Monte Carlo study of molecular weight distribution changes induced by degradation of ion beam irradiated polymers

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ABSTRACT

In this work we study a polymeric material that degrades upon irradiation due to the energy inhomogeneously deposited by heavy ion beams. Ion beam irradiation of polymers generates rather different effects than those induced by "classical" low ionizing particles such as electrons or gamma rays. This is due to the high electronic stopping power and the inhomogeneous distribution of deposited energy. This energy is transferred to the material within a small volume along the ion path forming the so called "nuclear track" or "latent track". The track size primarily depends on the ion velocity, and it is determined by the secondary electrons (delta rays) generated along the ion trajectory. By means of Monte Carlo simulations we first obtained equilibrated polymer configurations using a coarse-grained model, and then investigated the spatially inhomogeneous chain scission process due to the passage of the ions. The number average molecular weight, weight average molecular weight and the polydispersity were calculated as a function of track radius, scission probability within the ion track and irradiation fluence. Finally we compared our results with a numerical implementation of a model for random homogeneous degradation.

1. Introduction

Polymers modified by different types of ionizing radiation have been widely used in the last decades in diverse fields such as biotechnology, coatings, recycling, microelectronics and medicine. Also, a deeper understanding of the radiation-polymer interaction is of great interest when choosing or developing materials that will be used, for example, in space applications, i.e. satellites, or fusion reactors [1].

The effects induced in polymers by swift heavy ions (energies higher than 1 MeV per nucleon) can be very different from those induced by conventional ionizing radiation as electrons, neutrons or gamma rays [2]. The ions penetrate a limited depth in the sample, affecting only the surface without changing the properties of the underlying bulk material. Also, the linear energy transfer (LET) of an ion, i.e. the average energy deposited in the material by a particle along its path, is in general larger than that of gamma rays or electrons, and the dose distribution is very inhomogeneous [3,4]. When an ion beam penetrates a polymer, a large amount of energy is deposited in the surroundings of the ions trajectories. Each ion produces a damaged cylindrical zone, with a radius of a few nanometres, called nuclear track or latent track. The radius of the latent track depends on the target polymer and on the ion beam type and energy.

In this work we studied, by means of Monte Carlo (MC) simulations, the molecular weight distribution *MWD* changes of irradiated polymers that undergo chain scissions inside the ion tracks (spatially nonhomogeneous degradation), as a function of irradiation fluence (number of ions per cm²). The results were compared with the case of random homogeneous degradation, typical of gamma rays or electrons, identifying differences and similarities in the final polymeric samples subjected to both types of radiation.

2. Monte Carlo simulation

Two different MC simulations were used to investigate the evolution of a polymer sample *MWD* when chain scission occurs in localized zones that represent ion tracks. As a first step, we obtained thermodynamically equilibrated chain configurations and then the scission process was simulated on these samples.

2.1. Polymer configurations

Polymers were described with a widely used coarse-grained model that reproduces fairly the general properties of polymer melts in an ample range of thermodynamic conditions [5].

A certain number of chemical units of a given polymer is replaced for a single bead in the simulations. Chain connectivity and excluded volume interactions are accounted for in such a way that the polymers do not form crystalline structures easily, but rather organize in amorphous structures [6]. In addition, the potential parameters are set in order to make very unlikely the probability of bond-crossings. This constitutes a well suited "generic" coarse-grained model for polymer chains, whose matching to real polymers is obtained through comparisons of length, time and energy scales.

Polymer chains were modeled as N particles that interact through two different contributions to the potential energy:

1. A truncated and shifted Lennard Jones potential, which represents the excluded volume among all the monomeric units:

$$\widetilde{V}_{LJ}(r) = \begin{cases} V_{LJ}(r) - V_{LJ}(r_c) & r \leqslant r_c \\ 0 & r > r_c \end{cases} \tag{1}$$

   where $r_c = 2 \cdot 2^{1/6}$ and $V_{LJ} = 4\epsilon : [(\sigma/r)^{12} - (\sigma/r)^6]$

2. A finitely extensible nonlinear elastic (FENE) potential, for the monomers along a chain, to account for chain connectivity:

$$V_{\text{FENE}} = -33.75\epsilon \ln \left[1 - \left(\frac{r}{1.5\sigma} \right)^2 \right] \tag{2}$$

The potential parameters are chosen such that the most probable distance between bonded neighbours is 0.96σ, which is smaller than the most probable distance 1.12σ between non-bonded monomers. The parameters ϵ and σ set the scale for the system energy and length, respectively.

