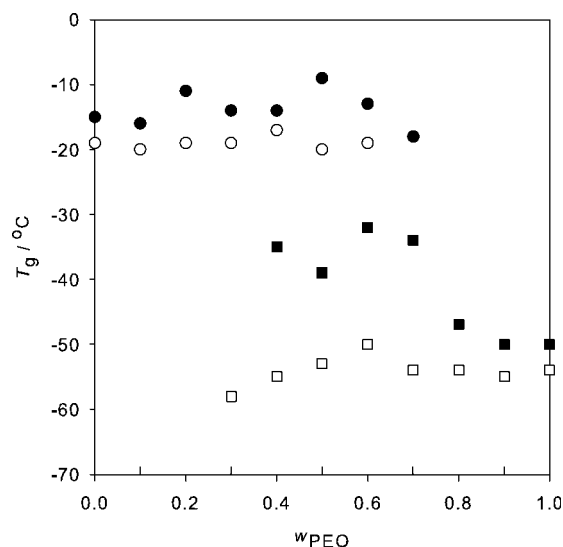


Figure 1 Glass transition temperatures of PEO and ENR in blends and in solid solutions with $Y = 12\%$ of LiClO_4 . Blends: open squares, PEO; open circles, ENR; closed markers refer analogously to salt-containing blends.

$\sigma = L/(R_b A)$. Quantities L and A denote thickness of the polymer electrolyte film and its surface area in contact with the stainless steel disk electrodes. Diameter of the electrode is 10 mm. The average of thickness L was calculated from three measurements of thickness on the dry polymer film at three different positions that were in contact with the stainless steel disk electrodes. Thickness was measured by use of Mitutoyo Digimatic Caliper.

RESULTS AND DISCUSSION

Glass transition temperature

Blends and solid solutions with Li-salt were exposed to thermal procedure ii, described in experimental section, for determination of glass transition temperatures T_g . Glass temperatures were estimated from the second heating runs. Figure 1 shows the results. Two glass transition temperatures, corresponding to those of the neat constituents, were found in both the salt-free and the salt-comprising systems. These results reveal two facts. First, the polymers are immiscible over the entire composition range, and second, addition of salt leads to an increase of both T_g s. This indicates that the Li-salt is soluble in PEO as well as in ENR. Glass transitions of neat ENR and PEO are found at 254 K (-19°C) and 219 K (-54°C), respectively. Addition of $Y = 12\text{ wt } \%$ of LiClO_4 causes a constant increase of glass transition temperatures by $\sim 5\text{ K}$ over the entire concentration range. This gives some hint about the distribution of salt in the two polymer phases. Using concentration Y of eq. (1), one may define Nernst's distribution coefficient

TABLE II
Ranges of Isothermal Crystallization for PEO

Polymer sample	Temperature range (°C)
PEO in PEO/ENR blends	44–54
PEO in solid solutions	24–35

cient as follows:

$$K = \frac{Y_{\text{ENR}}}{Y_{\text{PEO}}} \quad (2)$$

where concentration Y_i refers to the respective phase i . It follows for the salt concentration in the PEO phase in the blend with $Y = m_{\text{salt, total}}/m_{\text{blend}}$

$$Y_{\text{PEO}} = \frac{Y}{W_{\text{PEO}} + W_{\text{ENR}}K} \quad (3)$$

Quantity W_i symbolizes the mass fraction of component i in the blend. An analogous expression follows for Y_{ENR} . It is obvious that the change in T_g is a function of salt concentration. Moreover, Figure 1 shows that this change is constant for ENR to a good approximation over the whole range of blend compositions when $Y = \text{const}$:

$$\Delta T_g^{\text{ENR}}(Y_{\text{ENR}}) = \text{const} \quad \text{for } Y_{\text{ENR}} = \text{const} \quad \text{and } W_{\text{ENR}} \leq 1 \quad (4)$$

Equation (4) implies $Y/Y_{\text{ENR}} = 1$, and hence, the distribution coefficient of eq. (3) has to be equal to unity, $K = 1$. This result is bound to the change of T_g with salt concentration as given by eq. (4). If eq. (4) also holds true for PEO, then it follows according to thermodynamics also $K = 1$ for PEO. Figure 1 reveals that this is indeed obeyed in the range of low ENR concentrations. In the middle range of blend composition, deviations occur that plead for $K < 1$ and point toward modification of eq. (4). We may conclude that findings for T_g suggest dissolution of salt is slightly favored in PEO in a certain range of salt concentration.

