Proton NMR Determination of Crystallinity in Poly(ethylene Terephthalate)

C. M. Roland, J. H. Walton† and J. B. Miller*

Chemistry Division, Code 6120, Naval Research Laboratory Washington, DC 20375-5342, USA

The results of proton NMR T_{1xz} measurements on poly(ethylene terephthalate) (PET) films and fibers processed under various conditions are presented. Consistent with previous results, two domains are found in isotropic, amorphous PET. The NMR results provide an accurate measure of crystallinity in PET films and fibers, without requiring any assumptions about the semi-crystalline morphology of the polymer. The NMR technique is particularly advantageous for PET fibers where orientation effects interfere with the more traditional density determination of crystallinity.

KEY WORDS NMR ^{1}H NMR Crystallinity Poly(ethylene terephthalate)

INTRODUCTION

Although it is obviously of interest to quantify the degree of crystallinity in polymers, for poly(ethylene terephthalate) (PET) it has been found that no correlation exists among results obtained by different methods.[1–5] Of course, to the extent that experiments probe different physical features of the material, no correlation is expected. The usual determinations are based on mass density, the heat of fusion as determined by differential scanning calorimetry (DSC), infrared absorption[6,7] and x-ray diffraction intensities. The last method is good in principle but problematic in practice. Absolute crystallinity determinations from x-ray scattering require painstaking measurements of the amorphous background scattering, along with extrapolations over extended angular ranges.[8,9] The contribution to the diffracted intensity from small or imperfect crystallites may be neglected. 'Crystallinity indices,' which are, at best, only proportional to the degree of crystallinity, are often used instead of absolute crystallinities.[10]

There are serious problems with the use of DSC data for absolute crystallinity determinations in polymers. The most obvious is the fact that the act of measuring disrupts that which is being measured. Crystallization during the course of a temperature scan can introduce error, a particular problem with PET. DSC results are also sensitive to superheating, the propensity for which depends on the crystal structure.[11] Absolute determinations from DSC require a knowledge of the perfect (equilibrium) heat of fusion, the correct value of which can be in doubt owing to the effects of crystal defects and the finite crystal size.[12] In PET, and also other polymers, the value of the perfect heat of fusion varies significantly with temperature, as do the heat capacities

of both the amorphous and crystalline phases. Although procedures to minimize these problems have been proposed,[13–15] such complications reduce the accuracy of the DSC method. From an assessment of the error involved only in determining the perfect heat of fusion of PET, it was concluded that the correct value is known to no better than ±14%.

Infrared spectroscopy is less commonly employed for studying crystallinity in polymers.[6,7] The main drawback to this technique is achieving quantitative measurement of strong absorption bands in the presence of interference from scattered light. This is particularly a problem with fibers. Industrial PET yarn typically consists of bundles, each containing thousands of individual filaments; therefore, surface scattering usually overwhelms the light transmitted at the wavelengths of interest.

The most common method for quantifying the extent of crystallization in a polymer is from the mass density. If a two-phase morphology can be assumed, knowledge of the crystal and amorphous densities permits a facile calculation of the degree of crystallinity. Unfortunately, in PET both of these quantities are uncertain. From x-ray analysis of the unit cell, a range of values have been reported for the crystal density of PET, including 1.455,[16] 1.495,[17] 1.515[18] and 1.529 g ml^{-1}.[19] At least some of this discrepancy may arise from a dependence of the unit cell dimensions on the crystallization conditions. Huisman and Heuvel[20] have reported that the crystalline density of PET is a function of the processing conditions. A similar problem exists with regard to the amorphous density. Since PET can be quenched into a completely amorphous state, the unoriented amorphous density is well established (1.335 g ml^{-1}).[16] Unfortunately, the density of PET is a function of amorphous orientation,[1,21,22] thus negating any simple relationship between sample density and degree of crystallinity. In fact, it has been found that during spinning a density as high as 1.349 g ml^{-1} can be achieved in completely amorphous PET.[23]

NMR has been used for some time for the analysis of crystallinity in PET. There are two principle methods:

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lineshape analysis and relaxation time measurements. Differences in lineshape can arise from variations in chemical/physical environment or, as with relaxation time measurements, from variations in the frequency and amplitude of molecular motions in different polymer domains.

