

Compton Scattering from PTFE: Probing Electron-Charge Redistribution in Polymer Phase Transitions

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Compton profiles of polytetrafluoroethylene (PTFE) at room temperature and at higher temperatures up to and above the melting point are reported. For the first time, one has experimental evidence that thermally induced conformational excitations of the polymer chains are accompanied by a charge transfer, related to the σ - and π -molecular orbitals (MO) of the C-F bond. It is argued that localization of the π -MO related to the fluorine atom facilitates the translational movements of the chains, while the weakening of the C-F bond and the transition from a crystalline to an amorphous phase are associated with delocalization of σ -MOs. [S0031-9007(98)06632-0]

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Polymer chain conformations are of paramount importance in determining the properties of bulk polymeric materials. The shapes adopted by macromolecular chains depend on the nature of their constituent bonds. In particular, the dependence of potential energy on the torsion angle of a given σ bond along the chain plays a major role in the equilibrium, as well as dynamic, behavior of polymers. In a polymer backbone containing large numbers of carbon atoms, torsion angle potentials of neighboring σ bonds are, in general, interdependent. Although it is widely recognized that a proper understanding of polymer chain conformations requires accurate quantum mechanical calculations, the details of these interactions, and the ensuing electron charge redistribution around the interacting atoms, are generally concealed in an "effective" potential barrier between alternative conformational states. Barriers to internal rotations in simple molecules can be determined from spectroscopic or thermodynamic data [1,2]. In macromolecules, however, such barriers are not known to a great precision, and are often based on heat capacities or entropy fitting [2,3] or inferred from spectroscopic measurements on model compounds of low molecular weight [4].

In the present study, we employ the Compton scattering technique to probe experimentally, for the first time, the effects of subtle changes in the electronic structure of a polymer and their conformational implications. We have performed Compton scattering measurements on polytetrafluoroethylene (PTFE), a polymer that has been studied extensively in the past [5,6], at a series of temperatures ranging from room temperature up to and beyond the melting point of the polymer.

In a Compton scattering experiment an incident monochromatic beam of x- or γ -ray photons is scattered by the sample. The inelastically scattered radiation, deflected through a fixed scattering angle, is measured as a function of energy. By converting this spectrum from energy to a momentum scale, the so-called Compton

profile (CP) is obtained. The CP is the projection of the electron momentum density, $n(\vec{p})$, of the scatterer along the scattering vector \vec{k} , which is the vector difference between the wave vectors of the scattered and incident beams, respectively. By taking the direction of \vec{k} as z axis, and using the impulse approximation, the CP is given by the expression [7]

$$J(p_z) = \int_{p_x} \int_{p_y} n(p_x, p_y, p_z) dp_x dp_y. \quad (1)$$

Since $n(\vec{p})$ is a probability density, the CP is constrained by the normalization rules $\int_{-\infty}^{+\infty} J(p_z) dp_z = \int_{-\infty}^{+\infty} J(q) dq = Z$, where Z is the total number of scattering electrons, and q a scalar momentum variable $q = k\vec{p}/|\vec{k}|$. Furthermore, the CP is symmetric with respect to the so-called Compton peak $J(0)$ [7] [see inset of Fig. 1(a)]. The electron momentum density (EMD) is related to the momentum wave function $\chi(\vec{p})$, by $n(\vec{p}) = |\chi(\vec{p})|^2$, which, by Fourier transform, yields the real space wave function $\psi(\vec{r})$. In this way, Compton scattering experiments provide information on the electronic structure of materials.

Since the position and momentum space wave functions of a system weigh inverse regions of their respective spaces, it is well established in Compton spectroscopy [8] that when the charge density is spatially localized the EMD is extended, and hence the corresponding CPs become broader. Physically this corresponds to tightly bound electrons. In the case of electrons involved in a chemical bond, this broadening occurs when the bond becomes more polar [9]. The opposite is expected during the weakening of the bond; that is, the EMD and the corresponding CP become more contracted. In the present work, by varying the temperature of the material PTFE, a redistribution of EMD was observed. It is attributed to a charge transfer in the C-F bond associated with conformational changes, leading ultimately to the melting transition.