Crystallinity

Melting enthalpies of PEO, ΔH_m , are employed to examine PEO crystallinity in blends and solid salt solutions. The heat of melting was determined according to thermal procedure (i) in the reheating cycle after crystallization at selected T_c for five half times, $t_{0.5}$. Quantity $t_{0.5}$ is defined as time taken for half of the crystallinity to develop in the isothermal crystallization process. Ranges of crystallization temperature with appreciable rate of crystallization by

DSC are summarized in Table II. We selected crystallization temperatures for blends and solid solutions, where approximately the same rates of crystallization were observed (cf. Fig. 4).

Melting enthalpy can be used as measure of crystallinity X since it is proportional to X , $X \propto \Delta H_m$, with the reference enthalpy given in Table I as the factor of proportionality. Accordingly, the crystallinity of PEO amounts here to 69% and drops to 37% when 12 wt % of Li-salt is added. Figure 2 reveals that the degree of crystallinity of PEO in blends with ENR only slightly decreases as compared to neat PEO. This effect disappears in solid solutions as the dotted curve in Figure 2 shows. If the degree of crystallinity of PEO in solid solutions would follow the dotted line of Figure 2, we could say that Nernst's distribution coefficient K of eq. (2) is unity and constant over the range of blend composition. However, this is not fulfilled as the dashed curve shows. The steeper slope of this curve implies that in this range of blend composition, coefficient K decreases or the relative amount of salt dissolved in PEO increases as compared to ENR. This seems to be in contrast to the discussion on glass transition temperatures in the previous paragraph. The reason for this apparently controversial result can be simply explained by the different responses of the system. Glass transition temperature reflects the behavior of the amorphous phase in a system. The thermal history applied for determining the glass transition temperature is not associated with a change of amorphous phase. The melting enthalpy on the other hand is related to transformation of crystalline phase in

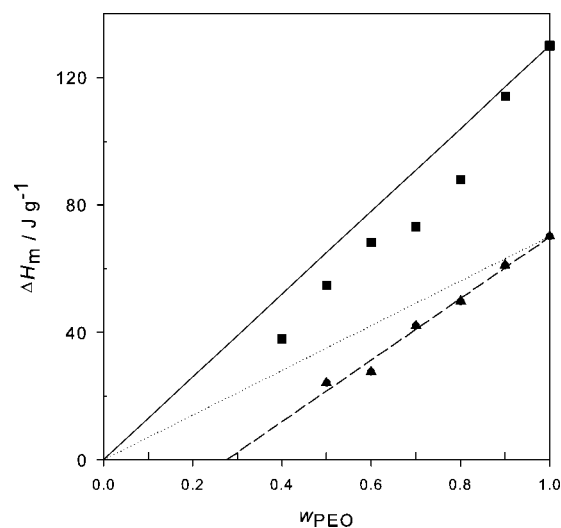


Figure 2 Melting enthalpy of PEO in blends with ENR (solid squares) and in solid solutions with 12 wt % of LiClO₄ (solid triangles); cf. text. Blends were crystallized for five half times at 49°C and solid solutions for equivalent periods of time at 30°C.

amorphous phase after isothermal crystallization. Hence, crystallization as well as melting depends on the salt content. In other words, the degree of crystallinity itself depends on salt content and this in turn also causes changes of the salt content of the amorphous phase. Therefore, glass transition temperature is determined under condition of constant salt concentration of the amorphous phases, whereas crystallinity can be only observed under constant overall concentration of salt in the system, but not under constant salt content of the phases. The phase transformation is accompanied by a change in salt solubility and hence, a change in distribution coefficient K .