We obtained a set of thermodynamically equilibrated polymer samples. Each configuration consists on a box of size $L \times L \times H$, where $L = 25\sigma$ and $H = 30\sigma$, with 231 molecules of degree of polymerization 64, number density $\delta = 0.79\sigma^{-3}$, end-to-end distance $R_e = 9.6\sigma$ and radius of gyration $R_g = 3.9\sigma$. The samples were equilibrated for 3×10^6 MC steps approximately, at a temperature of $T = 1.2\epsilon/k_B$. During this process the monomers evolve with local and reptation MC moves [7].
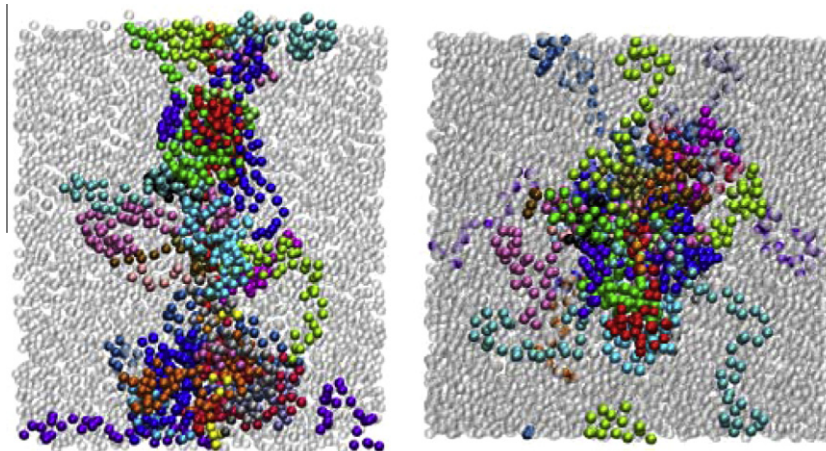
2.2. Chain scission

The equilibrated polymer configurations were used in a second simulation setup to study the effects of inhomogeneous chain scission.

Firstly, we simulated a random homogeneous degradation, characteristic of gamma rays, and compared the results to a theoretical calculation developed by Saito [8], for different values of scissions per monomeric unit τ, i.e. each bond was broken with a probability equal to τ regardless of its position.

Then, we performed the scission simulation for the track case, i.e. inhomogeneous degradation typical of ions. We studied track sizes of radii $R/\sigma = 1$, 2 and 4, with fixed scission probabilities τ_{track} inside the tracks. The investigated τ_{track} values ranged from 0.01 to 0.1.

For each pair of R and τ_{track}, the configurations suffered chain scissions inside the tracks. The irradiation was taken perpendicular to the sample surface and the ions passed through the material without changing their directions. Each ion, randomly distributed in the sample, generates a cylindrical zone whose axis is the ion trajectory. An example of this track produced by the ions as obtained from the simulations, is depicted in Fig. 1, where darker beads belong to chains that were broken due to ion energy and lighter beads belong to chains of original length. The irradiation fluence (number of ions per cm^2) is $\phi = n/A_0 = n/625\sigma^2$, where n is the number of ions that hit the sample and $A_0 = L \times L = 625\sigma^2$ is the sample area. The fraction of sample area covered by the tracks is given by

$$\frac{A}{A_0} = \left[1 - \exp \left(-\pi R^2 \frac{n}{A_0} \right) \right] \tag{3}$$

The studied fluences were chosen up to a value such that the maximum A/A_0 was 0.945: for $R/\sigma = 1$ n varied from 4 to 576, for $R/\sigma = 2$ from 2 to 144 and for $R/\sigma = 4$ from 1 to 36.