The γ -ray (59.54 keV) Compton spectrometer employed utilizes an ^{241}Am source in a 160° scattering angle geometry, and the instrument has a total resolution of 0.54 a.u. of momentum [7,8]. More details on the setup, as well as the detecting system, are given elsewhere [10]. The sample, a rectangular bar (15×15 mm, 3 mm thick) of commercially available PTFE, was positioned in the center of a cylindrical furnace made of alumina, and the whole system was placed in a vacuum chamber evacuated to 10^{-3} mbar. The temperature, continuously monitored, was stabilized within $\pm 1^\circ\text{C}$ to the set point. More than 2×10^7 counts were accumulated under the CP for each spectrum. The CPs were measured at different temperatures, from room temperature up to and above the melting point, in order to investigate possible modifications in the EMD of PTFE during the transition from the crystalline to the amorphous state. Clearly, only *differences* between CPs, ΔJ , are of interest, and therefore data processing includes only background subtraction and normalization to the total number of electrons. All other corrections (multiple scattering, etc.) do not affect the ultimate ΔJ s as these corrections cancel out in the subtraction process. All the CPs were normalized to a total of 48 electrons, between -7 and 7 a.u. of momentum [7], which is the sum of all electrons in a $(-\text{CF}_2-\text{CF}_2)$ unit.

Any alterations in the EMD in this range of temperature should be revealed by subtraction of the corresponding CPs. So $\Delta J(q)$ has been obtained by a point by point subtraction of the room temperature profile from each of the higher temperature profiles. $\Delta J(q)$ is a function of q , and it should be zero if there is no alteration in the EMDs with temperature. A nonzero $\Delta J(q)$ indicates an electron momentum redistribution with temperature. The integral of $\Delta J(q)$ is zero, as $J(q)$ is normalized to the total number of electrons. As a check for reproducibility at each temperature, and in order to eliminate the possibility of any artifacts, ΔJ s corresponding to the *same* temperature were obtained by subtracting two independent data sets both measured at the same temperature. In each case, ΔJ was equal to zero within the experimental error. This can be seen in Fig. 1(a) for $T = 25^\circ\text{C}$.

Figures 1(b) to 1(e) show the evolution of $\Delta J(q)$ as a function of temperature. In the temperature range from room temperature up to 220°C , $\Delta J(q)$ is negative at low values of momentum, becoming positive with a maximum around 1.0 a.u. of momentum. Thus, an electron momentum redistribution appears to occur towards higher momentum values. As the temperature rises to 260 or 280°C , the peak in $\Delta J(q)$ shifts to about 0.5 a.u. of momentum [Fig. 1(d)]. By further increasing the sample temperature, in the range near and above the melting point of PTFE, there is a clear shift of the $\Delta J(q)$ peak from the largemomentum region to values around 0.0 a.u. [Fig. 1(e)], indicating a momentum redistribution toward smaller momentum values corresponding to about 0.1 electrons [11] per $[\text{CF}_2-\text{CF}_2]$ unit. This systematic

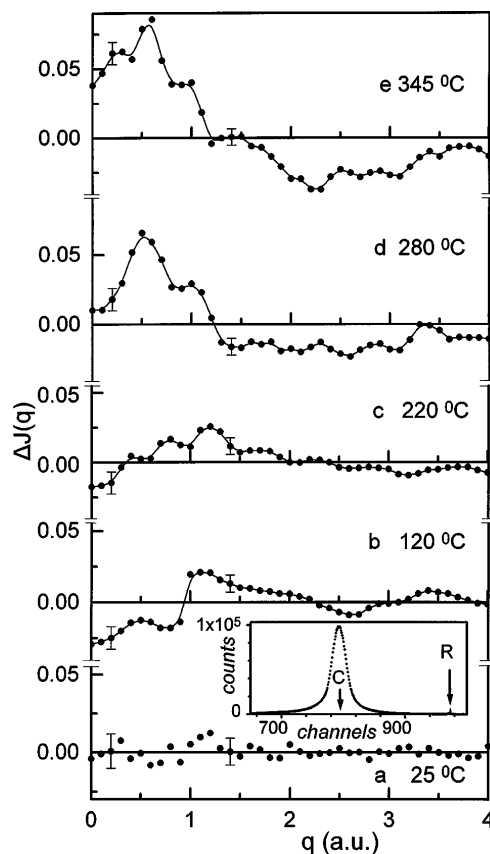


FIG. 1. Experimental difference Compton profiles (in electrons per atomic units of momentum) $\Delta J = [\text{CP at temperature } T] - [\text{CP at } 25^\circ\text{C}]$. Compton profiles were obtained at eleven different temperatures, but only five are shown for reasons of clarity. (a) $T = 25^\circ\text{C}$ (ΔJ was obtained by subtracting two independent sets of data both measured at the same temperature, i.e., 25°C). As expected, $\Delta J = 0$ within the experimental error; (b) $T = 120^\circ\text{C}$; (c) $T = 220^\circ\text{C}$; (d) $T = 280^\circ\text{C}$; (e) $T = 345^\circ\text{C}$. Error bars represent the statistical error. The solid line is drawn as a guide to the eye. The area under each curve [i.e., $\int_0^\infty \Delta J(q) dq$] is equal to zero (see text). Inset in (a): Raw data for a CP. R denotes the elastic peak and C the position of the Compton peak.

variation of $\Delta J(q)$ with temperature, coupled with the reproducibility observed at each temperature, weigh heavily against the possibility of the observed changes being due to artifacts.

