**Full Paper:** In recent papers we have used statistical mechanics to predict multiple phase formation in polymer liquid crystals (PLCs).[1, 2] Now we have performed molecular dynamics simulations of PLC copolymers as materials consisting of LC islands in flexible matrices. A method for creating such materials on a computer is described. The overall concentration of the LC units, island size, and spatial distribution of the islands (random, in rows, and evenly distributed throughout the material) were varied. Crack formation and propagation as a function of these parameters were investigated. The local concentration of LC units in each chain has been defined. We found that the probability of a crack initiation site goes symbiotically with the local LC concentration. The first small crack is sometimes a part of the path through which the material breaks, however, although several small cracks may evolve at first, some of these never evolve into larger cracks since crack arrest occurs. The results can be used for creation of real materials with improved mechanical properties.
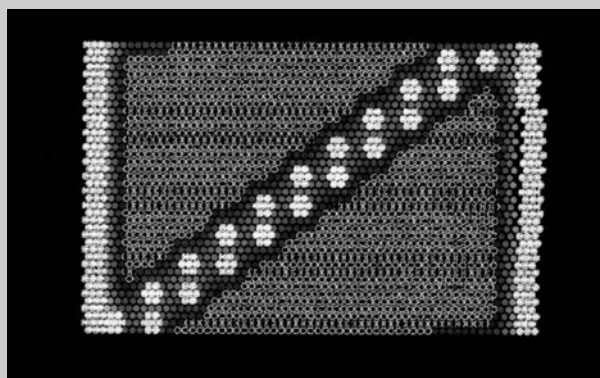
The local volume fraction description of a simulated hand-drawn PLC. The LC islands are shown as dark stars circumscribed by circles. Other shades indicate the local concentration – darker regions indicate higher concentration.

Crack Formation and Propagation in Molecular Dynamics Simulations of Polymer Liquid Crystals

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1 Introduction and Scope

Mesomorphic phases – intermediate between solids and isotropic liquids – are fascinating from a fundamental point of view. Three classes of such phases are known: liquid crystals (LCs), plastic crystals, and condis crystals, the last kind defined by Wunderlich and Grebowicz.[3] LCs are also important because of a number of current and potential applications. As discussed by Samulski, we have to distinguish between monomer liquid crystals (MLCs) and polymer liquid crystals (PLCs).[4] PLCs are significantly different from MLCs for the same reason that ethylene gas is different from polyethylene. PLCs are typically copolymers consisting of rigid (LC) sequences combined with flexible sequences. When compared to non-LC polymers, PLCs exhibit a number of advantageous properties,[5-7] including low thermal expansivity, stability at elevated temperatures (and thus large service temperature ranges), and much better mechanical properties than purely flexible polymers.

Given the complex structure of PLCs, they have been investigated by concomitant use of statistical mechanics,[8, 9] viscoelasticity,[10-12] experiments,[4-7] and only to a small extent by computer simulations, even though the latter can provide us with information that is not accessible experimentally. In particular, experiments such as scanning electron microscopy (SEM) can tell us

whether the fracture surface is brittle or ductile and thus can inform us about the morphology. However, SEM will not tell us where the original crack started, or how and by which route it propagated, eventually leading to fracture.

There are a certain number of options possible when choosing a computer simulation procedure. Öttinger has used the Brownian dynamics (BD) method and developed importance sampling to improve the efficiency,[13, 14] BD is useful for polymer solutions and has also been used by us for that purpose.[15, 16] The Monte Carlo (MC) method in combination with the Eyring chemical activation rate theory has been used by Termonia and coworkers to investigate tensile deformation of polymers such as polyethylene.[17–20] Finally, molecular dynamics simulations (MDSs) have been used in materials science in a variety of studies, including thermodynamic properties of simple fluids and polymer melts,[21, 22] melting, including that of thin layers on a substrate,[23–29] transport of fluids through a polymer membrane,[30] and comparison of the structure of simulated atactic polystyrene with X-ray results.[31] Several years ago we used MDSs to observe stress–strain behavior of PLCs,[32] and then to study stress relaxation in metals and in polymers.[33, 34] These results, obtained by others as well as by us, have shown that MDSs are convenient for dealing with solid polymers. A difficult issue faced in one method[32] was the overabundance of simulation results and the difficulty in extracting and presenting the significant findings. Progress in computer graphics,[35] including our own work aimed at PLCs,[36] have now made possible much more meaningful interpretation of simulation results.

