

The Molecular Structure of Polyacrylonitrile Fibers

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SYNOPSIS

In spite of considerable effort, the understanding of the molecular structure of polyacrylonitrile-based fibers is still incomplete. This paper shows that molecular modeling based on molecular mechanics and dynamics can be used to study the molecular structure of polyacrylonitrile-based fibers with appropriate strategies. Additional information has thus been obtained which is impossible to obtain by using other instrumental techniques. It is concluded that the chain conformations of polyacrylonitrile-based fibers are similar to those of nematic liquid crystal composites in which the chains are formed by the irregular combination of two or more species of unit groups. Hence the polyacrylonitrile molecules should be viewed as 'aperiodic chain molecules.' © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyacrylonitrile (PAN) and its copolymers have been studied for nearly a century. However, the molecular structure of PAN still remains unclear. The earliest studies on the molecular structure of PAN showed the crosslinked molecular architecture.¹⁻³ Thus, the polymer physical properties such as the insolubility and resistance to swelling in common organic solvents were attributed to the crosslinked structure. After some strongly polar solvents which could dissolve this polymer had been successfully found, the crosslinked structure was then replaced by the linear molecular structure with zigzag chain conformations and hydrogen bonds existing between the α -hydrogen atom of one chain and the nitrile nitrogen of an adjacent chain.^{4,5}

On the basis of the studies of low molecular weight organic nitriles, Saum proposed that a strong and rather specific interaction between pairs of CN groups was involved in the intermolecular forces leading to the formations of dimers.⁶ In comparison of the energy of N—H—C hydrogen bonds to the energy of nitrile groups in PAN materials, the interactions of the nitrile groups along the chains and

between the chains were found to be dominant, and thus an irregularly helical chain model was proposed, in which chains were packed in a hexagonal system of $a = b = 0.60$ nm.^{7,8}

So far the evidence for existence of this kind of irregular helical chain model has not been confirmed and a detailed picture of the chain conformation has not been presented yet. Whether the chain conformation of PAN materials is an irregular helix or zigzag is still in argument. The diffused reflections on the meridian of PAN and Acrylic fibers, measured by wide-angle X-ray photographic and diffractometry methods, suggest that there exist some local orders.⁹⁻¹¹ Therefore, an investigation on the chain conformation of PAN molecules is needed.

Of all the structural characteristic techniques, the X-ray method is one of the most important. However, the X-ray diffraction patterns of PAN materials provide insufficient information to allow structural analysis to be carried out to completion. This work tries to study the molecular structure of PAN materials using the molecular mechanics (MM) method. MM is essentially an energy minimization method in which the energy of a molecular system and the coordinates of nuclei are formulated and the structure of minimum energy is searched. Recently, this method has rapidly been emerging as an important technique of research in the study of polymers.

The earliest application of energy minimization to study the molecular structure of PAN polymer

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Table I Standard Bond Lengths and Angles Used for Constructing the Original Models

Bond	Length (nm)	Bond	Angle (deg)
C—H	0.111	C—C—H	109.5
C—C	0.154	C—C—C	109.5
C≡N	0.116	C—C≡N	180.0

was carried out by Krigbaum and Tokita,¹² using simple empirical rotational potentials for the energy minimization. McMahon and Tincher¹³ then evaluated the steric energies of disubstituted pentanes for all common conformations (*trans* and *gauche*) using Leonard–Jones potentials. Recently, Ganster et al.^{14,15} performed PCILO (perturbative configuration interaction using localized orbital) conformational calculations on model PAN molecules. The results obtained by the above authors are different since different kinds of *forcefield* were applied.

In this work, the commercial **Biosym** software (**InsightII** and **Discover**) is employed to search the minimum energy conformations of PAN molecules. **InsightII** is a highly comprehensive graphic package, while **Discover** is a molecular simulation program that performs molecular mechanics and molecular dynamics. Currently, these two packages are installed on a Silicon Graphic IRIS 4D series workstation, which is available in The University of Leeds, England. It is believed that the quality of the selected forcefield directly determines the simulated results. Hence, the results obtained in this work will be compared with those obtained by others so that the applicability of the employed forcefield to PAN molecules and the validity of the obtained results can be verified.