In order to examine the existence of an EMD redistribution, and the consequent charge transfer with temperature in PTFE in an alternative manner, the full width at half maximum (FWHM) of each CP has been plotted versus temperature (Fig. 2). It is evident that, up to about 150°C the FWHM increases, indicating the broadening of the EMD. At higher temperatures the FWHM decreases, until it reaches an almost constant value just above the melting point, indicating a contraction of the EMD. From the above findings, we argue that the temperature dependent behavior of the EMD in PTFE can be divided into two regions. In one region, from room temperature

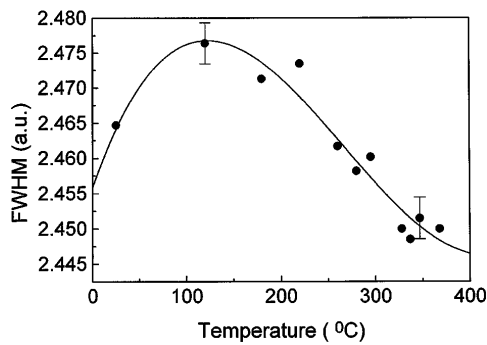


FIG. 2. FWHM of the Compton profiles versus temperature. The solid line has been drawn as a guide to the eye.

to about 150 °C, there is a spatial transfer of charge from less localized to more localized regions, and in the second region, from about 150 °C and up to the melting point, the situation is reversed and there is a charge transfer from more localized to less localized regions.

Additional information concerning the electron distribution in configuration space (\vec{r}) can be obtained from the CP, by using the function $B(\vec{r})$ which is the Fourier transform of the momentum density,

$$B(\vec{r}) = \int n(\vec{p})e^{-i\vec{p}\vec{r}} d\vec{p}. \quad (2)$$

It can easily be shown [12] that $B(\vec{r})$ is an autocorrelation function of the one-electron configuration space wave function $\psi(\vec{r})$:

$$B(\vec{r}) = \int \psi(\vec{r})\psi^*(\vec{R} + \vec{r}) d\vec{R}. \quad (3)$$

From (1) and (2) it follows that

$$B(z) = \int J(p_z)e^{-ip_z z} dp_z. \quad (4)$$

Thus, $B(z)$ represents the above autocorrelation along the z direction, and it is the one-dimensional Fourier transform of the directional Compton profile. Although this function is normally employed for the analysis of directional CP, in order to obtain a theoretical quantitative estimation of the charge transfer observed experimentally in the case of polycrystalline PTFE, we have used a spherically averaged $B(z)$.

Figure 3 shows the experimentally deduced difference $\Delta B_{\text{exper}} = B(z)_{345} - B(z)_{25}$ (curve *a*), where the subscript indicates the temperature in °C, along with the differences $\Delta B(z)_{\text{theory}}$ (curve *b*), as calculated for the C_2F_4 unit [13]. Good agreement is observed between theory and experiment, confirming that a charge transfer occurs from F to C as temperature rises up to and beyond the melting point. Curve *d* is the theoretical $\Delta B(z)$ taking into account *only* the $2p$ orbitals of fluorine, in a direction perpendicular to the C-F bond. It must be stressed that this is the only possible way to reproduce theoretically the negative part of the experimentally deduced $\Delta B(z)$ for

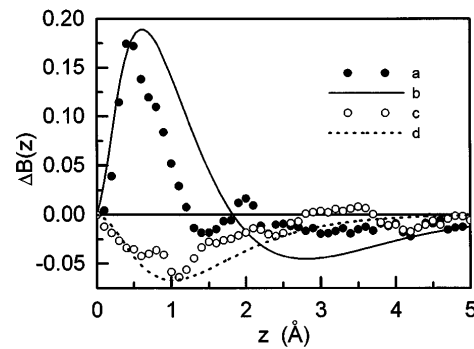


FIG. 3. Theoretical and experimental $\Delta B(z)$ for PTFE: (—) Theoretical $\Delta B(z) = B(z)_{\text{atoms}} - B(z)_{\text{ions}}$; (----) theoretical $\Delta B(z) = B(z)_{\text{atoms}} - B(z)_{\text{ions}}$ for $2p$ orbitals of fluorine; (●) experimental $\Delta B(z) = B(z)_{345} - B(z)_{25}$; (○) experimental $\Delta B(z) = B(z)_{120} - B(z)_{25}$.

lower temperatures [$\Delta B(z) = B(z)_{120} - B(z)_{25}$]. This fact strongly suggests that a π -molecular orbitals (MO) localization occurs in the low range of temperatures.

