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A NEW GENERATION OF FIRE RESISTANT POLYMERS: Part I
Computer-Aided Molecular Design

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ABSTRACT

Molecular dynamics modeling and experimental measurements are used to identify factors which reduce flammability by promoting the formation of heat resistant chars during the thermal degradation of polymers. Computer movies of the calculated trajectories reveal that cross-linked model polymers tend to undergo further cross-linking when burned. The presence of strong potential energy interactions with a surface or filler further facilitates the formation of high molecular weight, thermally stable chars.

INTRODUCTION

Flammability is a major concern when polymeric materials are used in buildings, aircraft, ships and clothing. A growing public awareness of this problem has prompted regulatory agencies to adopt more stringent performance standards for polymer flammability. The trend toward increasing regulation is international in scope and directly affects the ability of manufacturers to sell their products in the global marketplace. Thus, for example, the FAA has issued new requirements for aircraft materials and corrosivity tests for fire products have been implemented in Europe. The unification of material test standards by the EC will further change flammability performance criteria, with likely echoes in the U.S and Japan. As a result, many polymers will need to be modified or replaced. It is unrealistic to assume that these serious concerns can be successfully addressed by a band-aid approach applied to the final product. This realization has provided an impetus for the design of a new generation of fire resistant polymers.

Halogenated compounds are among the most widely used fire retardants for polymeric materials. Their mode of action is thought to involve the formation of gaseous intermediates which scavenge flame propagating free radicals (e.g., OH and H) thereby inhibiting chain branching reactions. The result of this process is incomplete combustion and a concomitant reduction in the rate of heat release. An increase in the products of incomplete combustion (PICs), which can be toxic and/or corrosive, is a necessary consequence. There are no known examples of halogenated flame retardants which are effective in reducing heat release rates without increasing the production of dangerous PICs. The same can be said of all fire

retardants which act by suppressing gas phase combustion. An alternative approach, which circumvents the problem of creating unwanted PICs, is to introduce chemical changes which enhance char formation during polymer burning. Charring increases the fraction of the fuel retained in the condensed phase so that less combustible, and otherwise hazardous, gases are evolved. It also forms a barrier which insulates the unburnt polymer, while at the same time, obstructing the outward flow of products generated in the degradation of the interior. The morphology and chemical structure of the char that forms is also an important factor in determining polymer flammability.

Research conducted in this laboratory has focused on elucidating the relationships between the chemical structure and char forming tendency of polymers. The progress we have made in identifying additives and structural features which promote the formation of heat resistant chars in burning polymers will be reviewed.

MOLECULAR DYNAMICS MODEL OF POLYMER DEGRADATION

We have used molecular dynamics modeling to explore mechanisms of char formation in the thermal degradation of polymers [1,2]. This approach consists of solving Hamilton's equations of motion

$$\frac{\partial H}{\partial p_i} = \frac{dq_i}{dt}, \qquad \frac{\partial H}{\partial q_i} = -\frac{dp_i}{dt} \qquad (i=1,2,\ldots,3N), \tag{1}$$

for each of the 3N molecular degrees of freedom. In this equation p_i and q_i denote the Cartesian components of momentum and position, respectively. The dynamic model consists of a central polymer chain surrounded by six additional chains in accordance with the experimentally determined crystal structure of polyethylene (PE). Each chain is made up of 50 carbon and 100 hydrogen atoms (Figure 1). The Hamiltonian of the model polymers has the form

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} + \sum_{i=1}^{N-1} V_s(r_{i,i+1}) + \sum_{i=1}^{N_c-2} V_b(\theta_{i,i+1,i+2}) + \sum_{i=1}^{N_c-3} V_t(\phi_{i,i+1,i+2,i+3}) + \sum_{i=1}^{N_c-3}\sum_{j=i+3}^{N_c} V_{nb}(r_{ij}) + \sum_{i=1}^{N_c}\sum_{j=1}^{N_x} V_{ext}(r_{ij}), \tag{2}$$

where N_C denotes the number of carbon and N_H the number of hydrogen atoms. The first term on the right hand side of Eq.(2) represents the kinetic energy of the $N = N_C + N_H$ atoms. The next terms are the potential energies for bond stretching (V_s) and bending (V_b) and a torsional potential (V_t) which restricts internal rotation around the C-C bonds. These are followed by non-bonded potential energy (V_{nb}) interactions between the atoms in the model polymers and themselves, as well as their interactions with an additional N_x atoms constituting neighboring chains in the bulk material or an external surface (V_{ext}). Values for the parameters which define the potential energy field represented by Eqs. (5)-(8) are listed in Table I.

