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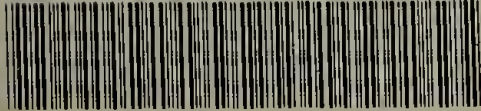
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**PREPARATION AND PHYSICAL STUDIES OF
POLYARYLENE VINYLENE COPOLYMERS AND THEIR
ANALOGOUS BLENDS**

A Dissertation Presented
by
ROBERTO Ma. S. GREGORIUS

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

September 1991

Department of Polymer Science and Engineering

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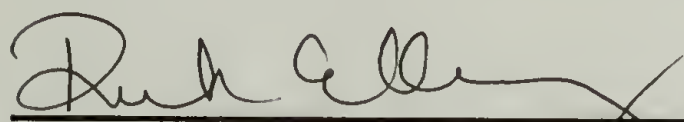
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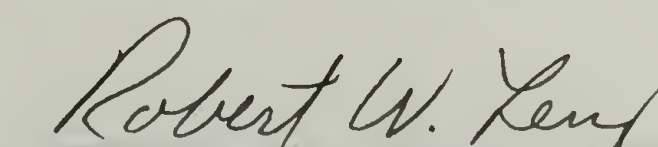
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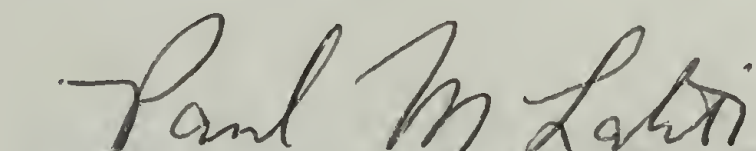
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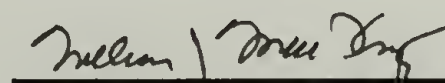
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Department of Polymer Science and Engineering

To the giants (and they know who they are)
on whose shoulders I stood
and been allowed to see such vistas,
in the hope that I may be worthy of being counted as one among them
- this thesis is dedicated.

ACKNOWLEDGEMENT

I am deeply conscious of the debt I owe to a number of people without whom this thesis would never have come to fruition. A graduate degree and the attendant thesis are such formidable aspirations that they may certainly not be achieved without the help of others. My only regret is that in acknowledging some of them here, I am bound to unintentionally overlook others whose help were no less important. I apologize and hasten to assure them that I am grateful.

I would like to take this opportunity to recognize the support that my siblings and one special friend, Anna, have given me this past years. My thanks go especially to my sister, Linda, without whom I would never have been able to come to the States to pursue a graduate degree. Her initial push was invaluable. I am grateful to my parents for instilling in me the desire for knowledge, for inspiring curiosity and having the wisdom to let me go when it was time. I wish my father were still here to see his son on the way to achieving the goals he awakened.

I am appreciative of the input my colleagues have provided both towards the project, to science in general and for simply being present, especially during those moments when results were slow in coming. I would especially like to mention my gratitude to Dr. Imrie, Dr. Lux and Dr. McCoy for their helpful discussions and suggestions.

I am indebted to the University of Massachusetts and to the Department of Polymer Science and Engineering in particular for providing me a proper atmosphere in which to work. I am grateful to

the Air Force Grant Office for providing the financial support to this project.

My mentors' benefaction is immeasurable. As I move on, Prof. Lahti's infectious enthusiasm and overflowing well of ideas will be missed. Prof. Lenz's availability during the gestation period of this research was invaluable. Lastly, but most certainly not least, I would like to show my appreciation here for the patience and faith Prof. Karasz has shown in allowing me to make my own mistakes and having the wisdom to know to call me in for meetings when he felt, rightly, that I had meandered from my goals. More importantly, for intentionally making sure that my education went well beyond academics, I am forever grateful.