In this light, we now examine more closely the experimental results from our investigation in two temperature ranges: room temperature to about 150 °C and about 150 °C to 370 °C. At a low temperature van der Waals interactions (primarily dipole-dipole forces) hold adjacent PTFE chains, or portions of chains, together to form a hexagonally packed crystalline structure. In fact, the orientational arrangement of the dipoles results in the well known helical PTFE structure described in the literature [5,6]. A consequence of such a dipolar alignment is the polarization of the charge density away from the F atom of a given C-F dipole and towards the opposing dipole with which it is interacting. Such charge delocalization results in *lower* electronic momentum, as noted previously. Increasing T , however, results in enhanced translational and rotational agitation. As segments of neighboring chains begin to move relative to each other their interaction weakens, since the dipoles become more distant and less well correlated. Note that, for spatially fixed permanent dipoles a distance r apart, the interaction energy varies as r^{-3} , while for freely rotating ones it is a much weaker dependence, namely, $(kT)^{-1}r^{-6}$.

As the dipolar interaction subsides, the electronic charge of the π orbitals associated with the $2p$ atomic orbitals of fluorine withdraws towards the F atom, leading to enhanced spatial localization, and hence an extension in the EMD towards *higher* momentum. This explains the increase in the FWHM upon initial rise of temperature, as shown in Fig. 2, and is the only way to account for the negative part of $\Delta B(z)$ in Fig. 3, as noted above. The C-F bond, and more specifically the σ -MO, seems to be very little affected initially, the redistribution of charge being largely confined to the π orbital at low to intermediate temperatures, i.e., in the range from room temperature to about 150 °C. This is to be expected, in

view of the fact that modification of the σ orbital requires more energy.

Thus, while at moderate temperatures only excitations to conformations with a small potential barrier are permitted, upon further increase of the temperature, rotation of the CF_2 group, around the C-C bond, is greatly enhanced. In particular, the transition between the (trans) t^\pm and t conformational states is likely to be affected first, on raising the temperature, since it is characterized by a rather small potential barrier of only about 2 kJ/mole [5]. This transition is favored energetically if the repulsive forces between opposing F atoms of the same molecule decrease. This could be the case if the charge density of the π -MO associated with the F atom withdraws toward its nucleus as has been observed in our experiments and further supported by $\Delta B(z)$ calculations (see curves c and d of Fig. 3). At still higher temperatures, and especially above the melting point $T_m \approx 330^\circ\text{C}$ [14], where the polymer is in the amorphous state, excitation to the (gauche) g^\pm conformations takes place, thereby increasing the freedom of the chains while simultaneously weakening the C-F bond. The latter effect is associated with a charge transfer within the σ -MO, away from the F atom and towards the C atom, and consequently leads to a decrease of electronic momentum. This is borne out by the results shown in Figs. 1(d) and 1(e), where the effect of such a charge delocalization can be clearly observed at the higher temperatures and is also consistent with energy considerations [15]. In this range of high temperatures, the charge localization emanating from the π -MO in F, which was dominant at low temperatures, is now completely swamped by the strong and opposite behavior of the σ bond, leading to an overall contraction of the EMD [see Fig. 1(e)] and a decrease of FWHM (see Fig. 2).

The weakening of the C-F bond associated with conformational transitions involving g^+ and g^- is supported by the theoretical work of Morokuma [16] and other experimental work [17]. Morokuma finds that, when the angle of rotation ω of adjacent CF_2 groups around the C-C axis approaches 60° (NB $\omega = 60^\circ$ corresponds to a gauche conformation), the C-F bond is weakened, with simultaneous charge transfer of $0.01e$ from F to C (commensurate with our experimentally deduced value about $0.025e$), while the strength of the C-C bond is not affected. Experimentally, the presence of a crystalline phase transition around $T_i = 150^\circ\text{C}$ was confirmed by an x-ray diffraction study [17]. This transition was ascribed to an intermolecular disorder, increasing rapidly as the temperature approaches T_i due to the excitation of t subunits in the chain.

In conclusion, we have probed experimentally the effects of subtle changes in the electronic structure of a polymer, and argued that these are related to chain conformations. For the first time, there is experimental

evidence strongly suggesting that thermally induced conformational excitations of the polymer chains are accompanied by charge transfer, related to the σ - and π -molecular orbitals of the C-F bond. Localization of the π -MO, related to the fluorine atom, facilitates the translational movements of the chains, while the weakening of the C-F bond and the transition from a crystalline into an amorphous phase are associated with a delocalization of σ -MOs.

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