

STUDY OF THE MOLECULAR ORIENTATION OF A KAPTON FILM

D. Nemirovsky, R. Moreh, Y. Finkelstein and J. Mayers[#]
Physics Department, Ben-Gurion University of the Negev, Beer-Sheva, Israel
[#]Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK

Introduction

Kapton films are made from polymerized structural units of the form $C_{22}H_{10}N_2O_5$. This molecule is usually assumed to be planar [1,2], with a small tilt angle between adjacent molecular planes (intra-connected via -O-bondings). In the polymer itself, all molecules were also thought to be oriented nearly parallel to the film surface. This assumption was based on the fact that during high temperature annealing of Kapton films [1,2], all O- and N-atoms are released as simple CO, O₂ or N₂ species. During this process, the hexagons of the molecular unit are left intact, the film contracts appreciably, resulting in highly oriented graphite surfaces of a quality comparable to that of highly oriented pyrolytic graphite (HOPG) with a mosaic spread of around 2°.

This behavior of the graphitized film was attributed to an assumed *planar* well ordered structure of the initial Kapton polymer film. If true, Kapton may be used as a highly anisotropic material where the strong C=C and the C-H bonds are well ordered in the plane, while the low energy vibrations of the atoms are normal to the plane.

Our purpose was to test the above expectations by studying the degree of anisotropy in the distribution of atomic momenta of the H- and C-atoms of the polyimide layers at room temperature. This was done by measuring the effective temperatures T_a and T_c of the H- and C-atoms of Kapton, along and normal to the plane of the film, by using the neutron Compton scattering (NCS) technique [3]. It may be noted that T_a and T_c are related to the corresponding mean square linear momenta $\langle p_a^2 \rangle$ and $\langle p_c^2 \rangle$ of the C-atoms by:

$$\langle p_c^2 \rangle = MkT_c \text{ and } \langle p_a^2 \rangle = MkT_a$$

with M the atomic mass and k the Boltzmann constant.

The results of the proposed measurements revealed a small anisotropy ratio of T_a/T_c which is far much lower than that deduced when assuming rigid planar Kapton molecules.

We first discuss the NCS technique and then explain how to calculate effective temperatures of the atoms of the Kapton molecule and also their anisotropy.

In the NCS method [3], epithermal neutrons (in the eV energy range) are scattered from single atoms of the sample. The scattered neutrons act as monitors of the

directional momentum distributions and kinetic energies (including the part of the zero-point motion) of the scattering atoms. In strongly bound atomic systems such as the Kapton molecule, the contribution of the zero-point motion is quite high and any anisotropy is expected to show up as a strong effect even at room temperature.

To obtain the momentum distribution and to interpret the NCS measurements, use is made of the impulse approximation (IA) which is strictly valid only at infinite momentum transfers [4-6]. To do so, consider a neutron transferring momentum \mathbf{Q} and energy ϵ by scattering from an atom of mass m. If the momentum of the atom is \mathbf{p} before collision, then momentum conservation requires that it is $\mathbf{p}+\mathbf{Q}$ after collision, and to conserve kinetic energy, the equation:

$$\epsilon = [(\mathbf{p}+\mathbf{Q})^2 - \mathbf{p}^2]/2m = (2\mathbf{p}\cdot\mathbf{Q} + \mathbf{Q}^2)/2m \text{ must be satisfied.}$$

Thus the component of atomic momentum along \mathbf{Q} is given by: $y = \mathbf{p}\cdot\mathbf{Q}/Q = (2m\epsilon - \mathbf{Q}^2)/2Q$.

Hence by measuring ϵ and \mathbf{Q} in certain directions, it is possible to deduce $J(\mathbf{Q},y)$ which is the probability that the atomic momentum component along \mathbf{Q} is y. Experimentally, our goal was to measure two distributions, $J(\mathbf{Q}_a,y)$ and $J(\mathbf{Q}_c,y)$ being the distribution of atomic momenta parallel and normal to the Kapton film surface, from which the effective temperatures T_a and T_c were deduced. In our analysis we also accounted for the final state effects (FSE) [4-6] which were introduced because of the finite momentum transfer \mathbf{Q} and the finite energy transfer ϵ .

In a *non-oriented* sample, the effective temperature T_e is isotropic and may be expressed in terms of T_a and T_c by: $T_e = (2T_p + T_c)/3$.