Melting behavior of PEO

Melting temperatures, T_m , were determined according to thermal procedure (i) after isothermal crystallization for five half times at the respective crystallization temperature, T_c . Data were evaluated after Hoffman–Weeks procedure.¹² Selected results are presented in Figure 3. The curves $T_m = T_m(T_c)$ for PEO do not change significantly in blends with ENR. The equilibrium melting point of PEO follows from Figure 3 to $T_m^0 = 83.6^\circ\text{C}$. It changes to $T_m^0 = 75.9^\circ\text{C}$ in solution with 12 wt % of Li-salt or to 73.5°C in 50/50 blends with ENR under the same condition. Functions $T_m = T_m(T_c)$, as shown in Figure 3, are strictly linear with correlations of 0.998. They read for the two systems of Figure 3.

$$T_m(\text{PEO})/^\circ\text{C} = 47.15 + 0.436T_c$$

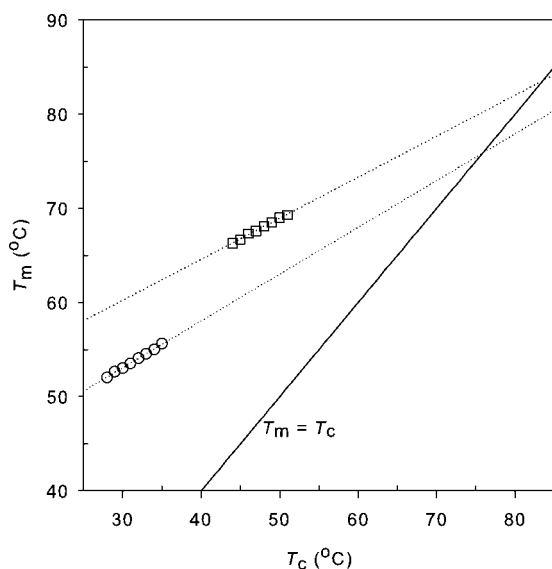


Figure 3 Hoffman–Weeks plots for PEO, crystallized from 44 to 51°C , open squares, and PEO with 12 wt % of LiClO_4 , crystallized from 28 to 35°C , open circles.

TABLE III

Avrami Parameters for Crystallization of Neat PEO and in Solution with LiClO_4

Avrami parameters	PEO	PEO in solution with 12 wt % of LiClO_4
	$T_c = 44^\circ\text{C}$	$T_c = 35^\circ\text{C}$
$100K_A^{1/n}(\text{min}^{-1})$	115 ± 1	2.8 ± 0.1
n	2.28 ± 0.01	1.53 ± 0.04

$$T_m(\text{PEO} + \text{salt})/^\circ\text{C} = 38.17 + 0.497T_c$$

If we assume the ratio $\Delta H_m(\text{PEO})/\Delta H_m(\text{PEO} + \text{salt}) = 1.85$ as given by data of Figure 2, it follows with $T_m^0(\text{PEO})/T_m^0(\text{PEO} + \text{salt}) = 1.10$ for the ratio of corresponding melting entropies $\Delta S_m(\text{PEO})/\Delta S_m(\text{PEO} + \text{salt}) = 1.68$. This means that both melting enthalpy and melting entropy of PEO descend when salt is added.

The Hoffman–Weeks functions

$$T_m = \alpha T_c + (1 - \alpha)T_m^0$$

given above might be easily related to the interfacial energy melt/crystallite per volume formulated here as the ratio of interfacial tension σ and thickness l_c of lamella. In Kelvin's approximation, it follows

$$\frac{\sigma}{l_c} = \Delta H_m^0 \rho \alpha \left(1 - \frac{T_c}{T_m^0}\right)$$

With the slopes α given in the text, one easily sees that

$$\left(\frac{\sigma}{l_c}\right)_{\text{PEO}} < \left(\frac{\sigma}{l_c}\right)_{\text{PEO} + \text{salt}}$$

It means for l_c and $T_c/T_m^0 = \text{const}$, the interfacial tension of the salt solution increases as compared to the solvent PEO or the salt acts as an interface-inactive substance.

