

Effects of Lithium Perchlorate on Poly(ethylene oxide) Spherulite Morphology and Spherulite Growth Kinetics

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ABSTRACT: Effects of lithium perchlorate (LiClO_4) on the crystallization behaviors of poly(ethylene oxide) (PEO) were investigated by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and polarized optical microscopy (POM) in PEO/ LiClO_4 system. DSC results indicate that there are nucleation effects of LiClO_4 on the crystallization of PEO. But, on the other hand, the coordination of lithium ion with the oxygen ether atoms of PEO can obviously reduce the crystallinity and spherulite growth rate of PEO. This contrary effect of LiClO_4 on the crystallization of PEO in PEO/ LiClO_4 complexes system was analyzed and discussed in

detail. The Lauritzen–Hoffman theory was used to describe the Li-coordinated crystallization kinetics of PEO spherulite. It showed that the nucleation constant (K_g) and folding surface free energy (σ_e) decreased with increasing LiClO_4 contents, and the energy necessary for the transport of segments across the liquid–solid interface (ΔE) increased on increasing the contents of LiClO_4 . © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1935–1943, 2012

Key words: lithium perchlorate; poly(ethylene oxide); crystallization kinetics; nucleation constant; folding surface free energy

INTRODUCTION

Poly(ethylene oxide) (PEO), owing to a specific structure and capability of dissolving metal ions, is widely studied and used as a polymer electrolytes material. Meanwhile, lithium is the most electropositive and lightest metal, which is widely included in the design of high density energy storage devices. Therefore, PEO-lithium salts based solid polymer electrolytes (SPEs), which is potentially a promising combination of materials in energy storage, have been extensively studied. The ionic conductivity in PEO-based polymer electrolytes is closely related to the transporting of Li^+ , and the motion of Li^+ is closely coupled to that of the polymer chains, as Li ions are coordinated with ether oxygen atoms. So the conductivity occurring in the amorphous phase of PEO is usually much higher than that in the crystalline phase.^{1,2} Due to its high polarity, the crystallinity of PEO is usually high at ambient temperature. Accordingly, the ionic conductivity is low at room temperature thus limiting the potential

applicability of PEO-based SPEs. However, the traditional view that crystalline polymer electrolytes are insulators has been challenged by the new findings of several groups.^{3–10} Bruce and coworkers al.⁷ found that some crystalline small-molecule electrolytes based on glyme ligands coordinating lithium salts exhibit promising ion mobilities and conductivity. Bruce's group^{8–10} also found that certain crystalline PEO polymer electrolytes, $\text{P(EO)}_6 : \text{LiX}$ ($\text{X} = \text{PF}_6, \text{AsF}_6, \text{SbF}_6$), $\text{P(EO)}_8 : \text{NaAsF}_6$, have a higher ionic conductivity than the analogous amorphous phases. These findings draw special interest on the correlation between the materials' crystalline structure and ion transportation. The research of the crystallization behavior and crystallization structure of complexes between lithium salts and PEO is helpful to understand the mechanism of ion transportation and improve conductivity of PEO-based SPEs at ambient temperature.

Because of the dimethoxyethane gauche conformation, PEO usually presents a solid-structure that consists of a mixture of a helical conformation (70–75%) and other conformation.¹¹ PEO usually crystallizes in a spherulite form and the spherulites are made up of PEO helices, growing radial from the nucleation center. Information concerning the crystallization morphology of PEO-LiX based polymer electrolyte was proved to be helpful on the interpretation of the conductivity changes during the crystallization process. Polarizing microscope observations was usually used to investigate the influence of crystallization phenomena on electrical

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properties of PEO–Lithium salt complexes.^{12–14} The investigations show that the ionic conductivity was directly related with the morphological varieties.

The combination of computer simulation^{15,16} and scattering experiments^{17,18} can be used to understand the mechanism of interaction of polymer electrolytes and dynamics with microscopic details. Müller-Plathe et al.¹⁵ investigated the effect of strong coulombic interaction between Li ion and the ether oxygens of PEO on the host polymer by molecular dynamics simulations. The results show that the addition of salt increases the gauche population of the O–C–C–O dihedral angles and throttles down the conformation transitions dynamics. Frech and Huang¹⁶ investigated the polymer CH₂ rocking vibration by Raman spectra and they indicated a similar effects when increase the gauche population of O–C–C–O dihedral angles with salt concentration. The mobility of PEO in PEO/LiX (X = I[−], LiClO₄[−], TFSI[−], BETI[−]) system has been reported^{17,18} using quasi-elastic neutron scattering (QENS). It is reported that because of the coordination of Li ions with ether oxygen atoms the segmental mobility of PEO decreased for all these system with the addition of lithium salt.

In LiClO₄ doped PEO system, when the concentration of salt is lower, the crystalline phase of pure PEO may be the dominant crystalline phase. Because of the strong interaction between Li ions and oxygen ether atoms, the reductions in spherulite growth rate of PEO can be observed. The slow spherulite growth rates provided the strongly interacting diluents with more time to diffuse over larger distances from the growth front, which is consistent with the predictions of Keith and Padden,¹⁹ and this is sure to influence the spherulite morphology. On the other hand, addition of salt can promote the crystallization process by introducing nucleation centers. However, the addition of salt can also inhibit crystallization behavior because of the strong interactions between the ions and PEO polymer chains, which slows down polymer chain mobility necessary for growth of spherulites. Some investigations already reported that the crystallization kinetics of PEO was slowed down with the addition of Li salt.^{14,20,21} However, to our knowledge, there are no reports about analyses on this behavior of Li salts doped PEO system in detail.

