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Crystallinity of poly(tetrafluoroethylene) using Raman spectroscopy

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Changes in the Raman spectra of quenched poly(tetrafluoroethylene) have been correlated with the crystallinity by differential scanning calorimetry, i.r. spectroscopy, density, and wide-angle X-ray scattering. An increasing tailing of the band at $\Delta\nu = 1381\ \mathrm{cm}^{-1}$ (CF_2 symmetric stretching fundamental) has been identified as the most marked effect of decreased crystallinity. A method for quantifying the band tailing has been devised. It was found that the band tailing so quantified can serve as a measure for the crystallinity.

(Keywords: poly(tetrafluoroethylene); crystallinity; Raman spectroscopy)

Introduction

One quantity employed to characterize the structure of partially crystalline polymeric solids is the degree of crystallinity (X_c). Methods utilized to determine X_c include calorimetry, density measurements, wide-angle X-ray scattering (WAXS) and, in the case of poly(tetrafluoroethylene) (PTFE), i.r. methods[1]. The aim of the work presented in this paper is to investigate whether it is feasible to determine X_c of PTFE using Raman spectroscopic methods. Raman spectroscopy provides a non-destructive and fast technique, complementary to i.r. spectroscopy and without any sample preparation requirements. Several authors[2–4] have suggested procedures where Raman methods might be used, but no satisfactory method is available at this time. We report here on a systematic correlation of spectral changes with varied sample crystallinity to identify changes which are specific and pronounced enough to prove useful for quantification.

At atmospheric pressure the phase diagram of PTFE exhibits three solid phases and the melt[5,6]. The equilibrium melting point lies, dependent on the chosen extrapolation[7], between 605 and 620 K. Two first-order crystal–crystal transitions are observed at 292 and 303 K, respectively. In the low temperature (LT) phase the molecules pack in a nearly perfectly ordered triclinic structure, adopting a 13/6 helical conformation having 13 equally spaced CF_2 groups in six turns. The intermediate temperature (IT) phase, between 292 and 303 K, is of hexagonal symmetry, with the molecular helix untwisting slightly to form a 15/7 helix. The lateral packing of the molecules remains hexagonal in the high temperature (HT) phase, the intermolecular separation increasing and the helical conformation further untwisting as the temperature is raised. Disorder is introduced into the crystal lattice of the IT phase by thermally activated librational motions of the chain segments and helix-reversal defects. In the HT phase, *trans* and *gauche* conformations are thought to become activated and translational motion sets in in the chain direction, disturbing the longitudinal order in the crystal lattice[5,6,8–13].

The different solid-state structures, and even the melt, show essentially the same Raman spectrum in terms of both the number and relative intensities of the Raman active vibrational modes[2,14,15]. All of the spectra are in accordance with group theoretical predictions based on an ideal, infinitely long and isolated PTFE helix. Line group analysis predicts 21 Raman active vibrational modes for either helical conformation, 14 of which can readily be observed[2,14,16,17]. There is still some uncertainty about the assignments of the symmetry species to the observed Raman bands, and we subsequently refer to the band assignment favoured by most authors and summarized by Bower and Maddams[18]. Variations in sample crystallinity are known to have little effect on the Raman spectra.

Experimental

Materials. As-polymerized commercial grade polymers were supplied in powder form by ICI, UK (Fluon G163) and Hoechst AG, Germany (Hostaflon TF1750 and KU02). According to Suwa *et al.*'s empirically derived relationship[19] between the number-average molecular weight and the heat of crystallization, the molecular weight was estimated at $44 \times 10^5\ \mathrm{g\,mol}^{-1}$, $22 \times 10^5\ \mathrm{g\,mol}^{-1}$ and $2 \times 10^5\ \mathrm{g\,mol}^{-1}$ for G163, TF1750 and KU02, respectively. The polymer powders were cold-pressed under vacuum at a pressure of $7500\ \mathrm{kg\,cm}^{-2}$ to form discs with a diameter of 13 mm and a thickness of around 120 μm. The discs were heated at 650 K – well above the peak melting temperatures of the polymers – for 1 h, subsequently quenched in an ice/water bath and then annealed for various times at temperatures between 590 and 600 K to yield samples of various crystallinities. Thermogravimetric

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*To whom correspondence should be addressed analysis confirmed that polymer degradation did not occur during quenching and annealing.

