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Crystallization of Stretched Polyimides: A Structure-Property Study

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Introduction

All-aromatic polyimides[1], the subject of this report, belong to a class of polymers containing "long bonds". The backbones contain rigid links connected by various "hinge" atoms. In the absence of hinges, the all-para-linked molecules are rodlike and they pack in parallel fashion.[2] In the commercially-important Kapton™ polyimide prepared from PMDA-ODA (pyromellitic dianhydride/4,4'-oxydianiline), the repeat unit contains a single hinge. The molecules spontaneously adopt some degree of order under the usual processing conditions,[3] but that order is usually described as smectic-like.[4,5,6] More complicated polyimide chain architectures can easily be designed, and a handful of these crystallize spontaneously with thermal treatments.[7-10] Other polyimides are nominally amorphous as synthesized, but they can be induced to crystallize by uniaxial stretching[9-12] or zone-drawing.[13]

Crystallization of polymers leads to improved strength, stiffness, solvent resistance and barrier properties. Increases of several hundred percent in the modulus and strength are typical.[14] It is of interest, therefore, to identify likely candidates for orientation-induced crystallization. In the following, crystallizability data on nineteen aromatic polyimides are related to simple molecular models of stretched chains.

Experimental Data

In Reference 14, a variety of polyimides with ether, carbonyl, and hexafluoroisopropylidene connecting groups were subjected to gradual heating under constant uniaxial load. This experiment is sometimes known as thermal deformation analysis (TDA) and has been used to obtain a first approximation to suitable conditions for fiber drawing.[12]

The TDA behavior of each polyimide film could be assigned to one of three classes as follows. In members of Class I, the curve of elongation vs. temperature was sigmoidal, with a well-defined plateau at high temperatures. Since the polymer is well above its glass transition at these temperatures, we infer that in the plateau, crystallites have formed effective crosslinks and that these limit the strain. Class II polymers have strain-temperature curves that begin to level off at high temperatures, but fracture occurs before a plateau is established. In this case, crystallization may be slow relative to the temperature ramp rate or the nascent crystals may be low-melting. The third class will be made up of those polymers which stretch steadily until they break, giving no evidence of strain-induced crystallization. An example of each type of TDA curve is shown in Figure 1. Monomer acronyms are defined in Table 1 and the 19 materials studied are listed in Table 2. Material 6 did not stretch measureably in the TDA experiment.

Models

Two simple molecular mechanics approaches were used in this work. First, an exhaustive search was conducted using a rotational isomeric state (RIS) approximation[15] with independent rotations. Bond angles and preferred torsion angles for the various hinge groups are given in Table 3. Each torsional potential was assumed to have four symmetrically-located minima of equal energy. For example, the phenyl ring adjacent to an ether oxygen in either a dianhydride or a diamine residue would prefer dihedrals of 40, -40, 140, and –140° relative to the C-O-C plane. In the cases where a para-linked phenyl group was joined to a phthalimide ring, all possible net rotations (sum and difference of the two joined torsion angles) were considered (see Figure 2). Table 4 summarizes the number of independent torsions for each model and the total numbers of conformations enumerated.

The second approach used molecular mechanics under the Cerius2™ environment (MSI Inc./Accelrys). Unconstrained minimizations on model compounds demonstrated that MSI's Universal force field gave equilibrium torsion angles in agreement with those in Table 3. For each polyimide, a single repeat unit was built. A terminal phenyl group represented the bond to the next repeat as shown in Figure 3. A restraint on the end-to-end distance of the repeat unit was imposed by means of an energy term that mimicked a spring with an arbitrarily-chosen stiffness of 10^3 kcal/mol/$Å^2$. A brief period of molecular dynamics (3 ps at 500 K) allowed torsional transitions in response to the restraint. With the restraint still in place, the energy was then minimized using a conjugate gradient technique.

Results and Discussion

The purpose of this work was to attempt to uncover molecular descriptors that correlate with stretch-crystallization. The crystallization process itself was not modeled. Rather, configurations of the 19 benchmark materials were examined in a search for trends.