The potential energy involved in stretching bonds is described by the function

$$V_s = S(r-r_d)D\{[1 - \exp(-\alpha_e(r-r_e))]^2 - 1\}, \tag{3}$$

where r is the distance between covalently bonded atoms. Standard values were used for the dissociation energies (D), equilibrium lengths (r_e) and force constants ($k_b = 2D\alpha_e^2$) of C-C, C-H and H-H bonds. The latter set was needed to describe the formation of H_2 in the reaction channels specified in Eqs. (13) and (15). The potential energy for bond bending is represented by

$$V_b = S(r_{i,i+1}-r_d)S(r_{i+1,i+2}-r_d)\frac{k_\theta}{2}(\cos\theta - \cos\theta_0)^2, \tag{4}$$

where θ denotes the angle defined by the dot product of the normalized bond vectors between three adjacent carbon atoms and k_θ is the corresponding force constant. Rotations about covalent bonds are restricted by a torsional potential

$$V_t = S(r_{i,i+1}-r_d)S(r_{i+1,i+2}-r_d)S(r_{1+2,i+3}-r_d)(\alpha\cos\phi + \beta\cos^3\phi), \tag{5}$$

where the dihedral angle, ϕ, is defined by the three bond vectors between four adjacent carbon atoms. The parameters, α and β, determine the position and height of the barrier to internal rotation. The switching function

$$S(r-r_d) = \frac{1}{2}(1 - \tanh(a(r-r_d))), \tag{6}$$

where a = 40 nm^{-1}, is used to ensure that the potential energy terms in Eqs.(4) and (5) fall smoothly to zero as the relevant bond lengths approach the dissociation distance, r_d (0.42 nm). Internal non-bonded potential energy interactions are represented by the function

$$V_{nb} = \epsilon[(\frac{r^*}{r})^{12} - 2(\frac{r^*}{r})^6] + \frac{Q_iQ_j}{r}, \tag{7}$$

where r denotes the distance between the atoms in the dynamic polymer chains and Q_k is the partial charge on atom k. Non-bonded interactions with N_s = 1300 external atoms constituting a rigid surface or neighboring chains in the bulk material are modeled by

$$V_{ext} = \epsilon[(\frac{r^*}{r})^9 - \frac{3}{2}(\frac{r^*}{r})^6], \tag{8}$$

where r is the distance between CH_2 groups in the dynamic chains and the surface atoms. The values of r^* and ε in Eqs.(7) and (8) define the position of the minimum and the depth of the potential well, respectively. In some simulations, larger values of ε were used for the external potential to account for the possibility that the interactions with an additive or filler might be considerably stronger than the internal forces between the polymer chains.

Two reactions which are thought to play a major role in the thermal degradation of polymers are hydrogen transfer and depolymerization. An example of intramolecular hydrogen transfer is depicted in the following scheme:

$$R\text{-}CH_2\text{---}CH_2\text{-}\overset{\overset{H}{|}}{CH}\text{-}R \rightarrow R\text{-}CH_3 + CH_2\text{=}CH\text{-}R. \tag{9}$$

The resulting fragments can react again and again in recursive fashion producing a broad spectrum of volatile hydrocarbons which are readily combusted. In the depolymerization reaction illustrated in Eq.(10),

$$R\text{-}CH_2\text{---}CH_2\text{-}CH_2\bullet \rightarrow R\text{-}CH_2\bullet + CH_2\text{=}CH_2, \tag{10}$$

the monomer splits off from a free radical fragment generated by the random scission of a C-C bond. These reaction channels, as well as the additional possibility of intermolecular hydrogen transfer between free radical fragments, are accounted for in the computer program. Both the hydrogen transfer and depolymerization reactions are modeled as concerted processes so that bond making occurs simultaneously with bond breaking. This is accomplished using the switching functions defined in Eq.(6). In the case of the depolymerization reaction, a new π bond forms at the same time as the adjacent σ bonds break. The potential energy of the π bond is

$$V = (1-S(r_{i,j}-r_d))(1-S(r_{k,l}-r_d))D'\{[1-\exp(-\alpha_e(r_{jk}-r_e))]^2-1\}, \tag{11}$$

with {i,j,k,l} denoting adjacent carbons and $D' = 0.759D_{C\text{-}C}$, the dissociation energy of a C-C π bond.

