# Segmental Shadowing Effect on Ultraviolet Depolymerization and Resulting Molecular Weight Distribution

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*Abstract* -Ultraviolet degradation of polymers in dilute solutions is simulated. The resulting molecular weight distribution and polydispersity evolutions are calculated for good, theta and poor solvents. Simulations show that, when the effect of shadowing among chain segments is taken into account, chain scission is not completely random. The effect is subtle, but it is observable in poor and theta solvents, especially in the 1/Mn and the d(1/Mn)/dt versus time graphics. Shadowing magnifies the increase in the polydispersity, when a polymer sample with a narrow molecular weight distribution is irradiated.

*Keywords*: Ultraviolet Irradiation; Molecular Weight Distribution; Simulation; Polymer Degradation; Kinetics

## 1. Introduction

Polymer based products can undergo partial or total degradation under the influence of various factors such as heat, light or chemicals. Polymer degradation is sometimes achieved intentionally to produce macro-radicals, or to control the molecular weight. It also occurs inadvertently as a side reaction (Karlsson, Albertsson 2004, Tyler, Chen 2004, Kumar, Gupta 2003). Various factors affecting the degradation and weathering of polymers have been discussed in the review article by Pimentel-Real (2011).

Thermal, ultrasonic and ultraviolet (UV) effects are commonly used for polymer degradation. In thermal degradation, bond scission mostly occurs at chain ends, and the monomers are cut off the chain one by one. Ultrasonic scission occurs in the middle of the chain (Pielichowski, Njuguna 2005). UV degradation is caused by photon absorption which can break any chemical bond in a polymer. Broken chain segments may recombine or crosslink. These processes change physical properties of the material (Singh et al. 1994). Scission process can be enhanced by use of oxidizing agents Shukla et al. (2009). Combined ultrasonic, thermal and photo degradation was investigated by Shukla and Madras (2012).
Polymer chain size distribution can be calculated using statistical mechanics (Staggs 2004). Wang et al (1995) developed a mathematical model for continuous kinetics of specific and random degradation processes. Kinetics of random scission, midpoint scission, chain-end scission and combination of random and chain-end scission were studied by Madras, McCoy and coworkers. (Madras et al. 1995, 1996a, b, 1997a, b, Madras and McCoy 1997, 1998, McCoy 1996, McCoy and Madras 1997, Wang et al. 1995). Effects of degradation are also investigated by methods which give the average molecular weight (Akyuz et al. 2008, 2009). Schauer et al. (2010) investigated and compared the photo and electron beam degradations in polysilanes. The basic goal of these experimental, theoretical and computational studies is to understand the time evolution of $M_n$, $M_w$ and MWD during degradation.

It is generally assumed that the probability of a photon impacting a given bond is independent of the position of the bond and the length of that chain. This assumption is valid for UV treatment in bulk or concentrated solutions, where scission probability is related with the distance of a particular bond from the exposed surface of the polymer (Nagai et al. 2005). In dilute solutions, where the concentration $c$ is less than $c^*$, the overlap concentration on the other hand, individual bonds are not statistically equivalent.

Segments of the chain are "shadowed" by other segments which are closer to the light source and in the light path. When a photon breaks a bond, it is absorbed. This protects the bonds, which lie on the path that photon would have followed. Here, this effect is called "the shadow effect". In concentrated solutions shadowing is dominated by other chains in the solution. For this reason, any statistical difference is expected to be between chains which are closer to the light source or deeper in the solution rather than segments within a chain. However in dilute solutions shadowing is dominated by segments of the same chain. The segments closer to the center are more likely to have a shadowing segment than the ones near the edges.

In this work, UV degradation kinetics of polymers in dilute solutions is simulated. The study assumes that there are abundant radical scavengers in the system so that broken chains quickly become inert and cannot recombine. The simulations are simplified by ignoring the thermodynamic effects on scission. The evolution of MWD is modelled with shadow effect for polymers in theta, good and poor solvents and also with no shadow effect. A narrow Gaussian initial MWD is used in the simulations. Molecular weight averages ($M_n$, $M_w$, $M_z$) are calculated as functions of time.