Experimental

The NCS measurements were carried out using the eVs spectrometer [3] of the ISIS neutron source at the Rutherford-Appleton Laboratory (UK). The time of flight (TOF) of the scattered neutrons was measured from the moderator to the detectors, after scattering from the Kapton foil. TOF spectra were taken with and without a resonance absorber of a gold (¹⁹⁷Au) foil

(placed in front of the detectors) which defined the final neutron energy at 4.912 eV. The shape of the resonance level in ^{197}Au is a Lorentzian having a half width at half maximum of 131 meV which limits the resolution of the system. The neutrons were detected using 32 Li-glass scintillators arranged in 4 banks each containing 8 detectors. Two banks were positioned around the scattering angles, 90° and 270° while the other two banks were placed at forward angles below 90° and above 270° for the detection of neutrons scattered from hydrogen. With this geometry, it was possible to simultaneously cover the momentum distributions of the C-, O-, N- and H-atoms in directions parallel and normal to the Kapton film surface. More details concerning the eVs spectrometer can be found elsewhere [7].

The Kapton sample (produced by Dupont), consisted of 5 rectangular foils, each with dimensions, $9.0 \times 4.5 \text{ cm}^2$, making a total thickness of 0.75 mm, was held on an aluminum frame at 45° to the incident n-beam.

Results and discussion

The TOF spectra from the Kapton film at scattering angles below 75° were measured. The spectra revealed a peak of the H-atom together with a combined broad peak of the C-, N- and O-atoms where the corresponding signals were not resolved because of the the proximity of the atomic masses and the large width of the instrumental resolution. The TOF spectra at larger scattering angles (above 90°) revealed only the (C+N+O) peak but no H-peak because of the kinematics of n-scattering from hydrogen.

Before extracting the effective temperatures from the TOF spectra, the final state effects were calculated and subtracted [4-6]. In the case of the H-atom, the FSE is large compared to that of the other heavier atoms. Experimentally, the full-width at half maximum (FWHM) widths of each peak in the TOF spectra, σ_a and σ_c , along and normal to the plane of the Kapton foil, were measured. These are related to the mean square momenta and hence to the effective temperatures T_a and T_c of the scattering atom (such as the H-atom), using the relations [7]:

$$T_a = h^2 \sigma_a^2 / 4\pi^2 M k, \quad T_c = h^2 \sigma_c^2 / 4\pi^2 M k$$

These equations were used to extract the anisotropy ratio T_a/T_c for the H-atom. The same procedure could not be applied to deduce the separate anisotropy ratios for C, N, and O-atoms whose contributions could not be resolved. We thus considered the combined TOF peak of C+N+O and defined an effective mass which is a weighted average obtained by multiplying the atomic mass of each element by the number of atoms in the molecule and by the scattering cross section. It may be noted that the value of σ_a/σ_c of the combined peak gave a good idea of the measured anisotropy ratio in the Kapton polymer. It was also used for deducing the effective temperature of the C-atom by taking the values of the N- and O-atoms from the results obtained using the GAUSSIAN98 AM1 code (see below) after assuming the same anisotropy ratio for the N and O atoms, namely 1.10. The results are given in Table 1 which show that the anisotropy ratio T_a/T_c for both the

H- and C-atoms is around 1.10 and is much lower than originally expected.

The performance of the experimental system was tested by using a sample of sample of Papyex (a form of partially oriented graphite) having the same dimensions and geometry as that of Kapton. At 295 K, the resulting effective temperatures [8] of the C-atoms, in Papyex: $T_a = 815 \text{ K}$ and $T_c = 530 \text{ K}$ being highly anisotropic, were in good agreement and consistent with the results of a previous study¹³ using a HOPG sample. This agreement gave us proved the reliability of using the NCS technique and the EVS instrument for the present study.

The calculation of T_a and T_c of the H-, C-, N- and O-atoms of Kapton, and their relation to the measured quantities is explained briefly below. First, note that the molecule should be terminated on both ends by an aromatic ring so as to form a symmetrical structure. Thus instead of 39 atoms which the Kapton monomer contains, we get $\text{C}_{34}\text{H}_{20}\text{N}_2\text{O}_6$, involving 62 atoms in the calculation. Note that not all the bonds of the C-atoms in Kapton are equivalent: out of 34 C-atoms, 20 have C-H bonds and the rest have C=C, C-O, and C-N bonds. Since the molecule has $N = 62$ atoms, hence it has a total of $3N-6 = 180$ independent internal normal vibrational modes which should all be accounted for in calculating the effective temperature. The procedure is to consider each mode and find the kinetic energy fraction shared by each of the C-atoms in the particular mode. A summation over the contributions from all modes is then carried out. Finally, one has to average out over all C-atoms of the molecule. A similar procedure was followed for the H-, N- and O-atoms.