The understanding of the crystallization behavior of metal salts doped polymer system is still in a nascent stage and this also can help our understanding of the crystallization mechanism of polymer. In this work, the influences of several factors on the depression in growth kinetics of PEO are discussed. The dominant factors, which were discussed in detail in this article, include a reduction in chain mobility and the changes in free surface energy of nucleation due to specific interactions. We thus focused on the effects of LiClO₄ on the crystallization behavior,

thermal property, and spherulite morphology of PEO. Two contrary effects of LiClO₄ on the crystallization of PEO will be discussed in detail. The interaction between PEO and LiClO₄ was investigated by infrared spectra technique. The spherulite growth kinetics has been discussed by the secondary nucleation theory of Lauritzen and Hoffman in the present article. The effects of LiClO₄ on the spherulite growth kinetics were also investigated in this article.

EXPERIMENTAL

Materials

PEO ($M_w = 2.0 \times 10^4$ g/mol) was purchased from Polysciences. LiClO₄ was obtained from Aldrich (regent grade), which was stored in the desiccator prior to use.

Preparations of PEO/LiClO₄ complexes

The complexes were prepared by dissolving predetermined amounts of PEO and lithium perchlorate in THF. After the solutions were stirred at room temperature for 8 h, the solvent was allowed to evaporate slowly at room temperature and the samples were further dried in a vacuum oven at 40°C for 72 h to remove any residual solvent.

Equipments and characterizations

Differential scanning calorimetry

Thermal analysis was performed on all samples using Perkin–Elmer Diamond differential scanning calorimetry (DSC) instrument. Indium and tin were employed for the temperature calibration and nitrogen gas purge was used to prevent oxidative degradation of the samples. The samples were first heated from 25 to 80°C and held at 80°C for 3 min to erase any thermal history, then cooled to 0°C, and finally heated to 80°C again. Both the heating rate and the cooling rate during the measurements were 10°C/min.

Fourier transform infrared spectroscopy

The conventional potassium bromide (KBr) method was employed to measure the infrared spectra of the polymer complexes system. All IR spectra were obtained with the range of 4000–400 cm^{−1} using a PE Spectrum 100 Fourier transform infrared spectroscopy (FTIR) spectrometer, operating at 64 scans and 1 cm^{−1} resolution.

POM

A Linkam optical stage (CSS450, made in UK) and a polarizing optical microscope (Olympus BX-51)

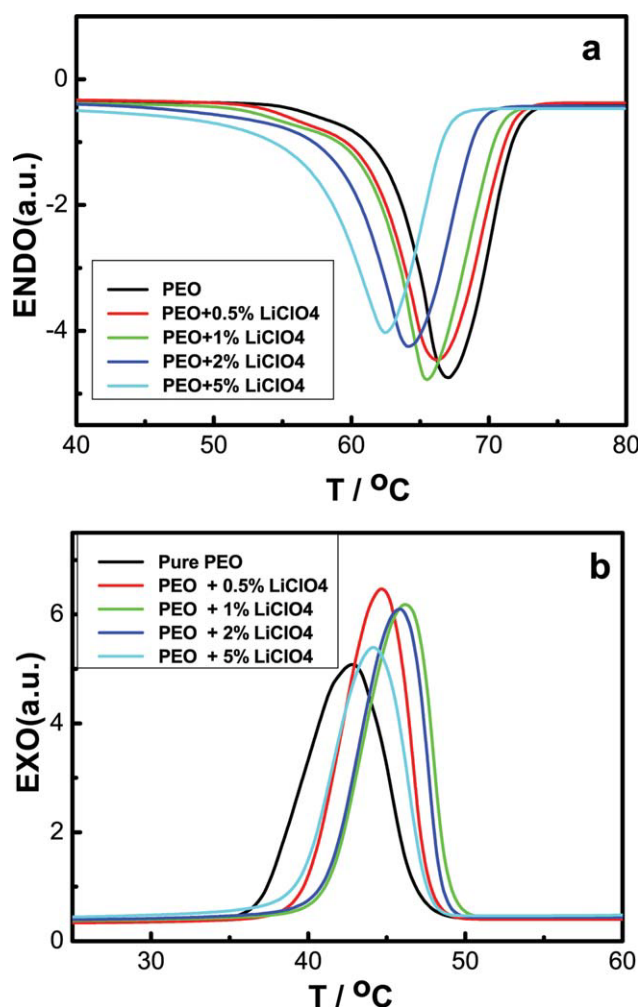


Figure 1 DSC curves of PEO/LiClO₄ systems. (a) Heating process, (b) cooling process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

equipped with a TV video camera (Olympus U-CMAD3) were used to observe the isothermal crystallization process of pure PEO and salt-coordinated PEO. All samples were held at 90°C for 3 min to erase any thermal history before the measurement, and then the melt was cooled to the crystallization temperature with a cooling rate of $-30^{\circ}\text{C}/\text{min}^{-1}$. The size of the growing spherulites was measured by taking the digital images at appropriate intervals of time with image processors (supplied by Linkam and Olympus).