Sample results from the RIS conformational search on a single molecule (ODPA/4,4'ODA) are plotted in Figure 4. Each conformation was characterized by the end-to-end distance of the repeat unit and by the angle between the initial bonds of successive repeats. The motivation for the latter choice is that in a crystal, the chain must pass continuously from one unit cell to the next; i.e. the chain must enter and leave the unit cell in the same direction. If the unit cell is one repeat unit high, this imposes a requirement that the starting bonds of successive repeat units have to align. Although alignment of the end bonds is clearly not a sufficient condition for a conformation to be crystallizable,[15] it is a useful starting point, as will be seen.

For the polymer used in the example shown in Figure 4, the misalignment angles for various conformations vary from as small as 8.4 degrees to as large as 170 degrees. It should be emphasized that each and every one of the RIS-generated conformations has the same energy. Due to the symmetry of the torsional potentials, many configurations are degenerate, but the redundancy does no harm.

Next the side-by-side packing of the chains in a polymer crystalline unit cell is considered. "Folded" chain configurations (ones that contain hairpin turns or large-scale loops) probably cannot efficiently fill space in the directions transverse to the overall chain direction.[6,19] We therefore adopt a fairly simple idea: we focus on conformations that are nearly fully-extended. Conformations with lengths closest to the maximum allowed end-to-end distance (subject to the RIS bond angle and torsion constraints) are regarded as the straightest and hence potentially the easiest to pack. The ratio of the end-to-end distance for a given configuration to the maximum attainable end-to-end distance will be called the degree of extension, ξ.

There are thus now two criteria to satisfy: (1) small misalignment of end bonds and (2) "extended" chain configuration. Although both these parameters are hypothesized to be related to crystallization, their relative importances are *a priori* unknown. Patterns are thus sought in the observed propensities to crystallize among our 19 polyimides (as summarized in the last column of Table 2).

A preliminary examination of the data showed that misalignments of up to 13° do not seem to be significant. That is, some Class I chains have <u>minimum</u> misalignments this large. Shifts of this magnitude can evidently be accommodated by minor torsional or angle-bending adjustments in the crystal.[21] Consequently, strict requirements on alignment seemed unnecessary. The analysis was therefore carried forward using the three best-aligned conformations found for each of the 19 polymers (i.e. 57 total candidate conformations).

Of these aligned conformations, those with large ξ tended to be concentrated in Class I as expected (Table 5). A χ^2 test indicates that this degree of concentration would occur by chance with a probability less than 0.005. It thus appears that the single criterion "degree of extension (at near minimum misalignment)" is effective as a screening criterion. To be specific, a cutoff at $\xi = 0.94$ correctly divides 9 out of 10 Class I materials from 7 out of 9 of the other types. Thus this criterion correctly assigns 84% of the test cases. Of course, it will be desirable to test the reliability of this correlation by predicting the behavior of additional polymers, and this is currently being done.

With a strictly empirical criterion like this, it is important to examine more closely molecules that were mis-classified. In the process, some feature might emerge that clarifies the missing physics and allows a more refined criterion to be established. A useful comparison, for example, would be between materials 7 and 8, which differ only in the substitution of a ketone for an ether connecting group. This would not be expected to have a large effect, and with aligned conformations at $\xi=0.97$, both exceed the cutoff. Yet material 7 is in Class I and material 8 is in Class III. It is perhaps worth noting that this is exactly contrary to the generalization of Carlier et. al.[22] Working with poly(arylene ether)s, they concluded that ketone linkages would promote crystallization by increasing the distance between the melting point and the glass transition temperature.

Extended conformations of molecules 7 and 8 were located by varying the constrained end-to-end distances in molecular mechanics energy minimizations. Starting from different initial conformations, the minimized energy was reproducible to within 0.5 kcal/mol at a given end-to-end distance. Plotting the strain energy as a function of end-to-end distance, it is easy to locate the distance at which the chains became taut. This fully-extended condition could be located within 0.5 Å or so by noting where the restraint increased (Figure 5). An example of an extended conformation was shown in Figure 3.

