LETTER TO THE EDITOR

Branching and vulcanisation of polymer chains

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Abstract. We study the effects of branching on linear polymers using a two-parameter position space renormalisation group. From the resulting phase diagram and the renormalisation group flows we find a new higher-order critical point. We propose that this critical point describes a vulcanisation process in which both the linear polymer and its branches become part of an infinite branched polymer network.

Linear polymers are formed when a large number of bifunctional monomers join to form a chain molecule. However, during the synthesis of linear polymers, branching sometimes occurs and leads to a polymer chain that is not perfectly linear (see figure 1(a)). An example is industrial polyethylene which has many three-functional branch points (de Gennes 1979). It is expected that the presence of a few branches in an already existing linear polymer should not affect the asymptotic scaling properties of the polymer. On the other hand, if the branches become comparable in length to the original linear polymer (see figure 1(b)), the asymptotic properties should be changed. In the following we develop a position space renormalisation group method to determine the phase diagram for a linear polymer solution in the presence of branching.
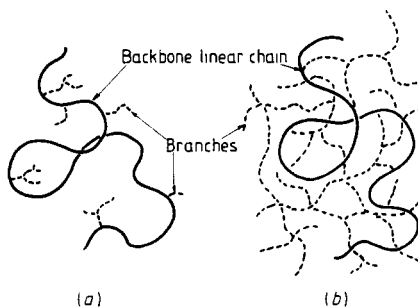

Figure 1. (a) Example of a linear polymer with short branches. (b) Example of a linear polymer with branches that are comparable in length to the original linear polymer.

The main result of our study is that when the length of the branches becomes comparable to that of the backbone chain, the polymer exhibits a new type of scaling behaviour different from that of both linear polymers and randomly branched polymers. We propose that this new higher-order critical point describes a vulcanisation process

in which both the backbone chain and its branches become part of an infinite branched polymer network. The properties of this new vulcanisation process are discussed below.

The application of position-space renormalisation group methods to the study of crossover phenomena in polymers has been the subject of recent reviews (Family 1983, Stanley *et al* 1982). We model a linear polymer in the dilute limit by a self-avoiding random walk on a lattice. To obtain a branched polymer, we enumerate all the possible branches that can be added to an already existing linear polymer. We use the approach of Family (1980) (see also Family (1983) and references therein) and model the system in a grand canonical ensemble and associate a fugacity K with a monomer in the backbone chain and a fugacity G with a monomer in the branches. To obtain explicit recursion relations for K and G, we discuss the model on a square lattice and partition it into cells of linear dimension $b = 2$. We assume that all polymer configurations which begin at the lower left corner and extend to the top of the cell are renormalised to a single backbone bond of weight K' in the vertical direction; we also use the same rule in the horizontal direction. Examples of configurations that contribute to K' are shown in figure 2(a). The resulting recursion relation is

$$K' = K^2 + K^2(2K + 2G + K^2 + 8KG + 6G^2 + 4K^2G + 16KG^2 + 11G^3 + 6K^2G^2$$
$$+ 18KG^3 + 12G^4 + 4K^2G^3 + 10KG^4 + 6G^5 + K^2G^4 + 2KG^5 + G^6). \quad (1)$$

Note that (1) reduces to the usual self-avoiding walk (linear polymer) recursion relation when $G = 0$. For $G = K$, (1) represents a branched polymer which has been constructed by adding branches to an already existing linear polymer.
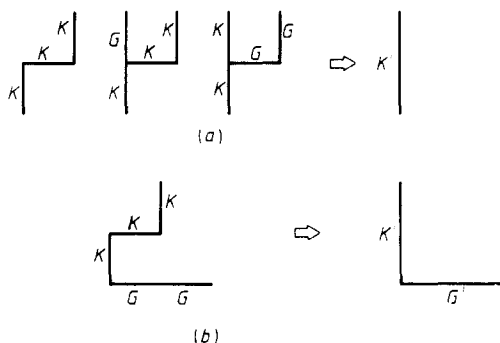

Figure 2. Examples of polymer configurations on a square lattice on a $b = 2$ cell. Weights K and G are associated with monomers (bonds) in the backbone linear chain and branches respectively. The configurations in (a) span vertically and contribute to K'. The diagrams in (b) span horizontally and vertically and contribute to both the K' and G' recursion relations.

In order to determine the recursion relation for G' it is convenient to introduce the *enhancement parameter g* defined by the relation $g = G/K$ and obtain the recursion relation for g' directly. The recursion relation for g' must satisfy the requirements that $g > 1$ ($g < 1$) favours (inhibits) the addition of branch monomers; the limit $g = 1$ corresponds to the case where monomers in the backbone linear chain and the branches have equal weight. These requirements imply that g' can be written as the sum of all branched configurations which span the cell in *both* the vertical and horizontal directions divided by the sum of the contributions from the same configurations with $g = 1$.

