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A Computer Simulation for the Aggregation of Associating Polymers

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ABSTRACT: A computer simulation (in 2-D) is used to model the aggregation process for self-avoiding flexible polymers which contain two "stickers", one at each chain end. We assume that the strong attractive interaction between these end sites leads the chains to aggregate and form clusters. By assuming that the monomer concentration of our aggregate is comparable to the monomer concentration at the overlap threshold for a solution of 2-D self-avoiding random walk chains, we have been able to correlate the radius of gyration for the cluster to n and N, the degree of polymerization and the number of chains, respectively. We find that $R_g \sim N^{1/2}n^{3/4}$. However, the presence of self-loops causes the cluster to contract in size and results in a small deviation from the predicted exponent relating R_g and N. We also demonstrate that the diffusion-limited network formation studied here is distinctly different from the small-particle diffusion limited aggregation.

Associating polymers are flexible macromolecules which contain a number of sites that strongly attract each other. The strong interaction between these sites leads the chains to aggregate and form clusters. This, in turn, gives rise to a variety of unusual physical properties.[1-6] Of particular interest are polymers in which the associating sites or "stickers" are located at the ends of the chains.[7,8] This feature is relevant in several self-assembling processes, such as the aggregation of telechelic ionomers,[9] mesophase formation in didiscotic liquid crystals,[10] and gel formation,[11] as well as the formation of microemulsions[12] and block copolymers. While there is considerable experimental evidence for the end-to-end association in the systems listed above, the exact size, shape, and number of stickers involved in these structures remain uncertain.[3]

In an attempt to understand the details of structures underlying these processes, we present below a computer simulation in two dimensions to model the aggregation process for flexible chains which contain two stickers, one at each chain end. In general, one of the key features in the above-mentioned processes is the lifetime of the association of the stickers.[13] This lifetime depends strongly on the chemical nature of the stickers. The computer simulation of such reversible associations of polymer chains with stickers is a very difficult task in terms of the necessary computer time. As a start, we consider only the case where the lifetime of the association is longer than the relaxation time of the individual chain and the characteristic time for the diffusion of a chain inside the aggregate. Consequently, we assume that the chains aggregate by a given end of a chain sticking irreversibly to either the other end of the same chain or an end of a different chain. Attention is focused only on the formation of a single aggregate.

The advantage afforded by this computer simulation is that it yields both a qualitative and quantitative means of understanding the factors which influence the size and shape of the growing cluster. First, the figures generated via this method allow us to actually visualize the growth and changes in the aggregate. Second, various features of the cluster, such as the radius of gyration or the number of intra- and inter-chain interactions are easily computed. Third, "experiments" to alter various polymer properties (such as chain length) are easily carried out, and hence we can examine how such variations affect the aggregation process. Finally, the procedure used here is similar to that used to study the class of problems known as diffusion-limited aggregation (DLA).[14] In these problems, diffusion of the particles to the surface of the aggregate is the rate-limiting step. As is common in this class of calculations, we will search for a scaling law that describes the evolution of the cluster.

The Model

The simulation is started by placing a seed chain, of specified length but with self-avoiding random configuration, at the center of a two-dimensional square lattice. The chain is taken to be composed of $(n - 1)$ bonds. All chains in the simulation obey the excluded volume criteria, in that no lattice site is permitted to be doubly occupied. The last bond at both ends of the chain is designated as a "tail". The configuration of the first chain remains fixed. Another chain of equal length is introduced and allowed to execute a self-avoiding random walk. In this paper we consider two limits which we call dilute and concentrated.

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In the dilute limit, a new chain starts its random walk with one end on the circumference of a circle, whose radius is equal to the sum of the current radius of gyration R_g of the cluster (in units of lattice spacing) and n. In the concentrated limit, this chain starts its movement from a location within a specified circumference, the radius of which is proportional to the number of chains already present.

The random walk executed by the mobile chain is composed of two parts: translation and a "wiggling" motion. First, the entire chain is translated in one of four directions to be picked at random: up, down, to the left, or to the right. Second, the chain dynamics is simulated by using the Verdier–Stockmayer algorithm.[15] The chain motion now attempted depends on the local conformation surrounding this bead: Some beads are less restricted in their motion (end beads), while other beads are not free to move (a bead colinear with its two nearest neighbors). Detailed discussions of this point can be found elsewhere.[15–18] The appropriate motion is attempted and is accepted if it meets the excluded volume criteria. We refer to this motion as "wiggling" the chain.