The total kinetic energy of the C-atom may be written as: $3kT_c/2$. It has contributions from the three kinetic energy components of the *entire* Kapton molecule, consisting of translation ($3kT/2$), libration-rotation ($3kT/2$) and internal vibrations ($\sum_1^{3N-6} k \alpha_j/2$). The factor 1/2 in this last term arises from the fact that the *kinetic* energy is equal to half the energy of the $3N-6$ vibrational terms, each represented by a harmonic oscillator. The C-atom shares only a fraction S_k ($k = t, r, j$) in each kinetic energy term. We may thus write:

$$T_c = (S_t + S_r) T + \frac{1}{3} \sum_{j=1}^{180} S_j \alpha_j$$

where S_t , S_r , S_j ($j = 1, \dots, 180$), the energy fractions shared by the C-atom in the translational, librational, and the j th internal vibrational motions of the entire Kapton molecule; T is the thermodynamic temperature. The total energy $k\alpha_j$ of each vibrational mode of frequency ν_j , represented as a harmonic oscillator, is: $k\alpha_j = h\nu_j [(\exp(h\nu_j/kT)-1)^{-1} + 1/2]$. The energy fraction S_t of the C-atom is obtained from the translational kinetic energy term of the whole molecule by multiplying by the mass ratio, hence $S_t = M(\text{C})/M(\text{C}_{34}\text{H}_{20}\text{N}_2\text{O}_6) = 12/570$. Similarly, the fraction S_r is deduced from the librational energy of the whole molecule by considering the axes of rotation and the

exact geometry of the molecule. S_j is obtained by noting that it is equal to the ratio of the vibrational energy of the j th atom relative to that of the entire molecule:

$$S_j = 4\pi\nu_j^2 M_i A_{ij}^2 / (4\pi\nu_j^2 \sum_{i=1}^{62} M_i A_{ij}^2)$$

with A_{ij} the amplitude of the i th atom in the j th vibrational mode of the molecule; these are deduced by utilizing computational methods of infra red spectroscopy[10]. To do so, we used the computer code, GAUSSIAN98, which yields the normal coordinate values for each atom in each internal vibrational mode of the molecule and along each one of the main molecular axes. S_j is deduced by squaring the calculated normal coordinate and multiplying by the relevant nuclear mass. It was computed separately for each one of the three principal axes of the Kapton film, yielding the effective temperature along any molecular direction. Note that the resulting T_e is the average over that of the 34 C-atoms of the Kapton molecule. More details concerning this calculation may be found elsewhere [11].

The resulting values of T_a , T_c , their ratio and T_e for the Kapton atoms are listed in Table 2 for systems containing one, two, three and four Kapton molecules. The values may be seen to be much higher than the thermodynamic temperature T . The reason is purely due to the effect of the zero-point motion and is responsible for the huge calculated anisotropy. It may be seen that the calculated anisotropy decreases drastically with increasing number of molecules. In fact, the ratio T_a/T_c for three and four molecules (see Table 1 and Table 2) is close to the measured value.

To understand the reason for the decreasing anisotropy, we studied the space structure of Kapton molecules using an optimization procedure which searched for a minimum in molecular energy. This was done by applying the GAUSSIAN98 package using AM1 semi-empirical HF model to four separate cases containing one to four Kapton molecules. Note again that in each case the chain has been terminated in such a way that the molecule formed a symmetrical structure, having an aromatic ring at both ends. The result for a single molecule, showed a relatively strong anisotropy. On increasing the number of molecules included in the calculation to two, three and then to four, the trend of deviation from coplanarity was found to increase while the ratio of T_a/T_c for the H-, C-, N-, and O-atoms was found to approach unity in relatively good agreement with experiment (compare the results of Table 1 and 2). It is of interest to note that the calculations using the GAUSSIAN98 code for the case of 4 molecules of Kapton included 179 atoms and took about 7 days of running time using a PC computer. Here, one has to consider 537 normal modes and to deduce all the kinetic energy fractions shared by each atom in all modes. Obviously, it was impractical to use ab-initio calculations because of the huge number of atoms.

The measured anisotropy is consistent with that calculated using the GAUSSIAN98 code (see Table 2). It may be noted that the relatively small measured anisotropy is very probably created during the manufacturing process of

Kapton where anisotropic stretching forces and stresses are applied on the film.

From Table 2, it is important to note that the measured effective temperatures are lower than the calculated values. This deviation is strongly related to the known problem of frequency scaling in the AM1 semi-empirical method employed in the GAUSSIAN98 code. Such deviations are of the order of 8% for all types of vibrations [12]. We thus multiplied the calculated frequencies by a factor of ~ 0.92 and obtained an improved agreement with the measured results (see last column of Table 2). A good agreement is obtained for the case of the C-atom, and a relatively large deviation exists in the H-atom.

