Large Enhancement of the Ionic Conductivity in an Electron-Beam-Irradiated [Poly(ethylene glycol)]$_x$LiClO$_4$ Solid Polymer Electrolyte

TH. JOYKUMAR SINGH,[1] GANESHSANJEEV,[2] K. SIDDAPPA,[2] S. V. BHAT[1]

[1]Department of Physics, Indian Institute of Science, Bangalore 560 012, India

[2]Microtron Centre, Mangalore University, Mangalagangotri 574 199, India

ABSTRACT: The effect of electron-beam (4–8 MeV) irradiation on the ionic conductivity of a solid polymer electrolyte, poly(ethylene glycol) complexed with LiClO$_4$, was studied. A large enhancement of the conductivity of nearly two orders of magnitude was observed for the highest dose of irradiation (15 kGy) used. The samples were characterized with differential scanning calorimetry, matrix-assisted laser desorption/ionization, and electron spin resonance spectroscopy. Although no free radicals were present in the irradiated samples, a decrease in the glass-transition temperature and an increase in the amorphous fraction were observed. Even though pure poly(ethylene glycol) underwent considerable fragmentation, unexpectedly, no significant fragmentation was observed in the polymer–salt complexes. The enhancement of the conductivity was attributed to an increase in the amorphous fraction of the systems and also to an increase in the flexibility of the polymer chains due to the irradiation. © 2004 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 42: 1299–1311, 2004

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INTRODUCTION

During the last two decades, solid polymer electrolytes (SPEs) have attracted considerable scientific and technological attention because of their interesting physics and wide application potentials in high-energy density batteries, electrochromic displays, sensors, and fuel cells.[1–4] Most of these studies have concerned high-molecular-weight polymers [e.g., poly(ethylene oxide) (PEO); molecular weight ∼ 10^6] complexed with alkali metal salts (lithium salts being the most stud-

ied[5,6]), and not much attention has been paid to the somewhat low-molecular-weight polymers (molecular weight ∼ 2000). It is known that polymers below a critical molecular weight (∼3200) have different viscosity and diffusion behaviors. A study on the effect of the molecular weight of a polymer on cation mobility by Shi and Vincent[7] has shown that even though the molecular weight has no significant effect on cation mobility above a critical limit of approximately 3200, below that an additional cation transport mechanism could be operating. In this low-molecular-weight region, called the Rouse region, there is a possibility of polymer chain diffusion in addition to segmental motion. Bearing these facts in mind, we have prepared a new SPE based on poly(ethylene glycol) (PEG; molecular weight = 2000) complexed

with lithium perchlorate salt. $LiClO_4$ has been chosen because it fulfils the electrochemical stability criteria[8] and has low lattice energy (723 kJ mol^{-1}), which is favorable for the formation of polymer–salt complexes.

It is generally accepted that polymer–salt complexes consist of three coexisting phases: a crystalline polymer, a crystalline polymer–salt complex, and an amorphous polymer–salt complex.[9] Most of the easily solvating host polymers, such as PEO and PEG, used for complexing with low-lattice-energy salts to form SPEs are partially crystalline in nature. It has been shown that the amorphous regions mainly contribute to the observed ionic conductivity.[10] Therefore, one of the most promising ways of achieving better ionic conductivity is increasing the amorphous fraction in the system. Different methods have been used to achieve this goal. Plasticization with a low-molecular-weight polymer[4,11] and the dispersion of insulating nanoparticle fillers into SPEs are two of the ways of increasing the amorphous fraction.[12,13] The irradiation of SPE systems with high-energy beams can also be used to achieve an increased amorphous fraction and, therefore, enhance the ionic conductivity. In principle, radiation damage can result in both chain scission (or chain fragmentation) and crosslinking. Extensive chain scission will lead to a reduction in molar mass and higher flexibility of the chains, whereas crosslinking will usually increase the molar mass, leading to a less flexible product.[14] Different types of irradiation [γ-ray irradiation, photoirradiation, electron-beam irradiation (e-beam irradiation), and ion-beam irradiation] can be used to irradiate polymeric systems. A few experimental studies on the effect of irradiation, mostly γ-ray irradiation and photoirradiation, on SPEs have been reported to date, and they have focused mainly on crosslinking. McCallum et al.[15] γ-irradiated complexes formed by high-molecular-weight (10^6) PEO and $LiClO_4$. The product thus obtained showed ambient ionic conductivity somewhat lower than that of unirradiated samples. This was understood to be a result of decreased chain flexibility caused by crosslinking, as evidenced by an increase in the glass-transition temperature (T_g). However, Song et al.[16] in their study of a PEO–$LiClO_4$ system, over a wide range of γ-irradiation doses, found an increase in the ionic conductivity up to 6.8×10^{-4} S/cm associated with crosslinking. It appears that crosslinking may lead to either an increase in the amorphous fraction or a reduction in the flexibility of the polymer seg-

ments. Therefore, one may observe either a reduction in the ionic conductivity[15] or an enhancement when the crosslinking is optimal, as achieved by Song et al.[16] Zhang et al.[17] recently reported the effect of radiation dose on the destruction of the crystallinity of PEO. They found, using wide-angle X-ray diffraction and calorific measurements, that about 3.5×10^6 Gy of γ-radiation was required to completely destroy the crystallinity and that this resulted in highly crosslinked, fragile, and glassy products. As is well known, such glassy specimens are mechanically unsuitable as useful polymer hosts. Also, because of the presence of excessive crosslinks, the ambient ionic conductivity was still rather low. The γ-radiolysis-induced chain degradation of PEO and the production of carbonyl groups at the end of the cleaved polymer chain were reported by Okamato and Cho.[18] They observed an increase in the conductivity by a factor of approximately 3 at room temperature upon γ-irradiation and reported that the effect of e-beam irradiation was similar. The photoirradiation control of some specific SPEs was also carried out by Kobayashi et al.[19] There are also a number of patents[20,21] related to the use of irradiation for enhancing crosslinking in polymer electrolytes and, therefore, increasing their mechanical stability. In this study, we used e-beam irradiation to cause chain scission and thus an increase in the flexibility of the polymer systems and enhanced ionic conductivity. We observed a large enhancement (nearly two orders of magnitude) in the ionic conductivity upon irradiation. To the best of our knowledge, there is no detailed report on the effect of e-beam irradiation leading to such a large enhancement of the ionic conductivity of an SPE.