The walk continues until a tail of the second chain is parallel and adjacent to a tail on the seed chain. Then, the aligning tail on chain 2 is stopped and remains stuck at this lattice site. The remaining portion of this chain can wiggle about so long as its other tail remains unattached. A chain with one stationary end will be referred to as "partially frozen". A third chain is now introduced onto the lattice. At this point, a chain is picked at random (in this case, either chain 2 or 3). A check is made to determine whether or not this chain contains any stationary tails. If it does not (chain 3), the chain is first translated and then wiggled. If chain 2 were to be selected, it is only wiggled: a bead on the chain is picked at random and an appropriate chain motion is attempted. A check is now made to see if the moves just executed have resulted in any two tails being located parallel to each other and one lattice unit apart. If not, a chain is again picked at random and the procedure described above is repeated. If, on the other hand, a new end–end pairing is found, another chain is added to the lattice and again the process above is repeated.

When a chain has both of its tails paired in the manner described above, the entire chain remains stationary and is referred to as frozen. A tail on a newly introduced chain is only permitted to align with a tail on a partially frozen or frozen chain. In this way, the new chain binds to one already attached to the growing cluster and the cluster keeps growing.

We note that at any given time, the cluster contains many partially frozen chains. The tails on these chains may align (where upon a new chain is added) before a loose chain can join the cluster. Therefore, there can be many loose chains on the lattice.

For a chain that is completely frozen, we can distinguish between two types of end–end associations: those arising from inter-chain or intra-chain interactions. In the first case, both ends of a given chain are paired with tails belonging to other chains. In the second case, the polymer forms a self-loop.

The simulation comes to a halt when a specified number of chains are incorporated into the cluster (specified number of chains = number of frozen chains + number of partially frozen chains). Then, the radius of gyration of the entire cluster, as well as other statistics, is calculated. As can be seen in the following figures, groups of frozen tails align to form horizontal or vertical "columns". The statistics gathered include the number of tails in a column and how many times a column of such length appears. Moreover, the number of self-loops present in the cluster is also tabulated.

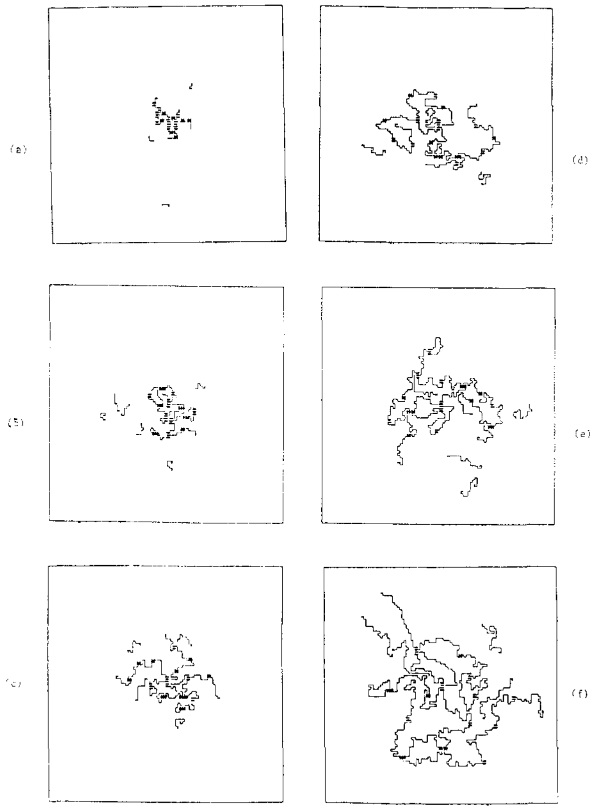

Figure 1. Clusters with 20 chains of uniform length in each. (a) – (f) correspond to chain lengths of 5, 10, 15, 20, 25, and 40 lattice sites, respectively. The "tail" sites on the chains are drawn with a thicker line to distinguish them from the rest of the chain. The "frozen" tails are drawn with the widest line to clearly indicate which ends are in the cluster. The simulations in this series were performed in the concentrated limit: the chains were introduced onto the lattice inside a circle, whose radius is proportional to the number of chains present.