Lineshape analysis in carbon-13 NMR has been applied recently to the study of semi-crystalline PET.[24,25] The carbon-13 resonances can be resolved into broad and narrow components, with a small shift difference between the components. The narrow component is associated with the crystalline fraction.[24] The latter, as measured by carbon-13 NMR, was found to exceed the degree of crystallinity deduced from other methods for all samples studied.[25]

The application of proton NMR to the study of PET has a longer history.[26,27] Eichhoff and Zachmann[26] relied on fitting the wide-line NMR signal measured above the glass transition temperature to a two-component function. In contrast to the carbon-13 NMR results, the broad component of the proton NMR line is associated with the crystalline fraction. The quantity of material associated with the broad component exceeds the degree of crystallinity found by other methods. This was ascribed[26] to the presence of taut amorphous chains contributing to the NMR response in a manner similar to the crystalline stems. The method has been used to assess the extent of taut tie molecules in PET.[28,29] These structures exert an important role in determining the physical properties of the fibers.

Interpretation of proton NMR experiments in terms of the concentration of crystalline and amorphous domains below the glass transition temperature is confounded by spin diffusion, which leads to the observation of a single broad line or relaxation time.[30] This problem is overcome, however, with a newer NMR technique based on spin–lattice relaxation behavior in the effective field of a multiple pulse line-narrowing cycle.[30] For the MREV-8 pulse cycle[31–33] this relaxation time, T_{1xz}, is sensitive to both the amplitude and frequency of motions, allowing the domains in the heterogenous PET morphology to be defined according to their mobility. The T_{1xz} determination effectively quenches spin diffusion. For this reason, the T_{1xz} approach is able to distinguish between components of different mobilities, the contributions from which are smeared by spin diffusion in the other NMR experiments.[30] The present study was directed to an assessment of this NMR method through measurements on PET processed in various ways.

EXPERIMENTAL

PET fibers and films were exposed to a variety of processes in order to produce morphologies differing in orientation and degree of crystallinity. Heated then quenched amorphous films (Goodyear Cleartuf 1006) were either drawn at 85 °C or isotropically annealed at 120 °C. One sample was annealed for an extended duration (several weeks) at 270 °C to yield a highly crystalline, high melting point polymer.[11] Spun fibers obtained from Allied-Signal Fibers, which had been

drawn to their maximum draw ratio followed by heat treatment, were used as received and after constant length annealing at 200 °C. One of these fibers was also relaxed on an off-line draw roll at around 100 °C. A complete description of the Allied-Signal fibers can be found elsewhere.[34,35]

Mass densities were measured with a density gradient column and optical birefringence was determined using a polarizing microscrope. The amorphous orientation was estimated from the birefringence data using standard procedures.[36]

The proton NMR measurements were made on a Bruker MSL-300 spectrometer at 300 MHz. The MREV-8 cycle time was 48 μs and the 90° pulse length was 1.8 μs. The NMR relaxation curves were fitted to a multi-exponential function. It was determined by least-squares analysis that three exponentials were required to fit the relaxation data, with the exception of the completely amorphous films, which could be adequately fitted with two exponentials. The shortest time constants, of the order of 1 ms, are assigned to 'amorphous' material; the intermediate time constants, of the order of 10 ms, are assigned to 'constrained amorphous' materials; the long time constants, of the order of 100 ms, are assigned to 'crystalline' material. The bi-exponential fits to the data for the amorphous materials produced time constants of the order of 1 and 10 ms, in line with the time constants of the amorphous and constrained amorphous materials obtained from tri-exponential fits to the data for the semi-crystalline materials. This description (amorphous, constrained amorphous and crystalline) follows terminology suggested previously;[30] ascertaining its correctness was an objective of the present work.

RESULTS

Our NMR data for amorphous PET are adequately fitted wiht a bi-exponential function, with time constants appropriate to amorphous and constrained amorphous material. Interestingly, the data for isotropic, amorphous PET required two exponentials for fitting. It is not obvious what the two fractions correspond to, since the material is presumably homogeneous. In contrast, multi-exponential signal decay in the absence of spin diffusion, using time suspension techniques, has generally not been observed in other unoriented, amorphous polymers.[37] When we draw initially amorphous PET without inducing crystallization, as determined from x-ray diffraction, no long time component is evident in the NMR data, even though the density increases. This densification is due to orientation of the amorphous material. However, none of the NMR fit parameters, time constants and percentage of components, change during drawing under these conditions (Table 1). This is consistent with the conclusion of Havens and VanderHart[30] that the constrained amorphous phase does not consist simply of oriented amorphous chains. In this important respect, the present NMR experiment differs from the earlier proton NMR studies.[26–29]