## 2. Theoretical

### 2. 1. Shadowing Probability

The shadowing probability of a bond is proportional to the solid angle subtended by bond $j$ at bond $i$, that is, $P_{shad}(i, j) \alpha (1/r_{ij})^2$ where $r_{ij}$ is the distance between the shadowing unit "$j$" and the unit being shadowed "$i$" in Figure 1.
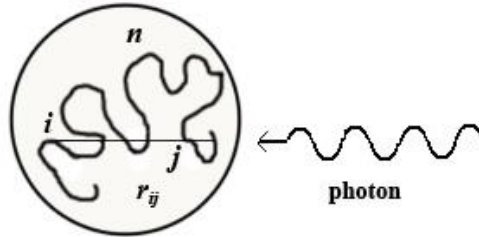


Fig. 1. Schematic depiction of shadow effect: Monomer j shadows monomer i and prevents a scission at that point.

The distance from $i^{th}$ to $j^{th}$ unit $r_{ij}$, is proportional to $\sqrt{|i-j|}$ in theta solvents, to approximately $|i-j|^{3/5}$ in good solvents and to $|i-j|^{1/3}$ in poor solvents (Flory 1969). In theta solvents the shadowing probability is proportional to,

$$P_{shad}(i,j) \alpha \left( \sqrt{|i-j|} \right)^{-2} = 1/|i-j|$$ (1)

A random coil with length n can be treated as two random coils with lengths $i$ and $n-i$ beginning at the $i^{th}$ bond of the chain. The probability that an incident photon is absorbed by another bond within the chain before it reaches the $i^{th}$ bond, is approximately proportional to the sum of this probability for all bonds from $i+1$ to n plus the sum from 1 to $i-1$.

$$P_{tot\_shad}(i,n) \alpha \left( \sum_{j=1}^{i-1} 1/|i-j| + \sum_{j=i+1}^{n} 1/|i-j| \right)$$ (2)

In the long chain limit we can approximate this sum with the integral,

$$P_{tot\_shad}(i,n)\alpha\left(\int_{j=1}^{i}\frac{dj}{j}+\int_{j=1}^{n-i}\frac{dj}{j}\right)=\ln(i)+\ln(n-i) \tag{3}$$

$$P_{tot\_shad}(i,n)\propto\ln\left(i(n-i)\right) \tag{4}$$

Here, $P_{tot\_shad}(i,n)$ is the probability that a bond, "$i$" units from an end of a chain of length "$n$" is shadowed. Note that the shadowing probability depends on both the chain length $n$ and the position of the bond within the chain.

In the Flory approximation for good solvents, the shadowing probability is proportional to,

$$P_{tot\_shad}(i,n)\propto\left(2-i^{-\frac{1}{5}}-(n-i)^{-\frac{1}{5}}\right) \tag{5}$$

For poor solvents, the shadowing probability is proportional to

$$P_{tot\_shad}(i,n)\propto-\left(2-i^{\frac{1}{3}}-(n-i)^{\frac{1}{3}}\right) \tag{6}$$

It is seen that when the shadow effect is taken into consideration, scission probability depends on solvent quality, chain length and whether the segment lies around the middle or near an end of the chain. Due to this effect shorter chains are more easily broken than longer chains, and scissions are more likely to occur near the ends than in the central parts of long chains. Scission is hindered if the chain is in a compact conformation in theta and poor solvents. In good solvents the shadow effect is not significant.

## 2. 2. Evolution of the Molecular Weight Distribution

Scission of a chain with length $n$, at the $i$'th bond creates two chains; one with a length of $i$ and the other $n$-$i$. Because it is assumed that the use of radical scavengers prevents any recombinations among chain fragments, the differential equations are linear and can be written in matrix form.