Dynamics of isothermal crystallization of PEO

Isothermal crystallization experiments were carried out according to thermal procedure (i), as described in the experimental section. Half times of crystallization, $t_{0.5}$, were estimated from the DSC traces as reported before. In the heterogeneous blend under discussion, phase boundaries may also influence the rate of crystallization. Therefore, Avrami equation¹³ will be applied here only to neat PEO and in solution with 12 wt % of LiClO_4 . It reads

$$X(t) = 1 - \exp\left[-K_A^{1/n}t\right]^n \quad (5)$$

The rate of crystallization of PEO in blends is simply characterized by the reciprocal half-time, $(t_{0.5})^{-1}$, which can be defined independently of eq. (5). In addition, results for pure PEO may serve as refer-

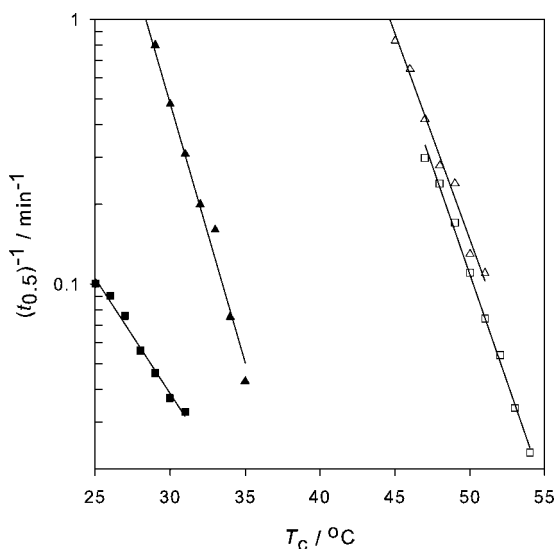


Figure 4 Rate of crystallization, $(t_{0.5})^{-1}$, at different T_c s for PEO in blends after the samples were exposed to thermal procedure I; salt content $Y = 12\%$. PEO/ENR blends: (Δ) 100/0, (\square) 50/50; PEO/ENR/LiClO₄: (\blacktriangle) 100/0, (\blacksquare) 50/50.

ence for evaluation of crystallization of PEO in blends. In eq. (5), the degree of conversion, $X(t)$, is the normalized crystallinity given as the ratio of the degree of crystallinity at time, t , and the final degree of crystallinity. Quantities $K_A^{1/n}$ and n represent the overall rate constant of crystallization and the Avrami exponent, respectively. Avrami plots for PEO are strictly linear up to conversions of 50% (correlation coefficients > 0.9990). Avrami parameters for neat PEO and in solution with salt were determined at $T_c = 44$ and 35°C , respectively, i.e., at crystallization temperatures with similar undercoolings, $\Delta T \approx 40$ K. Results are listed in Table III. Addition of 12 wt % of LiClO₄ to PEO suppresses its overall rate of crystallization by two orders of magnitude.

Figure 4 presents the crystallization rate of PEO in blends and corresponding salt solutions. As one expects for heterogeneous blends, the rate of crystallization does not change with the addition of ENR at least in the range where PEO is in excess. This situation changes, however, when salt is added. One observes in blends a dramatic decrease of the rate as compared to the salt solution with PEO. This is again an indication that for the distribution coefficient $K < 1$ holds true, i.e., the salt content in PEO exceeds that in ENR. The smaller magnitude of the slope for the 50/50 blend as compared to the PEO solution might be indicative of desaturation of PEO in blends with ascending temperature.

Spherulite growth rates of PEO

The radial growth rate, G , of PEO spherulites in blends with ENR and corresponding salt solutions

was determined by polarizing optical microscope under isothermal conditions at 49°C . In all mixtures, spherulite radii grew linearly with time to a good approximation. Resulting radial growth rates are depicted in Figure 5. The error of the rates is less than 8%. The figure shows that at 49°C the rate constant of PEO is not only constant in blends with ENR but also in solutions with salt. This result confirms the tendency indicated in Figure 4 that with increasing temperature the distribution coefficient approaches unity.

Blend morphologies

Figure 6 shows selected examples of PEO spherulite morphologies that developed in blends with ENR and in blend solutions with salt at $T_c = 49^\circ\text{C}$. When PEO is in excess in blends with ENR, spherulites exhibit fibrillar fine texture. The fibrillar texture disappears gradually in the opposite composition range. Addition of salt to the blends leads to nonspherical shapes caused by anisotropic growth rates. Moreover, one observes amorphous regions within the morphological structures that could not be rearranged interspherulitically.