PLCs are typically copolymers, with each chain containing flexible and relatively rigid LC sequences. SEM and wide-angle X-ray scattering tell us that the LC sequences flock together forming LC-rich islands[37]; thus we simulate systems containing two phases. Our questions on crack formation and propagation therefore become more specific: do the cracks form inside the flexible matrix because it is weak; inside the islands because these are rigid and relatively brittle; or at the interface between the two phases? What effects do the island size, spatial distribution, and overall LC unit concentration in the PLC have on the strength of such a material? The present paper reports on an attempt to answer these questions.

2 Creation of Polymers on a Computer

We have performed simulations on polymers created on a two-dimensional triangular lattice. A difficulty of the simulation procedure is creating materials that accurately capture the essential features of the real three-dimensional ones. Such a simulation was previously done for a cubic-island geometry,[32] however, this geometry is unrealistic since real LC islands have been shown to conform to spheres and ellipsoids, not cubes. Therefore, we have created PLC materials on the computer with islands as close as possible to circles and ovals, the two-dimensional analogs of spheres and ellipsoids.

Unfortunately, defining realistic materials on the computer in terms of Cartesian coordinates and momenta is not an easy task. Previously, less accurate procedures were applied to square lattices.[32] Needless to say, in a purely rectangular island configuration, LC concentrations on the square lattice are relatively easy to calculate since all chains have proportional segments. Furthermore, with purely rectangular island configurations, a small portion of the lattice could be created and then simply repeated to produce a larger representation. By contrast, in our triangular lattice with polygonal configurations, the island configuration within the lattice is far from uniform. This poses the problem of obtaining an accurate measure of LC concentration while maintaining relatively uniform distances between neighboring islands within the lattice. Also, a periodic arrangement is more difficult to implement for polygonal configurations. Necessarily, the procedures described below are more complicated. However, the results obtained are far more accurate than previous ones and show much more realistic material responses to tensile deformation – a vital feature of reliable computer simulations.

Real materials usually have rigid LC islands randomly placed in the flexible matrix, and we have developed an algorithm that allows us to create such materials. This algorithm places one rigid LC island at a time on the flexible matrix by random sequential addition. The LC islands are not permitted to overlap or touch, thus preventing the formation of more complicated clusters. To do this, the flexible segments surrounding the islands are "locked", while still labeled as flexible, as the material is built. The islands are placed until the desired LC concentration is achieved. Using this algorithm, we can create materials with 1×1, 3×3, 5×5, or 7×7 rigid LC island sizes. The numbers pertain to the edge length of the island. The maximum concentration of rigid LC units depends on the island size, and ranges from 35 to 45%. The material size is also a parameter in the program.

As seen in Figure 1, the relation between the number of rigid LC segments and the number of locked flexible segments is not linear. Larger island sizes have fewer locked flexible segments per rigid LC segment, which means higher concentrations can be achieved for larger island sizes.

The hexagonal shape of the islands represents a geometry as close as possible to circles. Obviously, this is a problem with smaller island sizes, but as the island size increases, the islands become a more accurate representation of the desired geometry.

The material size is also an issue. If we work with small sizes, it is not possible to obtain exactly any specified concentration; the islands have a constant size and
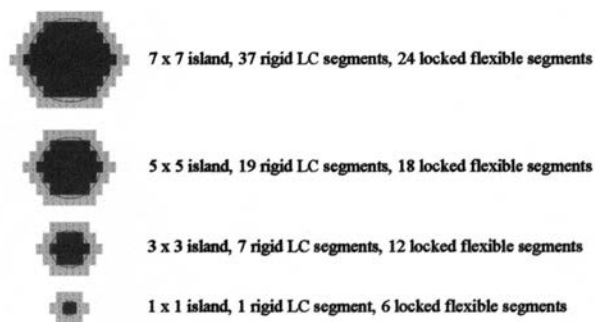
Figure 1. Rigid islands of different sizes. The dark blocks represent rigid LC segments and the light blocks represent the positions locked as flexible segments when the island is placed on the matrix.

we cannot use "partial" islands to try to match the concentrations. This problem diminishes when we use larger material sizes, but that also slows down the simulation procedure. In order to solve this problem, we analyze all results using the exact concentration of each material, which may or not be the desired one (for instance we may have a concentration of LC segments of 14.95% instead of the desired 15.00%).