Sample characterization. Step-scan diffractograms were recorded in reflection at 298 K with a Philips 1700 diffractometer using nickel filtered CuKα radiation. The data were corrected for polarization and scattering angle before deconvoluting the overlapping amorphous halo and the (1 0 0) diffraction peak[20,21]. Ratioing the integral intensities and correcting for density gives $X_{c,xray}$. I.r. transmission measurements in the range from 400 to 4000 cm^{-1} were made on a Mattson, Galaxy 2020 spectrometer at 2 cm^{-1} nominal resolution. Twenty spectra were co-added before processing the data, employing a method for the determination of X_c of PTFE proposed by Moynihan[1]. The method is based on the i.r. peak absorbances of an amorphous band at about 775 cm^{-1} and a band at 2367 cm^{-1} whose absorbance is considered to be insensitive to the molecular arrangement and hence to be dependent only on the sample thickness. According to Moynihan, the ratio $A(775\,\mathrm{cm}^{-1})/A(2367\,\mathrm{cm}^{-1})$ relates linearly to $X_{c,xray}$ and the sample density. Although our samples were some 120 μm thick, they were still thin enough to enable measurement of the relevant peak absorbances. Raman Stokes spectra with a resolution of 2 cm^{-1} were recorded on a Perkin–Elmer 1700x Fourier transform Raman spectrometer equipped with an indium gallium arsenide photodetector and a linearly polarized neodymium:YAG laser operating at a wavelength of 1064 nm. Scattered light of all polarization directions was collected in backscattering geometry. The laser power at the sample was 500 mW and the Norton–Beer medium apodization function[22] was chosen for Fourier transforming the interferograms. In order to improve the signal-to-noise ratio, 60 spectra were co-added. Specimens were mounted in a purpose-built sample holder equipped with a Peltier-element-driven temperature stage to allow variable-temperature Raman spectra to be obtained. Absolute density measurements utilizing the sink/swim method were conducted in compliance with international standard ISO 1183:1987, Method C. The measurements were carried out at 296 K using 1,4-dibromobutane and dibromomethane as immersion liquids. Heats of fusion were determined from the melting endotherms obtained with a Perkin–Elmer DSC-7 scanning calorimeter at a heating rate of 20 K min^{-1}.

Results and discussion

Preliminary experiments on virgin and quenched samples were conducted in the range between 250 and 395 K in order to evaluate how both the room temperature phase transitions and thermally introduced disorder affect the Raman spectra. Continuous annealing at 395 K did not affect the d.s.c., i.r. and WAXS derived values of X_c in both virgin or quenched samples. Interest was focused on the eight strongest, and therefore potentially most suitable for quantification, Raman bands at $\Delta\nu = 1381, 1301, 1216, 732, 576, 386, 382$ and 293 cm^{-1}. Over the entire temperature range all of the listed peaks can be satisfactorily and consistently fitted with a Lorentzian model, and subsequently quoted band parameters refer to Lorentzian curves fitted to the data.

Effect of temperature and crystallinity on Raman spectra. Shifts of band position with temperature and crystallinity are not very significant and may not exceed experimental error. All of the bands show a more or less pronounced broadening between 283 and 308 K, followed by a further linear increase of the bandwidth within the HT phase. A sharp, step-like doubling of the bandwidth close to 285 K is revealed in the bands at $\Delta\nu = 1216, 576$, 382 and 293 cm^{-1}, and can serve to monitor the onset of the first solid–solid transition. The increase in bandwidth associated with a decrease in crystallinity varies with the vibrational mode, and is slightly larger in the HT than in the LT phase. For our set of samples, this increase in bandwidth ranges, dependent on the specific mode, from 20 to 60% of the minimal bandwidth measured for one mode as $X_{c,xray}$ falls from 0.85 to 0.45. It is worth noting that virgin polymer, which has the highest crystallinity by d.s.c., i.r. and WAXS, does not show the smallest bandwidth of all the samples examined. Turning now to relative band intensities in the Raman spectra, either these do not change systematically with crystallinity or the changes are not particularly pronounced. The tail forming on the low frequency side of the peak at 1381 cm^{-1}, the depolarized symmetric CF$_2$ stretching mode (A_1 symmetry species), is the most marked effect of decreased crystallinity (see *Figure 1*).

