

# Heuristic Search for the Polymer Straightening Problem

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A simplified rotational isomeric state model of aromatic polymers was explored. "Straight" conformations (ones for which the end bonds of a repeat unit align) were identified using a tabu search procedure. The optimization method was tested with three polyimides and shown to be effective in locating the vicinity of the global optimum.

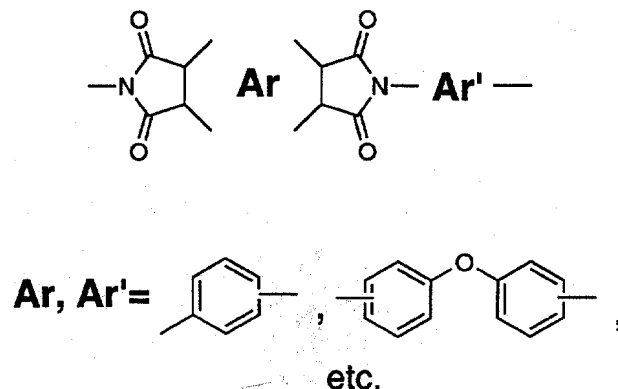
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## INTRODUCTION

Molecular chemistry contains many difficult optimization problems that have begun to attract the attention of the optimization community. Problems such as protein folding,<sup>1</sup> molecular conformation,<sup>2</sup> molecular similarity,<sup>3</sup> and molecular matching<sup>4,5</sup> have been studied. Minimum energy conformations for simple molecular structures such as water clusters, Lennard-Jones microclusters, and short polypeptides have dominated the optimization literature to date. Here, we introduce a new combinatorial optimization problem that we call the polymer straightening problem (PSP).

One of the major divisions among synthetic polymers is between amorphous and crystallizable structures. In particular, we are interested in the crystallization of high-performance aromatic polyimides.<sup>6</sup> These molecules consist of rigid aromatic rings connected to "hinge" groups by single bonds (Figure 1). X-ray data indicate that in some cases the backbone in such materials may adopt a zig-zag<sup>7,8</sup> or helical<sup>9</sup> structure. More generally, we assume that in order for a polymer repeat unit to correspond to a crystallographic repeat, the first and last bonds in the repeat unit must line up. In other words, the backbone must enter and leave the unit cell in the same direction. This is probably not a sufficient condition for crystallizability, but it provides a useful starting point.

The crux of our research, then, is to determine a priori if there exists a conformation for which a given



**Figure 1.** Generic polyimide structure with representative aromatic groups. *Ar* and *Ar'* might be benzene, diphenyl ether, benzophenone, or other aromatic groups.

polyimide may crystallize. To further simplify the model, bond angles and lengths will be regarded as fixed and each backbone torsion will be limited to discrete rotational isomeric states, corresponding to the potential minima for the bond rotations in an isolated chain. This simplification is justified by the observation that these rotational positions are usually preferred in published polymer crystal structures — the requirements for crystalline packing generally do not seem to override the single-chain energetics. Bond lengths, bond angles, and locations of torsional minima were taken from the literature.<sup>10-12</sup> The role of the optimizer is to determine if a straight line con-

formation for a given polyimide exists among all possible combinations of allowable (minimum energy) torsion angles for the rotatable bonds. The total number of combinations may be quite large. For example, a polyimide with ten bonds, each with eight allowable torsion angles, would have 100 million combinations.

### MATHEMATICAL FORMULATION OF PSP

For each polyimide assume there are  $B$  virtual bonds. The joints between the bonds are characterized by bond angles  $\pi - \theta_i$ , for  $i = 1, \dots, B$ . In addition, associated with each bond is a set  $\{\phi_i\}$  of torsion angles, with the  $\phi$ 's measured relative to  $\phi = 0$  in the *trans* arrangement.<sup>13</sup> Each chain conformation is given by a set of  $B$  two-tuples (one for each bond) consisting of the supplement of the bond angle and a torsion angle. Next, we require a measure that differentiates between conformations that are straight and those that are not. We use bond-centered Cartesian coordinate systems, or frames of reference, to look down the repeat unit of a polyimide and project the last bond onto the coordinate system defined by the first bond.<sup>13</sup> In order to perform the coordinate transformation, an orthogonal matrix  $T_i$  is used to transform the frame of reference for bond  $i + 1$  to the frame of reference for bond  $i$ .