RESULTS AND DISCUSSION

DSC results

To characterize the thermal properties of PEO/LiClO₄ system, the melting point, the crystallization temperature, and the crystallinity were obtained via DSC measurements. Typical DSC traces of PEO/

LiClO₄ system are shown in Figure 1. In Figure 1(a), the endothermic peak at T_m obtained in the second heating cycle, which is attributed to the melting of PEO rich crystalline phase, broadens, weakens, and shifts to lower temperature with increasing salt content. Figure 1(b) shows the exothermic peak of the samples investigated during the cooling process. The T_m and T_c obtained from DSC results are displayed in Figure 2. The results in Figure 2 indicate that the crystallization temperature increases obviously when the content of LiClO₄ is less 1%, then increases a little with more addition of LiClO₄ compared to the crystallization temperature of pure PEO. The increase of T_c indicated that the low content LiClO₄ acted as a nucleating agent for crystallization of PEO. The melting temperature of LiClO₄ doped PEO is lower than that of pure PEO, as shown in Figure 2, implying that the lamellae thickness and free energy of crystalline phase of PEO decreased with the addition of LiClO₄.

The crystallinity (X_c) of PEO/LiClO₄ system according to DSC results was calculated by following equation:

$$X_c = \frac{\Delta H_f}{x_A \times \Delta H_f^0} \quad (1)$$

where ΔH_f is the heat of fusion of per gram of the samples, x_A is the weight percentage of PEO in the salt doped PEO system, and ΔH_f^0 is the thermodynamic heat of fusion per gram of 100% crystalline PEO. Using the $\Delta H_f^0 = 222.07 \text{ J/g}$,²² the calculated results are shown in Figure 3. From Figure 3 it can be seen that the crystallinity of PEO decreased sharply by adding LiClO₄ up to 1 wt % and then

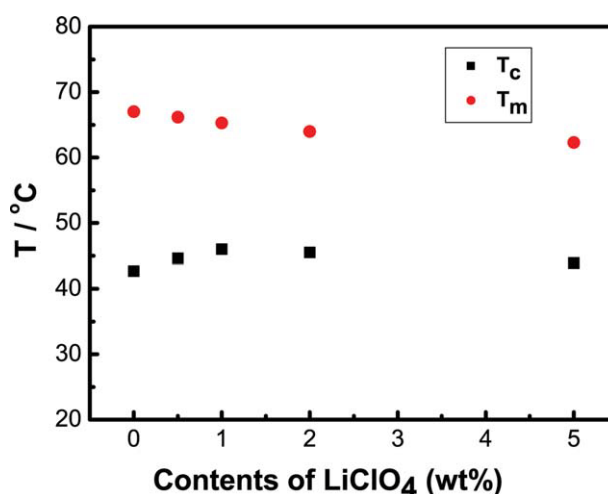


Figure 2 Crystallization and melting temperatures of PEO, PEO/LiClO₄ systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

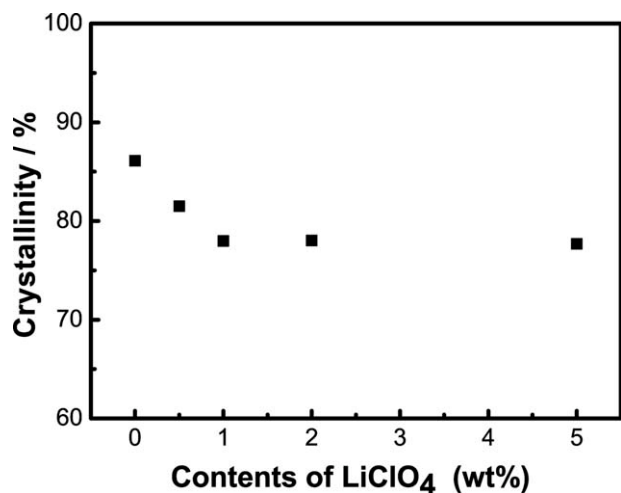


Figure 3 LiClO₄ dependent PEO crystallinity in PEO/LiClO₄ system.

decreased smoothly when the content of LiClO₄ is up to 5%.

From the results of DSC, we can see that low content LiClO₄ may have the nucleation effects on crystallization of PEO, which result in the increase of crystallization temperature of PEO. But the crystallinity of PEO decreased with the addition of LiClO₄, indicating the strong interactions between LiClO₄ and PEO suppressed the crystallization process. The analysis of LiClO₄ effects on the crystallization behavior would be discussed according the Lauritzen–Hoffman theory later in detail.