The degradation process terminates when reactive fragments combine to form more stable products. One such mechanism, which is also accounted for in the computer model, is the radical recombination reaction illustrated in Eq.(12).

$$R\text{-}CH_2\bullet + \bullet CH_2\text{-}R \rightarrow R\text{-}CH_2\text{-}CH_2\text{-}R \tag{12}$$

We also allow for a number of other reaction channels which are normally inactive in the thermal degradation of PE. Radical sites are generated whenever a bond begins to break. These in turn are eligible to react with other radical sites to form new bonds. This is simulated in the computer program by the following algorithm. When the length of any bond exceeds the value $r_d - r_e$, an attempt is made to form a new bond by examining all possible covalent interactions. The potential energy is given by Eq.(11), where D′ is the dissociation energy of the new bond that forms between atoms j and k when the i-j and k-l bonds break. The trajectories are updated only on the basis of the forces corresponding to the minimum energy subject to the constraints that there are never more than four bonds to a carbon and more than one bond to a hydrogen atom.

In addition to the vinylic compounds and monomers which are produced in the reactions outlined in Eqs.(9) and (10), vinylenic, cyclic, and cross-linked hydrocarbons are also formed. Examples of the chain stripping, cyclization and intermolecular cross-linking reactions which give rise to these products are illustrated in Eqs.(13)-(15).

$$R-\underset{\underset{H}{|}}{CH}-\underset{\underset{H}{|}}{CH}-CH_2-R \rightarrow R-CH=CH-CH_2-R + H-H \tag{13}$$

$$R-\underset{\underset{H}{|}}{CH}-(CH_2)_4-\underset{\underset{H}{|}}{CH}-R \rightarrow R-\underset{\underset{\underset{CH_2-}{|}}{CH_2}}{\underset{|}{CH}}-\underset{\underset{\underset{CH_2}{|}}{CH_2}}{\underset{|}{CH}}-R + 2H\bullet \tag{14}$$

$$\begin{matrix} R-\underset{\underset{H}{|}}{CH}-CH_2-CH_2-R \\ H \\ \underset{\underset{RCH-CH_2-CH_2-R}{|}}{} \end{matrix} \rightarrow \begin{matrix} R-CH-CH_2-CH_2-R \\ | \\ R-CH-CH_2-CH_2-R \end{matrix} + H-H \tag{15}$$

The chains are in a planar zig-zag conformation at the onset of the simulations (Figure 1). Thermal motion is initiated by giving each atom a three dimensional velocity chosen at random from a uniform distribution. Once the atoms in the model polymers are set in motion, they quickly adopt a Maxwell-Boltzmann velocity distribution [2]. The equations of motion are integrated using the differential equation solver ODE [3]. This routine is based on a predictor-corrector algorithm and uses a variable step-size. All forces are evaluated analytically from the first derivatives of Eqs.(3)-(8). Simulations are carried out for 5 to 10 picoseconds at temperatures ranging from about 500 K, which is typical of the pyrolysis of PE, up to about 2000 K. These calculations require about 1 hour of CPU time on NIST's Cray Y-MP[1] computer. Trajectories are downloaded to a Silicon Graphics 4D/310 GTX workstation where they were viewed in the form of movies.

The progression depicted in Figures 2 and 3 is representative of what happens in simulated thermal degradations of PE and other linear polymers. The chains fragment into fuel for gas phase combustion before a significant number of inter-molecular cross-links (highlighted in white) can form. In contrast, an incipient char is produced when a significant number of hydrogens (exceeding 20% of the total) are removed from the model polymers at the onset of the simulations. This gives cross-linking reactions a head start so that they can compete with fragmentation (Figures 3 and 4). The stability of the chars were observed to increase with the magnitude of the interaction between the surface and the polymer chains. When large values of ε were used in V_{ext} (Eq.(8)) the resulting chars contained more cross-links and were

[1] Certain commercial equipment and materials are identified in this paper in order to adequately specify procedures. Such identification does not imply recommendation or endorsement, nor does it imply that they are the best available for the purpose.

more persistent. Presumably, this is because the chains are brought closer together as a result of their mutual attraction to the surface. This observation suggests that a filler, particularly one that has a strong affinity for the polymer, will facilitate the formation of a heat resistant char.