Conductivity

In solid solutions of a salt in a polymer, salt molecules, especially cations, are solvated by chain segments. Therefore, properties of these systems are strongly governed by interactions between salt molecules and segments. We take these correlations approximately into account by formulating the molar

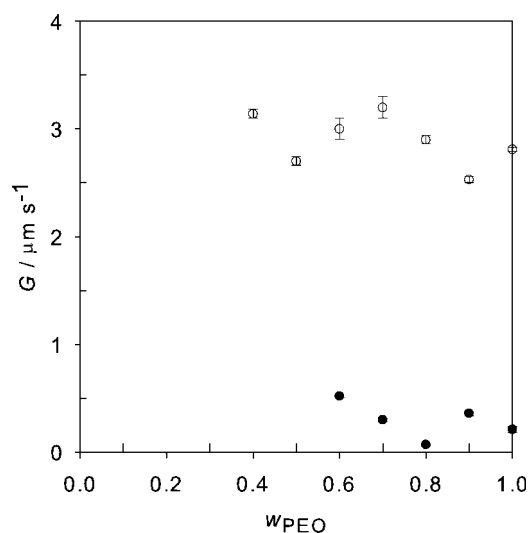


Figure 5 Radial growth rate (G) of PEO for PEO/ENR and PEO/ENR/LiClO₄ blends as a function of weight fraction of PEO in the blends after the samples were exposed to thermal procedure iii at $T_c = 49^\circ\text{C}$; salt content $Y = 12\%$. (\circ) PEO/ENR blends; (\bullet) PEO/ENR/LiClO₄.

