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Physical Principles of Ion-Beam Processing of Polymeric Materials and Applications*

E. H. Lee
Oak Ridge National Laboratory
Metals and Ceramics Division
P.O. Box 2008
Oak Ridge, TN 37831-6376

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Physical Principles of Ion-Beam Processing of Polymeric Materials and Its Applications

EAL H. LEE
Oak Ridge National Laboratory, Metals and Ceramics Division, P.O. Box 2008, Oak Ridge, TN 37831-6376 USA

Abstract

Irradiation of polymeric materials with energetic ions in the range of several hundreds of keV to several MeV causes drastic changes in physical, chemical, and mechanical properties. Studies indicate that irradiation produces many active radicals which then react with each other, transforming spaghetti-like tangled polymer chains into a highly cross-linked network structure. Analysis of experimental data shows that the most important parameter for cross-linking is the deposited energy density along the ion track, often expressed in terms of *linear energy transfer* (LET) in units of eV/nm. High LET produces a high number of free radicals over many neighboring molecular chains and thereby facilitates cross-linking. On the other hand, under low LET conditions, radicals are produced so sparsely that cross-linking efficiency decreases. Moreover, the deposited energy in the chain often leads to chain scission when there are no radicals in the neighboring chains for crosslinking. This paper reviews the current understanding of cross-linking mechanisms in terms of nuclear and electronic stopping and their impact on materials' properties.

Introduction

In the past, radiation effects in polymeric materials have been the domain of radiation chemistry, namely for the study of radiolysis and polymerization mechanisms induced by electron beams or γ-rays [1,2]. In recent work at ORNL, however, it was shown that the quality of such ionizing radiation sources and their impact on materials' properties were quite different from those produced by *high energy ion-beams* (HEIB) in the energy range of several hundred keV to several MeV. Property changes induced by HEIB were quite dramatic, over 50 fold increase in hardness [3], as high as 20 orders of magnitude increase in electrical conductivity [4,5], drastic improvement in wear and chemical resistance [6], increase in optical density [7], and changes in permeability [8], to name a few. While such property changes are of great interest for industrial applications, ion-beam polymer interaction mechanisms involved with HEIB have been the challenging subject for investigation at ORNL for the past several years. In the following, the recent understandings in the ion-beam polymer interaction mechanisms are reviewed. Due to the page limitation, only limited application examples are presented to aid in the explanation of the mechanisms. For those who are interested in application areas, detailed examples can be found in reference 3.

Ion-Beam/Polymer Interaction Mechanisms

When a charged particle traverses a polymer medium, it loses its energy by two main processes, namely, by interacting with target nuclei and by interacting with target electrons. The former process is called *nuclear stopping* and the latter *electronic stopping*.

The nuclear energy loss arises from collisions between energetic particle and target nuclei, which causes atomic displacements and phonons. Displacement occurs when the colliding particle imparts an energy greater than a certain displacement threshold energy, E_d, to a target atom, otherwise the energy is dissipated by vibrating lattice atoms (phonons). E_d is an energy that a

recoil requires to overcome the lattice forces and to move more than one atomic spacing away from its original site. Since the nuclear collision occurs between two atoms with electrons around protons, the interaction of ion with target nuclei is treated as the scattering of two screened particles. Nuclear stopping is derived in consideration of the momentum transfer from ion to target atom and the interatomic potential between two atoms. Thus nuclear stopping varies with ion velocity as well as the charges of two colliding atoms. Nuclear stopping becomes important when ion slows down to approximately the Bohr electron velocity (orbital electron velocity). For this reason, for high energy ions, the maximum nuclear energy loss occurs near the end of the ion track.