We earlier investigated a $(PEG)_x LiClO_4$ system (molecular weight of PEG = 2000; x is the ratio of ether oxygens to Li^+) and found that the room-temperature ionic conductivity had a maximum value of 7.27×10^{-7} S/cm for $x = 46$.[22] In this article, we report detailed studies on the effect of e-beam irradiation on the morphology, thermal properties, and the ionic conductivity of the SPE. We use three different doses: 5, 10, and 15 kGy. We have found that the maximum ionic conductivity increases as the irradiation dose increases. We have characterized the samples, showing the largest ionic conductivity (i.e., the one irradiated with 15 kGy) by matrix-assisted laser desorption/ ionization (MALDI), electron spin resonance (ESR), and differential scanning calorimetry

(DSC) studies. We also offer a possible explanation for the enhanced ionic conductivity.

EXPERIMENTAL

Sample Preparation

PEG (molecular weight = 2000; Fluka) and LiClO$_4$ (Fluka) were used without further purification. LiClO$_4$ was dried in an oven overnight at 100–110 °C to remove the moisture before use. The (PEG)$_x$LiClO$_4$ (x = 20–500) samples were prepared with the solution-casting method with methanol (analytical-reagent-grade) as the common solvent. The solutions were magnetically stirred for 7–8 h at room temperature, and this was followed by another hour at approximately 50 °C in a nitrogen atmosphere. The viscous solutions were then poured into Teflon rings (diameter ~ 7 mm, thickness ~ 500 μm to 1 mm) and kept in a glove box under a nitrogen atmosphere over night, and the solvent was allowed to evaporate slowly. The solidified samples were transferred to a vacuum desiccator for vacuum drying under continuous pumping. These methods were used to dry the samples thoroughly, as they were hygroscopic. For the same reason, they were also stored inside a vacuum desiccator before the various experiments were performed.

E-Beam Irradiation of the Samples

Thin film samples with various salt concentrations were irradiated in a 4–8-MeV pulsed electron accelerator (Microtron Centre, Mangalore University, Mangalagangotri, India). The electron beam was emitted from a LaB$_6$ single crystal. The samples were sealed in ultrathin and transparent polythene sheets and were irradiated directly in air at room temperature. Typically, the pulse duration was 2.3 μs with a repetition frequency of 50 Hz. A dose rate of 1 kGy/min was used. The samples were irradiated in one stretch. Still, there was no noticeable heating of the samples, mostly because of the very small average beam wattage. The samples were irradiated for a few minutes to achieve three different doses: 5, 10, and 15 kGy. The doses were monitored with a current integrator.

X-Ray Diffraction (XRD)

XRD patterns for unirradiated and irradiated PEG 2000 were recorded (Scintag XDS 2000,

United States) at a scanning rate of 10°/min in the 2θ range of 10–80° to study the changes in the crystalline fraction. This slightly high scanning rate was used so that the samples did not absorb moisture. The samples were prepared on glass slides so that their insertion into the XRD machine would be easier. The areas of the films on the glass slides were kept the same for both unirradiated and irradiated PEG 2000 so that a comparison of intensities would be possible.

Mass Spectrometry

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) is a soft ionization technique in which the energy from a laser is dissipated in volatilizing the matrix rather than in degrading the polymer. The matrix material also leads to the isolation of the polymer molecules from one another.[23] We used a MALDI-TOF MS instrument (Kompact SEQ, Kratos Analytical Instruments, Manchester, United Kingdom) to analyze the molecular weight distribution of unirradiated and irradiated PEG 2000 and (PEG)$_x$LiClO$_4$ SPE samples. This mass spectrometer was equipped with a pulsed nitrogen laser (λ = 337 nm, pulse width ~ 4 ns). The instrument was operated in the positive polarity mode with a linear flight path. The samples were dissolved in methanol before being loading onto the mass spectrometer. The solvent prevented the aggregation of the polymer. Under vacuum conditions, the solvent was removed, and cocrystallized polymer molecules were left behind, homogeneously dispersed within the matrix molecules. 2,5-Dihydroxybenzoic acid (Gentisic Acid, Sigma Chemicals) was used as the matrix.

ESR

ESR (ER 200D-SRC, Bruker) spectra for the glass rod used to mount the unirradiated and 15-kGy-irradiated PEG 2000 and (PEG)$_{46}$LiClO$_4$ samples were recorded at a scanning rate of 60 Gauss/s from 0 to 6000 Gauss in forward and reverse magnetic field scans at room temperature. The modulation amplitude was 4 Gauss, and the microwave power was 150 mW.

DSC

DSC experiments were carried out to compare the thermal properties of the unirradiated and irradiated systems. An MDSC 2920 (TA Instruments)
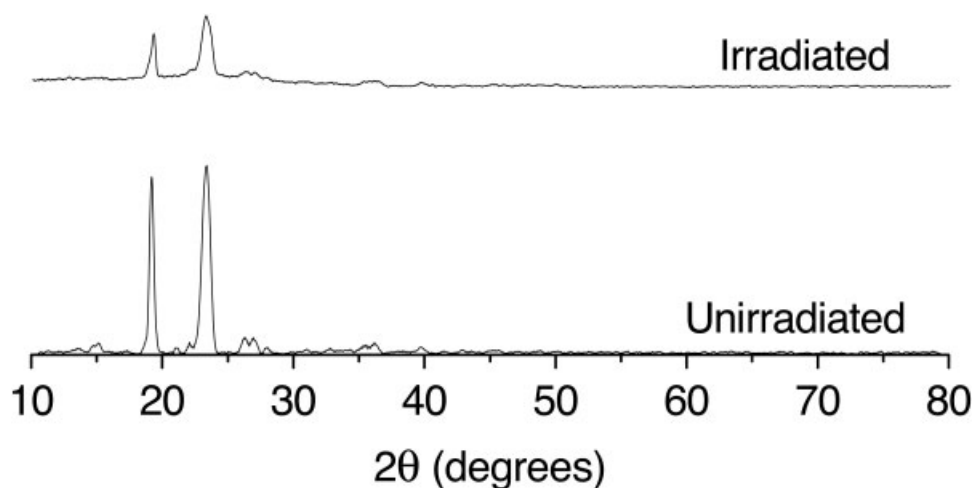
Figure 1. XRD patterns for unirradiated and 15-kGy-irradiated PEG 2000.

machine in the standard mode was used. Samples (10–12 mg) were heated to 90 °C at the rate of 10 °C/min, cooled to −90 °C, and then heated again. An empty aluminum pan was used as a reference. Dry nitrogen gas was used to purge the DSC sample cell at a rate of 25 mL/min.

