Chapter 6

Summary/Conclusions

This thesis has demonstrated that a single, continuously evolving, microstructural model can successfully reproduce all the WAXD features observed in P3ATs as a function of side chain length, temperature, casting conditions, regioregularity, and iodine concentration. The completeness with which this study has attempted to quantify microstructure, solely from the WAXD data from a semicrystalline material with a minimal number of available diffraction features, is unprecedented. This study has probed the limits regarding what can be discerned from a material that has only a small number of WAXD features present.

The pristine crystalline structure within the P3AT family of conducting polymers is characterized by well-organized lamellar structures whereby stacks of planar thiophene main chains are uniformly layered within a non-interdigitating alkyl side chain matrix. This provides this π-conjugated system with a large amount of π overlap, that is consistent with the observed electrical properties of this material.

There is evidence that side chain mobility allows for additional ordering at the interface formed by the alkyl side chain end groups. For P3ATs with side chains of 12 and longer, there is a well defined ordering with respect to the side chain/side chain interface that has been supported by both structure factor modeling and DSC measurements. This ordering behavior is not surprising for a predominantly "two phase" system, where the side chains and main chains have formed a structure whose phase separation has been maximized. The main chain and side chain ends are form well ordered regions within the polymer, while the side chains, out to the 8^{th} or 10^{th} CH_2 unit, form a more disordered transition region.

R-P3ATs cast from *m*-xylene nominally exhibit the same scattering features as their IR-P3AT counterparts, and hence similar crystalline structure, but when the solvent is evaporated off very slowly, these P3ATs show an additional crystalline structure in which neighboring stacks of thiophene main chains have completely interdigitated alkyl side chains. This secondary structure can be observed as a minority structural phase present in x-ray diffraction spectra consisting, primarily, of the original, non-interdigitating type-I structure. The molecular weight of the polymer, film processing, and the extent to which the side chains have been regularly attached to the main chain are all important factor influencing the presence of this type-II phase.

WAXD line profile analysis of P3DDT has revealed the function of crystal size and disorder in determining the peak shape of this particular polymer as a function of temperature. Although the application of the Warren and Averbach method for the separation of crystal size and disorder has not been often applied to polymer systems, it remains an interesting and useful tool for investigating how disordering mechanisms manifest themselves in polymer x-ray diffraction profiles. In this case, increased crystal size, as the major component in observed narrowing of these peak profiles has been found to be a misleading assumption. Variations in disorder have been found to be the dominant contributors in peak narrowing at temperatures greater than 60°C. Lattice parameter fluctuation decreased by a factor of two through the LC phase transition, while displacement disorder of the second kind is observed to maximize about this phase transition. This behavior may be a signature of the inhomogeneous melting of the alkyl side chains. The successful implementation of this method on P3DDT will hopefully encourage others to investigate simular polymer systems.

One significant contribution this thesis has made is the WAXD study of iodine intercalated P3AT structures. The use of *in situ* WAXD techniques has allowed for the complete 3D documentation of the previously unmodeled P3AT structural evolution as a function of dopant concentration. Oriented P3AT films intercalated, *in-situ*, by iodine vapor to I_3^- concentrations exceeding 50 mol wt. % per monomer, have been shown to exhibit a continuous and reversible structural evolution for P3HT and P3OT, while P3DDT exhibits a region of two-phase coexistence at intermediate doping levels. Structure factor modeling calculations show that the iodine intercalant causes a molecular restructuring involves both translational and rotational rearrangements of the host polymer, while the lamellar base structure of the pristine host polymer remains intact. Translational displacements of the polymer chains parallel to the main chain axes are found to occur within individual lamellae and this motion creates essentially 1-dimensional intercalant channels perpendicular to the main chain axis.

Although semicrystalline polymers generally exhibit a small number of scattering features, this fact does not preclude the ability to quantitatively understand the microstructure within these materials. By making use of all available, comprehensive WAXD scattering information, and remaining consistent with structural information from other parallel studies, one can construct and test models of various structures with good reliability, as demonstrated in this work.