The "stacking" of associating sites into triplets, quartets, etc., results, in this example, from the fact that each tail can stick to two other tails. Examples of this type of "multiplet" aggregation can be seen in systems where the associating sites attract each other thorugh a dipole–dipole[12] or electrostatic interaction.[9]

Results and Discussion

Several qualitative features about the structure of the aggregate become apparent by examining Figure 1. This figure reveals how the size and shpae of the clusters change as the length of the chain is varied. There are 20 chains of uniform length in each cluster, but the lengths are varied from 5 to 40 lattice sites in diagrams a–f. As can be seen in figure 1a, the short chain polymers form small and very tight aggregates. The ends or "stickers" are all within close proximity of each other, roughly centered around the initial seed chain. In contrast, the cluster composed of chains 40 lattice sites in length forms a diffuse structure that extends further out in space. The columns of stickers are located much farther apart from each other. Except for very short chains, the ends cluster predominantly in columns of twos or threes. These conclusions are further confirmed when we look at the larger clusters in Figure 2, , which dramatically illustrate the points above.

The figures also reveal that the end–end interactions are predominately of the "bridging" type: the flexible chain

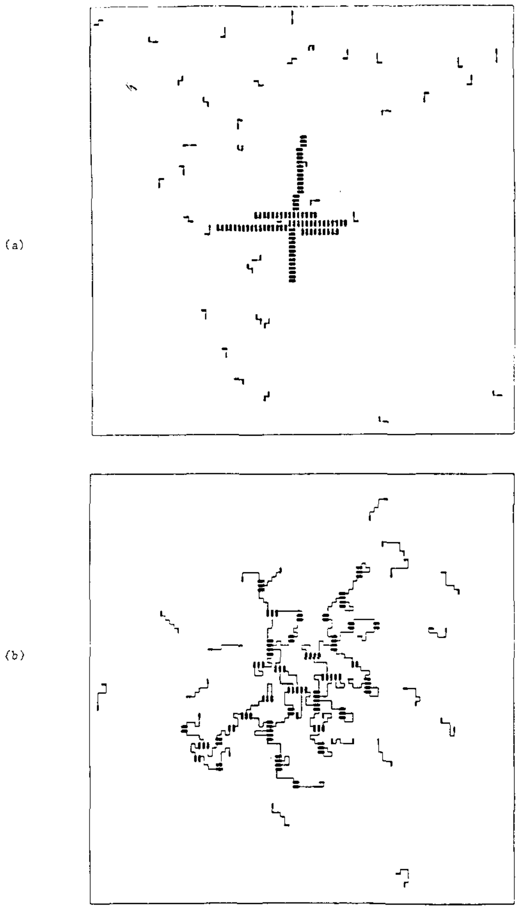

Figure 2. Chains containing 4 and 10 lattice sites. The chains in (a) are 4 lattice sites long. They form a compact structure of a few long columns, the longest of which contains 17 frozen ends. There is a total number of 42 frozen and 2 partially frozen chains. The chains in (b) are 10 lattice sites in length. Here, the cluster is composed of 48 frozen and 8 partially frozen chains. The columns predominantly contain only two or three "stickers". These simulations were peformed in the concentrated limit. Both frames represent the state of cluster growth after 50 000 computer time steps.

acts as a bridge between an end in one column and the other end located in yet another column. The number of self-loops is much smaller than the number of such bridges or inter-chain interactions. For example, there are 4 self-loops but 15 "bridges" in Figure 1b, while Figure 1e contains no self-loop at all. Finally, we note that it is entropically less favorable for the ends of a long flexible chain to become aligned than for ends located on short chains. Accordingly, the amount of time (number of computer steps) it took to freeze 20 chains in a cluster increases with the length of the polymer.

As we noted in the introduction, the growth of these clusters is diffusion-limited. Thus, in analogy with the small-particle diffusion-limited aggregates, one may attempt to obtain a scaling law that relates R_g and its mass which is proportional to Nn. However, mass alone is insufficient in describing the size of these clusters since the entropy of the associating chains clearly plays a crucial role in determining the radius of the aggregate. For example, an aggregate formed from a small number of longer chains is quite different from that from a larger number of shorter chains where the molecular weight of the aggregate is kept the same in both cases. Consequently, we are interested in studying the dependence of R_g on N and n separately. Futhermore, one may be tempted to view these clusters as diffusion-limited aggregates with a lattice spacing comparable to the radius of gyration of a single self-avoiding random walk chain. This implies that R_g is proportional to $N^{0.75}n^{0.6}$ where 0.75 and 0.6 are respectively the self-avoiding walk exponent and the size exponent[14] for small-particle diffusion-limited aggregates in 2-D. However, this is not the case as clearly shown in Figures 1 and 2. The extensive bridging and chain interpenetrations lead to more complicated networks, where chain length plays a more significant role than just setting up a scale for small-particle diffusion-limited aggregation.