Under normal circumstances, linear PE does not char when it is burned. This was confirmed in experiments using the NIST Cone Calorimeter [4]. Cross-linked polymers, which were prepared by irradiating linear PE with either γ or 1 Mev electron beam (e^-) radiation, did leave measurable amounts of char. Indeed, glowing combustion, as indicated by the formation of red-hot embers, was observed when the cross-linked polymers were burned. The critical flux to ignition was also significantly higher for the cross-linked than for the linear polymers (Table II). The behavior of the e^- irradiated samples was particularly striking. The more highly cross-linked layer on the top formed a thin char which retained the gases generated by the decomposition of the polymer in the interior of the sample. Eventually, the gases broke through and the sample ignited leaving behind a thin skin of carbonaceous material when the flame self-extinguished.

CONCLUSIONS

Molecular dynamic simulations provide new insights into the mechanisms of polymer degradation and should be useful in developing treatments for improving fire resistance. In particular, the prediction that cross-linking can increase the tendency of certain polymers to char when they are burned, and thereby contribute to a reduction in flammability, has been validated in experiments with both γ and e^- - irradiated PE. The behavior of the e^- - irradiated PE, in particular, suggests the possibility of using ionizing radiation to graft fire resistant shells on to pre-formed plastic. In this way, it may be possible to achieve a significant reduction in flammability without altering the bulk material.

Table I. Hamiltonian Parameters for Model Polymers[a]

V_b	V_a	V_t	V_{nb}[b]	V_{ext}
C-C: $D = 347.6$, $\alpha_e = 19.24$, $r_e = 0.1529$	$k_\theta = 130.0$	$\alpha = -18.41$	C-C: $\varepsilon = 0.2896$, $r^* = 0.3850$, $Q_C = -0.288$	$\varepsilon = 2.494$, $r^* = 0.2645$
C-H: $D = 405.8$, $\alpha_e = 18.88$, $r_e = 0.1100$	$\theta_0 = 113.3°$	$\beta = 26.78$	C-H: $\varepsilon = 0.2015$, $r^* = 0.3337$	
H-H: $D = 435.0$, $\alpha_e = 19.93$, $r_e = 0.0742$			H-H: $\varepsilon = 0.1402$, $r^* = 0.2927$, $Q_H = 0.144$	

a. All energies and lengths given in units of kJ/mol and nm, respectively.
b. Parameters for this potential energy function were taken from reference 5.

Table II. Ignition Times and Char Yields for Linear and Cross-linked PE

Polymer	Dose (MGy)	Flux (kW/m^2)	Time to Ignition (s)	Char Yield (%)
linear PE	0	20	285	0.0
γ-irradiated PE	0.5	20	923	2.7
e^--irradiated PE	1.0	21	1120	0.1