Cerius™ provides no facility to directly determine angular misalignment but angles and dihedrals between sets of atoms can be read out. Figure 6 illustrates schematically how the angles of the end bonds were determined relative to a line connecting them. Perfect alignment would require $\theta_1=\theta_1'$ and in addition, zero dihedral between their planes.

Results for molecules 7 and 8 are shown in Table 6, and on the basis of these mechanics results there is no clear reason to expect better alignment in the material with Class I TDA behavior. Thus despite the high success rate of the RIS search technique described earlier, the reasons for this failure are still unclear. It is possible that the models do not capture some essential aspect of the physics of crystallization. It is also possible, however, that differences in molecular weight or nucleation behavior[23] have affected some of the 19 polymers. Such hidden variables are common in structure/property studies. In the present case, care was taken to prepare all 19 polymers similarly[24], so this set of specimens should be more consistent than most.

The assumptions and approximations used will now be discussed briefly. First is the use of the RIS approximation. It enables one to rapidly summarize the distribution of available conformations. The method is well-established, and the use of it here is similar in spirit to its use in a paper by Abe[25] concerning the orientation of rigid cores in liquid crystalline polymers. The particular implementation described in the present paper is oversimplified in that it assumes independence of the torsions. This assumption has the effect of allowing certain combinations of adjacent torsions that are sterically improbable. Given the preliminary nature of this screening, the simplified version was thought to be adequate. In a more detailed study, the selected conformations could easily be examined for steric problems after the fact.

A second approximation is the neglect of intermolecular forces. Crystal packing considerations occasionally cause intramolecular torsion angles to deviate from their gas-phase values, although this is not a common finding. A formalism for simultaneous minimization of inter- and intramolecular degrees of freedom is available,[26] but it has not been widely used. In aromatic polymers in particular, however, polymorphism is fairly common[27,28] -- an indication that the crystal energy landscape is complex, with multiple minima that lie fairly close in energy. This being the case, experimental data (e.g. X-ray) are still a necessity when proposing a unit cell structure.

The simple chain-stretching screening presented here, while giving no information on the preferred unit cell, appears reliable enough to be useful to synthetic chemists and suggestive of the degree to which primary backbone chemistry determines crystallizability.

Conclusion

A simple rotational isomeric state model was used to detect the degree to which polyimide repeat units might align to give an extended crystal. It was found experimentally that evidence for stretch-crystallization was more likely to occur in materials whose molecules could readily give extended, aligned conformations. A proposed screening criterion was 84% accurate in selecting crystallizing molecules.

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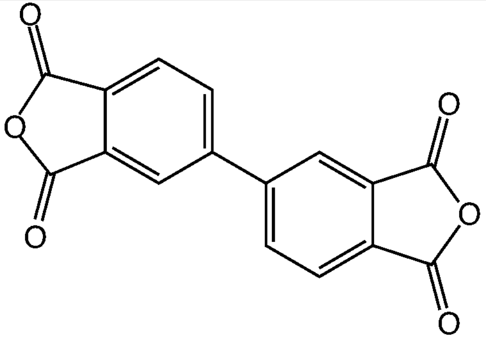
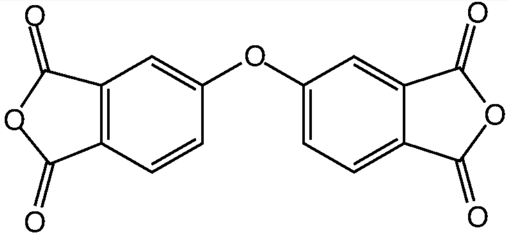
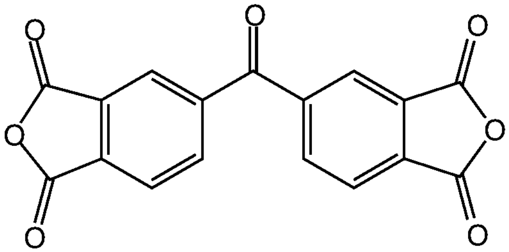
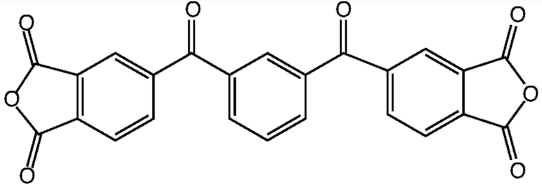
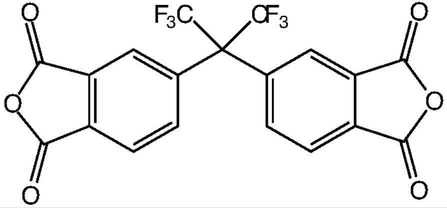
Table 1. Polyimide Monomers