Infrared spectroscopy results

The FTIR spectroscopy was used to probe the interaction between PEO and LiClO₄. Figure 4 shows infrared spectra recorded at room temperature. The band from 1400 cm⁻¹ to 1000 cm⁻¹ displays the bands representing oxygen ether stretching of PEO with different contents of LiClO₄. The C–O stretching vibration in PEO exhibits triplet peaks at 1144, 1114, and 1062 cm⁻¹. As shown in Figure 4, the coordination of Li cation with oxygen ether atom of PEO has almost no influence on oxygen ether stretching vibration when the content of LiClO₄ is less than 1%. However, the three stretching vibration peaks gradually disappeared at high content of LiClO₄ systems. IR spectra of the CH₂ wagging vibration for pure PEO and various PEO/LiClO₄ systems are also displayed in Figure 4. The pure PEO has two peaks, at 1343 and 1360 cm⁻¹, representing the crystalline phase.²² The crystalline conformation of PEO is partially destroyed when the LiClO₄ content increased. The peaks at 1236, 1244, and 1280 cm⁻¹ are due to the CH₂ twisting modes of PEO. The intensity of these twisting peaks decreased when the LiClO₄

content is high. It shows that the addition of LiClO₄ decreases the crystallinity of PEO.

As is known, the crystalline structure of PEO belongs to the monoclinic space group $P2_1/a(C_{2h}^5)$ and has a center of symmetry.²³ The corresponding IR-active modes were at 843 and 857 cm⁻¹. As can be seen in Figure 4, location of the characteristic peak shows almost no change with the addition of LiClO₄, indicating that the crystal form of PEO preserved monoclinic form when the content of LiClO₄ is lower than 5%. It is reported that the ClO₄⁻ band at 623 cm⁻¹ can be attributed to free ions, whereas the characteristic peak of contact ion pairs is at 630–635 cm⁻¹.²⁴ The band from 650 cm⁻¹ to 600 cm⁻¹ in Figure 4 shows the FTIR spectra recorded in free ClO₄⁻ vibration band for various PEO/LiClO₄ systems. While at low LiClO₄ content, only the free ions characteristic peak can be seen. With the increase of LiClO₄, due to the strong cation–anion interaction, there exist characteristic peak of free ions and contact ion pairs, which is consistent with other reports.²⁵ The presence of ion pairing may indicate that the number of Li ions coordinated with oxygen ether atoms of PEO decrease, which may also lead to the crystallinity of PEO decrease smoothly when the content of LiClO₄ is up to 5%.

Polarized optical microscopy measurements

Spherulite morphology of PEO/LiClO₄ complexes system

The spherulite morphology of pure PEO and its complexes were observed by polarized optical microscopy (POM) as shown in Figure 5. Figure 5 also shows the isothermal crystallized spherulite morphology of the PEO/LiClO₄ complexes system at

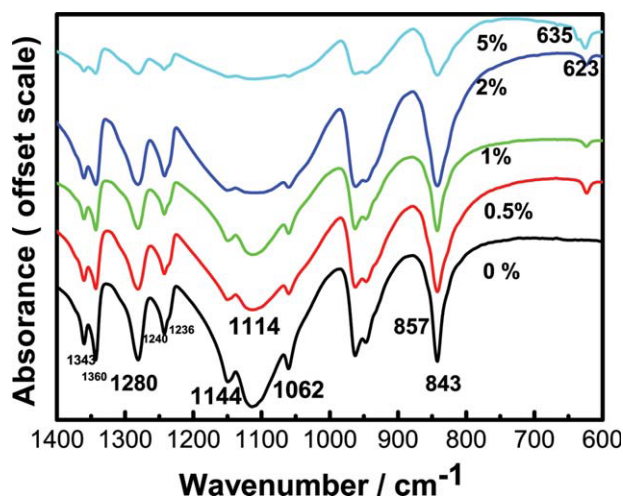


Figure 4 Infrared spectra for pure PEO and PEO doped with different contents of LiClO₄ with the range of 1400–600 cm⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