Method for quantifying the band 'tailing'. This band 'tailing' was further investigated at a temperature of 263 K, firstly in order to minimize thermally introduced inter- and intramolecular disorder and secondly to narrow the band, thus making the distinction between the main Raman peak and its low-frequency tail more obvious. It was found that the high frequency component of the 1381 cm^{-1} band and the complete bands at 1301 cm^{-1} (symmetric CF$_2$ stretching mode, depolarized, E_1) and 1216 cm^{-1} (asymmetric CF$_2$ stretching mode, depolarized, E_2) are almost perfectly fitted by Lorentzians. Based on this observation, the following procedure, as depicted in *Figure 1*, was adopted to quantify the band 'tailing'. Three Lorentzians and a straight baseline were fitted to the group of overlapping peaks in the interval

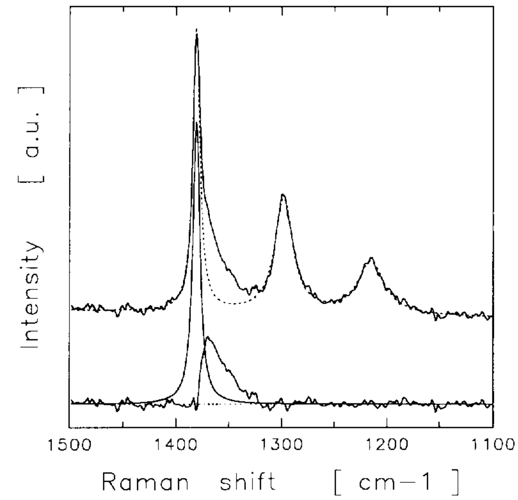

Figure 1 Part of a Raman spectrum of a low crystallinity sample of PTFE. The interval shown is relevant for curve fitting. Upper two curves: original and fitted (dashed curve) data. Lower two curves: fitted Lorentzian at 1381 cm^{-1} and difference spectrum as described in the text

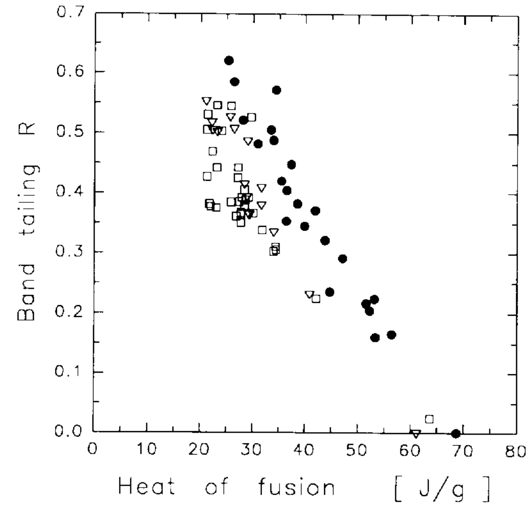

Figure 2 Band tailing R, as defined in the text, *versus* the heat of fusion: ●, sample KU02; ▽, sample TF1750; □, sample G163

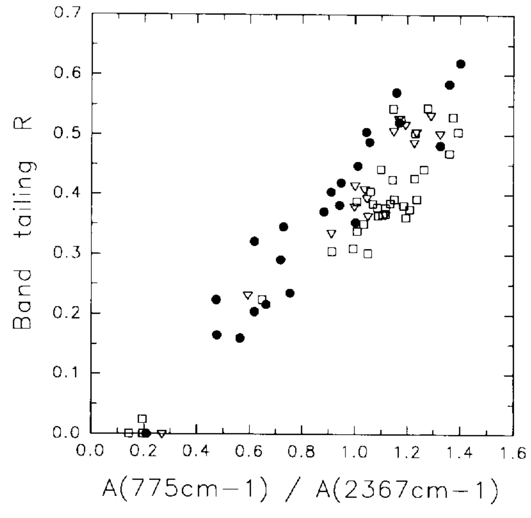

Figure 3 Band tailing R, as defined in the text, *versus* the ratio of i.r. peak absorbances according to Moynihan: ●, sample KU02; ▽, sample TF1750; □, sample G163

between 1100 and 1500 cm^{-1}, deliberately ignoring the data between 1300 and 1380 cm^{-1}. The fitted spectrum was then subtracted from the original data, yielding a difference spectrum with non-vanishing intensities between approximately 1325 and 1375 cm^{-1}, with a maximum intensity near 1365 cm^{-1}. As the last step, the areas beneath the broad peak in the difference spectrum and the fitted Lorentzian at 1381 cm^{-1} were ratioed, giving a relative measure of the band 'tailing'. *Figure 1* shows the recorded Raman spectrum of a low crystallinity sample, the entire model spectrum fitted to this data, the Lorentzian at 1381 cm^{-1} and the difference spectrum resulting from the subtraction. The intensity ratio R, defined as the quotient $I(\text{tail})/I(1381\ \text{cm}^{-1})$, can be reliably determined and is reproducible within a statistical error of around 4%. R is not affected by the solid–solid phase transitions and stays constant between 173 and 395 K. Neither any additional Raman peak nor a shoulder could be resolved at liquid nitrogen temperatures. In addition, there was no indication of the difference spectrum changing its shape and overall appearance with temperature and crystallinity, apart from a slight broadening as the temperature rose. This leads us to the assumption that an additional vibrational normal or combination mode is not the cause of the tailing and hence it is likely that the observed band asymmetry reflects inhomogeneous broadening due to a growing number of molecules adopting conformations different from a regular helix as the crystallinity decreases.