Table 1. Relaxation times and precentage content of the amorphous and constrained amorphous domains of isotropic amorphous films drawn to the indicated strains

Strain (%)	Amorphous		Constrained amorphous	
	$T_{1\rho}$ (ms)	Content (%)	$T_{1\rho}$ (ms)	Content (%)
0	1.7	64	7.3	36
52	1.9	75	8.9	25
150	1.8	72	7.5	28
200	1.8	75	9.4	25
260	1.9	75	9.2	25
280	1.7	71	8.0	29

Isotropic films were annealed while unconstrained, to yield different degrees of crystallinity, including an extreme degree of crystallinity obtained by high-temperature annealing.[11] As seen in Fig. 1, there is direct proportionality between the degree of crystallinity determined by NMR and that calculated from the density of the films. We conclude that both methods yield reliable relative measures of crystallinity, although they do not yield equivalent results. The crystallinity deduced from the densities always gives higher values for the crystallinity, even when using for the crystal density 1.529 g ml^{-1},[19] the highest value reported in the literature. This may reflect orientation developing in the amorphous chains as a result of the crystallization process, notwithstanding the absence of external constraints on the films during the crystallization.

When the data for the fibers are included in Fig. 1, the correlation between the two determinations of crystallinity deteriorates. There are two obvious sources for scatter of the fiber data about the line describing results from the isotropic films. The high orientation of the amorphous phase of the fibers will increase the density, leading to over-estimation of the crystallinity. As men-

tioned above, a 1% increase in density can be achieved in amorphous PET by orientation alone.[20] Based on the lowest value reported for the crystal phase density,[16] this would imply a degree of crystallinity of almost 13% if the effect of orientation on density were ignored.

It has also been found for PET yarns with high draw rations that the amorphous density can become anomalously low, presumably reflecting the development of voids.[6] This, along with a dependence of the crystal phase density on processing conditions,[1,20-22] contributes to the poor correlation of the fiber data in Fig. 1 with the results from isotropic samples.

The identity of the material having the intermediate relaxation time, referred to as constrained amorphous domains by Havens and VanderHart,[30] remains speculative. It is clearly not identifiable with the highly oriented 'taut tie chains' alluded to in interpretations of wide-line NMR measurements obtained on PET above the glass transition temperature.[26-29] This point was brought out in spin diffusion experiments carried out on PET fibers,[30] which indicates that the constrained amorphous domains were in equal physical contact with both the crystalline and unconstrained amorphous domains. In Fig. 2 we plot the amorphous orientation determined by optical birefringence as a function of the NMR-determined crystallinity for the various PET fibers. These data suggest that increased crystallinity comes at the expense of amorphous orientation, not a surprising result since crystallization arises primarily from the more oriented chains.[22,34,35] However, there is no correlation between amorphous orientation and the constrained amorphous content of the fibers, affirming that the latter is not an oriented phase.

In Fig. 3 we plot the amorphous and constrained amorphous content of annealed PET films (Fig. 1) as a function of NMR-determined crystallinity. We find, in agreement with earlier results[30] and as discussed above for our fiber samples, that crystallization does not occur at the preferential expense of the constrained amorphous material. This argues against its identification
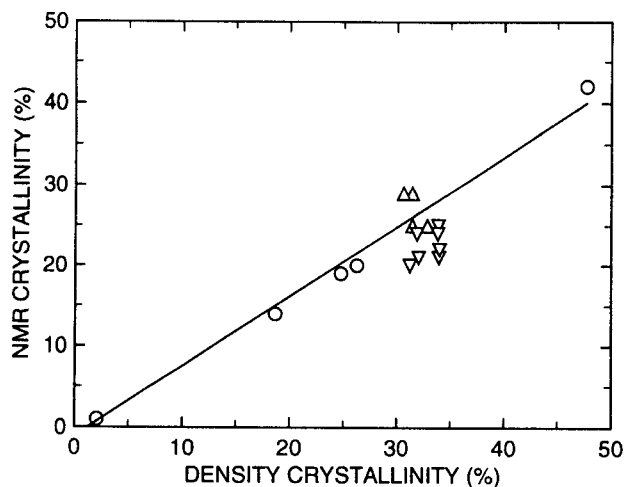

Figure 1. Plot of the NMR-determined crystallinity as a function of the crystallinity determined from density (using 1.529 g ml^{-1} as the crystal density.)[19] The circles are PET films annealed at 120 °C for various times, with the exception of the sample with the highest crystallinity, which was annealed for several weeks at 270 °C (as described in Ref. 11). △, Fibers as received; ▽, treated fibers. A complete description of the fibers can be found elsewhere.[34,35] The line is a least-squares fit to the film data (○).