Conclusions

We used the Neutron Compton scattering technique for studying the anisotropy of the atomic momentum distributions in a Kapton film. The measured anisotropy ratio of the effective temperatures was found to be small, namely, $T_a/T_c \sim 1.1$, which is far much lower than that deduced when assuming a rigid planar Kapton molecules, where the ratio is ~ 1.7 . The measured results are in qualitative agreement with calculations based on the AM1 semi-empirical method included in the GAUSSIAN98 package.

References

1. Inagaki M, Harada S, Sato T, Nakajima T, Horino Y, Morita K. *Carbon* 1998; 27: 253.
2. Hishiyama Y, Yoshida A, Kaburagi Y and Inagaki M 1992 *Carbon* 30 333.
3. Mayers J, Burke TM and Newport RJ. *J. Phys.: Condens. Matter* 1994; 16: 641.
4. Sears VF. *Phys. Rev. B*; 30: 44.
5. Reiter G, Silver RN. *Phys Rev Lett* 1985; 54: 1047.
6. Watson GI. *J. Phys.: Condens. Matter* 1996; 8: 5955.
7. Mayers J 1996 *J Phys: Condens Matter* 8 9423
8. Finkelstein Y, Nemirovsky D, Moreh R and Kimmel G 2000 *Physica B* 291 213
9. Fielding A L, Timms D N and Mayers J 1988 *Europhys. Lett.* 44 255
10. Herzberg G 1991 "*Infrared & Raman Spectra of Polyatomic Molecules*" New York: Krieger
11. Moreh R, Finkelstein Y and Shechter H *Phys. Rev.* 1996; B53: 16006.
12. Coolidge MB, Marlin JE and Stewart JJP. 1991 *J. Comput. Chem.*, 1991; 12(8): 948.

Table 1. Measured widths σ_a and σ_c of the H-atom and the combined (C+N+O) atoms obtained after applying multiple scattering corrections. The quantity $(\sigma_a/\sigma_c)^2$, related to the ratio of the effective temperatures, is also given. Note the magnitude of the measured anisotropy ratio which is 1.10. The asterisks refer to the effective temperatures of the C-atoms deduced from the combined (C+N+O) peak by taking the σ_a and σ_c values of the N- and O-atoms from the results of the GAUSSIAN98 AM1 code by assuming an anisotropy ratio of 1.10 for these atoms.

	H	C+N+O
σ_a (\AA^{-1})	4.61(0.10)	13.21(0.25)
σ_c (\AA^{-1})	4.39(0.10)	12.64(0.25)
$(\sigma_a/\sigma_c)^2$	1.092(0.06)	1.10(0.07)

	H	C
T_a (K)	1023(33)	705(23)*
T_c (K)	927(33)	644(20)*
T_a/T_c	1.104(0.05)	1.095(0.05)*
T_e (K)	991(33)	685(22)*

Table 2. Effective temperatures of the atoms in the one, two, three and four molecules of Kapton as calculated using the GAUSSIAN98 - AM1 code. The last column lists the corrected values obtained by multiplying all frequencies by a factor 0.92. The chemical symbols of the molecules used in the calculation are: (1) $C_{34}H_{20}N_2O_6$, (2) $C_{56}H_{30}N_4O_{11}$, (3) $C_{78}H_{40}N_6O_{16}$, (4) $C_{100}H_{50}N_8O_{21}$.

Number of molecules	T_a (K)	T_c (K)	T_a/T_c	T_e (K)	T_e^* (K)
H-atom					
1	1406	804	1.75	1205	1114
2	1248	1120	1.11	1205	1114
3	1241	1136	1.09	1206	1115
4	1198	1224	0.98	1206	1115
C-atom					
1	866	514	1.68	749	699
2	820	606	1.35	749	699
3	794	662	1.20	750	700
4	761	750	1.04	751	701
N-atom					
1	871	364	2.39	702	656
2	862	380	2.27	701	655
3	757	585	1.30	700	654
4	658	720	1.09	700	654
O-atom					
1	611	319	1.92	514	487
2	608	380	1.61	532	504
3	527	533	1.01	531	503
4	531	531	1.00	531	503

Abstract submitted by: [Raymond Moreh] Date: 28/2/2001 **File:Neon_AC1.doc**

Focus field: [Basic Carbon Science]

Authors: [D. Nemirovsky, R. Moreh, K. Kaneko, J. Mayers]

Address: [Prof. R. Moreh , Physics Department, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105]

E-mail address: [moreh@bgumail.bgu.ac.il]

Phone number: [972-8-6461569]

Fax number: [972-8-6472810

]