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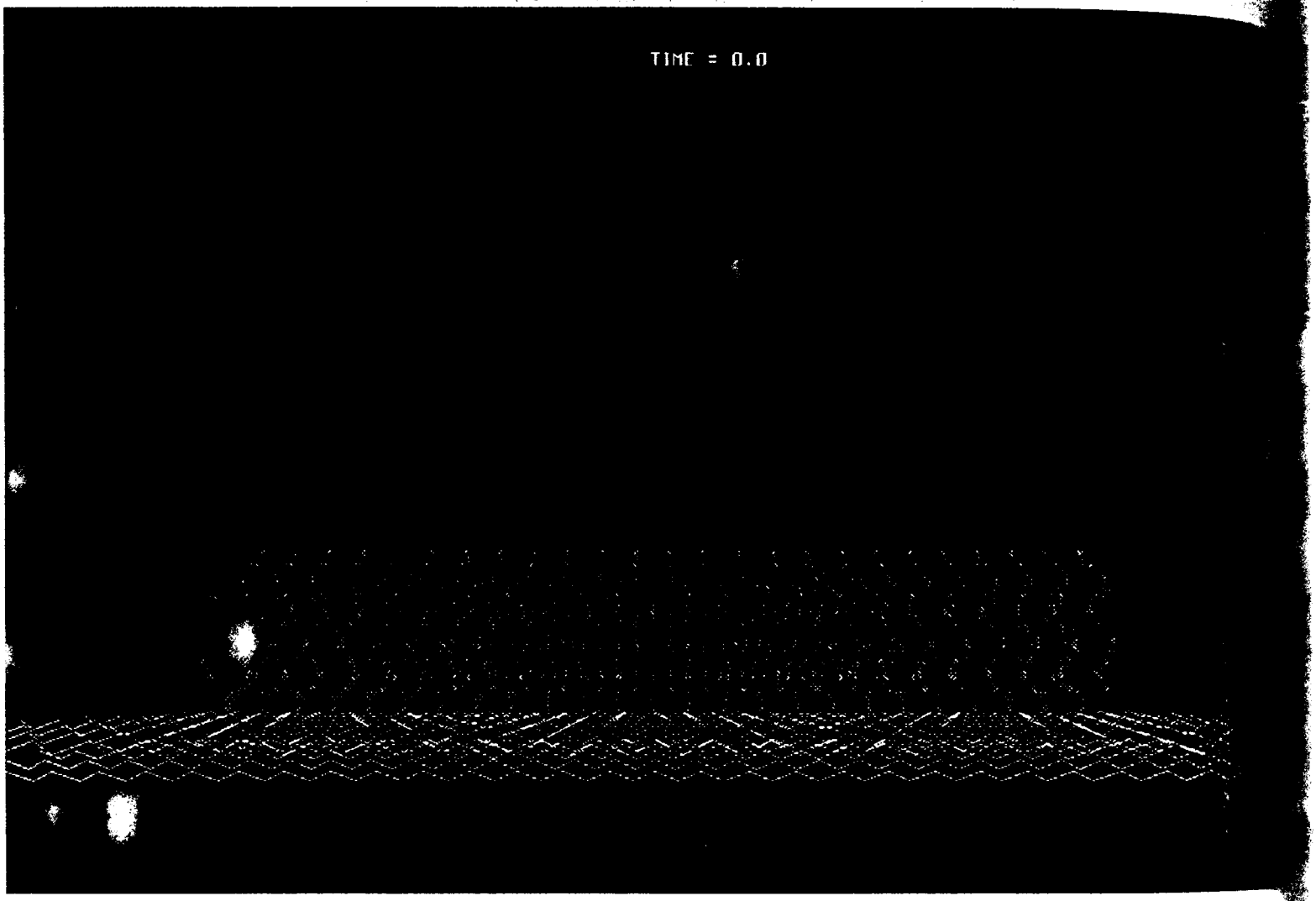
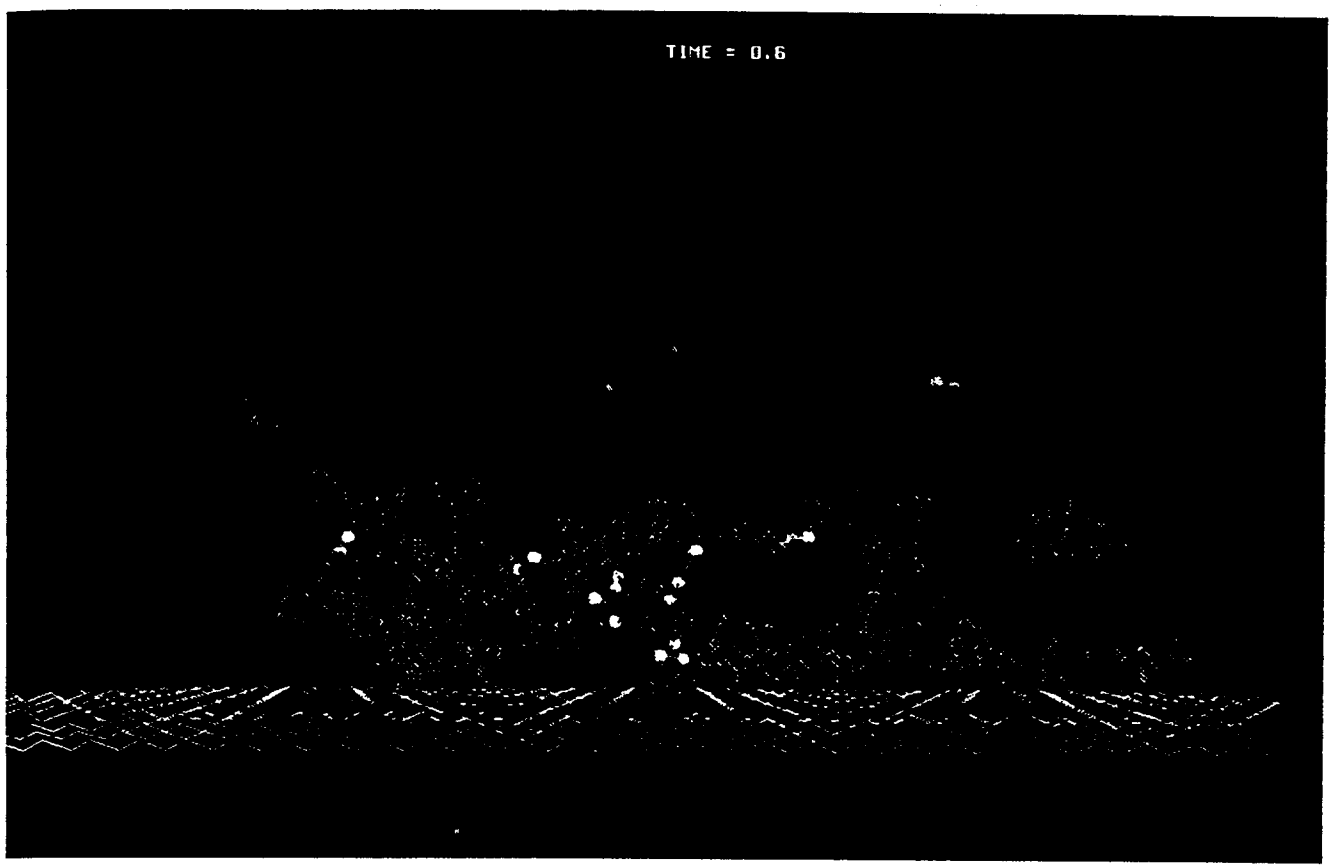