When an energetic particle passes through a medium, the orbital electrons of the ion are stripped off in varying degree depending upon the ion velocity (V_{ion}). The effective charge on a positive ion can be written as $Z^*_{eff} = Z[1-\exp(-a\beta/Z^{2/3})]$, where Z is the atomic number, $\beta = V_{ion}/c$ and c is the velocity of light. Somewhat different values have been assigned for the coefficient 'a' by various authors; a value of 25 was used by Pierce and Blann [9] and 130 by Barkas [10], for example, but both expressions give a similar trend. He-ions become completely stripped to an average charge of +2 at around 1 MeV or ≥0.3 MeV per nucleon.

The electronic energy loss arises from electromagnetic interaction between the positively charged ion and the target electrons and from elastic collisions between the ion and target electrons. The former process is called *glancing collision* (inelastic scattering) and the latter is called *knock-on collision* (elastic scattering). Both glancing and knock-on collisions transfer energy in two ways, namely by causing electronic excitation and ionization. All excited electrons eventually lose energy as plasmon decay. Electronic excitation is the process in which an orbital electron is raised to a higher energy level, whereas, in ionization, an orbital electron is ejected. The glancing collisions are quite frequent but each collision involves a small energy loss (<100eV). On the other hand, the knock-collisions are very infrequent but each collision imparts a large energy to a target electron (>>100 eV). These knock-on electrons are often called δ-rays or secondary electrons.

Nuclear collisions create recoil atoms and these recoil atoms lose their energy through nuclear and electronic processes until all excited atoms and electrons are thermalized by dissipating energy through phonons and plasmons. For most ion energy ranges of interest, nuclear stopping by small atoms such as H or He is small compared to electronic stopping because the momentum transfer from the low mass ions is small. Nuclear stopping, however, becomes important for ion species with a large number of protons. The unit eV/nm/ion or simply eV/nm is used for the energy loss per unit path length or linear energy transfer (LET).

An example of average energy partitioning per ion for 100 keV ions into polypropylene, calculated with Kinchin-Pease approximation using the Monte Carlo simulation program *Stopping and Range of Ions in Matter* (SRIM v.96) [11], is shown in Fig. 1. Displacements include vacancies and replacement collisions. In Kinchin-Pease approximation, replaced atoms are not counted, and only the vacancies are considered. The number of vacancies is calculated by employing NRT model [12], $\nu_{NRT} = 0.8E_v/2E_d$, where E_v is the energy used to cause atomic displacements (total phonon energy in SRIM). The electronic energy loss constitutes the ionization energy loss by the primary ion as well as by recoil atoms. The displacement processes involve breaking bonds and displacing atoms. Typical lattice binding energies, E_B, are 1-3 eV. E_B is the difference in energy for the atom in its lattice site and removed to an infinite distance. Every recoiling target atom loses Ed (E_B plus energy required to displace the atom over a lattice

potential) when it leaves its lattice site. The nuclear energy loss accounts for the energy used to break the bonds (E_B) and displace the atoms. All nuclear energy eventually decays as phonons. In SRIM Kinchin-Pease calculation, the bond breaking energy (vacancy number times E_B in SRIM) was calculated separately. Thus the nuclear energy loss is equal to the sum of phonon LET and vacancy LET. The integrated area under the six curves sums up to 100 keV, the energy received by the system. The phonon contribution from the recoils is large compared with that of the incident ion, because one ion produces many recoils.

During irradiation, various physical and chemical processes take place in the polymer. Nuclear collisions cause atomic displacements, which then can lead to chain scission or release of pendant atoms. Superposition of phonon waves can also lead to bond breakage, but the probability of such events is small because phonons have insufficient energy to start with. When a charged particle traverses a medium, an electromagnetic field sets up around the moving charged particle. The closer the distance to the track, the stronger the field. Electrons in the medium are pulled away by the positively charged ion as it moves and thus massive ionization occurs along the track, forming a cylindrical column of charged or excited atoms. The magnitude of ionization varies with ion velocity and its charge state. The δ-rays also cause electronic excitation and ionization along the track, producing active chemical species, bond stretching, and ionized atoms in the polymer chain. Coulombic attraction and repulsion among ionized atoms cause violent segmental motion of the polymer chains leading to cross-linking or bond breakage. Various gaseous molecular species are released during irradiation. The most prominent emission is hydrogen, followed by less abundant heavier molecular species which are scission products from the pendant side groups and chain-end segments, and their reaction products. Figure 2 illustrates various functional chemical entities created by irradiation. Crosslinking occurs when two free dangling ion or radical pairs on neighboring chains unite, whereas double or triple bonds are formed if two neighboring radicals in the same chain unite. An artist's rendition of the final product is depicted for polyethylene in Fig. 3.