Hand-drawn (as opposed to randomly constructed) materials (which we shall show later in Section 6) were also used in our simulations for several reasons. Some were chosen in such a way as to represent the alignment of the LC islands that takes place in real materials during processing, others were designed to study the behavior of specific island distributions.

3 Characterization of Computer-Generated Materials

While the local concentration of LC islands is macroscopically constant, it fluctuates on a local level. Such fluctuations have been shown to be relevant to a number of problems, including scattering by heterogeneous media,[38] transport through composites and porous media,[39] the study of noise and granularity of photographic images,[40−42] and the properties of organic coatings.[43] Furthermore, it has been suggested that these fluctuations influence the failure of composite materials,[44] including borosilicate glasses,[45, 46] and unidirectional composites.[47, 48]

Before investigating the failure of simulated polymers, we first quantitatively characterize these local concentration changes. Lu and Torquato defined the local volume fraction,[49] or local concentration, within an observation window υ in an arbitrary two-phase random medium that is statistically invariant under translation. The definition of the local concentration (ξ) is

$$\xi = (I(z) \cdot \theta(z) \cdot dz)/V \qquad (1)$$

where V is the volume of υ and $\theta(z)$ is the indicator function for υ

$$\theta(z) = \begin{cases} 1, & z \in \upsilon \\ 0, & \text{otherwise} \end{cases} \qquad (2)$$

In our case, I is the indicator function for the LC islands. In the limit of a very small observation window, ξ simply reduces to the indicator function I. On the other hand, as the window becomes very large, ξ will approach the macroscopic concentration level of LC islands.

For random media, the standard deviation and higher moments of ξ have been characterized.[49, 50] In related work, the full cumulative distribution function of ξ for various continuum (off-lattice) and periodic models of random media was investigated.[50, 51]

In Section 6 we shall show how the local concentration can be used as a predictor for crack propagation in PLCs.

4 Performance of Simulations

The procedure we use in performing the MDSs has been described in some detail in earlier papers.[33, 34, 36] This procedure has been used, among other things, to simulate stress relaxation in metals as well as in flexible one-phase polymers.[34] We also need to note that LC + LC interactions are represented by a fairly steep and narrow interaction potential well. The interactions between neighboring flexible units on the same chain are represented by a double well potential, which allows transitions from *cis* (short) to *trans* (long) conformations – in the same way they occur in real carbonic chains. The first simulations of PLCs subjected to mechanical forces have been reported by Blonski and Brostow.[32] As already noted, MDSs in general provide a wealth of information and extraction of that information has been a problem for some time. Only recently we have developed or adapted some animation techniques for meaningful representation of MDSs results.[36]

Moreover, earlier work was limited to materials consisting of 30 chains, each containing 50 segments. In the present work we have also developed larger materials and studied the effects of the system size. Materials consisting of 50 chains containing 80 segments each, and materials consisting of 70 chains containing 100 segments each have now been studied. These three different sizes correspond to systems of 1500, 4000 and 7000 segments, respectively. For these larger systems we have also studied the effects of island size, using islands of 3×3, 5×5, and 7×7, as in the smaller materials.

