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THE COMBINED ACTION OF IONIZING RADIATION OF POLYMER ELECTROLYTES

Dr. Pradyot Nanda

Assistant Professor, Physics Department, Dinabandhu Andrews College, Garia, Kolkata, West Bengal, India.

ABSTRACT

Ionizing radiation produces changes in various properties of polymers and is a useful technique to modify polymers. It is a very important way to generate new properties or improve existing properties in polymers. One characteristic property of polymer electrolytes is that at ambient temperatures the polymer has a tendency to crystallize. There are various ways to suppress crystallization and enhance addition of plasticizers, addition of insulating nanoparticles acting as fillers. This study examines the effects of gamma irradiation on polymer electrolytes, focusing on enhancing their structural, thermal, and electrochemical properties for applications like batteries, fuel cells, and sensors. Gamma irradiation induces cross-linking, chain scission, and oxidation in polymer matrices, which significantly impacts their conductivity, mechanical strength, and stability. While cross-linking enhances mechanical integrity and chemical stability, excessive irradiation can lead to chain scission, reducing molecular weight and strength.

INTRODUCTION

The combined action of ionizing radiation and oxygen on polymers may rapidly lead to a severe deterioration of the polymer properties. The resulting effects are strongly dependent on the chemical structure of the polymer. The radiation damage and oxidative degradation cause chemical changes in the polymer structure with build-up of a variety of new functional groups as carbonyls, carboxyl's, esters, hydroxyls etc.The property of the polymer alters significantly [2, 3] depending on the type of radiation used, nature of polymer and on dose. Studies have been made on the effect of various radiations like ion beam, electron beam, neutron beam, X- ray, gamma ray on polymer electrolyte systems [4]. The various physical and chemical properties of the polymer electrolyte can be studied using different experimental techniques like Differential Scanning Calorimetry, X-ray Diffraction, Fourier Transform Infrared Spectroscopy and Viscosity.

Polymer

A polymer is a molecular compound with high molecular mass and is composed of a large number of repeating units of identical structure called 'monomer'. The word 'polymer' is derived from the classical Greek words 'poly' meaning 'many' and 'meres' meaning 'parts' and was first used by Berzelius in 1827. Polymers offer unique properties and application prospects. Molecular weight of a polymer depends upon the degree of polymerisation. Polymers are tough, resistant to the action of water, acids and alkalis. Because of these, both natural and synthetic polymers play an ever increasing role in modern technology. The range of polymeric materials is so wide that they have found applications in practically every branch of industry [5-7].

Polymer Electrolytes

The present study aims at irradiation effects on physical and chemical properties of polymer electrolytes. Polymer electrolytes are solid ionic conductors formed by the dissolution of salts in suitable high molecular weight polymers. Polymer electrolytes are usually biphasic consisting of crystalline and amorphous phases. The solid polymer electrolytes (SPE) gained much attention due to various properties like high flexibility, low weight, transparency, and relatively high ionic conductivity. They have wide applications as sensors, in fuel cells, and in high energy density rechargeable batteries and electrochemical devices [8-12].

In years that followed much activity was observed in this field towards understanding the interactions involved in the formation of polymer electrolyte phases, synthesis of new polymer electrolytes and analysis of the various solid polymer electrolytes [13, 14].

The host polymer should have:-

1) Atoms/ groups, usually in the main chain with sufficient electron donor power to form coordinate bonds with cations of the salt

2) A suitable distance between such co-ordinating centres permitting formation of multiple intra polymer-ion bonds.

3) low barriers to rotation for atoms in the main chain so as to ensure high flexibility of the polymer and hence facilitate segmental motion and also provide sufficient volume to allow the ions to move through the polymer matrix.

Majority of the polymer electrolytes reported so far have been based on PEO (polyethylene oxide), PPO (polypropylene oxide), PEG (polyethylene glycol) using electrolytes like $LiClO_4$, LiSCN, NaI, NaSCN, NH_4ClO_4. Attention was mainly focussed on polyethylene oxide (PEO) based materials, owing to their ready availability at various molecular weights and their interesting mechanical properties [15].

Polyethylene oxide is a homopolymer with a repeat unit $[-(CH_2)O-]_n$. The commercial PEO (eg. polyoxresin) has a molecular weight ~$4x10^6$ with a density of 1.33 at 20°C. PEO is soluble in acetonitrile, dichloromethane, carbon tetrachloride, benzene etc. The crystal structure of PEO based on X-ray diffraction data was first suggested in 1964 by Tadokoro et al [16]. The crystal structure consists of 7/2 helix, i.e. seven monomeric units $(–O-CH_2-CH_2)$ turning two times per fibre period (here c axis of the unit cell is taken as the fibre axis) with symmetry isomorphous to the point group D_7. The fibre identity period is 1.93nm. The space group is $P2_1/a$ with unit cell parameters a=8.05Å, b=13.04Å, c=19.48Å, =125.4°. There is considerable distortion from the helical symmetry D_7. This means the molecular chain of PEO is more flexible and the intermolecular forces act on the main-chain atoms more strongly. Consequently, the large distortion of the PEO molecule may be attributed to the flexibility of the molecular chain and the intermolecular forces. It has been found that PEO usually takes the planar zigzag conformation although various other conformations in the crystalline complexes with other salts like urea, thiourea, $HgCl_2$ etc. have been reported [17].