The ability of a single structural model to successfully model P3AT structure as a function of many different variables is in effect a rigorous test of the model's reliability. The small number of diffraction features available for semicrystalline polymer systems makes any single successful structure factor model somewhat suspect. In fact, it might be difficult to argue confidently about the uniqueness of a structural model that is able to adequately reproduce all observed diffraction features for two types of undoped P3ATs, but the ability for a single model to reproduce all the observable feature available for P3ATs with three different side chain lengths, for a wide range of temperatures and iodine doping concentrations, makes the work presented here the best supported structural study available for P3ATs.

Bibliography

[1] C. K. Chiang *et al.*, Phys. Rev. Lett. **39**, 1098 (1977).

[2] H. Shirakawa *et al.*, J. Chem. Soc. Chem. Commun. 578 (1977).

[3] H. Naarmann and N. Theophilou, Synth. Met. **22**, 1 (1987).

[4] J. Tsukamoto, A. Takahashi, and K. Kawasaki, Jpn. J. Appl. Phys. **29**, 125 (1990).

[5] J. Tsukamoto and A. Takahashi, Synth. Met. **41**, 7 (1991).

[6] For the most recent International Conference on Synthetic Metals proceedings, see *Synth. Met.* **69**, (1995).

[7] *Handbook of Conducting Polymers*, edited by T. Skotheim (Marcel Dekker, New York, 1996).

[8] *Science and Applications of Conducting Polymers*, edited by W. R. Salaneck, D. T. Clark, and E. J. Samuelsen (Adam Hilger, Bristol, U.K., 1991).

[9] K. Y. Jen, R. Oboodi, and R. L. Elsenbaumer, Polym. Mat. Sci. and Eng. **53**, 79 (1985).

[10] C.-N. Hou, M.-Y. Hua, and S.-A. Chen, Mat. Chem. and Phys. **36**, 359 (1994).

[11] S. D. D. V. Rughooputh, S. Hotta, A. J. Hegger, and F. Wudl, J. Polym. Sci., Polym. Phys. Ed. **25**, 1071 (1987).

[12] J. P. Aimé *et al.*, Phys. Rev. Lett. **62**, 55 (1989).

[13] I. Watanabe, J. H. Cheung, and M. Rubner, J. Chem. Phys. **92**, 444 (1990).

[14] K. Yoshino, S. Nakajima, and R. Sugimoto, Jpn. J. Appl. Phys. **26**, L1038 (1987).

[15] T. A. Chen, X. Wu, and R. D. Rieke, J. Am. Chem. Soc. **117**, 233 (1995).

[16] R. D. McCullough *et al.*, J. Am. Chem. Soc. **115**, 4910 (1993).

[17] L. A. Harrah and J. M. Zeigler, J. Polym. Sci. Polym., Lett. Ed. **23**, 209 (1985).

[18] F. C. Schilling *et al.*, Macromolecules **22**, 3055 (1989).

[19] G. N. Patel, R. R. Chance, and J. D. Witt, J. Chem. Phys. **70**, 4387 (1986).

[20] G. Wenz, M. A. Muller, M. Schmidt, and G. Wegner, Macromolecules **837**, 17 (1984).

[21] L. M. Tolbert, Acc. Chem. Res. **25**, 561 (1992).

[22] M. G. Hill, K. R. Mann, L. L. Miller, and J.-F. Penneau, J. Am. Chem. Soc. **114**, 2728 (1992).

[23] K. F. J. Schoch *et al.*, IEEE Transactions on Power Delivery **7**, 1681 (1992).

[24] J. Miller, Adv. Mat. **7/8**, 587 (1993).

[25] J. Burroughs *et al.*, Nature **347**, 539 (1990).

[26] D. Braun and A. Heeger, J. Appl. Phys. Lett. **58**, 1982 (1991).

[27] G. Gustafsson *et al.*, Nature **357**, 477 (1992).

[28] G. Grem, G. Leditzky, B. Ullrich, and G. Leising, Adv. Mater. **4**, 36 (1992).

[29] Z. Yang, I. Sokolik, and F. Karasz, Macromolecules **26**, 1188 (1993).

[30] Q. Pei and Y. Yang, Adv. Mater. **7**, 559 (1995).

[31] D. Romero *et al.*, Solid State Commun. **95**, 185 (1995).