Ion-Beam Induced Property Changes

It has been well established that mechanical, physical, and chemical property changes in polymers are determined by the magnitude of crosslinking and scission, and that crosslinking enhances mechanical stability while scission degrades mechanical strength [13]. Cross-linking generally increases hardness and slows diffusion, improves wear and scratch resistance, and decreases solubility in chemical solvents. Electrical conductivity and optical density increase due to the formation of cross-links and conjugated double and triple bonds by irradiation. The delocalized π-electrons in the conjugated bonds are loosely bound and thus more mobile than the covalently bonded electrons. Furthermore, charge carrier mobility increases by cross-links which facilitate the transport of charge carriers across the chains. Otherwise, charge carriers must hop across the chains for conduction. The loosely bound π-electrons also can be excited by the energies of visible light, and color changes occur because light is absorbed when it passes through. Energetic blue light is absorbed first and thus the color changes from pale yellow to reddish brown and eventually to a dark color with increasing irradiation dose. At very high doses, a metallic luster appears because light is scattered by abundant π-electrons as in metals by free electrons. On the other hand, scission causes bond breakage and increases solubility of polymers in solvents. This feature has been used in lithography for positive-resists in the electronic industry [14].

Electronic vs Nuclear LET

An important question is what controls the magnitude of cross-linking and scission? As pointed out already, both electronic and nuclear energy transfer can induce crosslinking as well as scission. However, experimental evidence suggests that electronic stopping causes more crosslinking while nuclear stopping causes more scission [15, 16]. In Fig. 1, the contribution from the nuclear energy loss is considerable but relatively small compared to electronic energy loss. With increasing ion energy, electronic LET increases and nuclear LET decreases. As can be seen from Fig. 4, electronic LET becomes an even more important factor for ions of 1 MeV compared to 100 keV. Polymers have a fairly large free volume, often larger than 20 %, and the displacement cascade density (crudely said, a stressed field where atomic motion becomes larger than the thermal vibration by a nuclear collision) in such a loose system is relatively small compared to that in a medium with a compact lattice structure, such as a metal. Therefore, in polymers, most nuclear collisions occur fairly independently. The probability to cause simultaneous displacement of two atoms from neighboring chains and create two radical pairs for cross-linking is small in nuclear processes. Nuclear collisions are likely to cause scission. Heavy and low energy ions with less than a few keV have large nuclear LET and are thus generally not desirable for cross-linking. An excellent example for the nuclear displacement damage effect was demonstrated by Hunn and Christensen [17]. They were able to lift free-standing, single crystal diamond layers by selectively oxidizing the damaged layer underneath the crystalline diamond surface, in that a maximum displacement damage was produced at ~2 μm depth by using 4-5 MeV C-ions. On the other hand, high energy ions influence a considerable volume around the ion projectile via the coulombic force and δ-rays produced by glancing and knock-on collisions, respectively, thereby facilitating cross-linking.