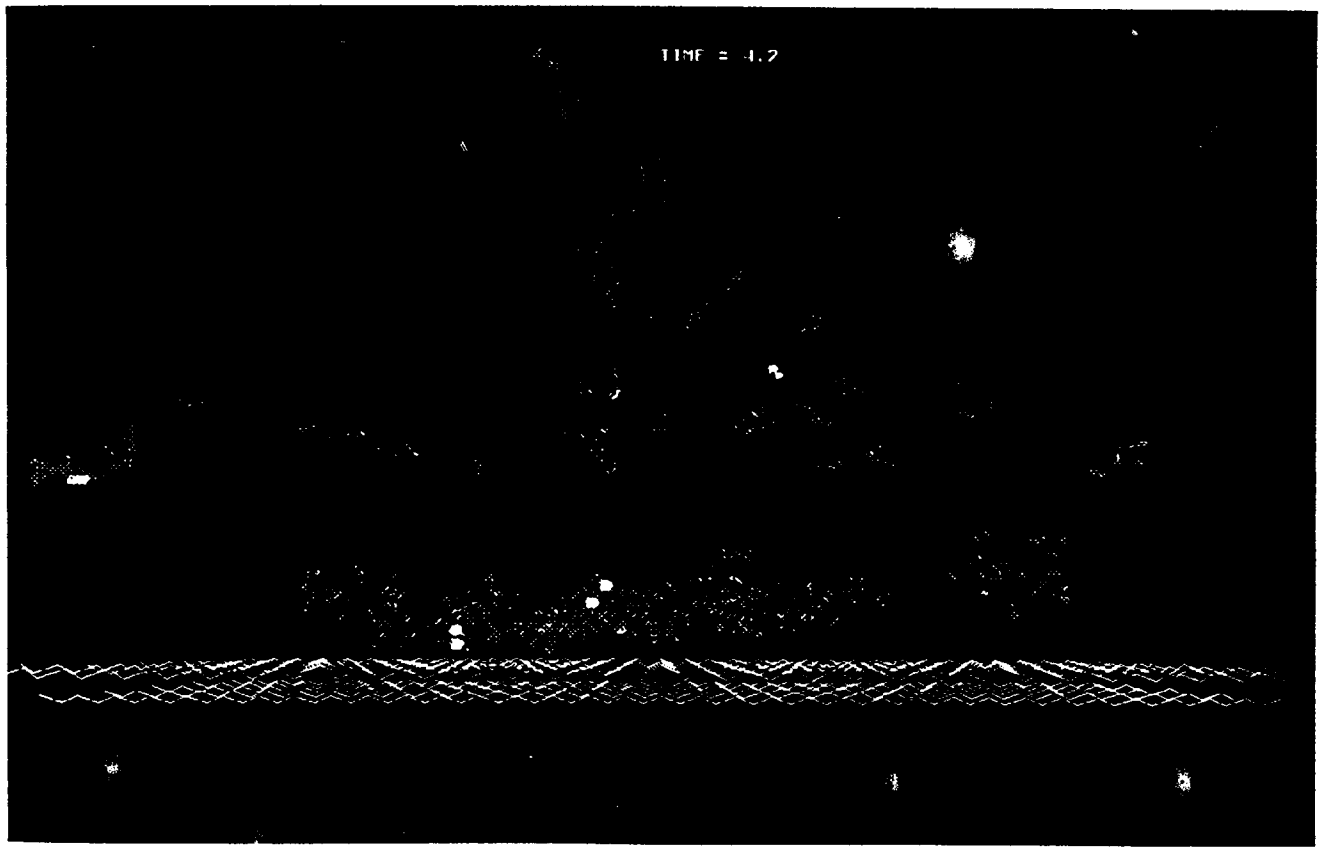
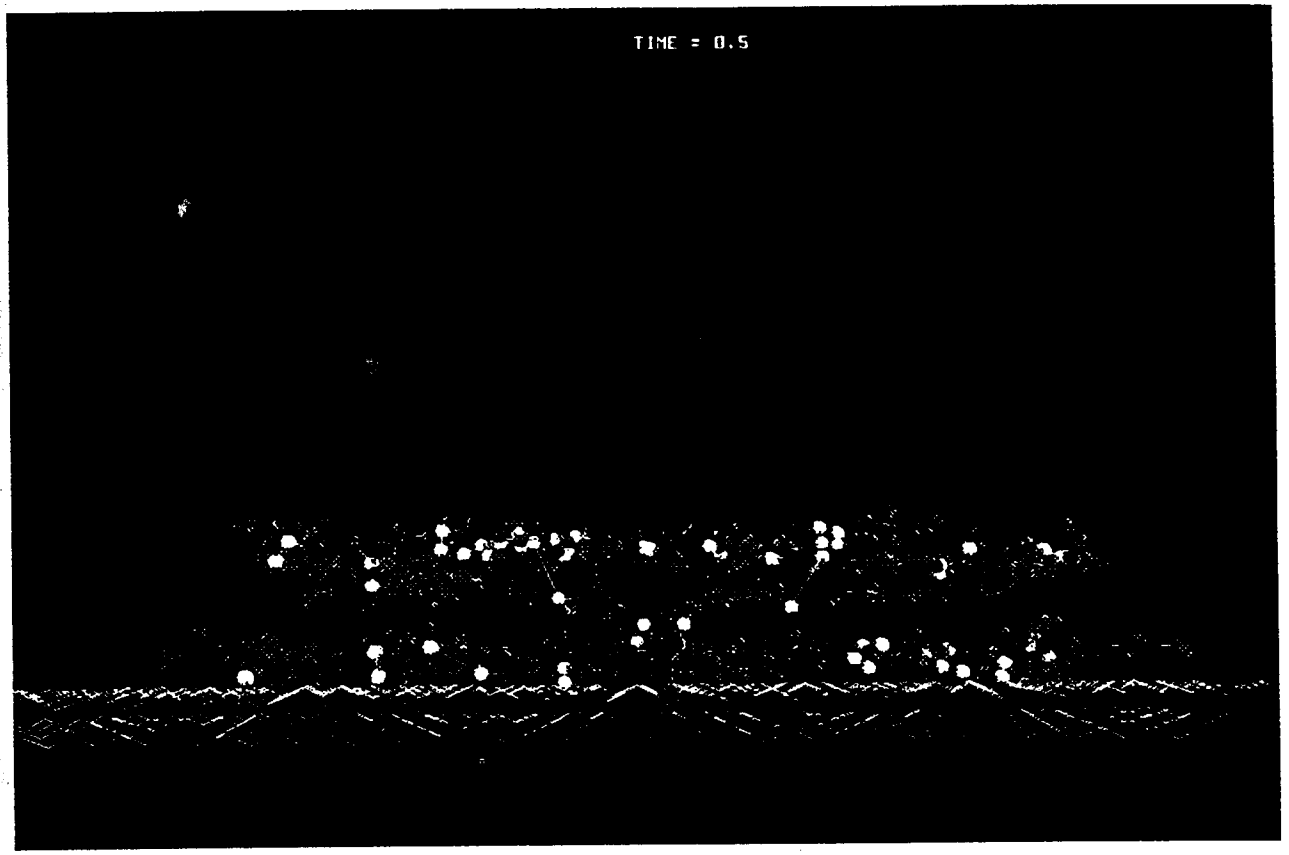