SYSTEM SETUP AND STRATEGIC APPROACH

Discover is a semi-empirical code molecular modeling package which approximates some integrals needed with empirically fit functions. A CFF91 forcefield was employed in which quadratic polynomials were used for the bond stretching and angle bending, and a three-term Fourier expansion was used for torsion. All cross-terms, out-of-plane coordinates, Coulombic, and van der Waals interactions are included.

PAN compounds of meso- and racemic-2,4-dicyanopentane were chosen as models for the study since

these two small molecules have the constitution and configuration corresponding to those in iso and syndiotactic sequences of PAN polymers. The original models of meso- and racemic-2,4-dicyanopentane molecules [$\text{CH}_3\text{—CHCN—CH}_2\text{—CHCN—CH}_3$] were constructed using the **Builder** modules of **InsightII** with various standard fragments of the library. The standard bond lengths and angles used in this work are summarized in Table I. All these original models were constructed in *trans* conformations, which are shown in Figure 1. The potential energies and the dihedral angles of these two original models are listed in Table II.

The energy minimization calculations for these two molecules were performed from the initial points

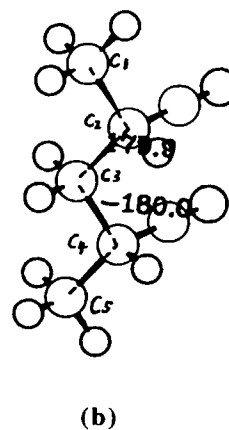
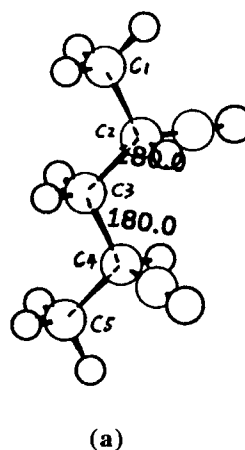


Figure 1 Original models of meso- and racemic-2,4-dicyanopentane in the planar *trans* conformations, (a) the meso, (b) the racemic.

Table II The Key Structural Parameters and Potential Energies of the Original and Minimized Models

Model	Di-AN	VDW	Elect (kcal/mol)	Total	α (deg)	(ϕ, ψ) (deg)
Original	meso	108.7	3.1	111.8	109.5	(180.0, 180.0)
	racemic	16.8	2.3	19.1	109.5	(-180.0, -180.0)
Minimized	meso			9.1	117.2	(-179.8, 71.9)
	racemic I			8.9	118.0	(-180.0, -180.0)
	racemic II			9.2	116.3	(-71.9, -71.9)

Di-AN: Dicyanopentane (meso- or racemic-2,4-).

VDW: van der Waals interaction energies.

Elect: Electrostatic (Coulombic) interaction energies.

α : The angle of $C_2-C_3-C_4$.

(ϕ, ψ) : The dihedral angles of $C_1-C_2-C_3-C_4$ and $C_2-C_3-C_4-C_5$.

of the original models under restraints. Unconstrained or unrestrained energy minimization would probably lead to a local minimum close to the starting conformation, and not the global minimum. This is because the minimization is specially designed to ignore conformations if the energy increases. Thus, it does not generally push a system over energetic barriers but down into the nearest valley. Therefore, modified strategies are needed to search the conformational space more thoroughly.

Torsionforce restraints were employed in this work. By using torsionforce restraints, the system would set the two dihedral angles (ϕ for $C_1-C_2-C_3-C_4$, ψ for $C_2-C_3-C_4-C_5$) so that they would start from an angle of 180° and change to an angle of -180° in increments of 10° . The energy minimization was performed each time the values for the two dihedral angles had been updated. During the minimization, all the degrees of freedom (except those of an active dihedral angle which was being forced to a target value) were free to relax, the structure was minimized, and the molecule was forced to adopt new conformations.