Ionic Conductivity Measurements

The ionic conductivity of the unirradiated and irradiated samples was measured with the complex impedance method. A vector lock-in amplifier (PAR 5210) in the frequency range of 2 Hz to 120 kHz with a signal of 500 mV was used for this purpose. The sample was loaded into the sample cell with a spring-fit stainless steel blocking electrode and was kept in a vacuum desiccator for the room-temperature ionic conductivity measurements. The samples were soft and were deposited into Teflon rings to maintain the intactness of the shape during the conductivity measurements. The measurements were also carried from 250 to 315 K. For the temperature variation studies, the sample cell was kept in a glass dewar, and cold nitrogen gas produced from boiling liquid nitrogen flowed continuously. The temperature was changed at intervals of 5 K during heating with a Bruker VT-1000 temperature controller. After the desired temperature was set, the cell was kept at that temperature for 20–25 min to stabilize at the set value. All the experimental spectra were analyzed with Boukamp's Equivalent Circuit software.[24]

RESULTS AND DISCUSSION

XRD Patterns

XRD patterns for unirradiated and irradiated PEG 2000 are shown in Figure 1. The two prominent peaks at $2\theta = 19.18°$ and $2\theta = 23.36°$[25] are present in both patterns, indicating the crystalline nature of PEG 2000. The intensity of these two peaks for irradiated PEG 2000 is reduced and slightly broadened. Most of the weaker peaks also disappear after irradiation. This result signifies a decrease in the crystalline fraction of the polymer after irradiation.

Mass Spectroscopy

The molecular weight distributions of unirradiated and irradiated PEG 2000 and $(PEG)_x LiClO_4$ ($x = 20, 46,$ or 100) were determined with MALDI-TOF MS. Table 1 gives the MALDI results for unirradiated and irradiated PEG 2000 and $(PEG)_{46}LiClO_4$. Similar results (not shown) were also obtained for samples with $x = 20$ or $x = 100$. The average molecular weight of unirradiated PEG 2000 quoted by Fluka was approximately 2000. This was confirmed with MALDI-TOF MS. A mass/charge (m/z) distribution from 1600 to 2600 can be observed for commercially obtained PEG 2000 with the molecular weight at the maximum peak value, M_p, at 2062.1 [Fig. 2(a)]. MALDI for 15-kGy-irradiated PEG 2000 shows a different distribution of m/z from 300 to 2600 with a new M_p value at 1010 [Fig. 2(b)]. In addition, the m/z distribution for irradiated PEG

Table 1. MALDI Results for PEG 2000 and (PEG)$_{46}$LiClO$_4$

Sample	Dose (kGy)	M_p	M_n	M_w	PDI
PEG 2000	Unirradiated	2062.1	2056.7	2071.6	1.007
PEG 2000	5	1889.2	1996.9	2024.6	1.014
PEG 2000	10	2023.7	1967.8	1998.5	1.016
PEG 2000	15	1009.5	1131.0	1337.4	1.182
(PEG)$_{46}$LiClO$_4$	Unirradiated	1919.5	1926.6	1950.2	1.012
(PEG)$_{46}$LiClO$_4$	5	1830.3	1896.8	1921.4	1.013
(PEG)$_{46}$LiClO$_4$	10	2007.3	1974.2	2003.4	1.015
(PEG)$_{46}$LiClO$_4$	15	1919.2	1962.6	1995.1	1.017

2000 is broader than that of the unirradiated PEG 2000. Thus, MALDI-TOF MS shows the fragmentation of PEG 2000 after the irradiation and a decrease in its molecular weight. MALDI results for unirradiated and irradiated (PEG)$_{46}$LiClO$_4$ are shown in Figure 2(c,d). The polymer–salt complexes do not undergo any significant fragmentation of the polymer chains, unlike pure PEG, and this signifies the radiation resistance of PEG complexed with the salt.

We also calculated the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI; i.e., M_w/M_n) of the various samples (Table 1).

In comparison with unirradiated PEG and polymer–salt complexes, the irradiated samples show larger PDI values. This means that the irradiated samples are more disperse and inhomogeneous. Furthermore, this increase in PDI after irradiation is much greater for pure PEG than for the complexes. In this context, it is worth mentioning that the measurements of the self-diffusion coefficient of polymer chains show that the wider the molecular weight distribution is, the faster the polymer chains diffuse.[26]

This first MALDI study of irradiation effects in an SPE has led to a couple of unique results. First is the absence of any sign of crosslinking. Earlier studies have shown that irradiation with γ-rays[15,16] or an electron beam[18] can lead to chain scission, crosslinking, or both, depending on the irradiation conditions. Although this needs to be confirmed by further studies, there is some evidence that if the irradiation is carried out *in vacuo*, crosslinking results, whereas if it is done in the presence of oxygen or air, scission is more likely.[27] In our experiments, the samples were irradiated with an electron beam in the presence of air, and this explains the observed chain fragmentation for the pure PEG samples.

The second and more difficult to understand result is the absence of any chain fragmentation in the PEG–LiClO$_4$ complexes, whereas the pure PEG sample underwent chain scission. We can only speculate about the possible cause of this difference at present. Although short-living PEG radicals, which induce chain scission, are generated in both PEG and PEG–salt complexes upon e-beam irradiation, it is likely that in the presence of the salt, the dissipation of energy is more effective, and this could result in a much shorter lifetime and thus limited the chain reactions that may contribute to fragmentation. We thank one of the referees for pointing out this possibility. It is also likely that because of the enhanced ionic conductivity of the PEG–salt complexes, the recombination process may be more effective and, therefore, reduce the radical lifetimes.