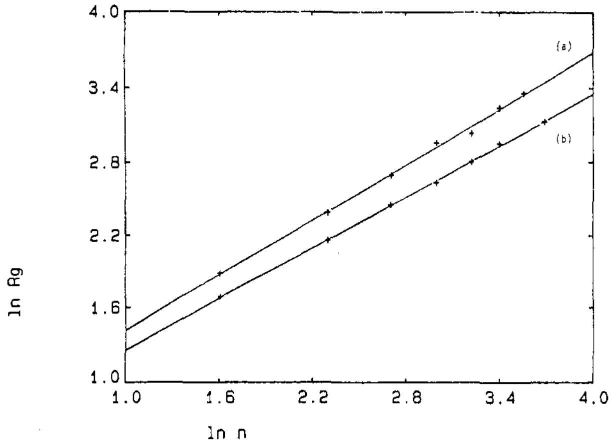

Figure 3. Natural logarithm of R_g in units of the lattice spacing plotted against ln n. The value of the slope for the dilute case, (a), is 0.755 ± 0.02, while this valuue is 0.699 ± 0.008 for the concentrated case, (b).

To quantify our observations concerning the variation in cluster size with changes in chain length, the radius of gyration of the 20-chain cluster was calculated for various chain lengths. Assuming a power law dependence, we made a log–log plot of R_g vs. n. Figure 3 shows a plot of ln R_g vs. ln n. Each value of R_g represents an average over 5 different runs for each chosen value of n (n varies from 5 to 35 in the dilute limit and from 5 to 40 in the concentrated limit). A least-squares fit of the data points gives the slope and standard deviation. The value of the slope for the dilute case, 0.755 ± 0.02, is slightly higher than in the concentrated limit (0.699 ± 0.008).

By holding the chain length constant at 10 lattice sites ($n = 10$) and varying the number of chains from 20 to 375 (350 in the dilute limit), we calculated the radius of gyration at various sizes as the cluster evolved (see Figure 4). As demonstrated in Figure 5, we find $R_g \sim N^{\alpha}$, where $\alpha = 0.424 \pm 0.015$ and 0.450 ± 0.009 for the dilute and concentrated cases, respectively. The values of R_g in Figure 5 again represent an average over five runs.

In order to formulate a model for the system, we regard our problem as the formation of a network from monodisperse polymer chains in two dimensions and apply the classical Flory theory[19,20] to understand the radius of gyration of the aggregate. Since each chain is taken to be a fully equilibrated self-avoiding random walk at every stage of aggregate growth, we can consider our cluster to resemble a solution of polymers at the overlap threshold, C^*. Furthermore, the aggregate is expected to assume a size such that its monomer concentration is proportional to the overlap concentration. the monomer concentration in our cluster is proportional to (Nn/R_g^2). The overlap concentration of self-avoiding chains in two dimensions follows as

$$C^* \sim \frac{n}{R_0^2} \sim \frac{n}{n^{3/2}} \sim n^{-1/2} \tag{1}$$

Here R_0 is the radius of gyration for a single chain with

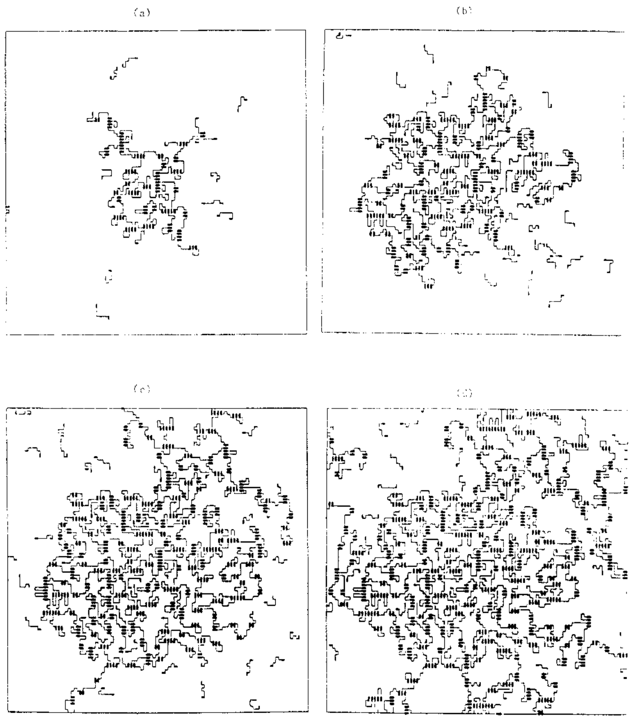

Figure 4. Chains containing 10 lattice sites. In (a), 50 chains have been incorporated into the cluster, in (b) there are 150 chains in the cluster, in (c) there are 250 chains, and in (d) there are 375 chains.