$$\frac{d\mathbf{N}}{dt}=\mathbf{M}\cdot\mathbf{N} \tag{7}$$

Here $\mathbf{M}$ is the $\left(n_{max}\times n_{max}\right)$ matrix representing the formation and destruction rates of polymers of all lengths during the scission process. The number concentration of chains with length 'n', is represented as the vector $\mathbf{N}$ of length $n_{max}$, where $n_{max}$ is the number of segments in the longest chain considered. The initial chain size distribution is denoted by the vector $\mathbf{N_0}$. In the simulations $\mathbf{N_0}$ is taken either as a Gaussian,

$$N_{0n}=\frac{e^{-(n-\mu)^2/2\sigma^2}}{\sqrt{2\pi}\sigma} \tag{8}$$

Where $\mu$ and $\sigma^2$ are the mean and variance of the distribution or as a Poisson distribution,

$$N_{0n} = \frac{n^\mu e^{-n}}{\mu!} \qquad (9)$$

The upper triangular ($i < n$) part of $\mathbf{M}$ gives the formation of chain fragments. The matrix elements $M_{i,n-i} = 2P_{i,n-i}$, where $P_{i,n-i}$ is the probability that the bond $i$ is broken per unit time. There is a factor 2 in the equation, because, for $i \neq n/2$ two breaking points lead to same final chains, and for $i = n/2$ two chains of length $i$ are formed by a single scission. The diagonal elements which give the destruction of chains are equal to the half of the sum of the upper elements in the same column,

$$\mathbf{M}_{nn} = -\frac{1}{2}\sum_{i=1}^{n-1}\left(\mathbf{M}_{in}\right). \qquad (10)$$

The lower triangular part of $\mathbf{M}$ is zero because recombinations are not allowed.

No differential equation is needed for the monomers (chains of unit length) because they cannot be broken and their number can be calculated using the conservation laws. Thus the ($n_{max}$-1) x ($n_{max}$-1), scission matrix is,

$$\mathbf{M} = \begin{pmatrix} -P_{1,1} & 2P_{1,2} & 2P_{2,2} & 2P_{2,3} & \cdots & 2P_{2,n\max-2} \\ 0 & -2P_{1,2} & 2P_{1,3} & 2P_{2,3} & \cdots & \vdots \\ 0 & 0 & -(P_{2,2}+2P_{1,3}) & 2P_{1,4} & \cdots & \vdots \\ 0 & 0 & 0 & -(2P_{2,3}+2P_{1,4}) & \cdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & 0 & -\sum_{i=1}^{n\max-1} P_{i,n\max-i} \end{pmatrix} \qquad (11)$$

The equation set can be solved numerically by finite differencing but since the set is linear, it is more efficient to solve it semi-analytically. The solution of this equation with the initial MWD given by $\mathbf{N_0}$ is,

$$\mathbf{N}(t) = e^{\mathbf{M}t} \cdot \mathbf{N_0} \qquad (12)$$

In this work, the matrix exponent is calculated using the MATLAB intrinsic function expm().

## 3. Results and Discussion

The narrow initial MWD studied here is a Gaussian distribution with the mean, $\mu$=450 and the half-width, $\sigma$=30. Maximum chain length in the calculation is 600, 5$\sigma$ more than the mean. The chains are assumed to be in random chain conformation in theta solvent. Short range interactions are neglected. Each segment represents not a monomeric repeat unit but a Kuhn length.

Figure 2a shows the MWD evolution during scission without shadow effect and Figure 2b shows the evolution with shadow effect in theta condition. The horizontal axis is the degree of polymerization and the vertical axis is the log of the concentration of chains of the corresponding length. The initial Gaussian distribution, seen as a parabola in the semi logarithmic plot, evolved towards an exponential distribution which appears as a line with negative slope. This evolution is rapid and uniform without shadow effect (Figure 2a), but when the effect is taken into account, the longer chains tend to live longer and distort the distribution (Figure 2b).

Figures 3a and b show the evolution of the number concentration of chains without shadow effect and with shadow effect in theta solvent respectively. Long chains with lengths 480, 520, 560 and 600 and shorter ones with lengths 200, 240, 280, 320 are depicted. Chains of 480 to 520 units are initially the most

abundant however as they are broken their numbers diminish while the number concentration of shorter chains of 200-300 units increase. The concentrations of the shorter chains start to decrease after the longer chains are depleted. The shadow effect increases the lifetimes of longer chains, as seen in Figure 3b.
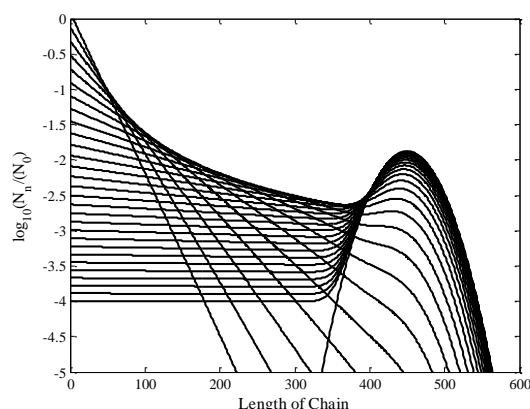