Thermal Properties

The DSC curves for unirradiated and irradiated PEG 2000 and the SPE (PEG)$_{46}$LiClO$_4$ are shown in Figure 3. The curves for the other compositions (not shown) are similar to that of the $x = 46$ composition. PEG 2000 and all the SPE samples exhibit a relatively sharp endothermic peak, which could be attributed to the melting of a PEG-rich crystalline phase. The melting temperature (T_m) decreases as the salt concentration increases for the (PEG)$_x$LiClO$_4$ systems.[28] Also, a minimal decrease in T_m for the irradiated systems can be observed, and so it can be concluded that the thermal stability of the polymeric systems does not degrade after irradiation. A weaker second peak can be observed for pure PEG 2000 in the second heating cycle. This could be due to the segregation of two types of crystalline regions after the first heating and cooling cycle. Further studies have to be carried out to verify this conjecture.
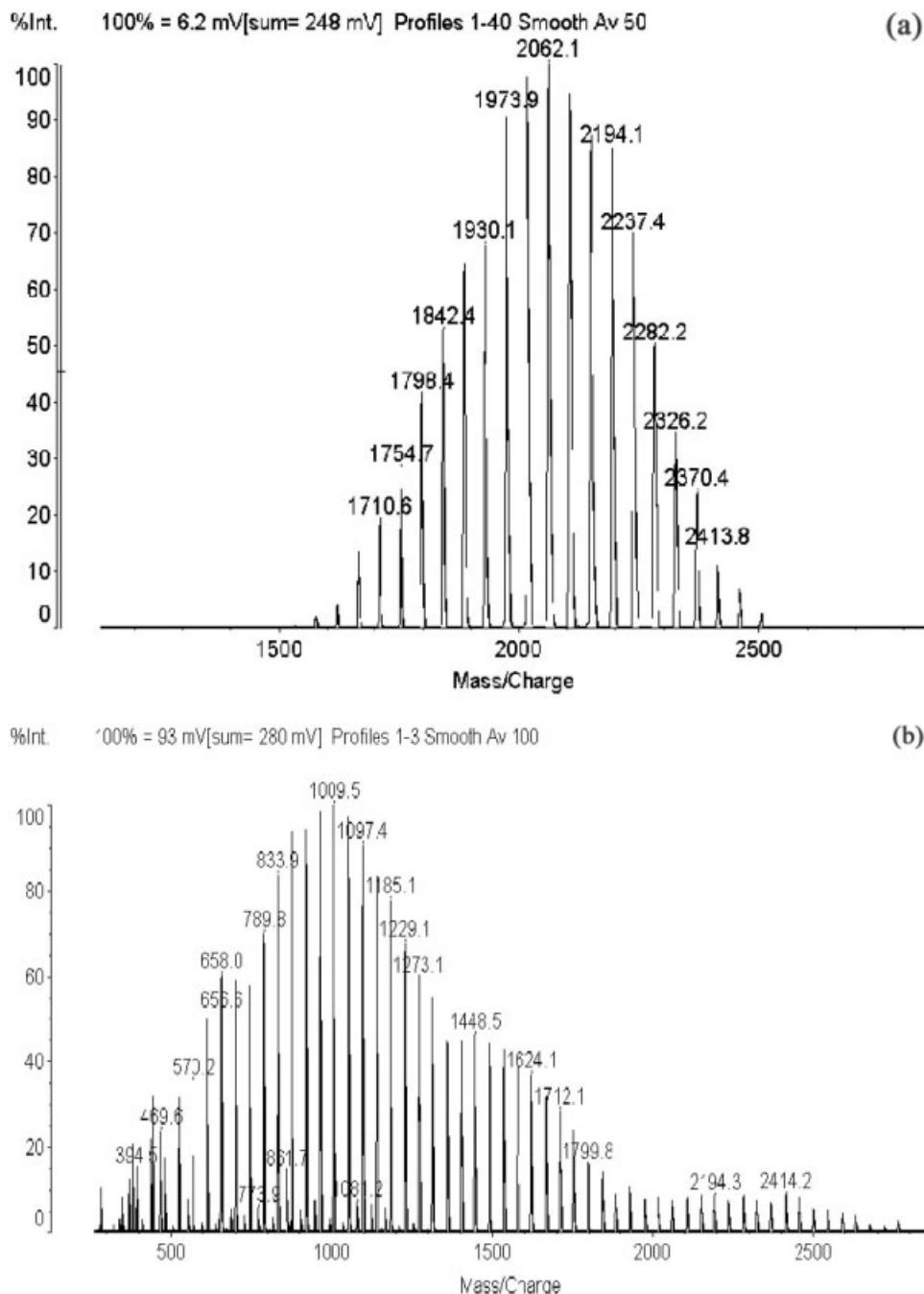
Figure 2. MALDI spectra for (a) unirradiated PEG 2000, (b) 15-kGy-irradiated PEG 2000, (c) unirradiated $(PEG)_{46}LiClO_4$, and (d) 15-kGy-irradiated $(PEG)_{46}LiClO_4$.

However, the area under the curve of the melting endotherm, which gives the latent heat of melting (ΔQ_m), is dependent on the composition of the specimen. As is well known, one can obtain the crystallinity percentage of a sample by comparing this value of ΔQ_m with that of a sample of a known crystallinity percentage. We earlier de-