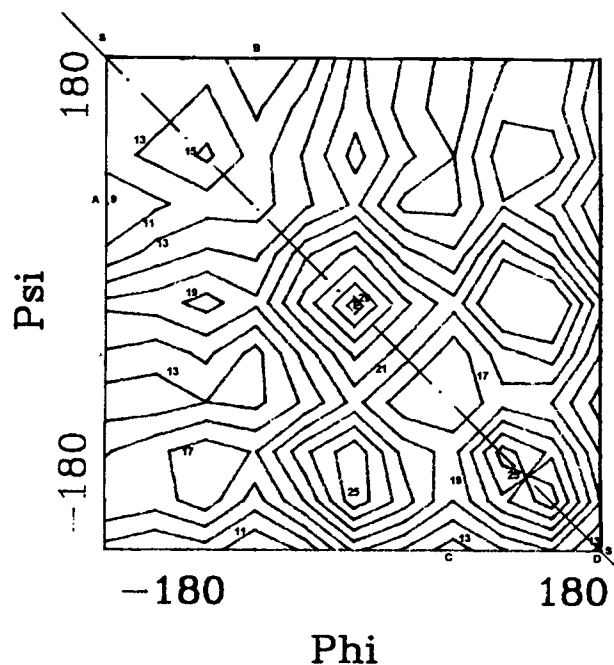


Figure 2 Conformational energy contours for meso-2,4-dicyanopentane obtained by running torsionforce constrained energy minimization. The contour level is 2 kcal/mol.

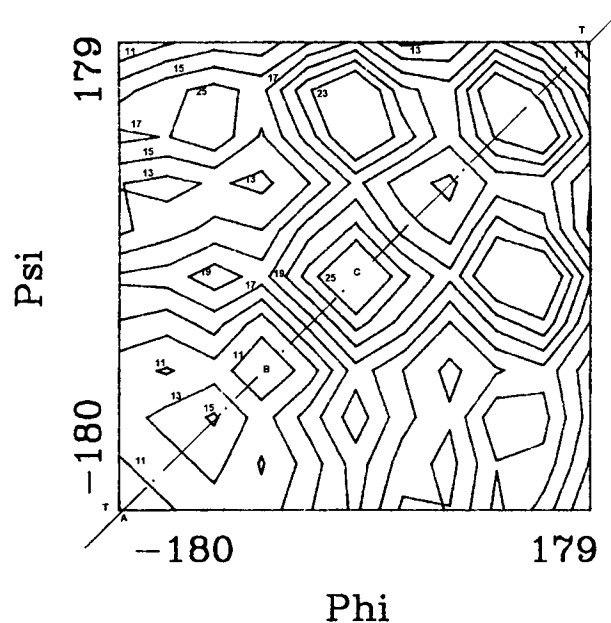


Figure 3 Conformational energy contours for racemic-2,4-dicyanopentane obtained by running torsionforce constrained energy minimization. The contour level is 2 kcal/mol.

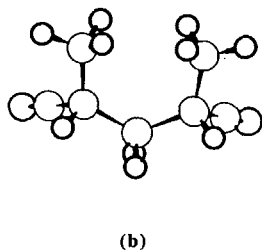
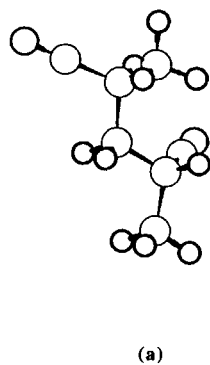


Figure 4 Minimal and maximal energy molecular structures of meso-2,4-dicyanopentane obtained by running torsionforce constrained energy minimization, (a) the minimal, (b) the maximal.

The robust minimization algorithm of steepest-descents was first used to perform 100 iterations in order to save computational time and avoid unstable results. The quasi-Newton-Raphson algorithm method was then selected to perform 1000 iterations or until the derivative was less than 0.001 kcal/mol, whichever occurred first. The minimized energies and structures after each iteration were recorded. The resultant energy maps were used to quantify low energy pathways across conformational barriers so that the global minimum was identified.