The fraction of polymer molecules of length p, $n(p)$, and the weight fraction of polymer molecules of length p, $w(p)$, were obtained as a function of fluence. From them, the number average molecular weight M_n, the weight average molecular weight M_w and the polydispersity $PD \equiv M_w/M_n$ were calculated.

3. Results and discussion

In the case of random homogeneous chain scission, the MWD was obtained for different values of τ, the number of scissions per monomeric unit. τ is related to the irradiation dose by the following expression:

Fig. 1. Side (left) and top (right) views of a simulated track. Dark spheres belong to chains that have been broken inside the ion track.

$$\tau = \frac{M_n^0}{\mu} \frac{G(S)}{0.965 \times 10^6} D \tag{4}$$

where M_n^0 is the number average molecular weight and μ is the number average degree of polymerization before the irradiation, $G(S)$ is the number of scissions per 100 eV of irradiation and D is the dose in Mrad.

To quantify the amount of radiation received by a sample in the case of ion beams, the fluence is more appropriate than the dose. In the case of nonhomogeneous scission, we obtained the fraction of broken bonds for each fluence value. Therefore, we expressed all the magnitudes as a function of τ and compared the different MWD for the same fraction of broken bonds in the sample. The bonds were broken either randomly (homogeneous degradation case) or in specific localized zones that represent the ion tracks.

3.1. Random degradation

In order to compare the MWD that results from the track simulation with the case of random degradation, typical of gamma or electron radiation, we also performed a simulation for the latter one. The inset of Fig. 2 shows the polydispersity calculated with the simulation together with the value predicted by Saito [8] for an initial monodisperse configuration

$$PD(\tau) = 2PD(0) : \frac{\exp(-\mu\tau) - 1 + \mu\tau}{(\mu\tau)^2}(1 + \mu\tau) \tag{5}$$

In our case, the values $\mu = 64$ and $PD(0) = 1$ were used. Saito [8] showed that for any initial distribution the final MWD becomes Poisson-like. In the simulations one has a finite number of chains, the starting sample is monodisperse (delta-distributed in chain of length 64) and the final state, after breaking all the bonds, will be another monodisperse configuration (all the chains will be of length 1). Therefore, we expect that the polydispersity grows from a value of 1, reaches a maximum and then decreases towards 1 again. Fig. 2 inset shows how the simulation data departs form Saito's expression as τ increases. This is also true for the other magnitudes calculated in this work, and to avoid this effect, that arises from the fact that we work with a finite number of polymeric molecules, we only compared the results obtained from simulations.

3.2. Inhomogeneous degradation

Fig. 2 shows the polydispersity as a function of τ for chain scissions occurring inside the tracks, for radii $R/\sigma = 1, 2$ and 4, and for
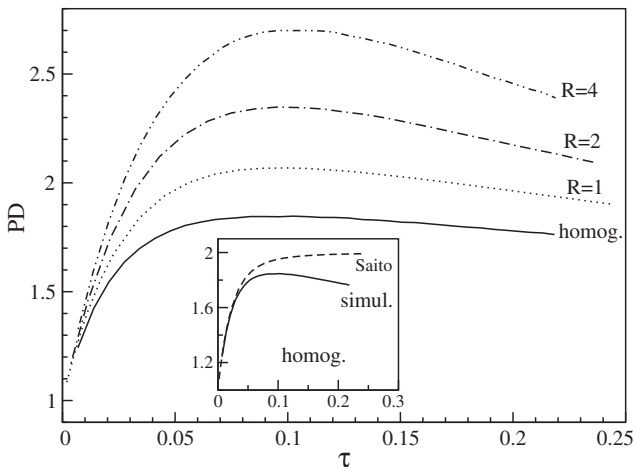
$\tau_{\text{track}} = 0.1$. All the samples show a polydispersity greater than the random case. This is also true for the other τ_{track} values studied.

In the case of the number average molecular weight M_n, we didn't find significant differences between homogeneous and non-homogeneous simulations. There is a small departure from the theoretical value for the greatest values of τ studied, again due to the fact that we have a finite number of molecules.