HEIB (high LET) vs e-Beam or γ-Rays (low LET)

As discussed already, the magnitude of ionization depends upon the deposited energy along the ion track or LET. The electronic (or ionization) LET for 1 MeV Ar is about 960 eV/nm for polystyrene, whereas those of e-beam and γ-rays are in the range of 0.2 - 0.36 eV/nm. Increasing the energy of e-beam or γ-rays does not increase the LET due to the limited effective charge or ionizing capacity; only the depth of penetration increases with increasing energy beyond a certain energy. When a charged particle traverses the medium, it deposits energy discretely, not continuously. Electronic excitation is restricted by quantized energy levels and a certain ionization potential must be overcome to release an electron from the orbit. Atomic displacement also requires a certain threshold energy to break the bonds and move the atom over a certain potential barrier due to surrounding atoms. Creation of an ion pair involves a removal of two or more electrons, for example, one electron from a hydrogen atom and one or more from a carbon atom. Most ionization events involve energy loss less than 100 eV, an average energy loss per event (or approximately an average energy required to produce one ion pair) being between 30 and 40 eV [18, 19]. This energy loss entity is often called a 'spur'. For 1 MeV Ar ions, about 24 (960/40) ion pairs or spurs are created per nm, whereas, for e-beam or γ-rays, only 0.009 (0.36/40) spurs are created per nm. In other words, the average distance between the spurs is 0.042 nm (40 eV/ 960 eV/nm) for 1 MeV Ar and 111 nm (40 eV/0.36 eV/nm) for e-beam or γ-rays. In the case of high LET, spurs overlap, the probability for two radical pairs to be in neighboring chains is increased, and cross-linking is facilitated. For low LET, spurs develop far apart and independently, the deposited energy tends to confine in one chain (not in neighboring

chain), and scission occurs more often when the deposited energies overlap in the chain. For this reason, e-beams are used in photolithography to dissolve the irradiated area. Finally, cross-linking is also polymer structure dependent, low LET ionizing radiation sources such as e-beam and uv can be used to achieve a limited degree of cross-linking for certain polymers.

Conclusions

The concepts of nuclear and electronic energy loss mechanisms have been reviewed, and their specific roles in polymer processing discussed. The mechanisms elucidate that electronic processes enhance cross-linking whereas nuclear processes enhance scission. Concepts of LET and 'spur' were described. Along a high LET track, spurs overlap and thus cross-linking is facilitated, whereas, for a low LET track, spurs develop independently, more often leading to scission. Since electronic LET depends upon the ion velocity and its charge state, high LET can be achieved by increasing ion energy and by employing high atomic number projetiles. Both cross-linking and scission have different application merits; some application examples were presented. Based on the fundamental principles presented, desirable material properties can be tailored for industrial applications.