Examples of configurations contributing to g' are shown in figure 2(b). The resulting recursion relation for g' for a $b = 2$ cell on the square lattice is

$$g' = G'/K' = N/D,$$

$$N = 3KG + 2G^2 + 2K^2G + 10KG^2 + 7G^3 + 5K^2G^2 + 16KG^3 + 11G^4$$
$$+ 4K^2G^3 + 10KG^4 + 6G^5 + K^2G^4 + 2KG^5 + G^6,$$

$$D = 5K^5 + 19K^3 + 32K^4 + 20K^5 + 4K^6. \tag{2}$$

Equations (1) and (2) constitute a coupled set of recursion relations for K' and G' (or g'). The resulting phase diagram and the renormalisation group flows are shown in figure 3. Although this phase diagram was obtained for a $b = 2$ cell on the square lattice its main features are expected to be independent of b and applicable to three dimensions as well.
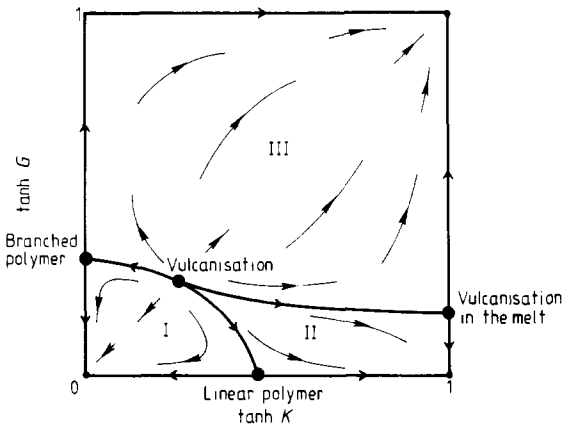

Figure 3. Resulting phase diagram and the renormalisation group flows obtained from the coupled recursion relations (1) and (2).

In addition to the three trivial fixed points at $(K^*, G^*) = (0, 0)$, $(\infty, 0)$ and (∞, ∞), there are four non-trivial unstable fixed points as shown by the full circles in figure 3. The fixed points at $K^* = 0.4656$, $G^* = 0$ and $K^* = 0$, $G^* = 0.3215$ correspond to the limits of a linear polymer (self-avoiding walk) and randomly branched polymer (lattice animal) respectively. Note that for $G < K$, the flow on the phase boundary is toward the linear polymer fixed point. This direction of flow implies that along the phase boundary the asymptotic critical behaviour is that of a linear polymer even though the polymer may have branches present.

For $G = K$ the length of the branches becomes comparable to the backbone linear chain and a new universality class develops as evidenced by the fixed point at $K^* = G^* = 0.2603$. This new fixed point describes a vulcanisation process in which both the backbone chain and the branches simultaneously become critical. Linearisation of (1) and (2) near this fixed point and the calculation of the largest eigenvalue of the linearised renormalisation group transformation matrix (details of this procedure are discussed in Family (1983), Stanley *et al* (1982)) lead to a fractal dimension $d_f = 1.8$ associated with this fixed point. (For comparison (1) and (2) yield $d_f = 1.4$ and $d_f = 2.0$ for the self-avoiding walk and lattice animal fixed points respectively.) Note that as

K decreases from $K^* = 0.2603$ along the phase boundary, the length of the backbone chain becomes finite and the branches grow in size in order to keep the polymer network connected. Hence the flow is from the vulcanisation fixed point toward the randomly branched fixed point on the G axis.

In addition to the three fixed points discussed above, there is another fixed point at $K^* = \infty$, $G^* = 0.1123$ which has physical significance. In the limit $K \to \infty$ linear polymers densely pack the lattice such that every lattice site is occupied by a monomer belonging to the polymer. If there were more than one chain present, the limit would describe a linear polymer melt. Hence in this limit the number of branch monomers required to form a vulcanised network is small and $G^* \ll 1$.

The critical lines divide the phase diagram into three regions: region I corresponds to the sol phase with polymers of finite size, region II corresponds to an infinite linear polymer with finite branches, region III corresponds to the gel phase where an infinite polymer network is present. Note that the vulcanisation fixed point is a higher-order critical point at which the correlation length of both the linear backbone and its branches become infinite simultaneously.

In the usual model of vulcanisation of linear chains (Flory 1953, de Gennes 1979), linear polymers in a melt are randomly cross-linked to form an infinite molecule. The present model of vulcanisation is more general, since two monomers of different chains can cross-link regardless of their distance apart. Hence in contrast to the usual model in which vulcanisation can occur in the melt only, in the present model it can also occur in the dilute and semi-dilute regions. An important aspect of our model is that whereas the critical behaviour for vulcanisation in the melt is of a mean-field type (de Gennes 1977), vulcanisation in the dilute and semi-dilute regimes exhibits non-mean-field behaviour (Daoud 1979, Coniglio and Daoud 1979). The present model complements the model of vulcanisation investigated by Coniglio and Daoud (1979) in which each cross-linking bond occurs with probability p and is absent with probability $1 - p$. Hence in the limit in which no linear backbone chain is present, Coniglio and Daoud obtain percolation critical behaviour rather than the critical behaviour of randomly branched polymers (lattice animals) as obtained in the present work.

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