[32] J.-K. Lee, R. R. Schrock, D. R. Baigent, and R. H. Friend, Macromolecules **28**, 1966 (1995).

[33] M. Berggren, M. Granstrom, O. Inganäs, and M. Anderson, Adv. Mater. **7**, 900 (1995).

[34] P. Burn *et al.*, Nature **356**, 47 (1992).

[35] R. Hosemann and S. N. Bagchi, *Direct Analysis of Diffraction by Matter* (North-Holland, Amsterdam, 1962).

[36] A. Hindeleh and R. Hosemann, J. Phys. C **21**, 4155 (1988).

[37] S. Brüchner, W. Porzio, and F. Wudl, Makromol. Chem. **89**, (1989).

[38] F. Garnier, G. Tourillon, J. Y. Barraud, and H. Dexpert, J. Mat. Sci. **20**, 2687 (1985).

[39] R. Yang, D. F. Evans, L. Christensen, and W. A. Hendrickson, J. Phys. Chem. **94**, 6117 (1990).

[40] M. J. Winokur *et al.*, Synth. Met. **28**, C419 (1989).

[41] G. Gustafsson, O. Inganäs, H. Österholm, and J. Laakso, Polymer **32**, 1574 (1991).

[42] M. Leclerc, F. M. Diaz, and G. Wegner, Makromol. Chem. **190**, 3105 (1989).

[43] J. Mårdalen, E. J. Samuelsen, O. R. Gautun, and P. H. Carlsen, Solid State Commun. **77**, 57 (1991).

[44] K. Tashiro *et al.*, Synth. Met. **41**, 571 (1991).

[45] M. J. Winokur *et al.*, Macromolecules **24**, 3812 (1991).

[46] W. Brostow, Polymer **31**, 979 (1990).

[47] M. Ballauff, R. Rosenau-Eichin, and E. W. Fischer, Mol. Cryst. Liq. Cryst. **155**, 211 (1988).

[48] M. Ballauff and K. Berger, Mol. Cryst. Liq. Cryst. **1557**, 109 (1988).

[49] Guinier, *X-ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies* (W.H. Freeman, San Francisco, 1963).

[50] B. E. Warren, *X-ray Diffraction* (Dover, New York, 1969).

[51] J. Ballon, V. Comparat, and J. Pouxe, Nucl. Instrum. and Meth. **217**, 213 (1983).

[52] M. Evain, P. Deniard, A. Jouanneaux, and R. Brec, J. Appl. Cryst. **26**, 563 (1993).

[53] O. Inganäs, W. R. Salaneck, H. Österholm, and J. Laakso, Synth. Met. **22**, 395 (1988).

[54] R. D. McCullough and S. P. Williams, J. Am. Chem. Soc. **115**, 11608 (1993).

[55] J. Moulton and P. Smith, Synth. Met. **40**, 13 (1991).

[56] J. Moulton and P. Smith, Polymer **33**, 2341 (1992).

[57] R. D. McCullough, R. D. Lowe, M. Jayaraman, and D. L. J. Anderson, J. Org. Chem. **58**, 904 (1993).

[58] T. Matsuyama *et al.*, Synth. Met. **55**, 690 (1993).

[59] T. Matsuyama *et al.*, J. Phys. Soc. Jpn. **52**, 2238 (1983).

[60] P.-A. Albouy *et al.*, Makromol. Chem. **193**, 853 (1992).

[61] R. H. Baughman, N. S. Murthy, G. G. Miller, and L. W. Shacklette, J. Chem. Phys. **79**, 1065 (1983).

[62] K. Tashiro *et al.*, Polym. Pre. Jpn. **41**, 4595 (1992).

[63] P. Ewald, Z. Krist. **56**, 129 (1921).

[64] L. E. Alexander, *X-ray Diffraction Methods in Polymer Science* (Wiley, Interscience, New York, 1969).

[65] P. M. deWolff, J. Polym. Sci. **60**, S34 (1962).

[66] *International Tables for X-ray Crystallography* (Kynoch Press, Birmingham, 1974), Vol. IV.

[67] R. P. Millane and S. Arnott, J. Macromol. Sci., Phys. **B24**, 193 (1985).