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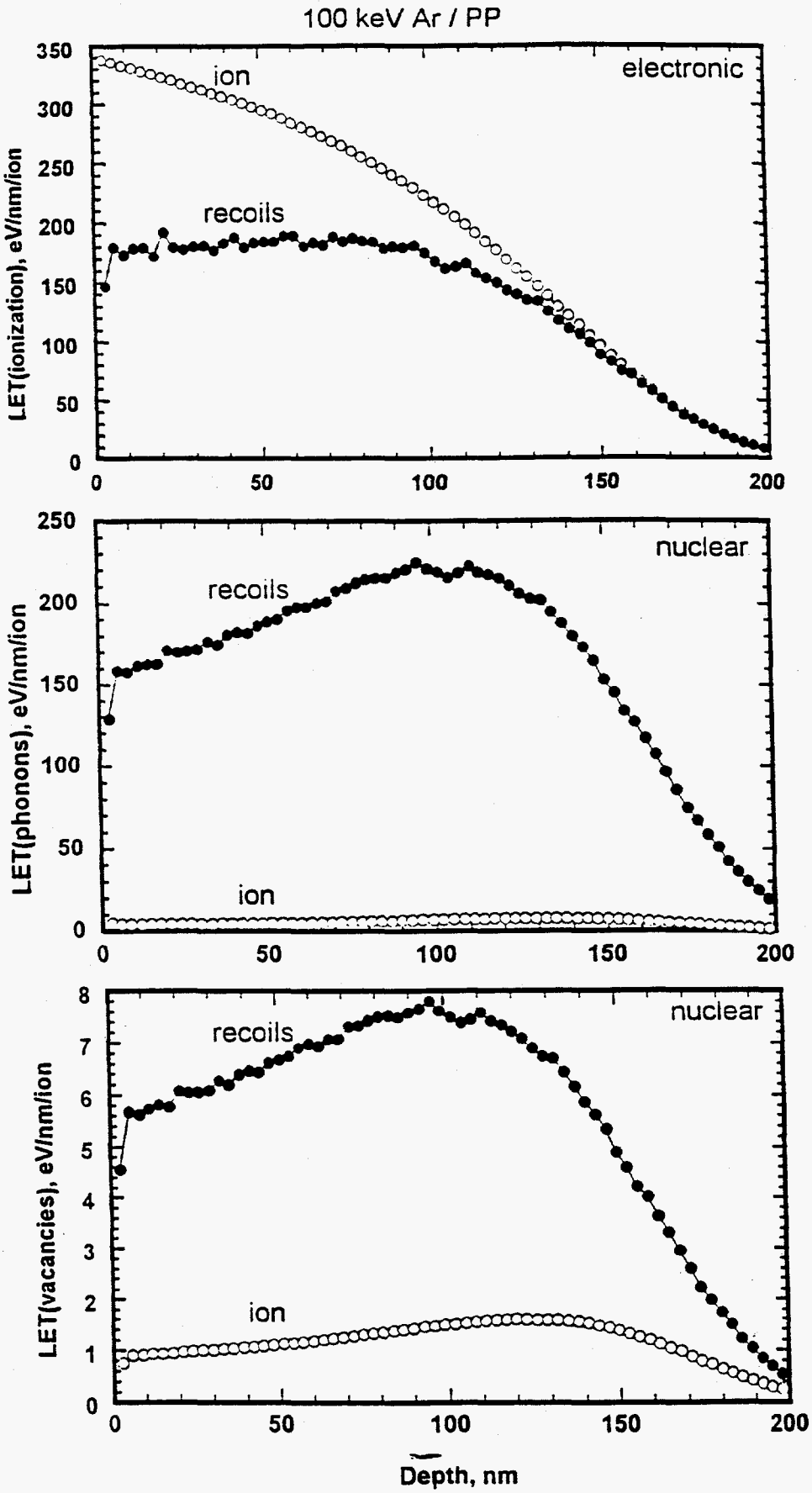
Figure Captions