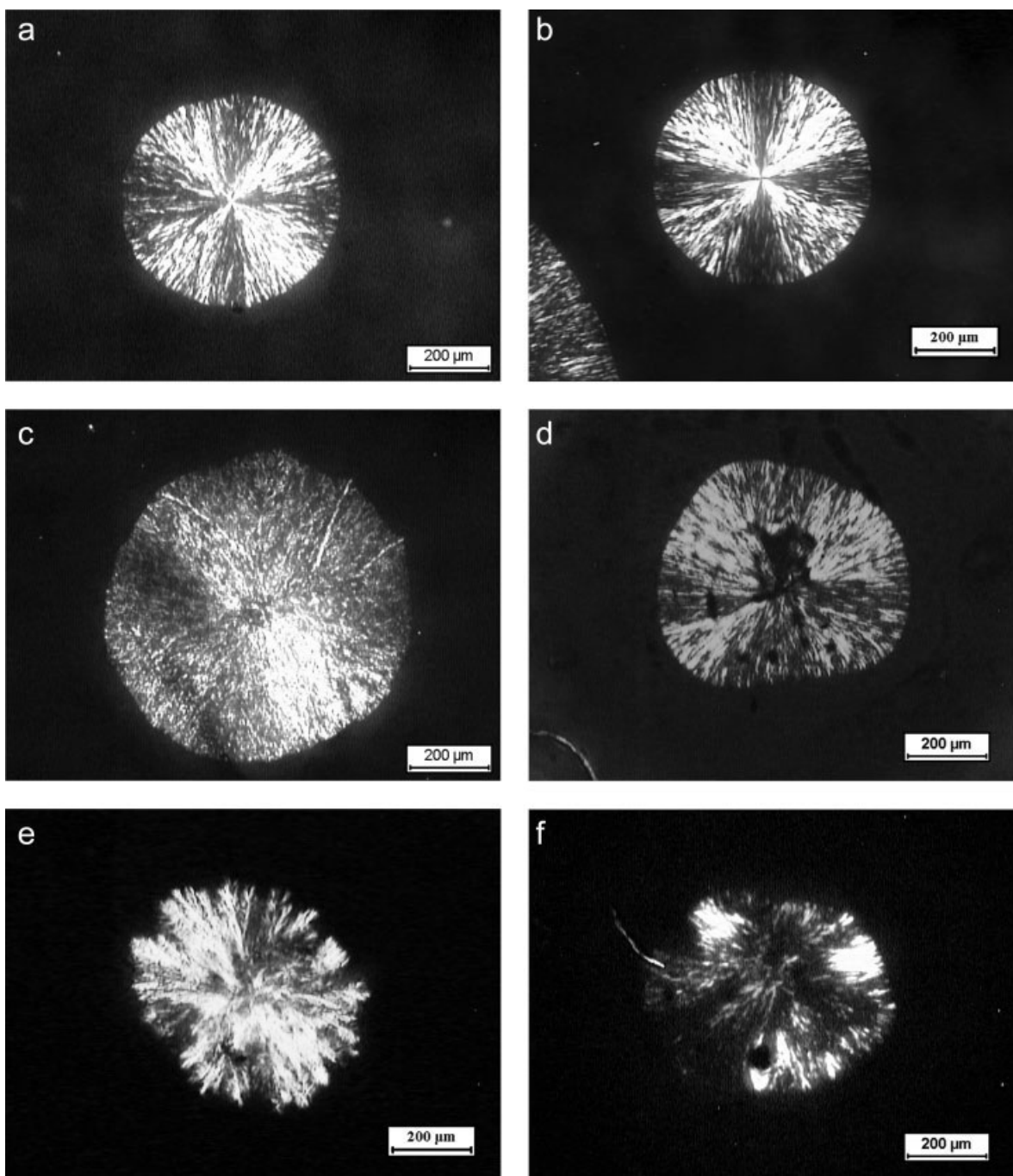


Figure 6 Morphology of PEO/ENR and PEO/ENR/LiClO₄ blends, isothermally crystallized at $T_c = 49^\circ\text{C}$. Micrographs taken at 49°C . Magnification: $\times 5$. The bar corresponds to $200\ \mu\text{m}$. PEO/ENR blends: (a) 100/0, (b) 80/20, (c) 40/60; PEO/ENR blends with $Y = 12\%$ of LiClO₄: (d) 100/0, (e) 80/20, (f) 60/40.

salt concentration as follows:

$$C_{\text{salt}} = \frac{1}{a^3 N_A} \left(\frac{\Phi_{\text{salt}}}{\Phi_{\text{poly}}} \right)^x = \frac{1}{a^3 N_A N_o^x} \quad (6)$$

with N_o the number of segments per salt molecule, $N_o = N_{\text{monomer}}/N_{\text{salt}}$, and the volume a^3 of a segment

given by

$$N_A a^3 = M_{\text{monomer}}/\rho_{\text{polymer}}. \quad (7)$$

Exponent x gives the extent of correlations between salt molecules and segments. For $x > 1$, eq. (6) indicates that the volume where correlations are important is larger than the natural volume $a^3 N_o$, whereas it is smaller for $x < 1$. As mentioned earlier

[see eq. (1)], the concentration measure Y is frequently applied. It can be easily related to N_o

$$Y = \frac{M_{\text{salt}}}{M_{\text{monomer}}} \frac{1}{N_o} \quad (8)$$

Applying eqs. (6)–(8), we get for concentration dependence of ionic conductivity

$$\sigma = eN_A\mu \frac{\rho_{\text{poly}}}{M_{\text{mono}}} \left(\frac{M_{\text{mono}}}{M_{\text{salt}}} \right)^x Y^x \quad (9)$$

In eq. (9), the ion mobility is symbolized by μ . A double-logarithmic plot of conductivity versus concentration Y yields exponent x and mobility μ .

Equation (9) is only valid in a certain range of concentration Y . This range might be estimated as follows. The Bjerrum length l_B gives the distance between two charges where Coulomb interaction equals thermal energy. It reads with the usually applied symbols

$$l_B = \frac{e^2}{4\pi\epsilon_0\epsilon k_B T} \quad (10)$$

for $T = 300$ K, one gets

$$l_B = \frac{55.58}{\epsilon} \text{ nm} \quad (10')$$

which results for water to $l_B \approx 0.7$ nm. At distances smaller than l_B , electrostatic energy exceeds thermal energy and recombination of ions will occur. The average distance between two salt molecules in the solid solution of concentration $c_{\text{salt}} = N_A C_{\text{salt}}$ is

$$r \cong c_{\text{salt}}^{-1/3} \quad (11)$$

It follows, eq. (9) should be valid as long as

$$\frac{l_B}{r} < 1 \quad (12)$$

The corresponding maximum value of concentration, Y_{max} follows directly from (12)

$$Y_{\text{max}} = \frac{M_{\text{salt}}}{M_{\text{mono}}} \left(\frac{M_{\text{mono}}}{\rho_{\text{poly}} N_A} \right)^{1/x} \frac{1}{l_B^{3/x}} \quad (13)$$