Comparison of Raman data with crystallinity by d.s.c., i.r., density and X-ray diffraction. Plots of R *versus* the measured heat of fusion, the ratio of the i.r. peak absorbances and the density are shown in *Figures 2, 3* and *4*, respectively. Clearly, R correlates linearly with all of the aforementioned quantities for the low molecular weight polymer KU02. The statistical significance of the correlations, expressed as the squared regression coefficient, falls by 10 to 20% from values around 0.95 if, in addition, the two higher molecular weight polymers are included. The correlation with d.s.c. data is the most affected, as can be seen in *Figure 2* where the data points of samples of different polymers lie on different straight lines. Increasing scatter occurs for the polymer G163 as the heat of fusion decreases. We presume that a molecular weight dependence of the morphology could be the underlying cause. Both polarizing light microscopy of microtomed specimens and scanning electron microscopy of cold fractured samples give supporting evidence for this view. Furthermore, on the basis of d.s.c. measurements and transmission electron micrographs, Suwa *et al.*[23] suggested that melt-crystallized PTFE forms lamellar or fibrillar structures for polymers with molecular weights above 10^6 g mol^{-1} and below 3×10^5 g mol^{-1}, respectively. Correlations of the ratio R with i.r. data and density are little affected by the molecular weight. The extrapolated value for the crystalline density at 2.272 g cm^{-3} at 298 K is in good agreement with n.m.r. measurements[24].

Flat-plate X-ray photographs of quenched specimens revealed a considerable degree of planar orientation[25,26] for polymers G163 and TF1750. Consequently, only

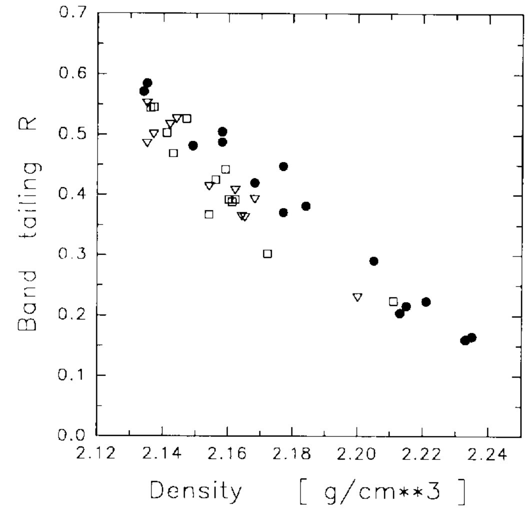

Figure 4 Band tailing R, as defined in the text, *versus* the absolute density: ●, sample KU02; ▽, sample TF1750; □, sample G163

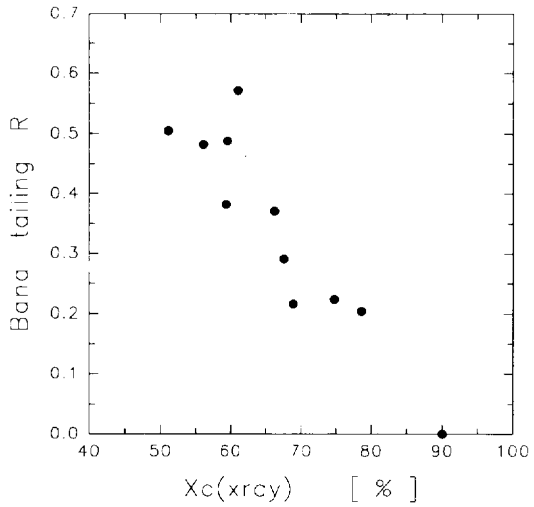

Figure 5 Band tailing R, as defined in the text, *versus* the degree of crystallinity by WAXS: ●, sample KU02

step-scan diffractograms of the polymer KU02 were employed to determine $X_{\mathrm{c,xray}}$. Although the data points in *Figure 5* are somewhat scattered, band tailing clearly increases as $X_{\mathrm{c,xray}}$ falls.

We intend to compare the routinely used i.r. method by Moynihan with the Raman procedure described here in detail in a subsequent publication.

Conclusions

A procedure for quantifying the band tailing of the Raman peak at 1381 cm^{-1} has been devised. Comparison of this phenomenon with d.s.c., i.r., density and WAXS measurements shows that a Raman spectroscopic method for determining the crystallinity can be based on this spectral feature. The correlation with the heat of fusion is presumably affected by the polymer morphology.

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