Dianhydride	Structure
s-BPDA	
ODPA	
BTDA	
IDPA	
6FDA	

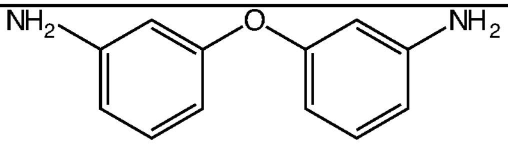
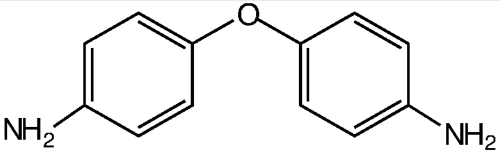
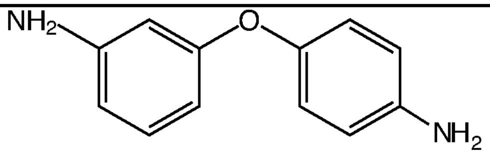
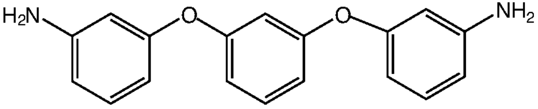
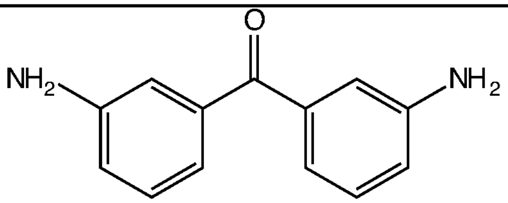
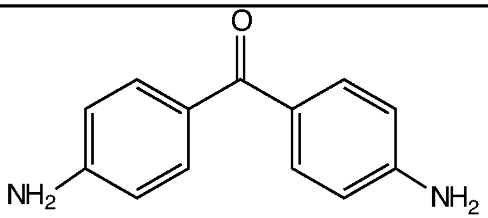
Diamine	Structure
3,3'-ODA	
4,4'-ODA	
3,4'-ODA	
1,3-APB	
3,3'-DABP	
4,4'-DABP	

Table 2. Polymer structures and TDA classifications

Structure number	Dianhydride	diamine	class
1	s-BPBA	1,3-APB	III
2	s-BPDA	3,3’-ODA	III
3	s-BPDA	3,3’-DABP	I
4	s-BPDA	3,4’-ODA	I
5	s-BPDA	4,4’-ODA	I
6	s-BPDA	4,4’-DABP	--
7	ODPA	4,4’-ODA	I
8	ODPA	4,4’-DABP	III
9	ODPA	3,4’-ODA	I
10	BTDA	3,4’-ODA	I
11	BTDA	4,4’-ODA	I
12	BTDA	3,3’-ODA	II
13	ODPA	3,3’-DABP	II
14	BTDA	3,3’-DABP	II
15	IDPA	4,4’-ODA	I
16	ODPA	3,3’-ODA	III
17	IDPA	3,3’-ODA	II
18	6FDA	3,3’-ODA	II
19	BTDA	4,4’-DABP	I

Table 3. Equilibrium bond angles and torsion angles

bond	bond angle, degrees	torsion angle, degrees	reference
ether	117	40	15
ketone	121	30	15
-C(CF3)2-	109	90	16
imide	--	58	17
biphenyl	--	45	18

Table 4. Numbers of conformations examined by RIS program

Polymer	Rotatable backbone links per repeat	Total conformations
1	7	16,384
2	5	1024
3	7	1024
4	4	512
5	3	256
6	3	256
7	4	1024
8	4	1024
9	5	2048
10	5	2048
11	4	1024
12	6	4096
13	6	4096
14	6	4096
15	6	4096
16	6	4096
17	8	65,536
18	6	4096
19	4	1024

Table 5. Conformations classified by degree of extension.