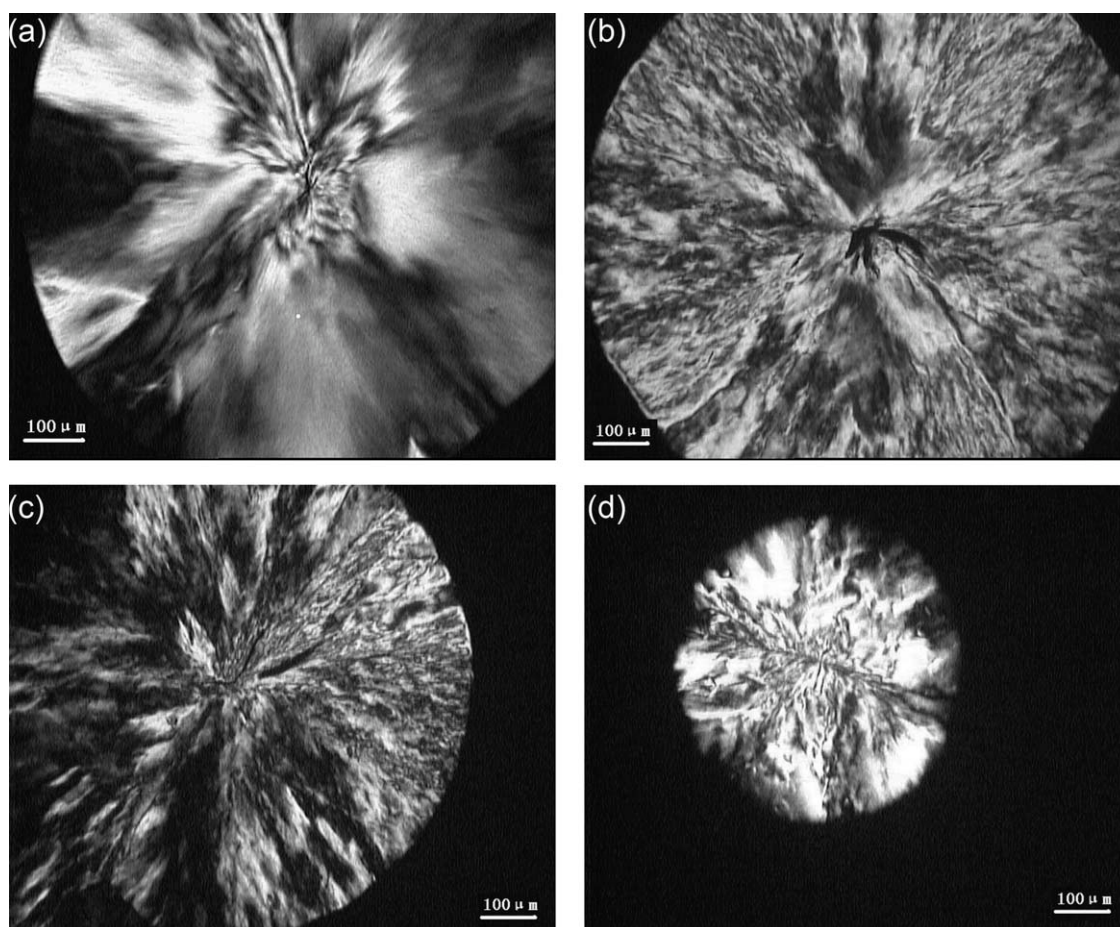


Figure 5 Spherulite morphology developed during isothermal crystallization at 52°C: (a) neat PEO, crystallization time: 50 s. (b) PEO with 0.5% LiClO₄, crystallization time: 200 s. (c) PEO with 2% LiClO₄, crystallization time: 240 s. (d) PEO with 5% LiClO₄, crystallization time: 500 s. The scale bar corresponds to 100 μm.

52°C. It can be seen that spherulite morphology of pure PEO has a very clear texture structure as shown in Figure 5(a). The morphology changed with the addition of LiClO₄ in the samples as shown in Figure 5(b–d). In these POM images, the salt-doped PEO shows a pattern of feather-like lamellar bundles. This crystalline morphology differs significantly from that of neat PEO. By comparison, with the increase of contents of LiClO₄, we can see that lamellar bundles are significantly coarsened and these lamellar bundles arranged around the nuclei loosely, forming immature and imperfect spherulite.

Generally, the feather-like spherulite morphology of PEO is found only in blend systems with strong-interaction between crystallization species and amorphous species.²⁶ The strong interactions between the ether oxygens in PEO and Li⁺ might be responsible for this peculiar morphology. Goldenfeld and coworkers^{27,28} have suggested that the dendritic feature (somewhat similar to the feather-like spherulite reported here) is a combined effect of the diffuse of the crystallizing material to the growth front in contact with the amorphous materials. The feather-like

morphology of the PEO spherulites in the PEO/LiClO₄ system may comply with the Goldenfeld and coworkers mechanism.

Spherulite growth kinetics for PEO/LiClO₄ complexes system

The interactions between PEO and LiClO₄ were found to influence the isothermal crystallization kinetics as well as the spherulite morphology of PEO. The isothermal crystallization process of pure PEO and salt doped PEO were observed by POM and the radius of spherulites was measured as a function of crystallization time. The spherulite radius increase linearly with the crystallization time, and the spherulite growth rates can be calculated by determining the slopes of the linear fittings in the plots of spherulite radius versus time.

Figure 6 shows spherulite morphology of pure PEO and PEO doped with 0.5% LiClO₄, both samples crystallized at 52°C. For a given time, the spherulite sizes of the salt doped sample are smaller than that of pure PEO, indicating that the spherulite