termined from the NMR measurements that pure PEG 2000 is 83% crystalline. The DSC results (Table 2) confirm the change in the crystalline fraction of the system. The degree of crystallinity (X_c) for both unirradiated and 15-kGy-irradiated PEG 2000 and $(PEG)_xLiClO_4$ systems has been calculated from a comparison of ΔQ_m of the sys-
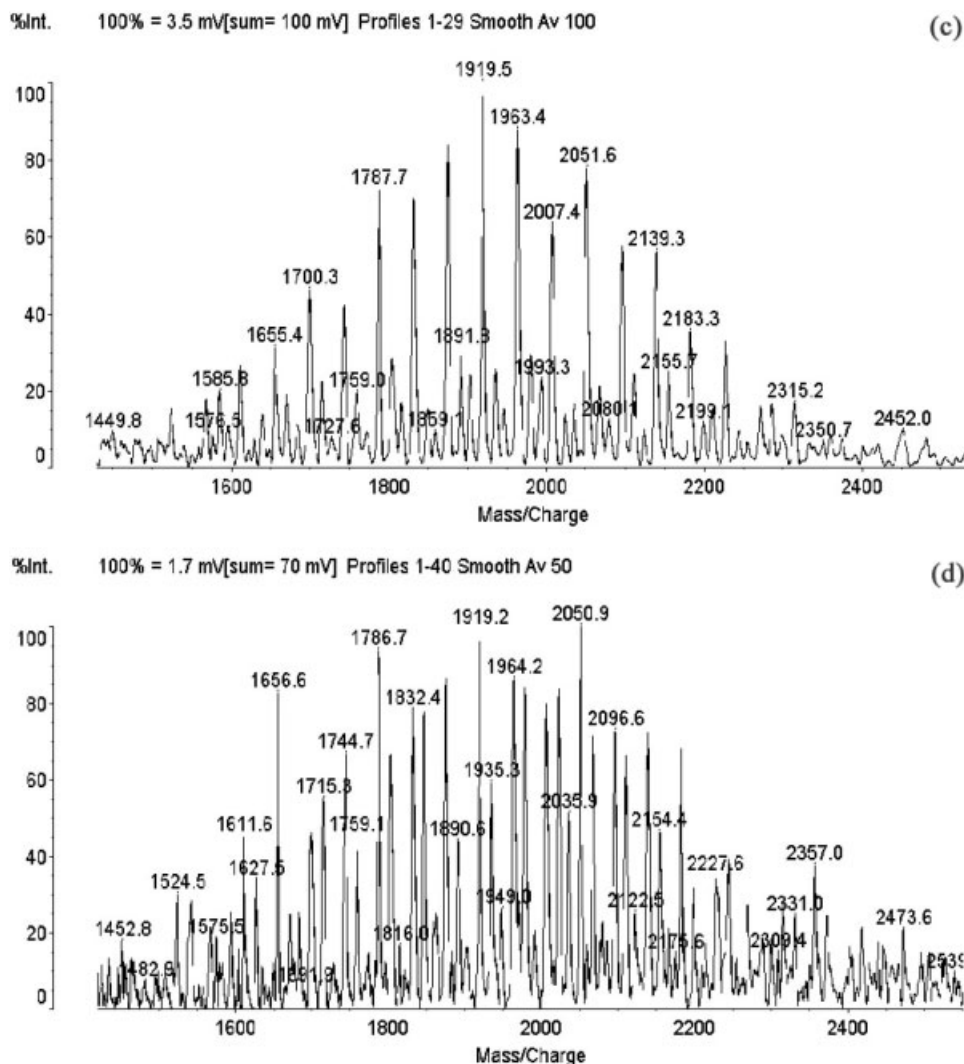
Figure 2. (*Continued from the previous page*)

tems used and the heat of melting of pure PEG 2000 scaled to 100% crystallinity (ΔQ_{mPEG} = 202.41 J/g) found from ^{1}H NMR spectra.[29] A decrease in X_c after the irradiation of the systems can be observed (Fig. 4). This may be due to the radiation-induced amorphization of the polymer chains, which is also complemented by the increase in the inhomogeneity shown in the mass spectrum. The inset in Figure 3 shows T_g for unirradiated and irradiated (PEG)$_{46}$LiClO$_4$ samples. T_g is lower for the corresponding irradiated systems. The decrease in T_g implies an increase in the flexibility of the polymer chains. In principle, radiation damage can result in both chain scission and crosslinking. Extensive chain scission will lead to a reduction in the molar mass, whereas crosslinking increases the molar mass,

leading to less flexible products.[14] In our case, there is chain fragmentation and the molecular weight of PEG 2000 decreases after irradiation, and there is no significant fragmentation for the polymer–salt systems with an increase in inhomogeneity for both, as observed in the mass spectra. Therefore, it can be inferred that a destruction of crystalline regions has occurred. Moreover, the possibility of an increase in the crosslink density is ruled out because a decrease in T_g is observed. T_g cannot be found for higher salt concentration samples, as they are highly crystalline.

Ionic Conductivity

Figure 5 shows the room-temperature conductivity versus the salt concentration for (PEG)$_x$Li-
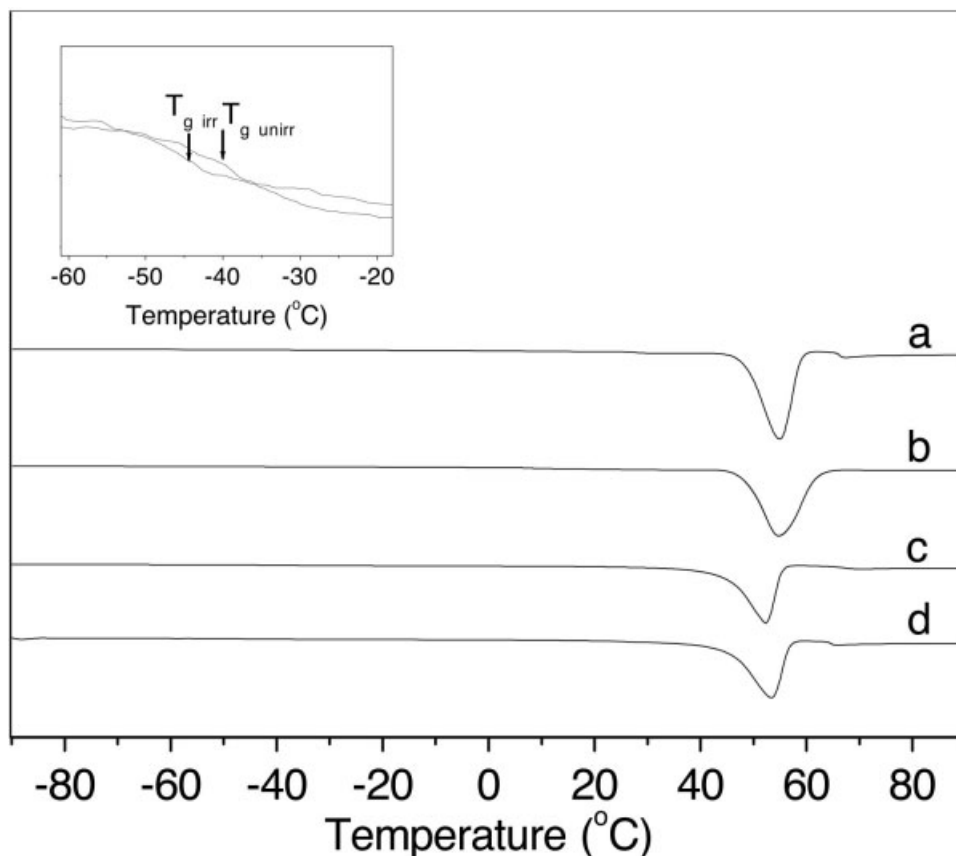
Figure 3. DSC curves for (a) unirradiated PEG 2000, (b) 15-kGy-irradiated PEG 2000, (c) unirradiated $(PEG)_{46}LiClO_4$, and (d) 15-kGy-irradiated $(PEG)_{46}LiClO_4$. The inset shows the expanded curves for unirradiated and irradiated $(PEG)_{46}LiClO_4$, indicating T_g's for both.