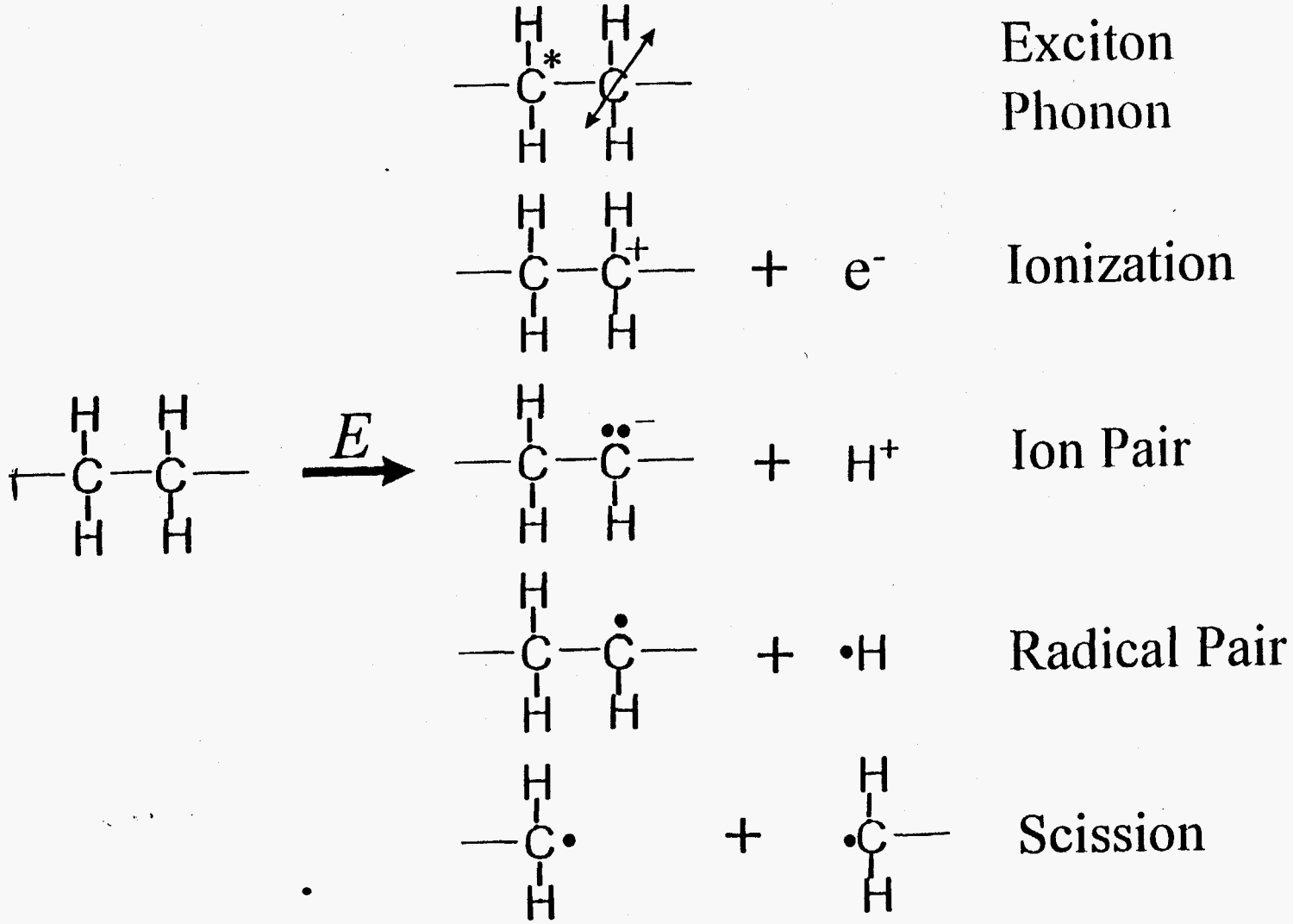
Fig. 1 SRIM calculated electronic (ionization) and nuclear (phonons and vacancy) energy losses for 100 keV Ar in polypropylene. For calculations, the values of 2 eV and 20 eV were used for the binding energy, E_b, and displacement energy, E_d, respectively.

Fig. 2 Typical consequences induced by ion irradiation in polyethylene, which include electronic excitation, phonons, ionization, ion pair formation, radical formation, and chain scission.

Fig. 3 Artist's rendition of irradiated polyethylene, showing single and double cross-links, double and triple bonds, and unpaired electrons. Chemical, physical, and mechanical properties vary with the magnitude of cross-linking, unsaturated bonds, and active chemical entities such as unpaired electrons, ionized atoms, and radicals.

Fig. 4 SRIM calculated electronic (ionization) and nuclear (phonons) energy losses for 100 keV and 1 MeV Ar in polypropylene


100 keV Ar / PP
ion
electronic
recoils
LET(ionization), eV/nm/ion
nuclear
recoils
ion
LET(phonons), eV/nm/ion
nuclear
recoils
ion
LET(vacancies), eV/nm/ion
Depth, nm