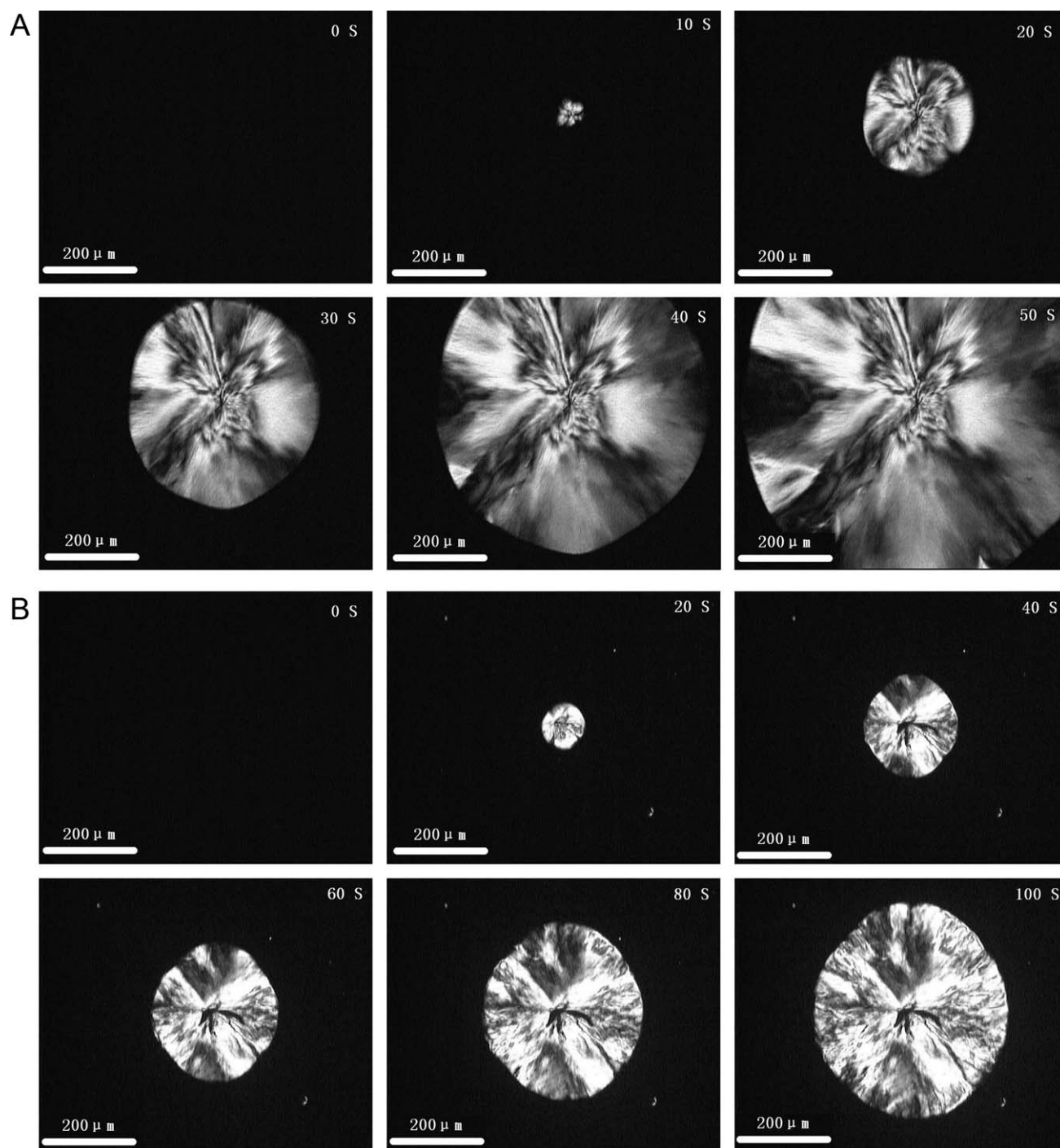


Figure 6 Time evolution of melt-crystallized spherulite pattern of PEO isothermal crystallized at 52°C: (a) Pure PEO; (b) PEO with 0.5% LiClO₄. The scale bar corresponds to 100 μm.

growth rates of PEO doped with LiClO₄ are slower than that of pure PEO. Similar phenomena can be observed from other salt doped PEO complexes system. The radii of spherulites developed with crystallization time at fixed temperatures are shown in Figure 7. The results in Figure 7 indicate that the spherulite radius increases linearly with the crystallization time for pure PEO and PEO doped with 0.5% LiClO₄ crystallized at different temperature. The

spherulite growth rates can be obtained by calculating the slopes of the linear fittings in the plots of time related spherulite radius. Similarly, the spherulite growth rates (G) of other samples can be obtained.

Figure 8 shows the calculated spherulite growth rates (G) of PEO with different contents of LiClO₄ as a function of temperature. As can be seen in Figure 8, PEO with higher LiClO₄ contents exhibit lower