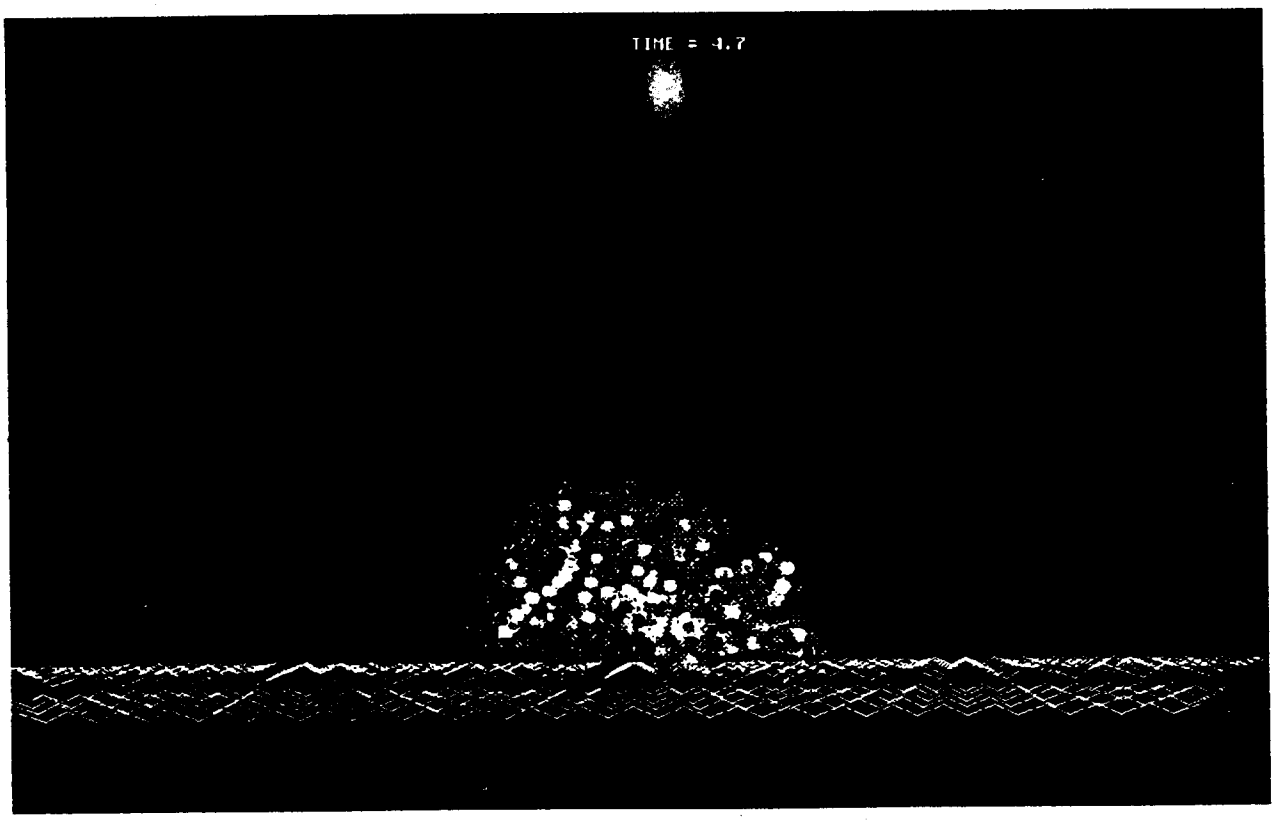
Figure 1. At time t=0, the seven polymer chains, each consisting of 50 carbon (large spheres) and 100 hydrogen atoms, are arranged in a planar zig-zag conformation. The static surface is indicated by white lines.





Figures 2 and 3. The chains fragment before strong cross-links (indicated white spheres) have a chance to form.





Figures 4 and 5. An incipient char forms when cross-linking is given a head start by removing hydrogens at the onset of the simulations.