$$T_i = \begin{pmatrix} \cos(\theta)_i & \sin(\theta)_i & 0 \\ \sin(\theta)_i \cos(\phi)_i & -\cos(\theta)_i \cos(\phi)_i & \sin(\theta)_i \\ \sin(\theta)_i \sin(\phi)_i & -\cos(\theta)_i \sin(\phi)_i & \cos(\phi)_i \end{pmatrix}$$

If we let  $v_B = (1, 0, 0)^T$  and successively pre multiply  $v_B$  by each of the  $T_i$  for  $i = B - 1, \dots, 1$  the result is that the  $B$ -th bond is projected on the frame of reference of the first bond in the repeat unit. That is,  $A = T_1 \dots T_{B-2} \cdot T_{B-1} \cdot v_B$  is the projection of the  $B$ -th bond onto the coordinate system of the first bond. Computing the dot product of  $A$  with the vector of unit length lying along the first bond yields the cosine of the angle between these two bonds. If this number is close to one, we consider the given conformation to be straight. Our optimization problem then is to find a conformation — a set of  $B$  two-tuples  $(\theta_i, \phi_i)$  — that maximizes the cosine of the projection of the  $B$ -th bond onto the first bond.

### TABU SEARCH HEURISTIC

Metaheuristics such as tabu search (TS) provide a shell within which a variety of other heuristics may be implemented. The definitions and notations that follow are taken from Glover<sup>14,15</sup> and Kincaid and Berger.<sup>16</sup> Let  $\Sigma$  denote the union of the sets of allowable torsion angle assignments and  $|\Sigma|$  denote the number of elements in this set. For each of the  $B$  bonds there are  $|U_i|$  torsion angles. Thus,  $|\Sigma| = \prod_{i=1}^B |U_i|$ . We call  $\Sigma$  the state space and let  $S$  denote an element of  $\Sigma$ . To differentiate between states we define a criterion function  $c: \Sigma \rightarrow [-1, 1]$ . For PSP

$c(S)$  measures the cosine of the angle between the first bond and the projection of the last bond onto the first bond coordinate system. We seek to maximize this value (a value of one for the cosine would correspond to zero degrees). To proceed from one state to another, we define a move set  $\Delta$ . A move  $\delta \in \Delta$  is a function from  $\Sigma \rightarrow \Sigma$ . For our purposes, the set of moves for any state  $S \in \Sigma$  are all possible interchanges of one torsion angle in the set  $U_i$  for another, for all  $i = 1, \dots, B$ . The outcome of applying all moves  $\delta \in \Delta$  to a state  $S \in \Sigma$  is the set of all states reachable from  $S$ . This is typically called the neighborhood of  $S$ . The *value* of a move is the difference between the objective function values after and before the move,  $c[\delta(S)] - c(S)$ . If this difference is positive, the move provides an improved solution (since our objective function is a maximization). The basic solution approach for Tabu Search (TS) consists of a *construction* phase that generates a starting solution and an *improvement* phase that seeks to iteratively improve upon the starting solution. After *max\_it* iterations of the improvement phase we do one of the following; *intensify* the search by restarting the improvement phase at the current best solution; or *diversify* the search by restarting the improvement phase in an unexplored region of the solution space; or stop and display the best solution found.

