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Competitive scission and cross linking in a solid polymer electrolyte exposed to gamma irradiation: Simulation by a fractal model

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HIGHLIGHTS

- The polymer system is modelled as deterministic Vicsek fractal.
- Theoretical simulation carried out on the polymer system perturbed by gamma irradiation.
- Simultaneous scission & cross-linking are considered as an effect of irradiation.
- Ionic motion is controlled by trapping phenomena & polymer segmental motion.
- Variations in conductivity & viscosity are simulated as a function of radiation dose.

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ABSTRACT

Gamma irradiation influences the microstructure of polymers that significantly affects the correlated properties of solid polymer electrolytes (SPEs). The present paper introduces a deterministic fractal model of polymer molecules and investigates the morphological changes due to gamma irradiation in SPE. The computer aided simulation is primarily based on radiation induced scission and/or cross linking of polymer molecules. The drift *velocity* of conducting ion which is proportional to conductivity, is calculated considering two competing effects, viz. trapping effect of ions diffusing inside a branched fractal molecule and the motion assisted by segmental motion of the polymer itself. Variations in ionic conductivity, molecular weight distribution, intrinsic viscosity etc., as a function of probability of scission and/or cross linking show significant correlation with microstructural change induced by gamma radiation of variable dose. The present theoretical study enables easy understanding for correlation of associated properties exhibited upon experimental system perturbation through gamma irradiation.

1. Introduction

The development of solid polymer electrolytes (SPEs) consisting of a polymer–salt complex is considered to be a breakthrough in the field of electrochemical devices. The prime peculiarity of polymer species is the co-existence of crystalline and amorphous phases. Researchers have shown that, majority of the ion dynamics occurs in the amorphous phase, where the transport properties viz. ionic conductivity, mechanical relaxations, diffusion, spin relaxation etc. are primarily associated

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with the segmental motion of the polymer [1–3]. Owing to the coupled behaviour of SPE systems, the ionic diffusion is supported by structural relaxation process and also occurs by the migration of ions [1]. However, such associated ionic conduction is hindered by the bi-phasic nature of the polymer followed by the performance deterioration of the solid state device. Based on the usual thumb rule applicable for polymers, the ionic charge carriers are transported through the amorphous regions and in addition the local motion of the host polymer tends to play a significant role [4]. Therefore, fast ionic transport occurs in the amorphous phases of the polymer electrolyte in which the conduction is found to be two/three order of magnitude higher than in the crystalline phase [5]. A number of techniques viz. addition of plasticizers, irradiation by gamma ray, inclusion of insulating particles etc. are engaged by many researchers round the globe [6–11] to improve the electrical, mechanical and rheological properties of SPE. The aforementioned techniques, in general, produce morphological changes in the polymer microstructure thereby modifying the related properties intrinsically. Among all the aforementioned techniques, irradiation is amongst the simplest procedure practised by the researchers. The advantages of gamma irradiation are its temperature independent, homogeneous, clean and controlled reactions producing sterile products without any chemical residue [7,12–14]. Polymer entities tend to undergo degradation as well as cross linking upon irradiation, owing to which the distribution of amorphous and crystalline regions alters significantly [15]. Experimental outcome of irradiation on polymers in terms of either scission or cross linking or both are highly dependent on the atmosphere viz. air or inert gas etc. which primarily controls the pattern of reaction [15–17]. Experimental research on irradiation effect encompasses a common shortcoming related to the formation of random products that fails to follow any pre-determined theoretical pattern. Such inconsistency in irradiation procedure affects the reproducibility of the technique thereby restricting its standardization.

The present article intends to homogenize the irradiation effect by considering a fractal model structure of the polymer moiety. Fractal modelling for long polymer macromolecules with entanglements and branches at different levels is reported in the prior arts [18,19]. However, in the present context, a simple deterministic model fractal structure is introduced representing the polymer system. Using such a theoretical model, the overall molecular weight distribution, intrinsic viscosity, ionic conductivity etc. are predicted through computer simulation. The simulated results enable the determination of physical properties for ordered perturbations over a wide range. This helps in easy understanding for correlation of associated properties exhibited upon experimental system perturbation through gamma irradiation.

2. Mathematical modelling: process dependent parameters based on the fractal concept

2.1. Fractal model of polymer electrolytes

The structure of polymer molecules can be described by random fractals which are stochastically self-similar [18]. Application of deterministic fractals [20] to model polymer molecules has certain advantages viz. assembling the fractals by definite mathematical rules through which exact results can be obtained analytically. In spite of the artificiality of deterministic model, their procedure may yield qualitatively significant results. In the present context, the Vicsek fractal, corresponding to a certain stage with a definite structure and length, is considered as a model polymer molecule. Owing to the inherent loop-less, finitely ramified branched morphology, the said fractal model is chosen where exact relations exist among the diffusion exponent (d_w), chemical exponent (d_l) and fractal dimension (d_f) [21,22]. Fig. 1(a)–(c) represent three consecutive stages for generation of the Vicsek fractal. The structure corresponding to Fig. 1(a) is considered as the monomer unit, consisting of 5 (five) basic blocks, each of unit molecular weight. A second stage pattern constructed using 5 (five) units of 1^{st} stage pattern connected self-similarly is shown in Fig. 1(b). Higher stage structures may be generated iteratively from its subsequent lower stage structures as shown in Fig. 1(c), i.e. five units of $(S-1)^{th}$ stage pattern forming the S^{th} stage when connected according to the particular fractal generation rule. Hence, if the linear scale increases by a factor of 3, the molecular weight increases by a factor 5. Based upon such consideration, the fractal dimension can be written as:

$$d_f = \ln 5/\ln 3 = 1.465. \tag{1}$$

Therefore, molecular weight increases as 5^S as the fractal stage [denoted by 'S'] increases. An assembly of these model fractal molecules with a chosen distribution in molecular weight constitutes the host polymer system of the present context. The mentioned distribution characterizes the initial (unirradiated) system. For the purpose of simulation, a mono-disperse polymer system having 1000 molecules is considered which corresponds to 7^{th} stage pattern of molecular weight being 5^7. The host polymer system is subjected to perturbation by means of high energy irradiation and the consequent effect in terms of intrinsic properties such as conductivity or viscosity of the parent polymer is the prime endeavour of the present study. The effect of the said perturbation is theoretically modelled based on certain considerations and is presented in the subsequent sections.

2.2. Perturbation through gamma irradiation: scission and/or cross linking

Ionizing radiation by proton, electron beam, gamma rays, etc. may cause the formation of new functional groups, rearrangement of bonds, scission and/or cross linking of polymer chains [7,12,23–26]. Scission and cross linking reactions occur simultaneously, but usually with dissimilar rates, depending on factors, viz. presence or absence of oxygen, radiation dose, nature of the polymer system, addition of plasticizers and other chemical species etc. [23,24,26]. Amid the