ClO_4 systems irradiated at three different doses (5, 10, and 15 kGy).

As the dose of the electron beam increases, there is an enhancement of the ionic conductivity. The 15-kGy-irradiated samples show the maximum ionic conductivity enhancement, by nearly two orders of magnitude. The ionic conductivity of

15-kGy-irradiated $(PEG)_{46}LiClO_4$ is 1.31×10^{-5} S/cm; the ionic conductivity is 7.27×10^{-7} S/cm for an unirradiated sample. The time dependence of the ionic conductivity was determined for unirradiated and irradiated $(PEG)_{46}LiClO_4$ systems. The ionic conductivity of the irradiated system remains unchanged for nearly 120 h, and it is

Table 2. DSC Results for Unirradiated and 15-kGy-Irradiated PEG 2000 and $(PEG)_xLiClO_4$

| x	Salt Concentration (mol)	Enthalpy of Melting ΔH (J/g)		T_m (°C)		T_g (°C)	
		Unirradiated	Irradiated	Unirradiated	Irradiated	Unirradiated	Irradiated
20	2.300	120.3	114.3	52.3	52.2	−36.4	−38.3
30	1.533	135.3	133.7	53.6	53.3	−39.6	−40.1
46	1.000	142.4	139.7	52.3	53.3	−38.9	−43.3
100	0.460	154.7	150.6	53.9	54.4	—	—
PEG	0	168.0	162.4	55.2	54.7	—	—
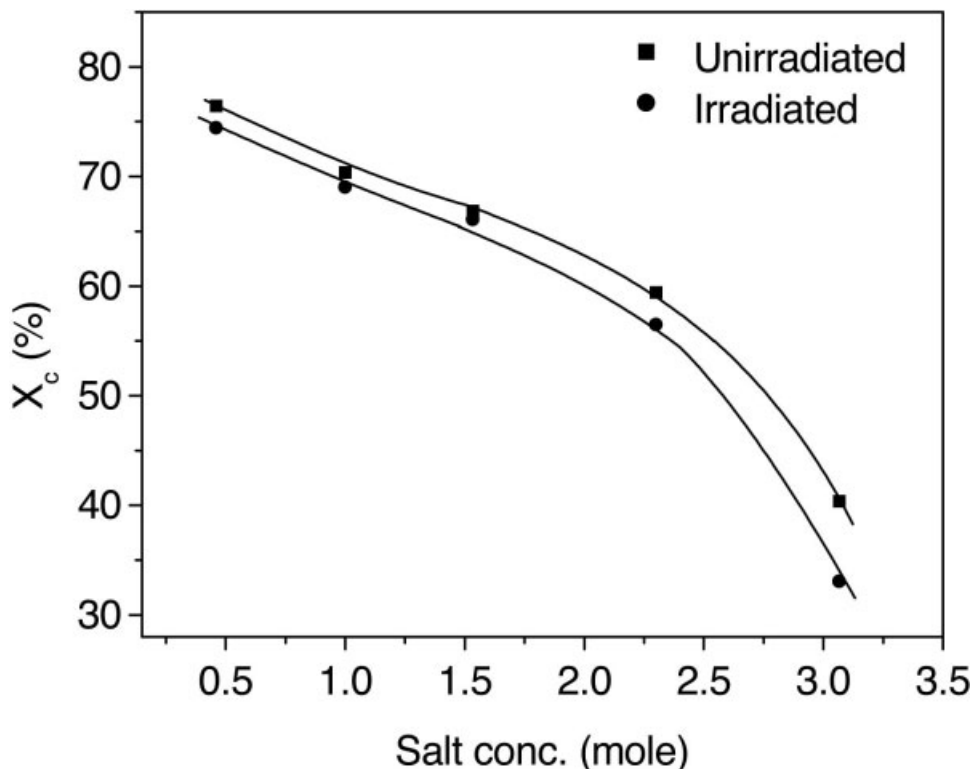
Figure 4. X_c versus the salt concentration for unirradiated and 15-kGy-irradiated (PEG)$_x$LiClO$_4$. The solid lines are guides to the eye.

likely that it continues to remain unchanged for a much longer period (Fig. 6). This indicates that nearly permanent changes have taken place in the samples after the irradiation. This result also indicates the stability of the irradiated SPE systems, which is one of the most important criteria for developing a suitable electrolyte for commercial use.

Because there is fragmentation and an increase in the inhomogeneity of the polymer chains, we can expect the possibility of the formation of free radicals due to irradiation and thus formed free radicals leading to an enhancement of the conductivity. To check for this possibility, we recorded ESR spectra for unirradiated and irradiated PEG 2000 and (PEG)$_{46}$LiClO$_4$ systems. However, no ESR signals were observed. Of course, some free radicals are expected to be generated during irradiation. However, because no ESR signals were observed, it can be concluded that their lifetime is very short and that they disappear in a relatively short time after irradiation. Thus, there is no contribution of the free radicals to the measured enhancement of the ionic conductivity. Furthermore, it is known that

in many polymer systems, the radicals trapped in crystalline regions can live for considerable time periods.[30] Therefore, the short lifetime of e-beam-irradiation-generated radicals points to the essentially different nature of these radicals. This conceivable difference between the results of photon irradiation and particle-beam irradiation deserves further study.