Fig. 3 shows the weight average molecular weight M_w as a function of τ for $\tau_{\text{track}} = 0.1$ and $R/\sigma = 1, 2$ and 4. We found that for all the cases studied in this work M_w is greater than the value obtained from the random simulation.

In order to understand why M_w and PD are greater for the nonhomogeneous scission case, let's examine the evolution of $n(p)$, the fraction of polymer molecules of length p, as a function of τ (or the corresponding irradiation fluence). Fig. 4 shows $n(p)$ for three different τ values. In the nonhomogeneous degradation case there is a larger number of short chains than for the random scission simulation. And also the peak at $p = 64$, which corresponds to the molecules that were not broken, is bigger for the track case. This is because in the track case, for the same fraction of broken bonds, there are at the same time unaffected chains and, inside the tracks, shorter segments from heavily fragmented chains.
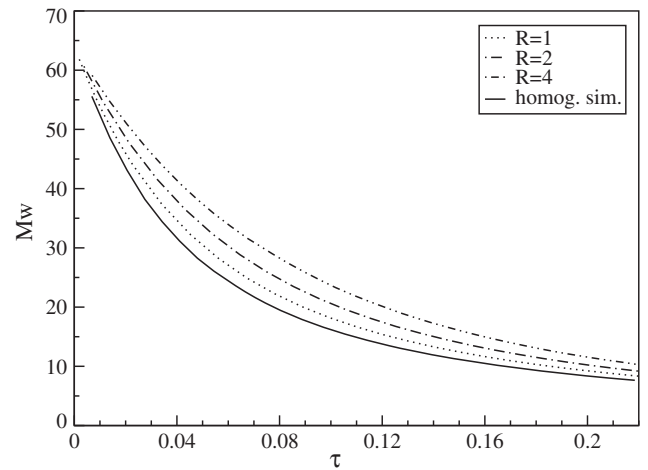

Fig. 3. Weight average molecular weight M_w vs. τ for track radii $R/\sigma = 1, 2$ and 4 and $\tau_{\text{track}} = 0.1$ together with homogeneous simulation result.

Fig. 2. Polydispersity vs. τ for track radii $R/\sigma = 1, 2$ and 4 and $\tau_{\text{track}} = 0.1$ together with the homogeneous simulation result. The inset shows a comparison between simulation and theory for the random degradation case.
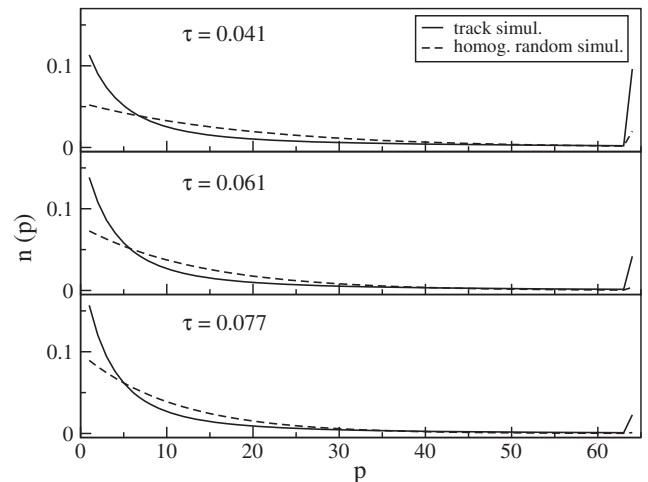