5 Crack Formation

One important aspect of the cracking phenomena is the appearance of the first few broken bonds. It is important
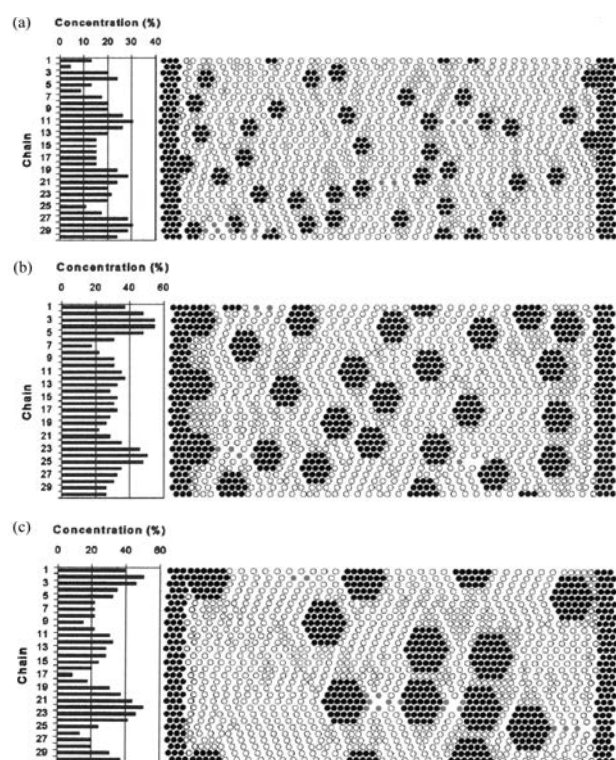
Figure 2.   a) Distribution of the LC concentration along chains for a 30 × 46 material with 3 × 3 islands. The macroscopic LC concentration of this material is 20%. Dark circles represent rigid segments, white circles represent flexible segments and gray circles represent segments between which the bond was broken. Broken bonds appear in chains 11, 21, 28 and 29. b) Distribution of the LC concentration along chains for a 30 × 46 material with 5 × 5 islands. The macroscopic LC concentration of this material is 35%. Broken bonds appear in chains 1, 3, 5, 23, 24 and 25. c) Distribution of the LC concentration along chains for a 30 × 46 material with 7 × 7 islands. The macroscopic LC concentration of this material is 30%. Broken bonds appear in chains 2, 20, 21, 22, and 25.

to locate the expected loci within the material where the broken bonds first appear, since these may evolve into small cracks, later causing failure of the material. We have observed that in some cases the first small crack is a part of the path through which the material breaks. In some other cases, several small cracks evolve at first, but then some of these never evolve into larger cracks since crack arrest occurs.

To pinpoint the location of the first broken bonds, the concentration of rigid LC segments has been calculated for each individual chain. We have observed that this concentration is, in most cases, directly related to the location of the first broken bonds. In order to predict those locations, we look at the LC concentration vs. chain number graphics, Figure 2. We find that chains with a LC unit concentration much higher than in the surrounding chains are likely locations for the appearance of the first broken bonds. When the placement of the islands in the material is a random process, some materials exhibit

approximately uniform distribution of the concentration of LC rigid segments along the chains, while some others have some local concentration maxima surrounded by chains with much lower LC unit concentration. In most cases, only certain chains will have the local maxima we have described. We have observed that this happens most often for larger island sizes and relatively low concentrations. However, in cases where that distribution tends to be relatively uniform, the probability of the appearance of the first broken bonds is similar for all the chains; in this case, this method will provide little help in predicting the location of the first broken bonds.

Another important characterization of initial crack formation is the location of the broken bonds inside a given chain. Again we can extract this information from our simulations. We have observed that the first broken bonds usually appear between islands separated by one, two, or three flexible segments. If the minimal distance between islands turns out to be much larger than that, the broken bonds will appear elsewhere between islands closer to one another.

For smaller systems it was previously observed that the deformation process starts by a conformational change of the bonds.[32] After all the bonds underwent the change from the *cis* to the *trans* conformation, broken bonds began to appear. Small cracks then started to form, and after some time, failure of the material would occur. We have observed that for larger systems broken bonds start to form even before the conformational transition is complete. In some cases, the number of those broken bonds is such that some small cracks develop in the material. This effect is more noticeable as the size of the material increases. We have also observed that the conformational changes occur starting from the edges and moving towards the center of the material. In large materials, this usually means we shall observe small cracks closer to the edges of the material while in the center we still observe bonds that have retained their initial short *cis* conformation.