TS begins with an initial state  $S_0 \in \Sigma$  that is either chosen at random or constructed algorithmically. For PSP, random solutions are easily generated by selecting one of the allowable torsion angles for each of the rotatable bonds. The improvement phase is a greedy local improvement scheme. That is, TS generates a sequence of moves  $\delta_0, \delta_1, \dots$  which determines a sequence of states through which the search moves. We select a move  $\delta_i$  from among all possible choices of torsion angles for each bond that satisfies  $c[\delta_i(S'_i)] = \max_{\delta \in \Delta(S_i)} c[\delta(S_i)]$ . We repeat this process until there are no more local changes available that lead to an improved solution. Hence, the final state  $S_f$  is a local optimum with respect to  $\Delta(S_f)$ . Tabu search attempts to avoid entrapment in local optima by keeping a list of previously selected moves and deleting them from the move set  $\Delta$  for a state  $S$  in the hope of avoiding a return to a previously observed state. We use a three-dimensional short-term memory list, where the attribute of a move is the triple  $(i, j, k)$ . The indices  $j$  and  $k$  denote the torsion angles interchanged for bond  $i$ . That is, torsion angle  $j$  is replaced by torsion angle  $k$  for bond  $i$ . A list of move attributes  $(i, j, k)$  of length *tabu size*, called a *tabu list* is constructed and updated during each iteration of the improvement phase of TS. An admissible move in TS is one that is either not on the tabu list or one that meets an aspiration level criterion. The *best admissible move* is one that yields the greatest improvement or the least degradation in the objective function value. The best admissible move,  $(i, j, k)$ , is appended to the tabu list at the end of each of *max\_it* repetitions of the improvement scheme. Once the tabu list becomes full, which occurs after *tabu size* repetitions of the improve-

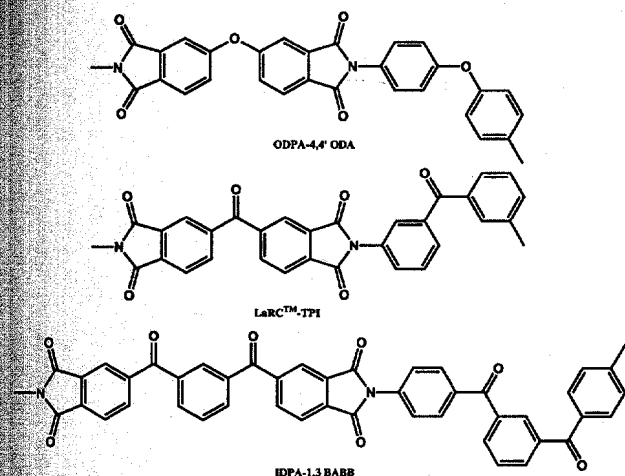


Figure 2. Chemical structures of test polyimides.

ment scheme, the "oldest" move, that is, the one that was at the head of the circular array, is removed. Thus, if  $\tau$  denotes the tabu list of moves, then within each repetition of the improvement scheme, moves are selected from  $\Delta(S) - \tau$ .

It is possible for a move on the tabu list to be selected provided that it meets one (or more) aspiration level criterion. The purpose of an aspiration level criterion is to choose "good" moves by allowing the tabu status of a move to be overridden if the move satisfies a particular condition. The goal is to do this in a manner that retains the search's ability to avoid returning to a previously generated state (typically referred to as cycling). If  $\delta \in \tau \subseteq \Delta(S)$  and  $c[\delta(S)] > c_{\text{best}}$ , then  $\delta$  is admissible. The tabu status is overridden, because the move is said to meet the aspiration level criterion. Cycling is avoided here, since if  $\delta(S)$  had appeared previously, then  $c[\delta(S)] > c_{\text{best}}$  would not be possible. This aspiration criterion, although easy to implement, treats all states with the same objective function value identically. A pseudocode outline of the method is given in the Appendix.

## RESULTS AND DISCUSSION

We tested our TS search code on the three polyimides shown in Figure 2. ODPA/4,4'-ODA, the polyimide from oxydiphthalic anhydride and 4,4'-oxydianiline<sup>17</sup> has four virtual bonds which are joined at the oxygen atoms and the centers of the phthalimide benzene rings; LaRC™-TPI, the polyimide from benzophenone tetracarboxylic dianhydride and 3,3'-diaminobenzophenone<sup>18</sup> has six links; and IDPA/1,3-BABB, which is prepared from 4,4'-isophthaloyl diphthalic dianhydride and 1,3-bis-(aminobenzoyl) benzene<sup>19</sup> has eight.