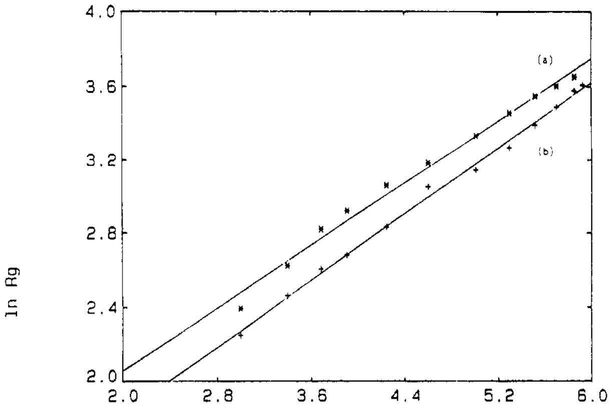

Figure 5. Natural logarithm of R_g plotted against ln N, where N is the number of chains. The slope for the dilute case, (a), is 0.424 ± 0.015, while the slope is 0.450 ± 0.009 for the concentrated case, (b).

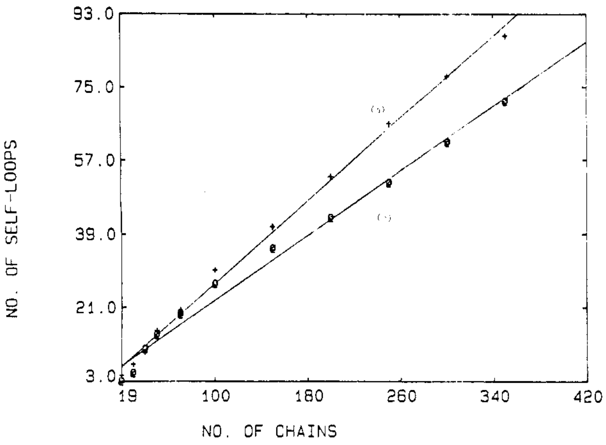

Figure 6. Number of self-loops plotted against N, the number of chains. The slope for the dilute case, (a), is slightly higher (0.253 ± 0.006) than for the concentrated case (0.198 ± 0.008), (b). Consequently, the number of self-loops for a given N is always higher in the dilute case.

self-avoiding walk statistics, and it is well-known[20] that $R_0 \sim n^{3/4}$. Therefore, the dependence of R_g on N and n is obtained from

$$\frac{Nn}{R_g^{\,2}} \sim C^* \tag{2}$$

to be

$$R_g \sim n^{3/4} N^{1/2} \tag{3}$$

As shown in Figure 3, the predicted relationship between the radius of gyration for the cluster and chain length, $R_g \sim n^{3/4}$, is supported in the dilute case. The value for this exponent is slightly lower for the concentrated case. In three dimensions, if the system were to behave like a melt, the excluded volume effect would be fully screened and $R_g \sim n^{1/2}$. In two dimensions, the chains in a melt are not quite ideal.[20] The observed exponent value of 0.699 ± 0.008 in our concentrated case falls between these two limiting values, due to partial screening of the excluded volume effect.

The observed exponent for the relationship between R_g and N (the number of chains) is slightly smaller than the predicted value of $^1/_2$ for both the dilute and concentrated cases. The smaller of the two values is observed in the dilute limit. This deviation from 0.5 can be explained by the presence of self-loops, which cause the size of the cluster to contract. As can be seen in Figure 6, for higher values of N, the number of self-loops increases linearly with the number of chains. Moreover, the number of self-loops for a given N is always higher in the dilute case. In the concentrated limit, there is a greater availability of ends belonging to another chain, while in the dilute situation, the density of such partners is less. Consequently, a chain may find its own tail before it finds one belonging to another chain. We have also observed that in the concentrated case, the number of such intra-chain interactions decreases monotonically with increasing chain length.