6 Crack Propagation

We now consider the problem of predicting the behavior of the cracks that propagate as the simulated polymer is stretched. As discussed in more detail below, we find that the cracks tend to propagate through the flexible bonds that have many rigid bonds nearby. This informal description can be made more precise by using the local concentration defined in Section 3 as the concentration of rigid bonds in a small observation window within the material. In the current context of LC islands on the triangular lattice, we choose observation windows that are centered on flexible segments, and we specify that the window is a 5 × 5 hexagon or a 7 × 7 hexagon. The shapes of such observation windows are shown as dark
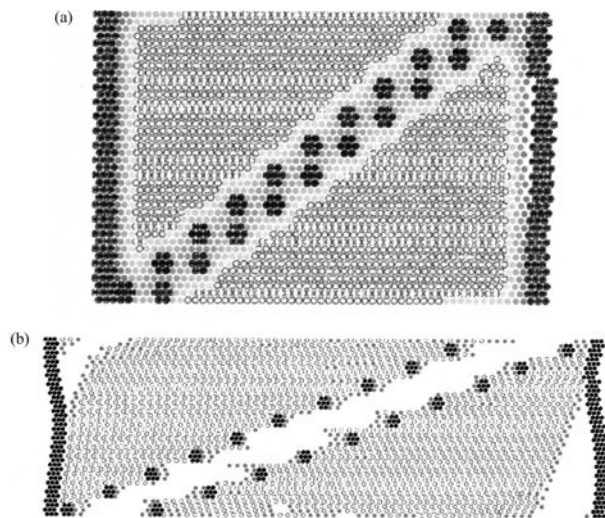
Figure 3. a) The local volume fraction description of a simulated hand-drawn PLC. The LC islands are shown as dark stars circumscribed by circles. Other shades indicate the local concentration – darker regions indicate higher concentration. b) The final step of the simulation at which fracture has been observed. Dark circles represent rigid segments, white circles represent flexible segments and gray circles represent segments between which the bond was broken.

regions in Figure 3. Before beginning the crack-propagation simulations, the concentrations of rigid segments within these observation windows are computed. For example, when 5×5 hexagonal windows are used, the local concentration must be an integer divided by 19.

Several figures shown in the present Section display local concentration information. In these Figures, bonds around which the local concentration of LC islands is larger than the macroscopic concentration are shown in shades of gray; darker shades of gray correspond to higher local concentrations. However, for the sake of clarity, we have not shaded flexible segments in regions where the local concentration is lower than the macroscopic concentration.

In Figure 3, as a test case, we show a hand-drawn polymer with a string of LC islands along the diagonal. Naturally, the flexible bonds surrounded by the highest local LC concentration occur between the islands. As the polymer is stretched, the crack forms also between the islands; this of course would be expected on physical grounds. Therefore, in this particular case, the crack ultimately forms in the portion of the flexible phase where the local LC unit concentration is the highest.

The same behavior occurs in randomly constructed LC structures. In Figure 4 and 5 we show two different random polymers at two different macroscopic concentration levels. In parts (a) of these figures the polymer is shown with the local concentration shading convention while part (b) shows the final step of the simulation at which fracture has been observed. In part (c), the locations of the cracks are superimposed onto the local concentration
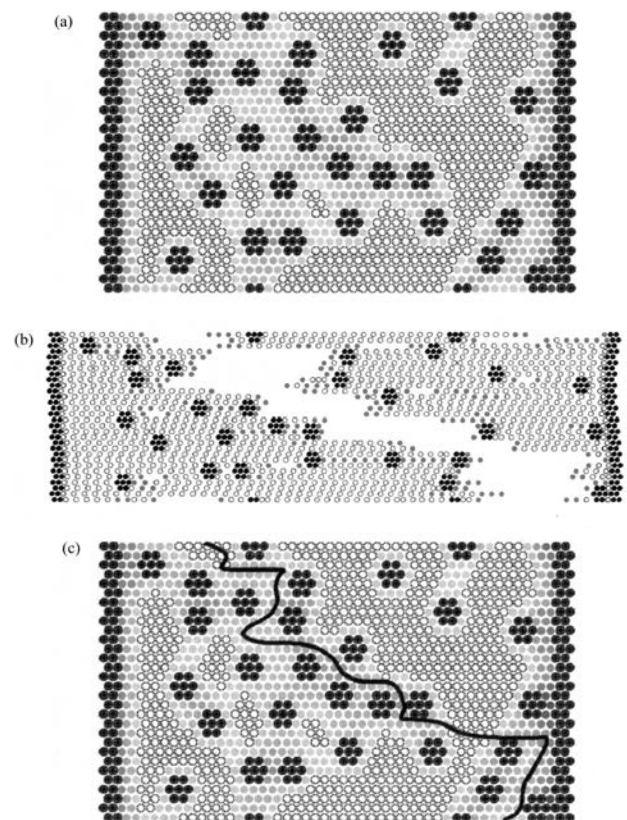