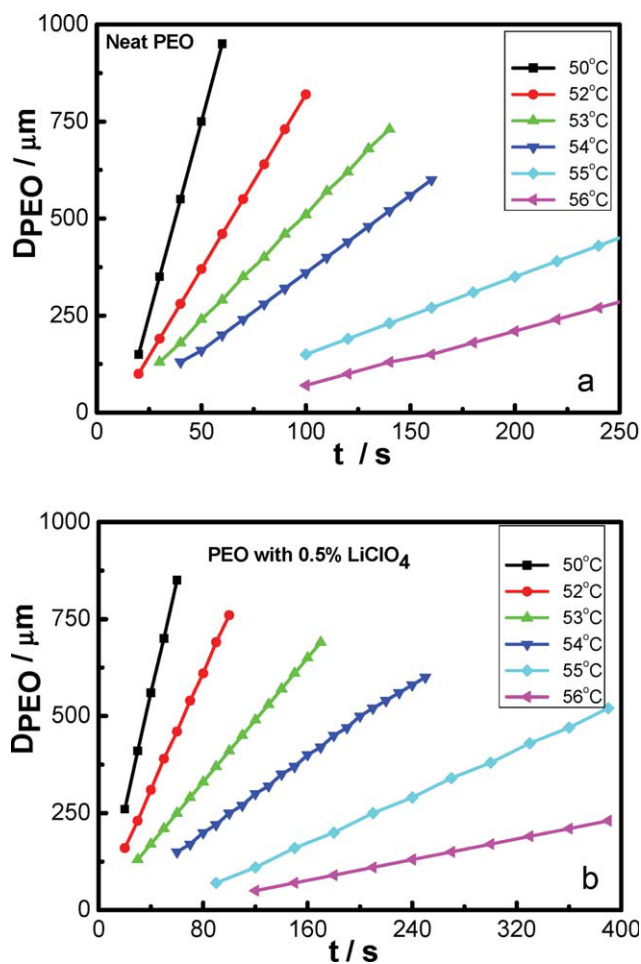


Figure 7 The radius of spherulites developed with crystallization time for PEO. (a) Neat PEO; (b) PEO with 0.5% LiClO₄ [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

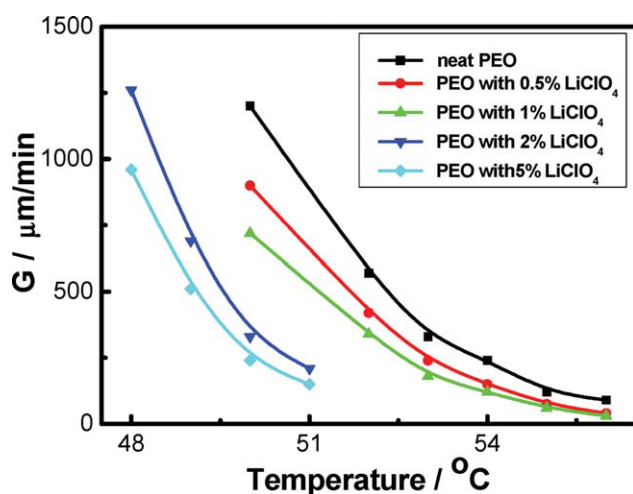


Figure 8 Crystallization temperature related spherulite growth rate of PEO/LiClO₄ systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

spherulite growth rates (G) at a given temperature. The spherulite growth rates (G) can then be plotted as a function of the temperature to analyze the parameters of spherulite growth kinetics of the investigated systems according to the secondary nucleation theory of Lauritzen and Hoffman²⁹:

$$G = G_0 \exp\left(-\frac{\Delta E}{R(T_c - T_g + C)}\right) \exp\left(-\frac{K_g}{T_c \Delta T f}\right) \quad (2)$$

where G_0 is a constant that depends on the regime of crystallization; ΔE is the energy necessary to achieve the transport of segments across the liquid–solid interface; R is the gas constant; T_g is the glass-transition temperature of polymer; T_c is the temperature of crystallization; C is the constant, which varies from one polymer to another; and K_g is the nucleation constant, ΔT is the degree of the supercooling determined by $(T_m^0 - T_c)$, T_m^0 is the equilibrium melting point, f is a correction factor given as $2T_c/(T_c + T_m^0)$.

The secondary nucleation theory proposed by Hoffman et al.²⁹ was used to analyze the spherulite growth kinetics of PEO and its complexes, as shown in eq. (2). K_g in eq. (2) is the nucleation constant, which represents the energy needed for the formation of nuclei in critical size, which is defined as:

$$K_g = \frac{nb\sigma\sigma_e T_m^0}{\Delta h_f k_b} \quad (3)$$

where b is the thickness of a monomolecular layer, σ is the lateral surface-free energy, σ_e is the folding surface free energy, Δh_f is the heat of fusion per unit volume, T_m^0 is the equilibrium melting temperature obtained from the Hoffman–Weeks plots. $n = 4$ for regimes I (lower ΔT) and regime III (higher ΔT) and $n = 2$ for regime II (medium ΔT), and k_b is the Boltzmann constant, $k_b = 1.380 \times 10^{-23}$ J/K. The crystallization of PEO in this study was considered to occur in regime II, corresponding to $n = 2$.

As mentioned above, low content of LiClO₄ has the nucleating effect on PEO and may promote the crystallization of PEO, which may surely affect the nucleation constant K_g . The coordination of Li⁺ with ether oxygen atoms of PEO may influence the transport of segments across the liquid–solid interface,

TABLE I
Parameters Used in Analysis

ΔE (J/mol)	11,979.9
b_0 (nm)	0.465
ΔH_f (J/m ³)	2.41×10^8
C (K)	51.6
T_g (°C)	-55
T_m^0 (°C)	72