Morphology

When crystallization occurs in polymer-based systems from melt or solution, it commonly takes place by the formation of spherulites, which are three dimensional structures consisting of sheet–like crystalline regions (fibrils of lamellae) embedded in amorphous material. Depending on the method of formation of a polymer electrolyte (nature of solvent used for casting etc.) and on its subsequent thermal history, various morphological states may be formed, each of

which has a characteristic influence on the thermal, electrical and other physical properties of the system. Wright and Co-workers [18, 19] showed that the solvent influenced the morphology of polymer electrolyte system, producing materials predominant in either high melting, highly ordered or low melting, partially ordered crystalline phases from the same stoichiometry. It was postulated that the predominating phase was controlled by competition between solvent and PEO for the salt.

Polymerisation

Polymerisation is the process in which simple units, called monomers, unite to form a complex polymer molecule. Monomers react chemically to produce polymers and the links forming the chains in the polymer are covalent in nature [20-22].

Classifications of polymers are based on:

(1) Polymerisation process

(a) Addition polymerisation –The monomers add up to form a polymer maintaining the original properties of the monomer.

(b) Condensation polymerisation – Chemical reaction also takes place between the monomers that add to form a polymer.

(2) Structure

(a) Linear – Polymerisation occurs in one dimension only.

(b) Branched – Linear polymerisation with branch formation takes place.

(c) Network –Three dimensional arrays or networks of molecules are formed.

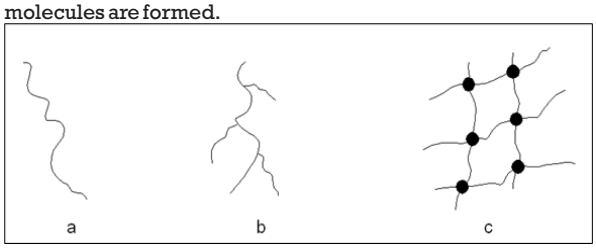

Fig: 1 Schematic representations of (a) a linear polymer (b) a branched polymer (c) a network polymer. (The symbol represents a cross-link point where two chains are chemically bonded together.)

(3) Properties

(a) Thermoplastics - Molecules in a thermoplastic are held by weak intermolecular forces so that they soften when heated and return to their original condition when cooled. Thermoplastics which are not cross linked can be reshaped once moulded. Usually linear or slightly branched polymers are thermoplastics. All the major thermoplastics are produced by chain polymerization. However, not all amorphous polymers are thermoplastics. The glass transition temperature (T_g) indicates whether an amorphous polymer is a thermoplastic. Thermoplastics already have a range of applications because they can be formed and reformed in many shapes. Some examples are food packing, insulation, automobile bumpers and credit cards [20].

(b) **Elastomers** – They are slightly cross linked and are reversibly stretchable to high extent. Some elastomers can be stretched to many times their original length and can bounce back into their original shape without permanent deformation. An elastomer must be above its glass transition temperature (T_g) and have a low degree of crystallinity. Examples of elastomers are natural rubber, styrene-butadiene rubbers, poly-butadiene rubbers, isobutylene-isoprene rubbers, ethylene-propylene polymers, nitrile butadiene rubbers.

(c) **Thermosets** are three-dimensional network polymers that are heavily cross-linked. Thermosets cannot be reshaped by heating. The heavy cross-linking restricts the motion of the chains. They are used to make toys, varnishes, boats, hulls and glues.

Crystallinity of polymers

Perfectly crystalline polymers are very difficult to obtain under laboratory conditions. Usually, polymers are partly in amorphous state and partly in crystalline state [23]. The amount of crystallinity of a polymer is described by the so called degree of crystallinity and expressed as a percentage [8-10]. Analysis of the X-ray diffraction (XRD) patterns of the polymers and Differential Scanning Calorimetry (DSC) provides information about crystallinity of a polymer [24].