For an estimation, we suppose $M_{\text{salt}} = M_{\text{mono}} = 100 \text{ g mol}^{-1}$, $\rho_{\text{poly}} = 1 \text{ g cm}^{-3}$ and use eq. (10'). It results

$$Y_{\text{max}} \cong \left(\frac{\epsilon}{100} \right)^{3/x} \quad (13')$$

Figure 7 gives the conductivity of solutions of LiClO₄ in PEO and ENR in the range up to $Y = 0.12$. The regression functions read

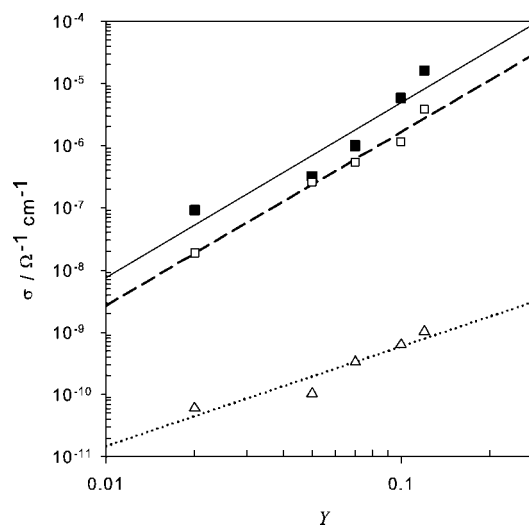


Figure 7 Electric conductivity of solid solutions as a function of Li-salt content at 30°C; dashed curve: LiClO₄ dissolved in PEO; dotted curve: LiClO₄ dissolved in ENR; solid curve: LiClO₄ dissolved in 60/40 blend of PEO and ENR.

$$\text{PEO: } \sigma = 9.96 \times 10^{-4} Y^{2.78} \quad (\Omega \text{ cm})^{-1} \quad (\text{correlation } 0.991)$$

$$\text{ENR: } \sigma = 2.35 \times 10^{-8} Y^{1.60} \quad (\Omega \text{ cm})^{-1} \quad (\text{correlation } 0.95) \quad (14)$$

With the molecular characteristics for the PEO system (ENR system) $M_{\text{salt}} = 106.5 \text{ g mol}^{-1}$, $M_{\text{mono}} = 44 \text{ g mol}^{-1}$ (152 g/mol), and $\rho_{\text{poly}} = 1.2 \text{ g cm}^{-3}$ (1.1 g cm⁻³), we can calculate the mobilities. It results

$$\text{PEO: } x = 2.78 \quad \text{and} \quad \mu = 4.4 \times 10^{-6} \text{ cm}^2/\text{Vs}$$

$$\text{ENR: } x = 1.60 \quad \text{and} \quad \mu = 1.9 \times 10^{-11} \text{ cm}^2/\text{Vs} \quad (15)$$

The figure shows that the conductivity of solutions with PEO is higher than that with ENR owing to the fact that the mobility in ENR is by five orders of magnitude lower as in PEO. This effect might be also influenced by the stronger correlation of ions in PEO, $x = 2.78$ as compared to 1.60 for ENR.

Figure 7 also gives the conductivity of a PEO/ENR 60/40 blend as a function of overall salt concentration Y . It follows for the regression function

$$\sigma = 3.28 \times 10^{-3} Y^{2.82} (\Omega \text{ cm})^{-1} \quad (\text{correlation: } 0.95) \quad (16)$$

The conductivity of ENR is by three orders of magnitude lower than the conductivity of PEO. Therefore, we may say that the conductivity of the PEO/ENR 60/40 blend is solely governed by the

conductivity of PEO. Figure 7 shows: At $\sigma = \text{const}$, the overall salt concentration Y of the blend is lower than the salt concentration Y_{PEO} of PEO. However, the salt concentration of PEO has to be the same in both systems according to our initial assumption. This allows easily for estimating the distribution coefficient K defined in eq. (2). We replace in eq. (16) the overall concentration Y according to eq. (3) by the concentration Y_{PEO} of the PEO phase and equalize eqs. (14) and (16). It follows adopting $\sigma = \sigma_o Y^x$

$$K = \frac{1}{W_{\text{ENR}}} \left[\left(\frac{\sigma_{\text{oPEO}}}{\sigma_{\text{oblend}}} \right)^{1/x(\text{blend})} Y_{\text{PEO}}^{\left(\frac{x(\text{PEO})}{x(\text{blend})} - 1 \right)} - W_{\text{PEO}} \right] \quad (17)$$