ABSTRACT

**PREPARATION AND PHYSICAL STUDIES OF
POLYARYLENE VINYLENE COPOLYMERS AND THEIR
ANALOGOUS BLENDS**

SEPTEMBER 1991

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UNIVERSITY**

PhD., UNIVERSITY OF MASSACHUSETTS

Directed by: Professor Frank E. Karasz

The synthesis and physical characterization of a series of poly(*p*-phenylene vinylene-co-2,5-thienylene vinylene) (PPV-co-PTV) were reported. The synthetic route used was a variation on the Wessling route to poly(*p*-phenylene vinylene) which involved a precursor polymer. The copolymeric nature of the materials produced were investigated by IR analyses of the *trans*-vinylene absorption of these systems. The results of the attempts to produce other polyarylene vinylene (PAV) copolymers were also reported. The conductivity and orientational properties of PPV-co-PTV in comparison with those of the blends of poly(*p*-phenylene vinylene) (PPV) and poly(2,5-thienylene vinylene) (PTV) were investigated. The interrelation of the PTV contents, sequence distributions, conductivities, draw ratios, morphology and order parameters for the copolymers and blends were discussed. The effects due to the random copolymeric nature of PPV-co-PTV were emphasized.

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CHAPTER 1

INTRODUCTION

1.1. The Importance of Conducting Polymers

Conducting materials based on organic systems have been, and continue to be, of considerable interest both theoretically and technologically. The remarkable physical and electronic properties of such polymers and their possible applied uses such as battery components¹, non-linear optical devices², anti-static cladding, electronic packaging and interconnections³, have stimulated an ongoing interest in the field. Moreover, the fact that these polymers are composed of very rigid chains make them highly interesting in themselves. The resulting physical properties as a function of chemical and structural modifications, the conducting behavior as a function of dopant and dopant levels, film and fiber formation, and morphology are only some of the ongoing concerns with conducting polymers.

Certainly, conjugated polymers as applied to secondary battery electrodes have stimulated quite a major research effort. The important considerations regarding such an application have been: conductivity, reversible electrochemical oxidation and reduction, facility in tailoring the redox potential, high energy densities, ease in fabrication and, to some extent, lesser waste hazard - all of which are clearly exhibited by conducting polymers based on organic π -conjugated systems^{4, 5}.

Rechargeable batteries have been prepared using polyacetylene (I, fig. 1.1)⁶, poly(*p*-phenylene) (II, fig. 1.1)⁷, poly(2,5-pyrrole) (III, fig. 1.1)^{8, 9} and poly(aniline)¹⁰.