The temperature dependence of the ionic conductivity was also studied in the range of 250–315 K for $x = 46$ and $x = 100$ [Fig. 7(a,b)]. The curvature that is often observed for noncrystalline SPEs is apparent. The Vogel-Tamman-Fulcher (VTF) equation, in the form $\sigma = A/T^{1/2} \exp\{-B/[k(T - T_o)]\}$,[31–33] where σ is the conductivity, k is the Boltzmann constant, T is the absolute temperature, T_o is the ideal glass-transition temperature (usually 30–50° below T_g; i.e., the temperature at which the configurational entropy vanishes), B is an apparent activation energy (dependent on the free-energy-barrier opposing configurational rearrangements), and A is a pre-exponential factor related to the number of carriers,[34] was found to fit the data best. The values of the best fit parameters are given in Table 3. A
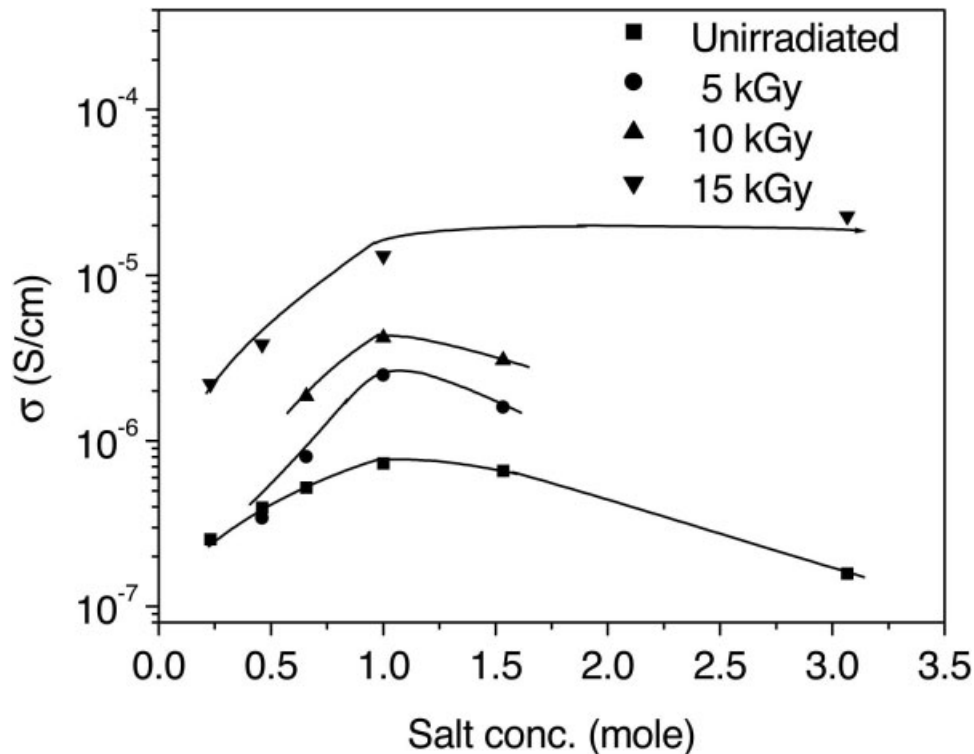
Figure 5. Conductivity (σ) versus the salt concentration for unirradiated and irradiated $(PEG)_x LiClO_4$ at three different doses. The solid lines are guides to the eye.
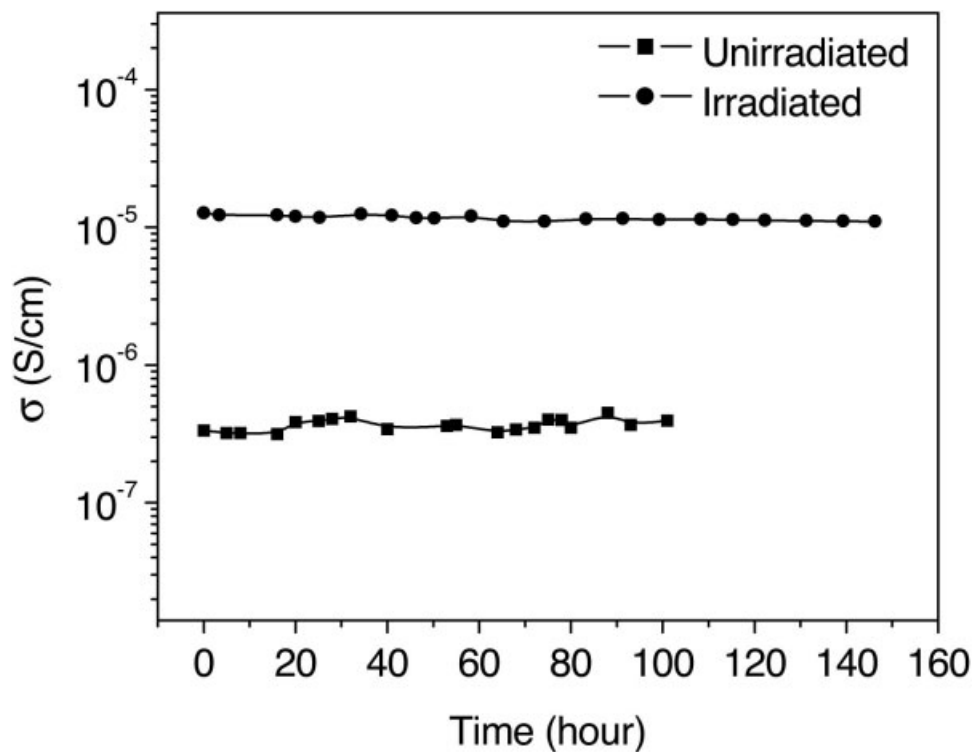
Figure 6. Conductivity (σ) versus the time for unirradiated and 15-kGy-irradiated $(PEG)_{46} LiClO_4$ at room temperature. The solid lines are guides to the eyes.
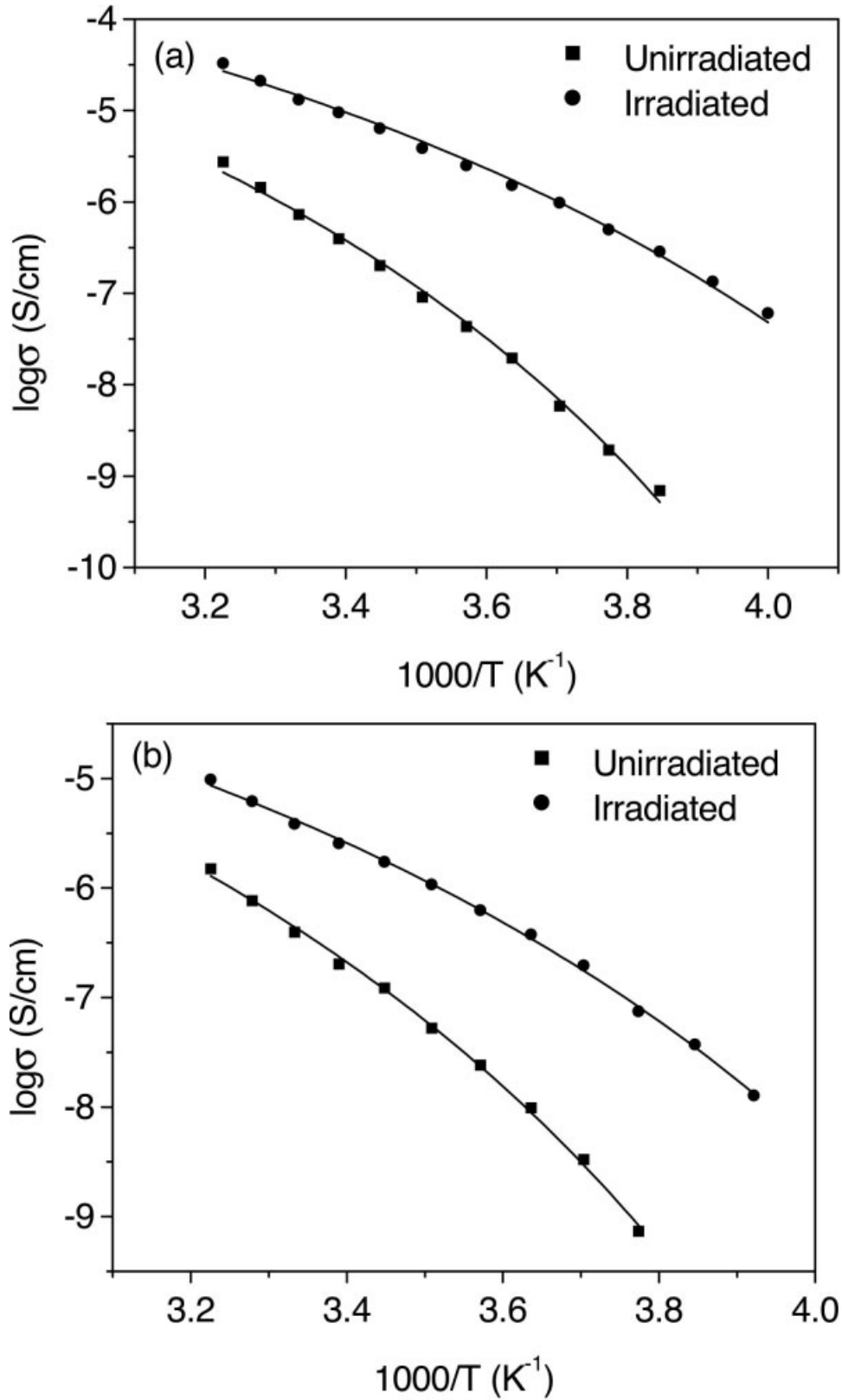
Figure 7. Conductivity (σ) versus the temperature for unirradiated and 15-kGy-irradiated (a) (PEG)$_{46}$LiClO$_4$ and (b) (PEG)$_{100}$LiClO$_4$. The solid lines are fits to the VTF equation.