	Conformations from class I	Conformations from other two classes
$\xi<0.94$	8	22
$\xi\geq0.94$	22	5

Table 6. Misalignment angles of fully-extended repeats

Molecule	Angles from end-to-end line, degrees	dihedral, degrees
7	177,136	123
8	178,135	107

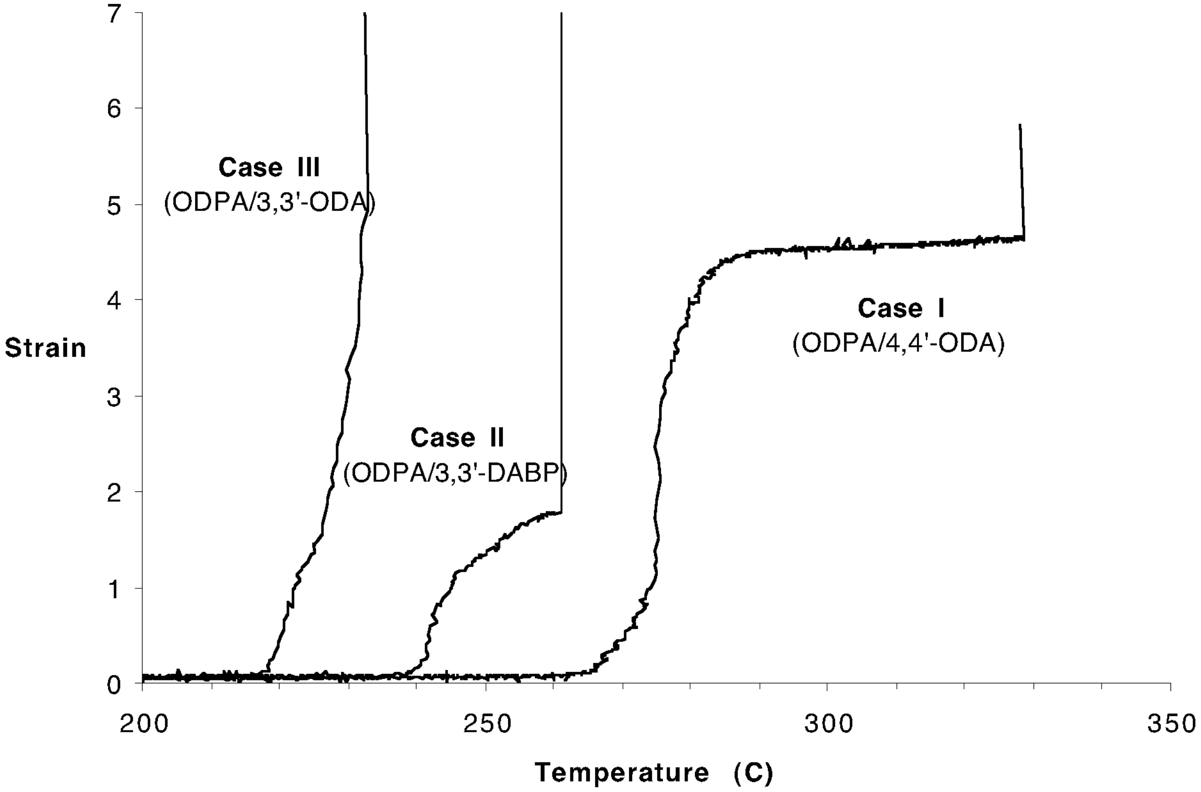


Figure 1. Representative TDA curves for the three classes of polymers.