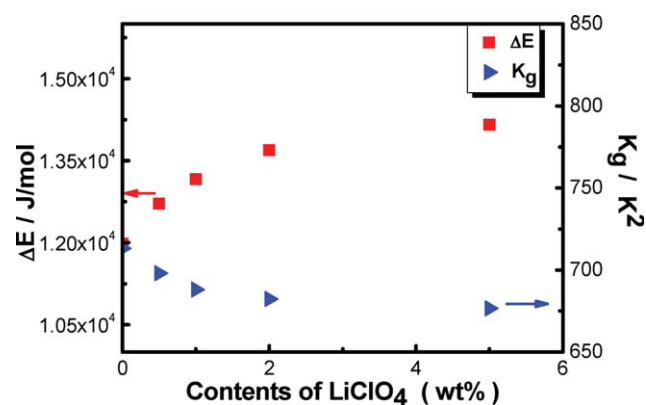


Figure 9 kinetic values of ΔE and K_g for PEO crystallization with different contents of LiClO_4 . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

which may change the ΔE value. As can be seen in eq. (2), for a given G_0 , the spherulite growth rates (G) of PEO mainly depends on ΔE and K_g . However, ΔE and K_g cannot be inferred simultaneously from eq. (2) just by simple mathematics calculation, because there is only one equation but two unknown variables. To investigate the influence of LiClO_4 on the ΔE and K_g of PEO, curve fitting method and optimization method are adopted to calculate the parameters of ΔE and K_g of PEO with different contents of LiClO_4 . For pure PEO, the parameters used in calculation are listed in Table I.²² To begin with, G_0 is calculated by plotting $\ln G + \Delta E/R(T_c - T_g + C)$ versus $10^4/fT_c\Delta T$. The plots fitting fits the value of G_0 (intercept). Then for the given G_0 and the ΔE of pure PEO which was shown in Table I, we can tune K_g to make the theoretical curve fits well with our experimental results. By this the K_g of PEO with different contents of LiClO_4 can be obtained. Then we fix the K_g at the median value, the ΔE is tuned to make the theoretical curve fits well with our experimental results and ΔE of PEO with different contents of LiClO_4 can be obtained. Next, we choose the median value of ΔE and continue to tune K_g to make the theoretical curve fits well with our experimental results. By this step optimization, for a given G_0 , we can calculate ΔE and K_g of the salt doped PEO, as can be seen in Figure 9.

From Figure 9, we can see that the values of K_g decrease when the LiClO_4 content increases, which indicates that the crystallization ability of PEO in the complexes increases with increasing LiClO_4 content. This result is consistent with the DSC result, which also shows that the crystallization temperature increases with increasing LiClO_4 content. This phenomenon may be due to the nucleation of LiClO_4 on PEO during the isothermal crystallization process. However, from the DSC results the crystallinity of

PEO decrease with the increase of LiClO_4 contents. It can be seen that LiClO_4 has two contrary effects on the crystallization of PEO. The decrease in crystallinity of PEO doped with LiClO_4 might be because the coordinated segments of PEO cannot enter into the crystallite unit of PEO. This may result in the increasing of amorphous component and decreasing the fraction of the crystalline phase of PEO.

The lateral surface free energy σ can be estimated by the Thomas–Stavely relationship³⁰:

$$\sigma = \alpha b_0(\Delta h_f) \quad (4)$$

where α is an empirical constant which is assumed to be 0.1 for vinyl polymers and $\alpha = 0.25$ for high melting polyesters. For a low melting point polyether, such as PEO, which has a long run of CH_2 groups like PE, a value of 0.1 was usually used. Then the surface energy values for PEO doped with different contents of LiClO_4 can be obtained. It is not difficult to find that K_g has the same trend with the surface-free energy of chain folding σ_e . The nucleation of LiClO_4 can reduce the surface free energy of chain folding and provides the driving force for crystallization of PEO. The surface free energy of chain folding is lower than pure PEO and would induce the smaller crystalline thickness,³¹ which is consistent with the melting temperature depression.

The amorphous component of salt doped PEO may play the role of a nucleating agent and increases the crystallization rate. However, the crystallization rate of PEO decreases with the increasing contents of LiClO_4 . According to the regime theory,²⁹ crystallization rate in regime II ($i \sim g$) is controlled by nucleation rate and substrate completion rate simultaneously at the middle region of crystallization temperature. The lower chain mobility of PEO may be an important reason which causes a slow crystallization isothermally. This influence is also found by some quasi-elastic neutron scattering (QENS) experiments,^{17,18} may play the crucial role during the isothermal crystallization process of PEO which result in the depression of crystallization process. The crystalline phase of pure PEO will form when the content of LiClO_4 is low and the coordination effect may make the concentration of pure PEO at the growth front decreases, which also can be attributed to the depression of crystallization rate. Moreover, the coordinated amorphous molecules are more difficult to diffuse away from 0 the crystallizing front, causing great hindrance for the advance of the crystal front. In addition, the glass transition temperature (T_g) of PEO in the PEO/ LiClO_4 complexes system increase with the LiClO_4 content.³² As can be seen in eq. (2), the

increase of T_g can also reduce the crystallization rate. All these factors made the crystallization rate of PEO decrease exponentially with the increase contents of LiClO₄.

CONCLUSIONS

In PEO/LiClO₄ complex systems, the crystallization behavior of PEO from the melt is strongly influenced by LiClO₄. Low content LiClO₄ which acted as a nucleation agent were found to enhance the crystallization temperature of PEO. The crystallinity of PEO decreased with the addition of LiClO₄, because of the strong interactions between LiClO₄ and PEO. The spherulite growth kinetics was analyzed quantitatively using the secondary nucleation theory of Lauritzen and Hoffman. From the analysis of the Lauritzen–Hoffman equation it can be found that with increase LiClO₄ contents, values of the nucleation constant (K_g) of PEO decreased and that the energy for the transport of segments across the liquid–solid interface increases.

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