Finally, we note that our exponent relating R_g and N differs from that obtained from the DLA calculations on small particles.[14] Here, the radius of gyration has been shown to vary with the number of subunits to the 0.6 power. The fundamental difference between the two simulations is that in the traditional DLA, a sticker already in the cluster can only bind to a new, incoming particle. In our simulation, a partially frozen chain is free to wiggle. Since the number of new chains is small, a free end is more likely to find its own tail or the tail belonging to another partially frozen chain than it is to react with a new chain. Consequently, there is a high fraction of self-loops and bridging between partially frozen chains. This is true at every stage of cluster growth. Thus, the emerging structure is more compact than the small-particle diffusion-limited aggregate. While the structure resulting from small-particle aggregation becomes highly dendritic as the cluster grows, the compact structure in Figure 4 resembles a gel at all length scales.

The difference between these two simulations can be further appreciated by noting that if the entire chain were frozen upon its sticking with a tail already in the cluster and if a given tail could only interact with one on a new chain, a highly branched cluster would emerge, similar to the small-particle DLA structures. Conversely, if the dendritic arms seen in the traditional DLA were allowed to wiggle, the diffuse structure would collapse and become more compact.

Thus, it is the wiggling of the partially frozen chains, which in turn allows these chains to form self-loops and bind with other partially frozen chains, that makes the resulting cluster fundamentally different from that seen in small-particle DLA. This difference is reflected in the different scaling behavior.

Conclusions

We have performed a Monte Carlo simulation in two dimensions of the diffusion-limited aggregation of monodisperse associating polymer chains. The chains can aggregate only through their ends. Except for the seed chain, the dynamics of the chains have been simulated using the Verdier–Stockmayer algorithm. Each member chain is free to move until both ends of the chain are anchored to the growing aggregate. The dependence of the radius of gyration of the aggregate on the chain length and the number of chains has been investigated.

First, we demonstrate that our diffusion-limited network formation is distinctly different from the small-particle diffusion-limited aggregation. By assuming that the monomer concentration of our aggregate is comparable to the monomer concentration at the overlap threshold for a solution of two-dimensional self-avoiding chains, we have been able to correlate the radius of gyration of the cluster with the chain length and the number of chains in the aggregate. The presence of self-loops causes the cluster to contract in the size and results in a small deviation from the predicted exponent relating the radius of gyration and the number of chains.

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Physical Gelation of a Multiblock Copolymer

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ABSTRACT: The thermoreversible gelation of a multiblock copolymer made up of poly(dimethylsiloxane) blocks ("soft" segments) and poly[(dimethylsilylene)phenylene(dimethylsilylene)-1,2-ethanediyl] blocks ("hard" segments) is studied. The thermal behavior as a function of polymer concentration is investigated which allows the phase diagram to be established. This phase diagram shows the occurrence of a monotectic transition which implies that the gel formation proceeds from a liquid–liquid phase separation frozen in at its early stage by crystallization. The mechanical properties through the determination of the compression modulus E are examined. It is found that the knowledge of the phase diagram enables one to account for the variation of E with temperature. This result leads to the conclusion that gel partial melting takes place at the monotectic transition rather than the abrupt disappearance of one type of crystal. Finally, swelling experiments are interpreted by means of a model involving microfibrils instead of the usual fringed micelle model.

Introduction

Physical gels constitute a particular class of materials. Numerous investigations carried out on gels from homopolymers are now available.[1–6] Yet, as far as copolymers are concerned, only a few studies have been reported. Berghmans et al.[7] have studied statistical copolymers (poly[(ethylene terephthalate)-*co*-isophthalate]) as have Takahashi and Mandelkern et al.[8] [poly(ethylene–butadiene) and poly[ethylene–(vinyl acetate)]]. To our knowledge, no extensive study dealing with multiblock copolymers, where crystalline and amorphous sequences alternate, have been achieved hitherto. This type of copolymer possesses some interesting particularities which can provide information on gelation as a whole. For instance, beyond a certain number of sequences the copolymer behaves in a homopolymer-like fashion. Thereby, light may be thrown on gelation of atactic polymers containing some stereoregular sequences. In addition, the synthesis procedure allows the composition and the average length of both or either sequence to be varied.

The purpose of this paper is to report on the thermal analysis and the phase diagram, the mechanical properties, and the swelling behavior of an organosilicic block copolymer. This study gives a new approach to the gel melting mechanism and shows that the mechanical properties as well as the swelling behavior can be accounted

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