Table 3. VTF Equation Fitting Parameters for Unirradiated and 15-kGy-Irradiated $(PEG)_x LiClO_4$

x	Salt (mol)	A_{unirr} (S K$^{0.5}$ cm^{-1})	B_{unirr} (eV)	$T_{o\ unirr}$ (K)	A_{irr} (S K$^{0.5}$ cm^{-1})	B_{irr} (eV)	$T_{o\ irr}$ (K)
46	1.00	1.793	0.111	195.75	1.321	0.095	176.14
100	0.46	1.852	0.116	196.43	0.875	0.099	182.57

lower T_o value for the irradiated systems, compared with that of the unirradiated systems, can be observed. This result substantiates the reduction of T_g observed by DSC. The large enhancement of the ionic conductivity could be due to the combined effect of an increase in the amorphous fraction and a decrease in T_g after the irradiation. The increase in the inhomogeneity of the samples inferred from the PDI, as observed in the mass spectra, could lead to better diffusion of the polymer chains, which could also be favorable for better ionic conduction. Even though we do not stress the microscopic picture of the systems under irradiation, semimacroscopically, an increase in the amorphous fraction and the flexibility of polymer chains due to radiation damage has been found to lead to enhanced ionic conductivity.

Chemical Changes

Irradiation is known to result in important chemical changes in polymers and polymer electrolytes. For example, Ferloni et al.[35] studied, using ESR, the effects of γ-irradiation on dry PEO and aqueous solutions of PEO and PEO–LiClO$_4$ complexes. Okamoto and Cho[18] reported a possible mechanism for the effects of γ-beam and e-beam irradiation on polymer electrolytes with a Tb^{3+} fluorescence probe. In these studies and a number of other studies, the following emerge as the likely processes after irradiation. The irradiation causes the formation of the scission carbonyl —OĊHC(=O)H, the hydrogen abstraction radical —OCH$_2$ĊHO—, and the chain-scission radical —OĊH$_2$ and can also lead to trapped electrons. These radicals and trapped electrons can lead to chain scission and crosslinking. In our samples, we do not observe any ESR signals, and this indicates the very short lifetime of the free radicals that may have formed during the irradiation. Therefore, it is not possible to draw any conclusions on the nature of the free radicals, except that there is no contribution to the enhanced conductivity from any free radicals. Low-temperature irradiation and ESR experiments may be able to throw some light on the nature of the free

radicals that are generated and their influence on chain scission and crosslinking.

CONCLUSIONS

The main result of this work is the observation of a large enhancement of the ionic conductivity of the polymer electrolyte $(PEG)_x LiClO_4$ after e-beam irradiation. A decrease in X_c and an increase in the flexibility of the polymer chains have been observed after irradiation. The possibility of free radicals contributing to the increase in conductivity has been ruled out because no ESR signals have been observed. The enhanced ionic conductivity remains constant with time for more than 100 h, and this signifies the nearly permanent changes in the system after irradiation. The enhancement of the ionic conductivity of the $(PEG)_x LiClO_4$ system after the irradiation is attributed to an increase in the inhomogeneity, a decrease in the degree of the crystallinity, and an increase in the flexibility of the polymer chains.

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