Molecular dynamics was also performed for these two molecules in order to observe the pathways for the conformational transitions and compare the results with those obtained using the approaches discussed above. The starting conformations for use in the dynamics were the minimized structures. 100 *initialize* iterations were selected to run, during which the system was raised to and equilibrated at the target temperature of 300 K with a Maxwell-

Boltzmann distribution of random velocities. 1000 *resume* iterations were set to be performed once the target temperature had been achieved. The time interval between each iteration was set at 1 Fs, which is smaller than that of the highest frequency vibration of C—H bond stretching (10^{-14} s) of the molecules. Too large a time step could cause instabilities in the system due to integration errors, leading to nonconvergence of potential and kinetic energy. Other parameters were set according to the same rules needed in the minimization. Data were then collected at each tenth frame throughout the whole dynamic running. These data can be used to replay and analyze the dynamic trajectory.

RESULTS AND DISCUSSION

The potential energies of these two original models of meso- and racemic-2,4-dicyanopentane are very high, particularly of the meso-2,4-dicyanopentane due to the geometrical positions of the nitrile groups. The distance between the two nitrile groups of the meso is 0.252 nm, which is quite small. This causes the high steric repulsion. It is of interest to note that the

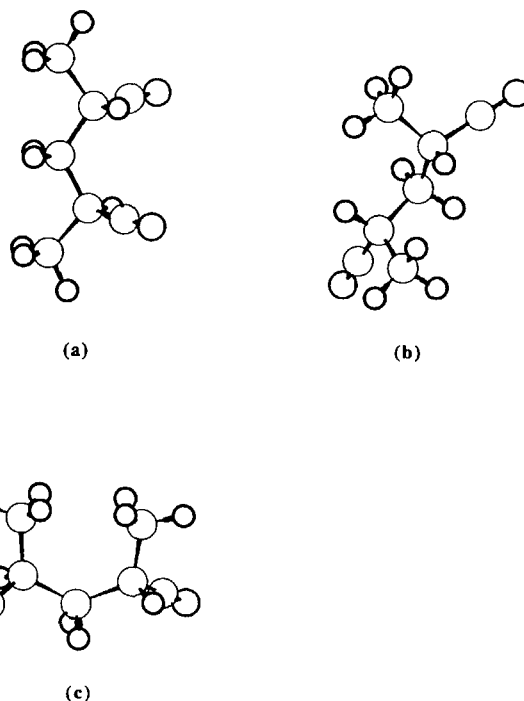


Figure 5 Minimal and maximal energy molecular structures of racemic-2,4-dicyanopentane obtained by running torsionforce constrained energy minimization, (a) the global minimal, (b) the local minimal, (c) the maximal.

Table III The Minimum Energy Conformational Parameters Compared with Those Obtained by Other Authors

Di-An	α	(ϕ, ψ)	Conformation	Method	Author
meso		(-180, 60)	(g't) or (tg.)	Classical electrostatics	Krigbaum and Tokita ¹²
racemic I		(-180, -180)	(tt)		
racemic II		(-60, -60)	(g'g')		
meso		(-180, 60)	(g't) or (tg.)	Lennard-Jones potentials	McMahon and Tincher ¹³
racemic I		(-180, -180)	(tt)		
racemic II		(-60, -60)	(g'g')		
meso	107.0	(-97.5, 152.5)	(g't)	PCILO	Ganster and Lochman ¹⁴
racemic I	106.5	(-147.5, -147.5)	(tt)		
racemic II		(-92.5, -92.5)	(g'g')		
meso	117.2	(-179.8, 71.9)	(g't) or (tg.)	MM	This work
racemic I	118.0	(-180.0, -180.0)	(tt)		
racemic II	116.3	(-71.9, -71.9)	(g'g')		
meso		(-180, 60)	(g't) or (tg.)	¹ H-NMR Experimental	Murano and Yamadera ¹⁷
racemic I		(-180, -180)	(tt)		
racemic II		(-60, -60)	(g'g')		

Di-AN: Dicyanopentane (meso- and racemic-2,4-).