Figure 4. a) The local volume fraction description of a simulated PLC. The LC islands are shown as dark stars circumscribed by circles. Other shades indicate the local concentration – darker regions indicate higher concentration. b) The final step of the simulation at which fracture has been observed. Dark circles represent rigid segments, white circles represent flexible segments and gray circles represent segments between which the bond was broken. c) The local volume fraction description of a simulated PLC with the locations of the cracks formed during the simulation superimposed on it.

description. We see that the crack ultimately joins regions of high local LC concentration. However, on some occasions the crack may propagate through regions of low LC concentration – if such a path efficiently joins regions with high local LC concentration. One can become proficient at predicting where major cracks will ultimately form based on the local concentration information. We also see that, in rows in which we do not have exceptionally high local LC concentration, the cracks may appear along the boundary.

We have also investigated effects of the island size on crack propagation. The same behavior is seen for 5×5 and 7×7 LC islands. Moreover, the same behavior was observed for larger materials, as shown in Figure 5.

7 Concluding Remarks

On starting this work, we could have equally well expected that crack propagation begins in the flexible matrix or in the rigid LC islands. Now answers to the
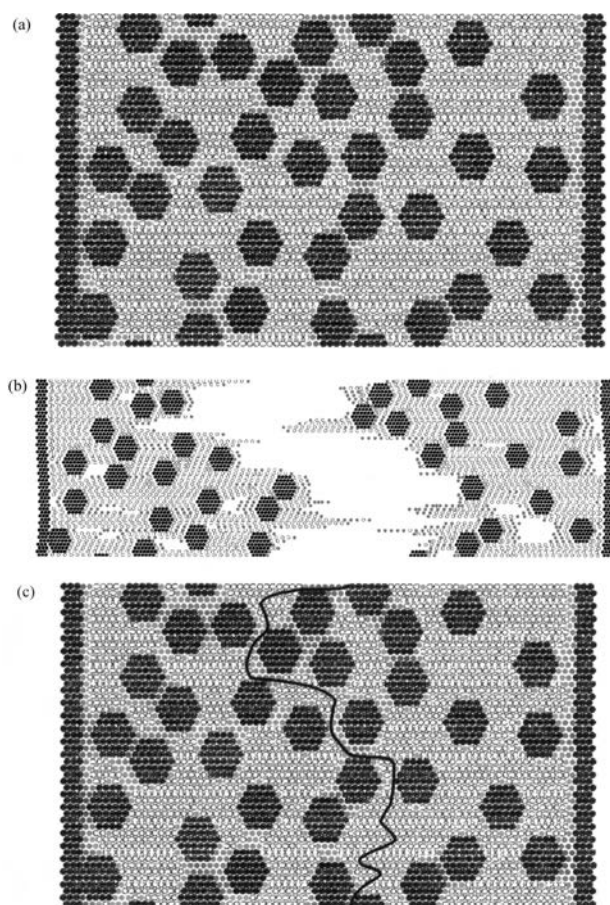
Figure 5. a) The local volume fraction description of a simulated PLC. The LC islands are shown as dark stars circumscribed by circles. Other shades indicate the local concentration – darker regions indicate higher concentration. b) The final step of the simulation at which fracture has been observed. Dark circles represent rigid segments, white circles represent flexible segments and gray circles represent segments between which the bond was broken. c) The local volume fraction description of a simulated PLC with the locations of the cracks formed during the simulation superimposed on it.

questions posed in the introduction begin to emerge. While LC-rich islands reinforce the material, their high local concentration facilitates the crack formation. We have defined a useful measure of that local concentration.

We have observed that the first cracks might become a part of the path through which the material breaks, but may also never evolve into larger cracks. We found that chains with an LC unit concentration much higher than in the surrounding chains are likely locations for the appearance of the first broken bonds. Also, we have observed that cracks form between islands or at the boundary, since these are high local LC concentration regions. The cracks ultimately join regions of high local LC concentration. As noted above, we have also seen occasions when a crack propagates through regions of low LC concentration provided that such a path efficiently joins regions with high local LC concentration. Given the several variables involved, further work will be useful. It is already clear that the spatial distribution of LC islands is more important than the overall concentration of the LC units in the polymer.

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