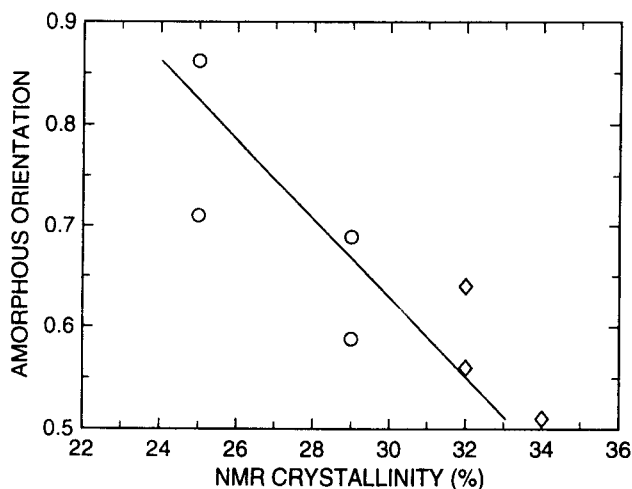**Figure 2.** Plot of the amorphous orientation as a function of the NMR-determined crystallinity. ○, Fibers as received; ◇, off-line relaxed fibers. The line is a least-squares fit to the data; it is included as a guide for the eye and does not indicate a linear relationship.
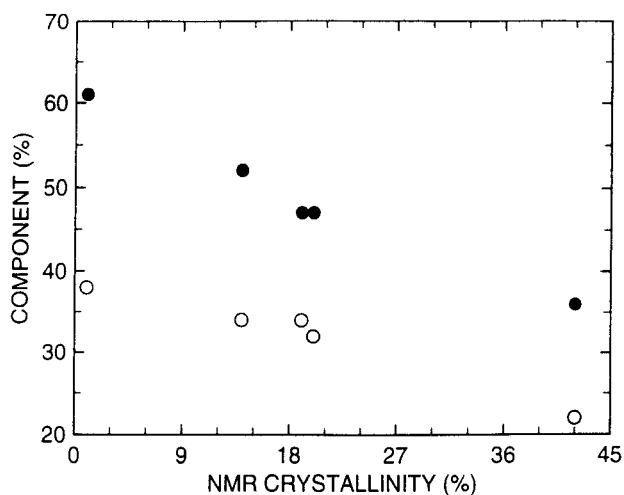
Figure 3. Plot of the (●) amorphous and (○) constrained amorphous content (%) as a function of the NMR-determined crystallinity of the annealed films.

with amorphous chains bordering the crystalline phase. Havens and VanderHart[30] suggested that the PET material of intermediate mobility might comprise the grain boundaries existing between crystallities in the mosaic block model of semi-crystalline PET.[3] This suggestion is at odds with the presence of the constrained amorphous phase even in completely amorphous PET (see Table 1). Finally, we point out that carbon-13 NMR results on PET fibers have been interpreted in terms of the existence of crystalline, amorphous and ordered amorphous domains.[25] However, this reference relied on density data, which are clearly unreliable for oriented PET.

CONCLUSION

The proton NMR method permits the quantitative analysis of the crystallinity of PET films and fibers. Unlike conventional techniques, this NMR method does not require any assumptions concerning the semi-crystalline morphology. The results presented demonstrate that the degree of crystallinity of PET is invariably overestimated when it is deduced from the density of the material. For PET fibers, orientation introduces a number of extra variables into the dependence of density on crystallinity. Accordingly, the NMR method becomes particular useful for this very important class of materials.

The finding that two domains, as defined by their mobility, exist in isotropic, amorphous PET is intriguing, since such material is expected to be morphologically homogeneous. The origin of this phenomenon, not seen in other polymers,[37] deserves further study.