α : The angle of C₂-C₃-C₄.

(ϕ, ψ) : The dihedral angles of C₁-C₂-C₃-C₄ and C₂-C₃-C₄-C₅.

van der Waals repulsion (VDW) is the dominant factor affecting the potential energies of these molecules. In contrast, the contribution for the electrostatic repulsion of nitrile groups is rather small. The VDW repulsions for the meso and the racemic are 108.715 and 16.814 kcal/mol, respectively. The electrostatic repulsions are 3.124 for the meso and 2.338 kcal/mol for the racemic, respectively. The structural parameters and the potential energies of the original models are shown in Table II.

Figures 2 and 3 show the energy contours against the two specific dihedral angles of the meso- and the racemic-2,4-dicyanopentane obtained by running the torsionforce restrained energy minimization, respectively. For the meso, the global minimum energy is 9.1 kcal/mol. The minimized energy structure corresponds to the conformation with a pair of the specified dihedral angles (ϕ, ψ) of $(-179.8^\circ, 71.9^\circ)$ (point A in Fig. 2). It is noticed that Figure 2 has the symmetry about the S-S axis. Therefore, point B has also the global minimum energy, since point B is the mirror image of point A. The C₂-C₃-C₄ angle is 117.2° . This means that the chain rotates approximately 108° (left or right) to a helical structure (g't) or (tg.). The structure corresponding to

the global minimized energy is shown in Figure 4(a). There are also some points C and D which have the local minimum energy. The local minimum energy is 11.2 kcal/mol. The global minimum energy is about 2 kcal/mol less than the local minimum energy, which is significant. The maximum energy is 30.0 kcal/mol (point E in Fig. 2). It corresponds to the conformation with dihedral angles of $(0.0^\circ, 0.0^\circ)$; the C₂-C₃-C₄ bond angles is 123.0° (shown in Fig. 4(b)). This means the *cis* conformation causes the maximum energy for this small molecule. The *trans* conformation $(-180.0^\circ, 180.0^\circ)$ with the C₂-C₃-C₄ bond angle of 121.0° is only a local minimum (point D in Fig. 2).

For the racemic, the global minimum energy is 8.9 kcal/mol (point A in Fig. 3). The local minimum energy is 9.2 kcal/mol, which is not significantly different from the global minimum (point B in Fig. 3). Therefore, the possibility of molecular conformation for the racemic increases. The corresponding structures for the global and the local minimum energies are the two specified dihedral angles of $(-180.0^\circ, -180.0^\circ)$ and $(-71.9^\circ, -71.9^\circ)$, respectively. The C₂-C₃-C₄ bond angles are 118.0° and 116.3° , respectively. The minimized structures are

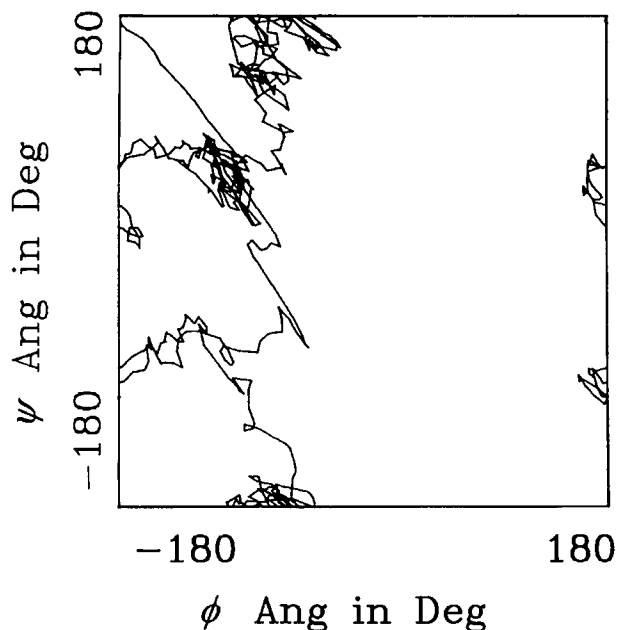


Figure 6 The two-dimensional graph of the potential energy surface against the two specified dihedral angles of meso-2,4-dicyanopentane obtained by running unconstrained dynamics.