Exciton
Phonon
Ionization
+ e⁻
E
Ion Pair
+ H⁺
Radical Pair
+ •H
Scission
+

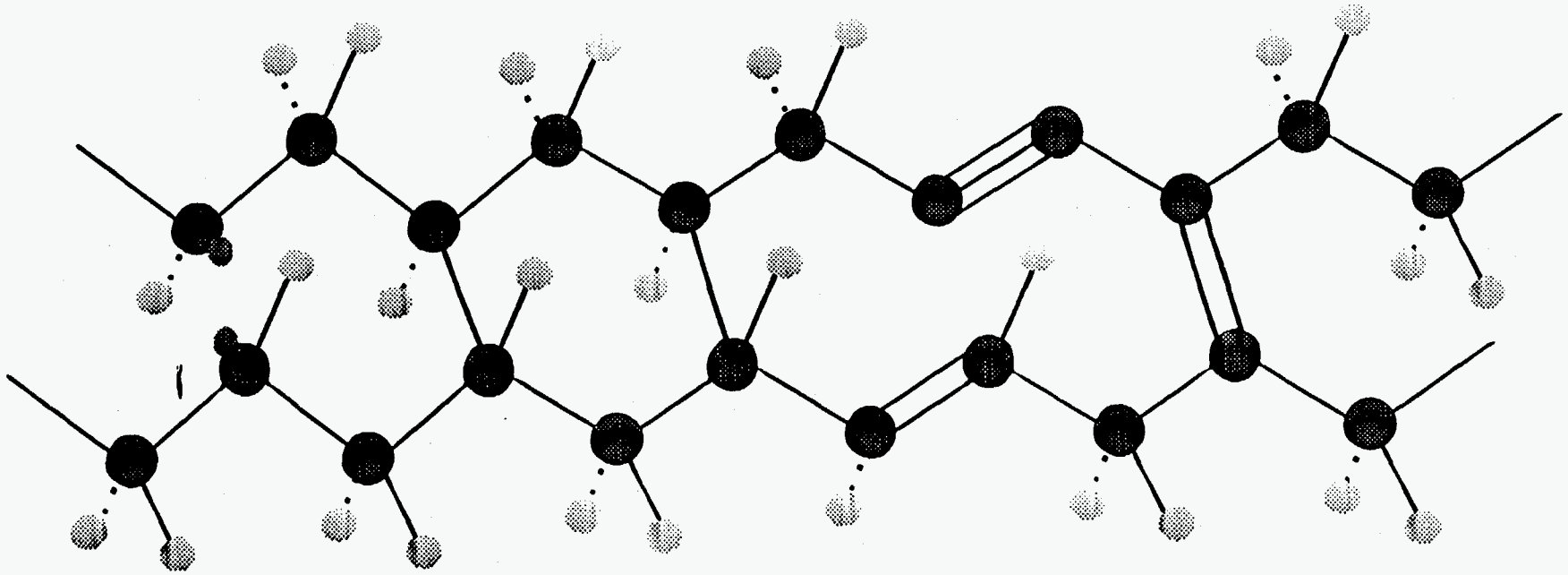
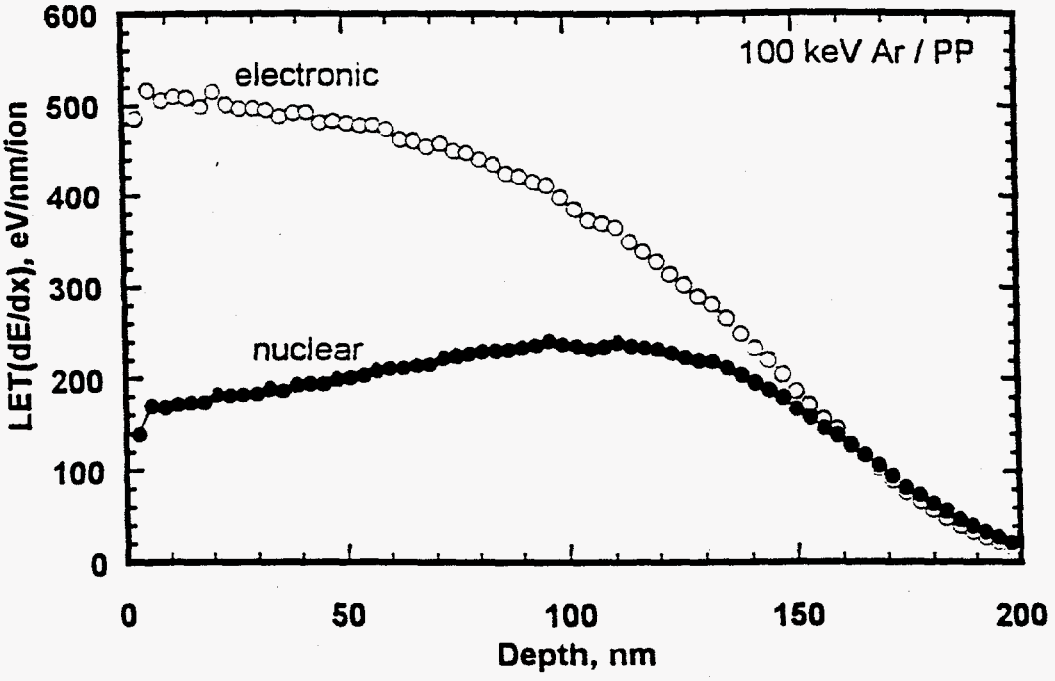