Fig. 4. Fraction of polymer molecules of length p, $n(p)$, for $R/\sigma = 4$ and $\tau_{\text{track}} = 0.1$, obtained from track and homogeneous random scission simulations, for three different τ values.
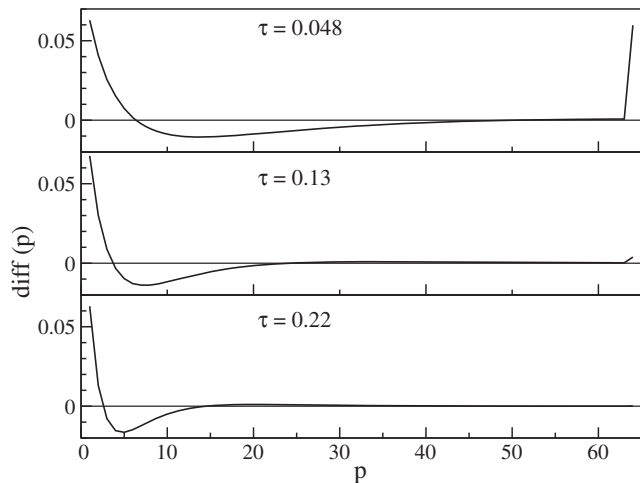
Fig. 5. Difference between $n(p)$ for nonhomogeneous and homogeneous scission simulations, for $R/\sigma = 4$ and $\tau_{track} = 0.1$, for three different τ values.
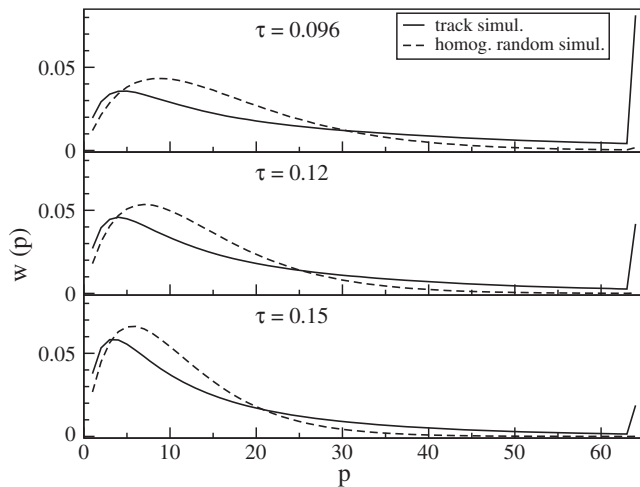

Fig. 6. Weight fraction of polymer molecules of length p, $w(p)$, for $R/\sigma = 4$ and $\tau_{track} = 0.1$, obtained from track and homogeneous random scission simulations, for three different τ values.

Fig. 5 shows the difference between $n(p)$ obtained from the track and homogeneous simulations

$$diff(p) = n(p)_{track} - n(p)_{homog} \qquad (6)$$

for three different τ values.

Finally, Fig. 6 shows $w(p)$, the weight fraction of polymer molecules of length p, also for three different values of τ.

All the figures presented here are for $R/\sigma = 4$ and $\tau_{track} = 0.01$, because the effects are more evident for these parameter values. For smaller R values, and also when τ_{track} decreases, the differences between the homogeneous and nonhomogeneous scissions are smaller.

4. Conclusions

We investigated the effects of spatially inhomogeneous chain scission on an equilibrated polymer sample by means of Monte Carlo simulations. The simulation setups serve as a model for the degradation of polymeric materials irradiated with swift heavy ions.

We obtained molecular weight distributions MWD as a function of fluence and compared them with the case of random homogeneous scission, characteristic of gamma or electron radiation. We found that the number average molecular weight M_n was not affected by the spatial distribution of the scissions. On the contrary, the weight average molecular weight M_w and the polydispersity PD are found to be higher for the inhomogeneous case for all the studied parameters. We observed that there was a higher fraction of short and long chains in the MWD when the scissions occurred inside the tracks. The effects are more evident when the radius of the tracks is increased, for a fixed scission probability inside the track τ_{track}, and also when τ_{track} is increased for a fixed radius. This suggests that ion radiation could be useful to tailor samples of polymer melts with coexisting very long and very short chains, which are likely to enhance phase separation in the presence of walls or regions of the substrate with higher rigidity.

This technique allowed us to obtain not only average values, but also the MWD, starting with a configuration of polymeric chains that is thermodynamically meaningful. Other initial distributions (Poisson-like, Gaussian, etc.) and a probability of scission that depends on the position inside the tracks could be tested with this method, as well. Finally, a comparison with experimental data of MWD could help to understand the mechanisms of chain scission by means of swift heavy ions.

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