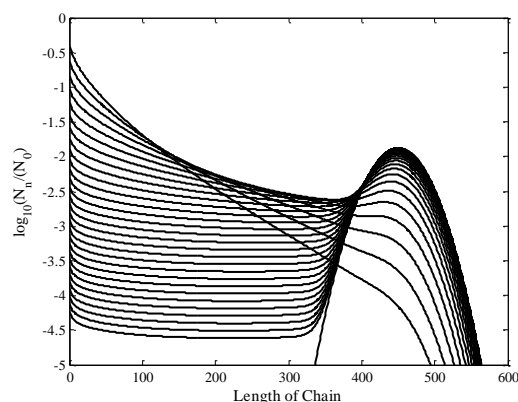Fig. 2a. Evolution of MWD during scission without shadow effect.



Fig. 2b. Evolution of MWD during scission with shadow effect in theta condition.

In theta condition evolutions of the number, weight, and z- average molecular weights, $M_n$, $M_w$, $M_z$ without shadow effect (in Figure 4a) are closer to each other than their counterparts with shadow effect shown in Figure 4b. This effect causes long chains to survive longer. The plot of the evolution of the polydispersity index (HI) with shadow effect in poor, theta and good solvents and with no shadow effect is shown in Figure 5. As seen in the figure, the shadow effect increases the polydispersity in poor and theta solvents.

The total polymeric mass in the reactor is constant, therefore inverse of the number average molecular weight $M_n$ is proportional to the number concentration of polymer molecules and the scission rate is proportional to the rate of increase of $1/M_n$.

If there is no shadowing among molecular segments, the scission rate is constant in the long chain approximation. (For finite chains the difference between the number of monomer units and the number of backbone bonds which is one less, causes a small deviation). Shadowing reduces the scission rate early in the irradiation. As the chain length is reduced, the shadow effect gradually loses its significance. For this reason, the existence of this effect can be detected as a gradual increase of scission rate during the process. Plots of $1/M_n$ versus time and $d(1/M_n)/dt$ versus time are expected to show the deviation from linearity. Figure 6a shows the evolution of $1/M_n$ with time in all solvents. In poor and theta solvents slope increases whereas in good solvents and without shadow effect there is no increase in the slope. An increase in UV scission rate was observed by Aarthi et al. (2007) but the data is not conclusive.
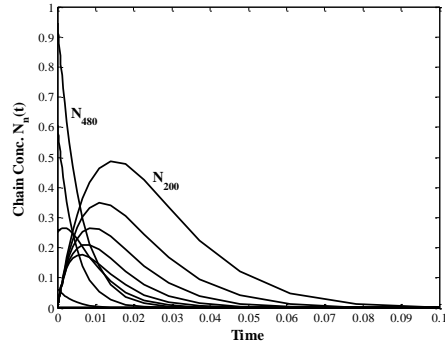
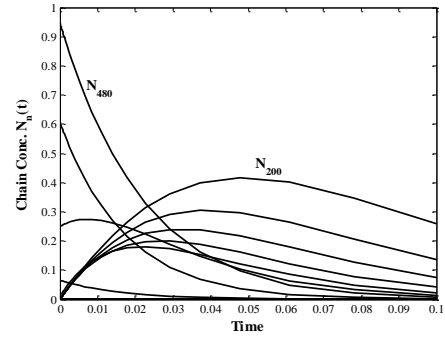Fig. 3a. Evolution of chain concentrations during scission without shadow effect



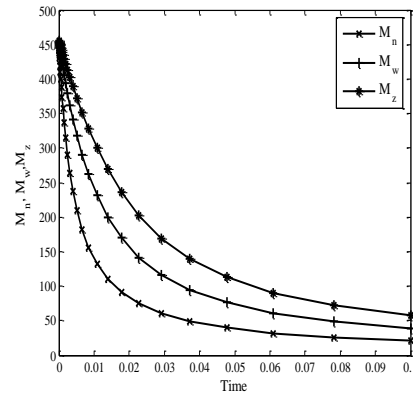Fig. 3b. Evolution of chain concentrations during scission with shadow effect in theta condition.