Acknowledgements

REFERENCES

1. G. Farrow and I. M. Ward, *Polymer* **1**, 330 (1960).
2. W. O. Statton, *J. Appl. Polym. Sci.* **7**, 803 (1963).
3. S. Fakirov, E. W. Fischer, R. Hoffmann and G. F. Schmidt, *Polymer* **18**, 1121 (1977).
4. F. Fontaine, J. Ledent, G. Groeninckx and H. Reynaers, *Polymer* **23**, 185 (1982).
5. D. E. Bosely, *J. Appl. Polym. Sci.* **8**, 1521 (1964).
6. R. G. J. Miller and H. A. Willis, *J. Polym. Sci.* **19**, 485 (1956).
7. S. R. Padibjo and I. M. Ward, *Polymer* **24**, 1103 (1983).
8. N. S. Murthy and H. Minor, *Polymer* **31**, 996 (1990).
9. N. S. Murthy, S. T. Correale and H. Minor, *Macromolecules* **24**, 1185 (1991).
10. J. H. Dumbleton and B. B. Bowles. *J. Polym. Sci. Part A-2* **4**, 951 (1966).
11. C. M. Roland, *Polym. Eng. Sci.* **31**, 849 (1991).
12. A. Peterlin and G. Meinel, *J. Polym. Sci., Part B* 783 (1965).
13. D. J. Blundell, D. R. Beckett and P. H. Willcocks, *Polymer* **22**, 704 (1981).
14. A. P. Gray, *Thermochim. Acta* **1**, 563 (1970).
15. M. J. Richardson *Plast. Rubber Mater. Appl.* **1**, 162 (1976).
16. R. de P. Daubeny and C. W. Bunn and C. J. Brown, *Proc. R. Soc. London, Ser. A* **226**, 531 (1954).
17. H. G. Kilian, H. Halboth and E. Jenckel, *Kolloid-Z.* **172**, 166 (1960).
18. S. Fakirov, E. W. Fischer and G. F. Schmidt, *Makromol. Chem.* **176**, 2459 (1975).
19. M. G. Northolt and H. A. Stuut, *J. Polym. Sci., Polym. Phys. Ed.* **16**, 940 (1978).
20. R. Huisman and H. M. Heuvel, *J. Appl. Polym. Sci.* **22**, 943 (1978).
21. J. H. Nobbs, D. I. Bower and I. M. Ward, *Polymer* **17**, 25 (1976).
22. C. M. Roland and M. F. Sonnenschein, *Polym. Eng. Sci.* **31**, 1434 (1991).
23. H. M. Heuvel and R. Huisman, in *High Speed Fiber Spinning*, edited by A. Ziabicki and H. Kawai, p. 295. Wiley, New York (1985).
24. M. D. Sefcik, J. Schaefer, E. O. Stejskal and R. A. McKay, *Macromolecules* **13**, 1132 (1980).
25. D. L. Tzou, P. Seai, A. S. Abhiraman and T.-H. Huang, *J. Polym. Sci., Polym. Phys. Ed.* **29**, 49 (1991).
26. U. Eichhoff and H. G. Zachmann, *Makromol. Chem.* **147**, 41 (1971).
27. A. Cunningham, A. J. Manuel and I. M. Ward, *Polymer* **17**, 126 (1976).
28. H. J. Biangardi and H. G. Zachmann, *J. Polym. Sci., Polym. Symp.* **58**, 169 (1977).
29. H. G. Zachmann, *Poly. Eng. Sci.* **19**, 966 (1979).
30. J. R. Havens and D. L. VanderHart, *Macromolecules* **18**, 1663 (1985).
31. P. Mansfield, *J. Phys. C* **4**, 1444 (1971).
32. W.-K. Rhim, D. D. Elleman and R. W. Vaughan, *J. Chem. Phys.* **58**, 1772 (1973).
33. W.-K. Rhim, D. D. Elleman and R. W. Vaughan, *J. Chem. Phys.* **59**, 3740 (1973).
34. D. W. Tomlin, C. M. Roland and L. I. Slutsker, *J. Polym. Sci., Polym. Phys. Ed.* **31**, 1331 (1993).
35. K. L. Peng and C. M. Roland, *J. Polym. Sci., Polym. Phys. Ed.* **31**, 1339 (1993).
35. R. J. Samuels, *J. Appl. Polym. Sci.* **10**, 781 (1972).
37. D. G. Cory, unpublished results.