[68] G. C. Rutledge, U. W. Suter, and C. D. Papaspyrides, Macromolecules **24**, 1934 (1991).

[69] F. V. Bolhuis *et al.*, Synth. Met. **30**, 381 (1989).

[70] S. Hotta and K. Waragai, J. Mater. Chem. **1**, 835 (1991).

[71] B. Orchard, B. Freidenreich, and S. Tripathy, Polymer **27**, 1533 (1986).

[72] N. S. Murthy, R. H. Baughman, and G. G. Miller, J. Chem. Phys. **89**, 2523 (1988).

[73] C. D. West, J. Chem. Phys. **15**, 689 (1947).

[74] S. Ergun, J. Appl. Cryst. **1**, 19 (1968).

[75] G. Caglioti, A. Paoletti, and F. P. Ricci, Nucl. Instrum. **3**, 223 (1958).

[76] H. Rietveld, Acta Cryst. **22**, 141 (1967).

[77] H. Rietveld, J. Appl. Cryst. **2**, 65 (1969).

[78] W. Łużny, S. Nizioł, and M. Zagòrska, Synth. Met. **64**, 59 (1994).

[79] J. Mårdalen *et al.*, Macromol. Chem. Phys. **196**, 553 (1995).

[80] A. Bolognesi, M. Catellani, S. Destri, and W. Porzio, Makromol. Chem., Rapid Commun. **12**, 9 (1991).

[81] A. Bolognesi, W. Porzio, F. Provasoli, and T. Ezquerra, Makromol. Chem. **194**, 817 (1993).

[82] W. Łużny, Acta Cryst. **B51**, 255 (1995).

[83] H. J. Fell, E. J. Samuelsen, J. Mårdalen, and P. H. J. Carlsen, Synth. Met. **63**, 157 (1994).

[84] J. Mårdalen, E. J. Samuelsen, O. R. Gautun, and P. H. J. Carlsen, Solid State Commun. **77**, 337 (1991).

[85] J. Mårdalen, E. J. Samuelsen, O. R. Gautun, and P. H. Carsen, Solid State Commun. **80**, 687 (1991).

[86] J. Mårdalen, E. J. Samuelsen, O. R. Gautun, and P. H. Carsen, Synth. Met. **48**, 363 (1992).

[87] J. Mårdalen, E. Samuelsen, and A. Petersen, Synth. Met. **55**, 378 (1993).

[88] J. Mårdalen, C. Riekel, and H. Müller, J. Appl. Cryst. **27**, 192 (1994).

[89] K. Tashiro *et al.*, J. Polym. Sci., Polym. Phys. **29**, 1223 (1991).

[90] S.-A. Chen and S.-J. Lee, Polymer **36**, 1719 (1995).

[91] J. Corish, D. A. Morten-Blake, F. Bénière, and M. Lantoine, J. Chem. Soc. Faraday Trans. **92**, 671 (1996).

[92] W. Porzio *et al.*, Synth. Met. **41**, 537 (1991).

[93] T. J. Prosa, M. J. Winokur, and R. D. McCullough, Macromolecules **29**, 3654 (1996).

[94] G. Gustafsson *et al.*, Synth. Met. **41**, 593 (1991).

[95] K.-S. Ho *et al.*, Synth. Met. **55**, 384 (1993).

[96] K.-I. Iwasaki, H. Fujimoto, and S. Matsuzaki, Synth. Met. **63**, 101 (1994).

[97] W.-P. Hsu *et al.*, Macromolecules **26**, 1318 (1993).

[98] H. J. Fell *et al.*, Synth. Met. **69**, 301 (1995).

[99] K. J. Ihn, J. Moulton, and P. Smith, J. Polym. Sci., Polym. Phys. **31**, 735 (1993).

[100] E. J. Samuelsen *et al.*, Synth. Met. **55**, 365 (1993).

[101] M. Lemaire *et al.*, New. J. Chem. **16**, 1009 (1992).

[102] T. J. Prosa *et al.*, Macromolecules **25**, 4364 (1992).

[103] J. D. Moulton, Ph. D. thesis, University of California at Santa Barbara, 1991.