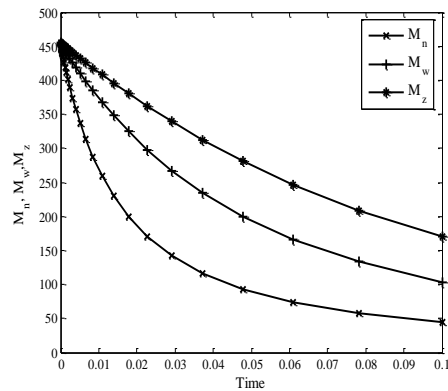Fig. 4a. Evolution of molecular weights scission without shadow effect.



Fig. 4b. Evolution of molecular weights during during scission with shadow effect in theta condition
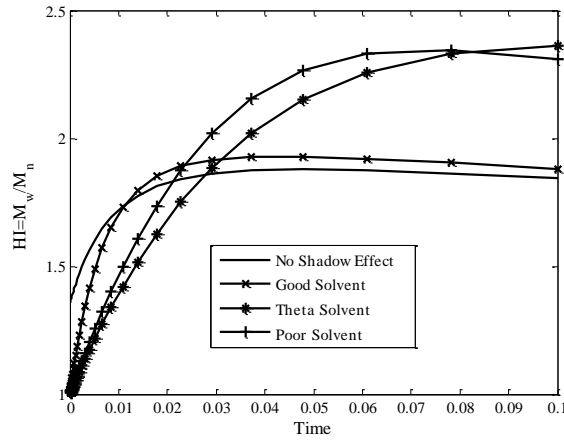
Fig. 5.  Evolution of the polydispersity index during scission for Gaussian initial MWD.

In figure 6b the derivative of the inverse of the number average molecular weight, $(d(1/M_n)/dt)$ shows the same trend seen in Figure 6a more clearly. The slight deceleration seen in the increase of $1/M_n$, in the trace for no shadow effect, is due to finite sizes of polymer molecules.

## 4. Conclusion

These simulations indicate that self-shadowing has a subtle effect on the evolution of the MWD of macro molecules undergoing UV depolymerization in dilute solutions. This effect, increases the polydispersity of the polymer because the longer chains are more difficult to break than shorter ones. It tends to disappear as the long chains are depleted. For this reason, evolutions of $1/M_n$ and HI are good places to look this effect.
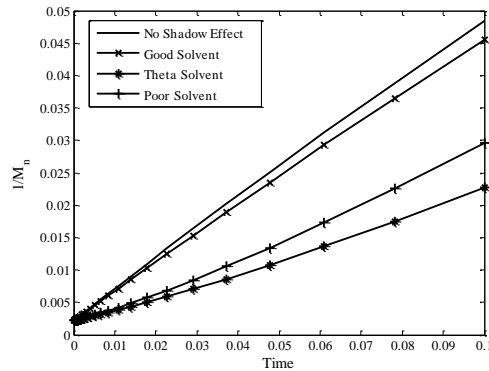


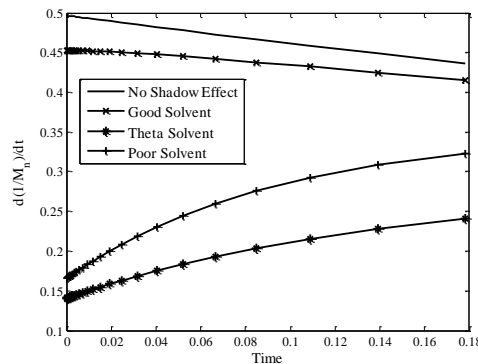Fig. 6a. The evolution of 1/Mn during scission for Gaussian initial MWD.



Fig. 6b. The evolution of d(1/Mn)/dt during scission for Gaussian initial MWD.

Shadow effect is expected to be experimentally observable for a high molecular weight sample in poor or theta solvents, especially if the initial MWD is narrow.

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