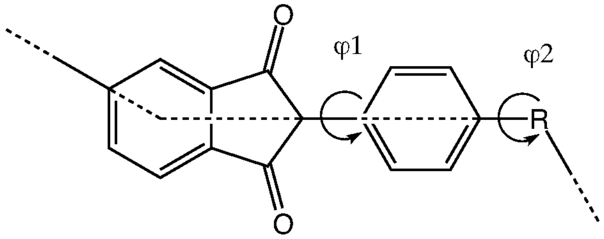


Figure 2. Illustration of virtual bonds (dotted) and summation of rotations about para-phenyl. R is a generalized hinge group. The torsion angle about the central virtual bond φ = ±φ1±φ2±180°. For example, if R is an ether oxygen, then φ1=58°, φ2=40°, and φ can assume the 8 values { ±98, ±18, ±82, ±162}.

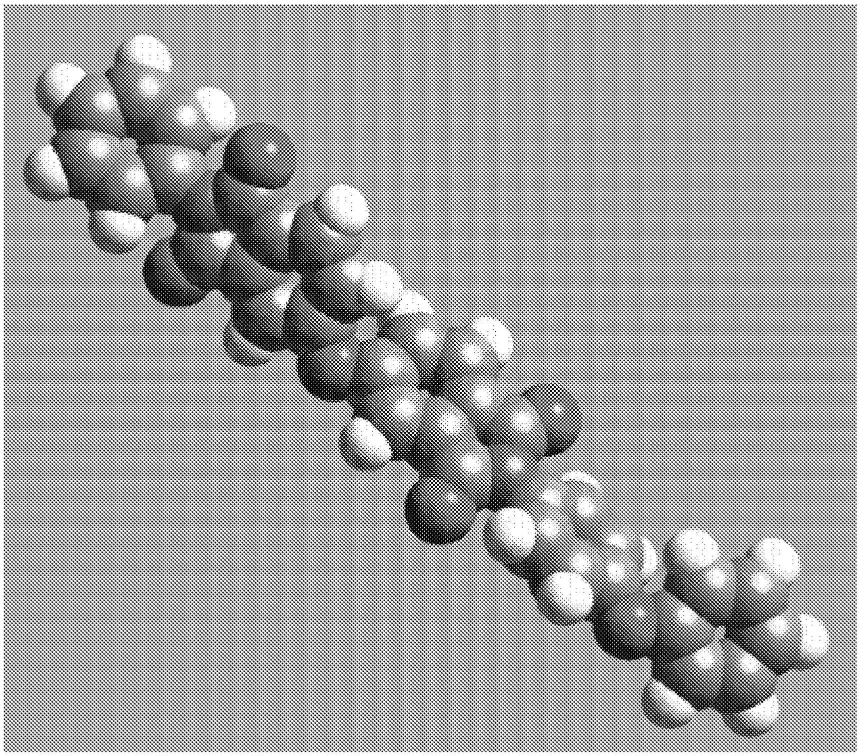


Figure 3. Taut conformation of ODPA/4-4′-ODA (molecule 7).

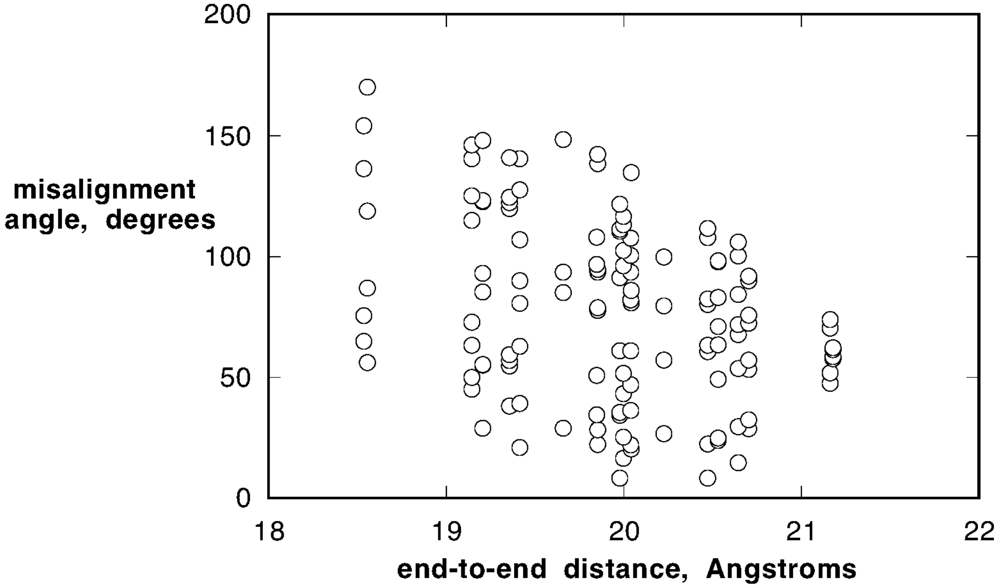


Figure 4. RIS conformations for ODPA/4,4′-ODA, molecule 7.