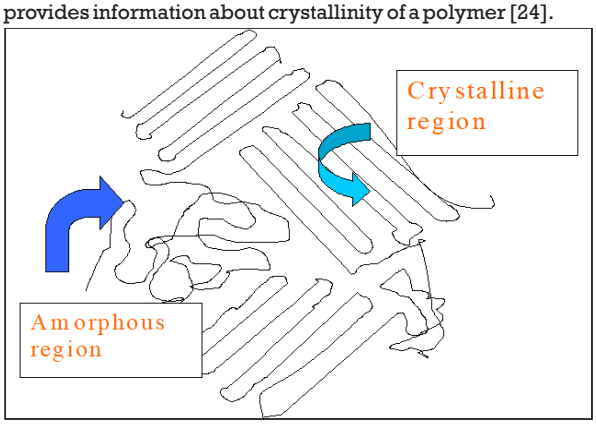

Figure 2: Schematic representation of crystalline and amorphous region of a polymer

The crystallinity (χ) of polymer is defined as

$$\chi = \frac{\Delta H_m \text{ of the sample}}{\Delta H_m \text{ of 100\% crystalline polymer}}$$

where ΔH_m refers to the enthalpy change.

Interaction Between Polymer And Salt

Some polymers behave as high molecular weight solid solvents and dissolve salts to form stable ion-polymer complexes. A salt dissolves in a polymer only if the energy and entropy changes associated with the transfer of its constituent ions from the crystal lattice to their equilibrium positions in the host medium produce an overall reduction in the free energy of the system [16]. The lattice energy is compensated by exothermic ion-polymer interactions. The total entropy change is determined by the gain in entropy brought about by the destruction of the crystal lattice and also, sometimes, by changes in the conformation of the host polymer. The solid polymer molecules have electron donor sites that can form weak linkages with the cation part of the salt. Such coordination sites are along the polymer chain and execute motion along with the normal thermal activation of the polymer chain. The degree of interaction between the coordinating sites on the polymer and the ions depends on interaction energy between the cation and/or anion and the polymer's ability to adopt conformations that allow multiple inter- and intramolecular coordinations [19].

Experimental characterisation of physical and chemical properties of polymer electrolytes

The various physical and chemical properties of the polymer electrolyte can be studied using different experimental techniques like Differential Scanning Calorimetry, X-ray Diffraction, Fourier Transform Infrared Spectroscopy and Viscosity.

Differential scanning calorimetry (DSC)

Differential scanning calorimetric measurements of a polymer help to study the thermal transitions and different phases of the polymer. The melting point and the glass transition temperature of a polymer can be determined by

DSC. In this process two pans are taken— the sample pan and the reference pan. The polymer is kept in the former and the latter is kept empty. The pans are then heated by a heater. A computer is fitted to turn on the heaters that supply heat to the two pans at a specific rate. The polymer in the sample pan takes more heat to keep the temperature of the sample pan increasing at the same rate as the reference pan. Plots of the difference in heat output of the heater against temperature are obtained [Fig.3].

The plot of heat flow vs. temperature shows a sudden shift upward, after a certain critical temperature, called glass transition temperature (T_g). However this change in heat capacity takes place over a temperature range. The polymers have a lot of mobility above the glass transition temperature and then at a suitable temperature they gain enough energy to crystallize. This produces a drop in the heat flow vs. temperature curve and the corresponding temperature in the lowest point of the dip is called the polymer's crystallization temperature (T_c) and the area of the dip gives a measure of the latent energy of crystallization for the polymer. When heated beyond T_c, the polymer starts melting. At melting temperature (T_m), the chains come out of their ordered arrangements and begin to move around freely. There is absorbance of heat which appears as a peak on DSC plot. The latent heat of melting is obtained by measuring the area of this peak. The temperature corresponding to the peak is the melting temperature (T_m). Since heat is absorbed, melting is called endothermic transition [21]. The degree of crystallinity of the sample can be measured by taking ratio of the area under the curve for the sample with a sample that is 100% crystalline [23].

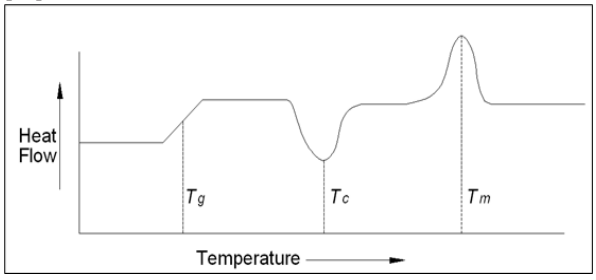

Figure 3: Heat flow vs. temperature in a typical DSC curve

CONCLUSIONS

Application of gamma radiation on polymer electrolytes can effectively enhance chain scission or degradation and crosslinking. Although both these processes occur simultaneously, usually, one dominates over the other, depending on the condition of irradiation and the shape, size and chemical nature of the polymer etc. Application of gamma radiation leads to variation in various morphological, physical and electrical properties of the polymer electrolyte. This has wide applications in analyzing the changes in the behaviour of polymers in radiation environments encountered in nuclear reactors, space crafts, particle accelerators etc. [24]

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