shown in Figure 5 (a) and Figure 5 (b). This means that the racemic takes the stable chain conformation of either the *trans* (*tt*) or the helical structure (*gg*). The maximum energy is 29.8 kcal/mol (point C in Fig. 3). It corresponds to the conformation with dihedral angles of $(0.0^\circ, 0.0^\circ)$ (shown in Fig. 5(c)). This means that the *cis* conformation causes maximum energy for the racemic. Obviously, the contour map has the symmetry about the T-T axis for this molecule.

All the above results showed some resemblance to those obtained by Krigbaum and Tokita¹² in which the two specific dihedral angles of $(-180.0^\circ, 60.0^\circ)$ and $(-60.0^\circ, 180.0^\circ)$ were minima for the meso, and $(-60.0^\circ, -60.0^\circ)$ and $(-180.0^\circ, -180.0^\circ)$ for the racemic. Ganster and Lochmann¹⁴ and Ganster, Fink, and Zenke¹⁵ proposed the two specific dihedrals $(-97.5^\circ, 152.5^\circ)$ for the meso, $(-147.5^\circ, -147.5^\circ)$ and $(-92.5^\circ, -92.5^\circ)$ for the racemic, using PCILO conformational energy calculations. Table III summarizes these results. Note that the angle of $C_2-C_3-C_4$ decreases in the work of Ganster et al. when the molecules approach the minima, while it increases in this work. Furthermore, the similar minimized structures have been reached for the meso; however, the minimized structure for the racemic varies more.

Figure 6 shows the two-dimensional graph of the potential energy surface against the two specified dihedrals of the meso obtained by running unconstrained dynamics. It is clear that the structures of the meso, characterized by the two specified dihedrals (ϕ, ψ) , vary widely during the dynamics running. The angle ϕ is almost always located within the range between -50.0° and -180.0° , although a few conformations with ϕ between 170.0° and 180.0° were also found. In contrast, the angle ψ is located through the whole range between -180.0° and 180.0° . The dynamics trajectory passes through legitimate minima and does not just fluctuate about a single minimum. Therefore, the flexibility of this kind of small molecules is confirmed immediately.

Figure 7 shows the two-dimensional graph of the potential energy surface against the two specified dihedrals of the racemic obtained by running unconstrained dynamics. The structures of the racemic are characterized by the (ϕ, ψ) fluctuation around the four points which are near the original point $(180.0^\circ, 180.0^\circ)$. This means the stable conformation could be the planar zigzag or distorted planar zigzag, namely the (*tt*) conformation. At room temperature, the potential energy both for the meso and the racemic fluctuate in the range of 20–30 kcal/mol during the dynamics running. This means that

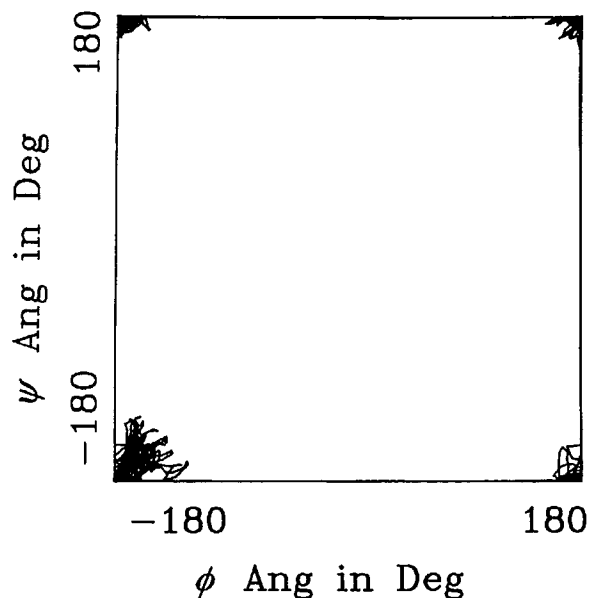


Figure 7 The two-dimensional graph of the potential energy surface against the two specified dihedral angles of racemic-2,4-dicyanopentane obtained by running unconstrained dynamics.