One recognizes that K depends slightly on Y_{PEO} , the salt concentration in PEO. For $Y_{\text{PEO}} = 0.1$, it follows with the data of eqs. (14) and (16) for $K = 0.19$. It means that an overall salt content of $Y = 0.068$ in the 60/40 PEO/ENR blend corresponds actually to a salt content in the PEO-phase of $Y_{\text{PEO}} = 0.1$. For $Y_{\text{PEO}} = 0.2$, the distribution coefficient descends to 0.18. With increasing salt content, the differences in salt concentration of the PEO- and ENR-phase ascend slightly.

CONCLUSIONS

Studies on solid solutions with blends reveal that LiClO_4 is preferably dissolved in PEO as compared to ENR. We characterize the salt solubility in equilibrium by the distribution coefficient K . It turns out that different conditions lead to different responses of the system. Measurements of glass transition temperature, made under condition of constant salt content of the blends, indicate almost equal solubility of the Li salt in the polymers. The situation changes when crystallization is involved. Both degrees of crystallinity and rates of crystallization point toward $K < 1$ that is

higher solubility of the salt in PEO. The same conclusion can be drawn by analyzing electrical conductivities as a function of salt content in the polymers and the blends. It is found that electrical conductivity displays a power-law dependence on salt concentration Y . Ions are solvated by chain segments. The mobility of those solvated ions governs the conductivity. The exponent of the power law may indicate the extent of correlations between segments and ions.

Thanks are due to E. M. Radman, J. Othman, T. I. A. Tunku Kudin, N. F. A. Zainal, S. N. Mohd. Zolkepli, and H. Hanibah who provided results that were incorporated in this study.

References

1. Fenton, D. E.; Parker, J. M.; Wright, P. V. *Polymer* 1973, 14, 589.
2. Armand, M. B.; Chabagno, J. M.; Duclot, M. In *Fast Ion Transport in Solids*; Vashista, P., Mundy, J. N., Shenoy, G. K., Eds.; Elsevier: Amsterdam, 1979; p 131.
3. Glasse, M. D.; Idris, R.; Latham, R. J.; Linford, R. G.; Schlindwein, W. S. *Solid State Ionics* 2002, 147, 289.
4. Baskaran, R.; Selvasekarapandian, S.; Kuwata, N.; Kawamura, J.; Hattori, T. *Mater Chem Phys* 2006, 98, 55.
5. Li, W.; Yuan, M.; Yang, M. *Eur Polym Mater* 2006, 42, 1396.
6. Ko, S. J.; Kim, S. J.; Kong, S. H.; Bae, Y. C. *Electrochim Acta* 2004, 49, 461.
7. Munich-Elmer, A.; Jannasch, P. *Solid State Ionics* 2006, 177, 573.
8. Chan, C. H.; Kummerlöwe, C.; Kammer, H. W. *Macromol Chem Phys* 2004, 205, 664.
9. Tan, S. M.; Ismail, J.; Kummerlöwe, C.; Kammer, H. W. *J Appl Polym Sci* 2006, 101, 2776.
10. Chee, M. J. K.; Kummerloewe, C.; Kammer, H. W. *New Polymeric Materials (ACS Symposium Series, 916)*; ACS: Washington, DC, 2005; p 282.
11. Scandola, M.; Focarete, M. L.; Adamus, G.; Sikorska, W.; Baranowska, I.; Swierczek, S.; Gudowski, M.; Kowalczyk, M.; Jedlinski, Z. *Macromolecules* 1997, 30, 2568.
12. Hoffman, J. D.; Weeks, J. J. *J Res Natl Bur Stand (A)* 1962, 66, 13.
13. Avrami, M. *J Chem Phys* 1939, 7, 1103.