For the ODPA/4,4'-ODA polymer we assumed

$$\theta = (30, 61, 30, 61),$$

$$\phi_1 = \phi_2 = (\pm 40, \pm 140),$$

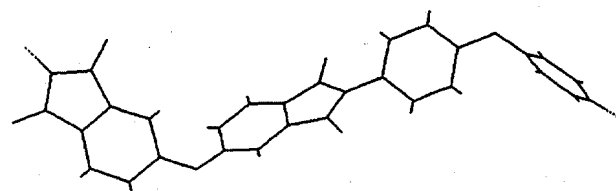


Figure 3. Two-dimensional projection of optimum conformation of ODPA/ODA.

and

$$\phi_3 = (\pm 112, \pm 168, \pm 12, \pm 68).$$

The latter set arises as the sum of (independent) rotations about the para bonds on one ring of the ODA moiety. Unlike the torsional potentials in aliphatic polymers, which typically have *trans* and *gauche* states of different energy, the potential for rotation of an unsubstituted or symmetrically substituted benzene ring about the bond connecting it to a neighboring atom has minima of equal energy. In posing the problem as we have, we are implicitly giving equal weight to each possible conformation.

The *neighborhood* of a particular conformation is found by generating all possible combinations of two-tuples by replacing exactly one of the torsion angles. For ODPA/4,4'-ODA each conformation has 13 neighbors. The size of our state space  $\Sigma$  for ODPA/4,4'-ODA is only  $4 \cdot 8 \cdot 4 = 128$ ; hence we can easily verify the optimal solution by completely enumerating  $\Sigma$ . This will not be possible for larger problems. Other validation procedures may be needed since there is no guarantee that tabu search will always produce the best possible choice of the torsion angles. By checking all combinations of torsion angles the following combination was found to be optimal:  $[\phi] = (0, -140, 40, 112)$ . Note that rotation  $\phi_1$  does not affect the angle between the first and last bonds and may therefore be set to zero. Examining the form of the transformation matrix  $T_1$  confirms this.

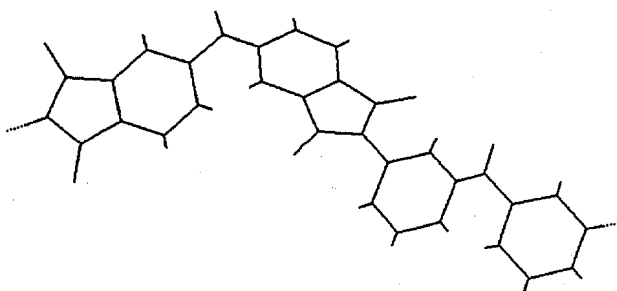
The same optimum was also found by tabu search. In fact, a tabu search was not even needed; a simple greedy local search scheme would suffice. This was the easiest problem, in that there appears to be only one local optimum. The solution, shown in Figure 3, corresponds to an arrangement of bonds that is about 10 degrees off-line. It is interesting to note that this polymer is said to be difficult to crystallize.<sup>20</sup>

For the LaRC-TPI polymer with six links

$$\theta = (30, 63, 30, 60, 63, 60),$$

$$\phi_2 = \phi_3 = \phi_5 = \phi_6 = (\pm 30, \pm 150),$$

and



**Figure 4.** Two-dimensional view of optimum conformation of LaRC™-TPI.

$$\phi_4 = (\pm 28, \pm 152).$$

By checking all combinations of torsion angles the following combination was found to be optimal:  $\phi = (0, -30, 150, 28, 30, -30)$ . Note again that  $\phi_1$  is always zero: it could take on any value. This conformation puts the first and last bonds about 3.5 degrees off-line.