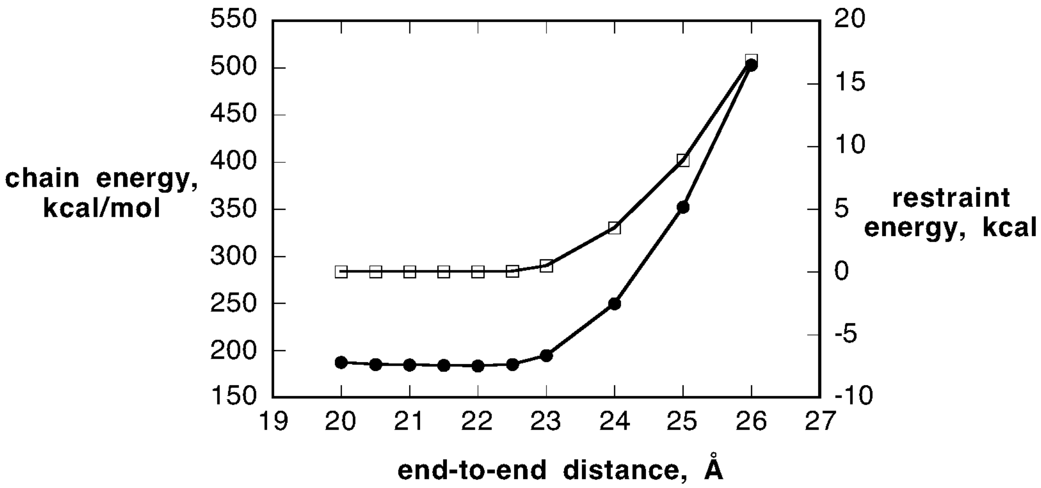


Figure 5. Results of molecular mechanics search with ends constrained

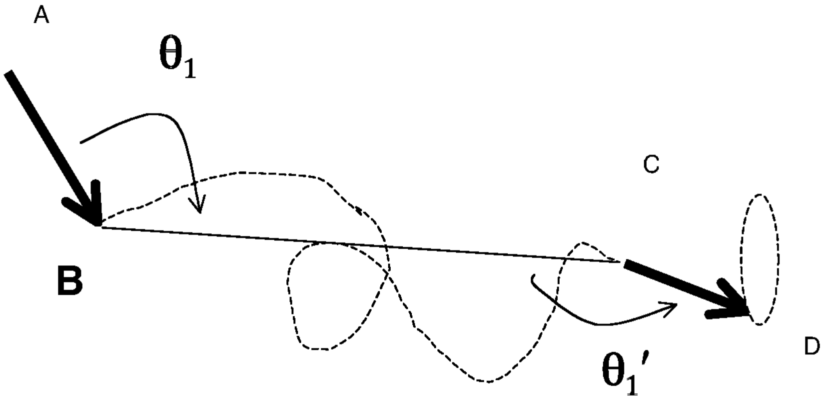


Figure 6. Bond angles θ are taken with respect to thin solid line BC joining first bond AB and first bond of following repeat CD. Dashed curve symbolizes remaining bonds. Dihedral is between planes ABC and BCD.

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13. ABSTRACT ***(Maximum 200 words)***

A simple rotational isomeric state model was used to detect the degree to which polyimide repeat units might align to give an extended crystal. It was found experimentally that the hallmarks of stretch-crystallization were more likely to occur in materials whose molecules could readily give extended, aligned conformations. A proposed screening criterion was 84% accurate in selecting crystallizing molecules.

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