[104] J. Mårdalen, Ph.D. thesis, Universitet I Thondheim, Norges Tekniske Høgskole, 1991.

[105] Klemman, B.; Koutsky, J. *unpublished*.

[106] J. J. Mallon and S. W. Kantor, Macromolecules **23**, 1249 (1990).

[107] M. J. Winokur and R. Clarke, Phys. Rev. Lett. **54**, 811 (1985).

[108] W. R. Busing, Macromolecules **23**, 4068 (1990).

[109] The "similar" β-phase of Bolognesi et al. is obtained by extremely slow cooling from the isotropic melt.

[110] R. Hosemann, Z. Phys. **128**, 465 (1950).

[111] R. Hosemann, W. Schmidt, A. Fischer, and F. Balta-Calleja, Anales De Fisica A **79**, 145 (1983).

[112] R. Bonart, R. Hosemann, and R. McCullough, Polymer **4**, 199 (1963).

[113] B. E. Warren and B. L. Averbach, J. App. Phys. **21**, 595 (1951).

[114] B. E. Warren and B. L. Averbach, J. App. Phys. **23**, 497 (1952).

[115] B. E. Warren, *X-ray Studies of Deformed Metals* (Pergamon Press, New York, 1959), Vol. 8.

[116] G. Bodor, Adv. Polym. Sci. **67**, 165 (1985).

[117] P. R. Howard and B. Crist, J. Polym. Sci. Polym. Phys. Ed. **27**, 2269 (1989).

[118] B. Crist and P. R. Howard, Advances in X-Ray Analysis **34**, 519 (1991).

[119] E. Jordan, D. Feldeisen, and A. Wrigley, J. Polym. Sci. **9**, 1835 (1971).

[120] H. Takahashi, J. Phys. Soc. Japan **27**, 708 (1969).

[121] B. Crist and J. B. Cohen, J. Polym. Sci. Polym. Phys. Ed. **17**, 1001 (1979).

[122] W. Vogel, J. Haase, and R. Hosemann, Z. Naturforsch. **29a**, 1152 (1974).

[123] J.M.Cowley, Acta. Cryst. A **32**, 83 (1976).

[124] E. Bertaut, Acta. Cryst. **5**, 117 (1952).

[125] R. Young, R. J. Gerdes, and A. Wilson, Acta. Cryst. **22**, 155 (1967).

[126] R. L. Rothman and J. B. Cohen, Advances in X-Ray Analysis **12**, 208 (1969).

[127] R. Delhez, T. H. DeKeijser, and E. Mittemijer, Fresenius Z. Anal. Chem. **312**, 1 (1982).

[128] R. Delhez, T. deKeijser, and E. J. Mittemeijer, National Bureau of Standards Special Publication **567**, 213 (1980).

[129] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran: The Art of Scientific Computing* (Cambridge University Press, New York, 1992).

[130] S. Wecker, J. Cohen, and T. Davidson, J. Appl. Phys. **45**, 4453 (1974).

[131] D. R. Buchanan and R. L. Miller, J. App. Phys. **37**, 4003 (1966).

[132] T. J. Prosa *et al.*, Synth. Met. **55(1)**, 370 (1993).

[133] T.J.Prosa *et al.*, Phys. Rev. B **51**, 159 (1995).

[134] T. Kawai, M. Nakazono, R. Sugimoto, and K. Yoshino, J. Phys. Soc. Jpn. **61**, 3400 (1992).

[135] T. Kawai, M. Nakazono, R. Sugimoto, and K. Yoshino, Synth. Met. **55**, 353 (1993).

[136] K. Tashiro *et al.*, J. Appl. Phys. **33**, L1023 (1994).

[137] T. Kawai, M. Nakazono, and K. Yoshino, J. Mater. Chem. **2**, 903 (1992).

[138] S. Y. Hong and M. Kertesz, Phys. Rev. Lett. **64**, 3031 (1990).

[139] M. Leclerc, F. M. Diaz, and G. Wegner, Makromol. Chem. **190**, 3105 (1989).

[140] D. Djurado *et al.*, Synth. Met. **34**, 683 (1990).