The same arrangement, shown in Figure 4, was found by tabu search as well. This problem needed both the short term memory (tabu list) and aspiration criteria to escape local optima. There are eight solutions with a value of 7 degrees or less. The optimal solution was found by tabu search on the twentieth iteration. Thirty-six tabu moves were uncovered and the aspiration criterion was invoked twice. That is, twice a tabu move was allowed because it had a superior objective function value.

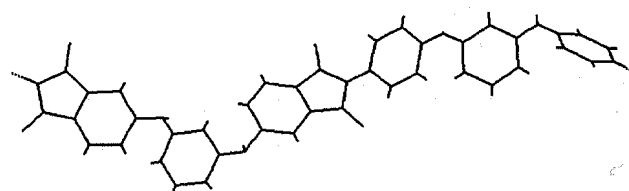
For the IDPA/1,3--BABB polymer with eight links

$$\theta = (30, 63, 60, 63, 30, 63, 60, 63),$$

$$\phi_2 \text{ through } \phi_8 = (\pm 30, \pm 150) \text{ except for,}$$

$$\phi_3 = (\pm 12, \pm 68, \pm 112, \pm 168).$$

By checking all combinations of torsion angles the following combination was found to be optimal:  $\phi = (0, -30, 30, 150, 30, 168, 30, 30)$ . This solution corresponds to an arrangement that is about 1 degree off-line. The best tabu search solution was about 1.34 degrees away from colinearity. There are 20 solutions with objective values of 2.5 degrees or less. Both the tabu list and aspiration criteria were needed to generate the 1.34 degree solution. More sophisticated tabu search techniques (recency based diversification and frequency based diversification) could be added to attempt to uncover the optimal solution. The difficulty appears to be the large number of solutions with nearly the same objective function value. Interestingly, similar molecules containing several ketone linkages are known to exhibit crystal polymorphism, perhaps as a result of the large number of accessible conformations. The optimum-straightness solution, shown in Figure 5, actually requires some serious atomic overlaps. These are permitted by our scheme because the torsions



**Figure 5.** View of optimum conformation of IDPA/BABB.

were assumed to be independent. More complicated rotational isomeric models incorporating conditional statistics could prevent these overlaps, but it was thought to be preferable to include them in the search.

For the above examples we have cheated a bit in using TS for determining whether or not a particular polyimide has a conformation that is straight. That is, we were able to enumerate all possible conformations and verify the quality of the solutions found by TS. For larger problems this will not be possible and other techniques for determining the quality of the best solutions will be required. Of course, if the best solutions are nearly straight ( $0^\circ$ ) then we would be done. However, in cases where TS does not find a nearly straight conformation we would like to know with certainty that there does not exist any conformation that is straight. With TS we cannot guarantee that this is so.

## ACKNOWLEDGMENTS

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## APPENDIX

### I. Pseudocode for tabu search heuristic

Inputs:  $S_1 = [(\theta_1, \phi_1), \dots, (\theta_B, \phi_B)]$  an initial conformation;  $T_j$  the set of allowable torsion angles for each  $\phi_j, j = 1, \dots, B$ ;  $max\_it$  the maximum number of iterations.

```

cbest = c(S1)
do i = 1, max_it
  Δcbest = -∞
  do j = 1, B
    do k = 1, |Tj|
      swap Tj,k with φj yielding S̄i
      compute Δc = c(S̄i) - c(Si)
      if (Δc > Δcbest) then
        check tabu status of swap
        if (swap tabu) then
          check aspiration criteria
          if [c(S̄i) > cbest] then
            make swap permanent
            Si = S̄i
            Δcbest = Δc
          else
            swap not allowed
        endif
      endif
    endif
  endif
endif

```

```

else
  make swap permanent
   $S_i = \bar{S}_i$ 
   $\Delta c_{best} = \Delta c$ 
endif
endif
end do
end do
update tabu list with best swap
if [ $c(S_i) > c_{best}$ ] then
   $c_{best} = c(S_i)$ 
endif
end do

```

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