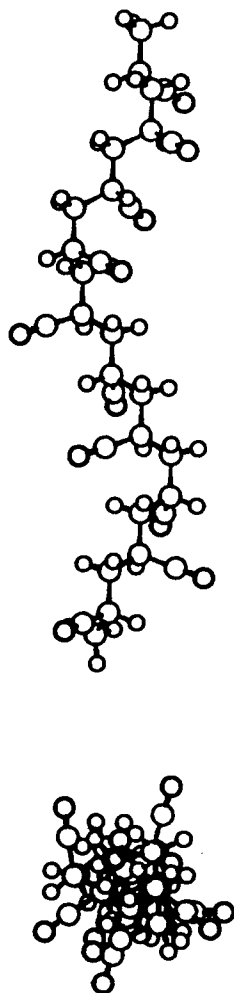


Figure 8 An example of atactic PAN chain model with 10 monomer units.

the system will pass through any energy barrier which is less than 10 kcal/mol.

Finally, the real atactic PAN chains were constructed from the segments based on the minimum energy conformers of meso- and racemic-2,4-dicyanopentane, using random sequences of the meso and the racemic with probabilities of 0.5. An example of such a chain is shown in Figure 8. It can be seen that the characteristic of the molecular structure of PAN is similar to that of nematic liquid crystal composite in which the chain was formed by the irregular combination of two or more species of unit groups. Although the unit groups (meso and racemic segments) in PAN homopolymer consist of the same kinds of atoms, the unit lengths of each group along the chain axis are different. That is why a diffuse X-ray

reflection corresponding to the d -spacing of approximately the mean length of the unit group sizes (0.23 nm) persisting on the meridian, for this represents the internal structure of the molecule in projection on the chain axis. Assuming that the chain cross-sectional area is 0.307 nm^2 (calculated from the X-ray equatorial scan of PAN fibers), the calculated density within the 'crystal' region is 1250 kg/m^3 . This is in good agreement with the estimate for 'crystalline' PAN.¹⁶ It is expected that the computer simulated X-ray meridional diffraction trace and the calculated birefringence based on the chain model would also be in good agreement with those obtained from the experimental.⁹

CONCLUSIONS

By using molecular mechanics and molecular dynamics methods, it is possible to study the chain conformations of PAN materials. Assuming pure isotactic PAN, the chain conformation would adopt the nearly, but not exactly, 3_1 helical structure; while assuming pure syndiotactic PAN, the chain would adopt roughly zigzag conformation. The real atactic PAN chains would adopt the structure mainly combining with the roughly 3_1 helical and distorted zigzag conformers randomly distributed along the chains.

Van der Waal interaction was found to be the dominant in the chain conformation. The *cis* conformations both for the meso and the racemic cause maximum potential energies, which indicates that the chain-folding in PAN fibers would cause maximum potential energy.

The validity of this structural model proposed in this work has been supported by $^1\text{H-NMR}$ experimental method.¹⁷ The simulated X-ray diffraction spectrum of the model is also in good agreement with the meridional wide-angle X-ray diffraction-oriented PAN fibers.⁹ It is suggested that the model is especially suitable when PAN is in a gas or liquid state. PAN molecules are much less constrained in gas or liquid state than those in the solid state. In the view of fiber manufacturing, PAN fibers are the most commonly produced by both wet-spinning and dry-spinning processes, although gel-spinning is also possible. Therefore, this model could be viewed as the first step in formulating the formation, structure, and property relationship of the fibers.

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