[141] S. Flandrios, C. Hauw, and B. Francois, Mol. Cryst. Liq. Cryst. **117**, 91 (1985).

[142] R. Baughman *et al.*, Mol. Cryst. Liq. Crys. **118**, 253 (1985).

[143] L. W. Shacklette and J. E. Toth, Phys. Rev. B **32**, 5892 (1985).

[144] D. Chen, M. J. Winokur, M. Masse, and F. E. Karasz, Phys. Rev. B **41**, 6759 (1990).

[145] M. J. Winokur *et al.*, Polymer **33(1)**, 296 (1992).

Appendix A

Key of Abbreviations

1D	one dimension
3D	three dimension
ACS	American Chemical Society
ADC	analog-to-digital converter
AsF_6	arsenic floride
BF_4	boron floride
C-C	carbon-carbon
DSC	differential calorimetry
$FeCl_3$	iron chloride
FTIR	Fourier transform infrared
FWHM	full width at half maximum
HH	head-to-head
HT	head-to-tail
I_3	iodine trimer
I_5	iodine pentomer
ID	interdigitated
IR-	regioirregular

KV	kilovolt
KW	kilowatt
LC	liquid crystalline
LED	light emmiting diode
NF_4	nitrogen floride
NMR	nuclear magnetic resonance
NSF	National Science Foundation
P3AT	poly(3-alkylthiophene)
P3DDT	poly(3-dodecylthiophene)
P3DT	poly(3-decylthiophene)
P3HT	poly(3-hexylthiophene)
P3OT	poly(3-octylthiophene)
PA	polyacetylene
PANI	polyaniline
PID	proportional integral derivative
PPP	poly(p-phenylene)
PPV	poly(p-phenylene vinylene)
PPy	polypyrrole
PT	polythiophene
P-TS	p-toluenesulfonate
R-	regioregular
TT	tail-to-tail
type-I	non-interdigitated P3AT structure
type-II	interdigitated P3AT structure
UV	ultraviolet
WAXD	wide angle x-ray diffraction
WAXS	wide angle x-ray scattering

Appendix B

Vita

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- B.S. in Physics and Math, May 1990, University of Wisconsin-Eau Claire, GPA: 3.76, Magna Cum Laude.

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- *Undergraduate Research*, June 1989 to August 1990, Department of Chemistry, University of Wisconsin-Eau Claire.

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- *Postdoctoral Reasearch Associate*, Sept. 1996, National Instituit of Standards and Technology, Gaithersburg, Maryland.

Publications:

1. "*Doping-Induced Side Chain Motion and Structural Transformations in Poly(3-n-alkylthiophenes)*",
   M.J. Winokur, **T.J. Prosa**, Jeff Moulton, Paul Smith, and A.J. Heeger,
   in *Polymer Preprints* **33(1)**, 296 (1992).

2. "*X-ray Structural Studies of Poly(3-alkylthiophenes): An Example of an Inverse Comb*",
   T.J. Prosa, M.J. Winokur, Jeff Moulton, Paul Smith, and A.J. Heeger,
   in *Macromolecules* **25**, 4364 (1992).

3. "*X-ray Diffraction Studies of Iodine-Doped Poly(3-Alkylthiophenes)*",
   T.J. Prosa, M.J. Winokur, Jeff Moulton, Paul Smith, and A.J. Heeger,
   in *Synthetic Metals* **55-57**, 370 (1993).

4. "*X-Ray-Diffraction Studies of the Three-Dimensional Structure within Iodine-Intercalated Poly(3-octylthiophene)*",
   T.J. Prosa, M.J. Winokur, Jeff Moulton, Paul Smith, and A.J. Heeger,
   in *Physical Review B* **51**, 159 (1995).

5. "*Evidence of a Novel Side Chain Structure in Regioregular Poly(3-Alkylthiophenes)*",
   T.J. Prosa, M.J. Winokur, and R.D. McCullough, in *Macromolecules*, **29**, 3654 (1996).

6. "*Line-Shape Analysis of Poly(3-dodecylthiophene): A Study of the Layer Disorder thru the Liquid Crystalline Polymer Transition*",
   T.J. Prosa, M.J. Winokur, and A.J. Heeger, in preparation.