Fig. 3


100 keV Ar / PP
electronic
nuclear
LET(dE/dx), eV/nm/ion
Depth, nm
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200
300
400
500
600
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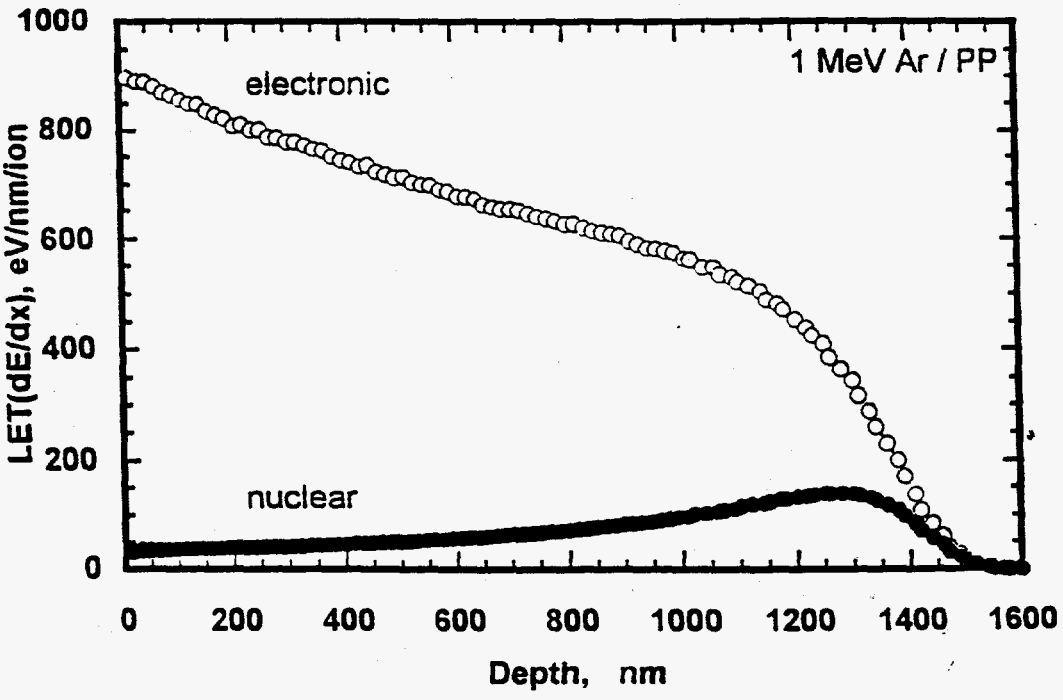
50
100
150
200


1 MeV Ar / PP
electronic
nuclear
LET(dE/dx), eV/nm/ion
Depth, nm
0
200
400
600
800
1000
0
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800
1000
1200
1400
1600