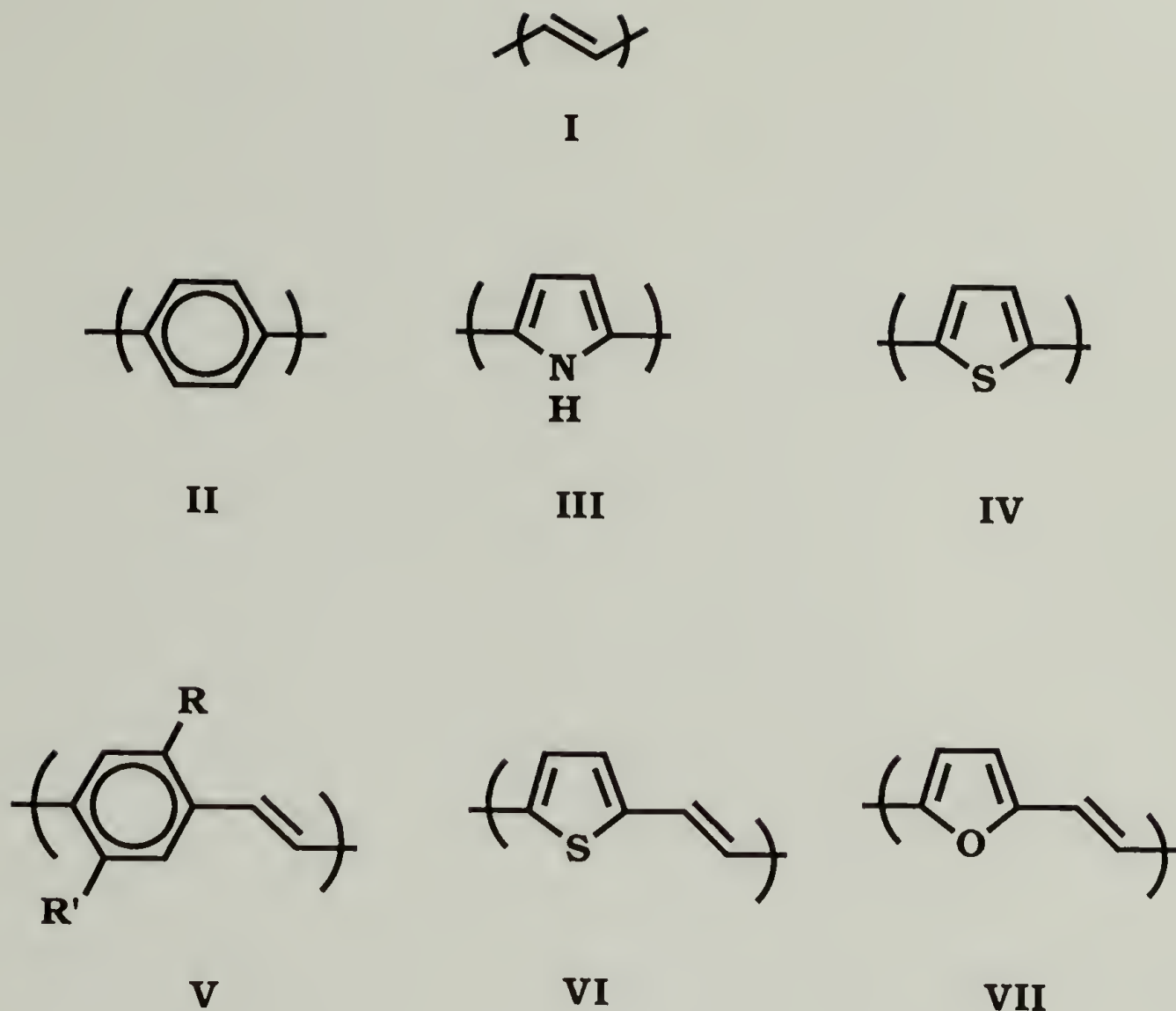


Fig. 1.1. Typical Conducting Polymers Based on Conjugated π -bonds.

Other applications using π -conjugated polymers have been investigated. Electronic devices such as field effect transistors using poly(2,5-thiophene)¹¹ (**IV**, fig. 1.1), Schottky diodes and heterojunctions¹² and optical display devices containing poly(2,5-pyrrole)¹³ have been reported. A discussion of possible future applications for such polymeric systems is given by Potember *et al.*¹⁴.

The need for fundamental research into the issues concerning organic conducting polymers can not be over-looked. In a multi-disciplinary field such as polymer science and engineering, the

inquiries and contributions of each field to an illumination of the concept of an organic and polymeric conductor can be overwhelming.

In the field of synthesis, questions regarding the mechanism of the reaction^{12, 15, 16}, the reactivity of monomers, the best synthetic pathways are only the beginning. The polymer chemist must ultimately understand the relationship of the varied chemical structures to the resulting conductivities.

Conductivity, however, is not only a function of chemical composition. The morphology of the sample often plays a major role in controlling the conductivity of the material. Inquiries into the morphology¹⁷ and sample processing¹⁸ must be considered with regard to their effect on the over-all conductivity.

A description of the mechanism of conductivity in π -conjugated organic polymers¹⁹⁻²¹ therefore, must not only describe the conduction mechanism of a single isolated polymer chain, but must also take into consideration the effects of the reaction scheme, the number of contiguous repeat units, molecular weight and molecular weight dispersity, crystallinity, orientation, dopants and dopant-levels, ionization potentials - just to name a pertinent few.

The field of organic π -conjugated conducting polymers is then truly an interdisciplinary endeavor for which the well-rounded polymer scientist was trained for. It is this particularly rich and interlocking research, meshing beautifully with other distinct but not separate fields that makes scientific inquiry very rewarding.

1.2. Objectives of this Dissertation

This dissertation was designed to show that certain questions regarding the polyarylene vinylene system such as monomer reactivity, reaction mechanism and conduction mechanism may best be answered by investigating the properties of copolymers and copolymeric reactions within the polyarylene vinylene system. The poly(*p*-phenylene vinylene-co-2,5-thienylene vinylene) (PPV-co-PTV) (fig. 1.2) system was investigated for this purpose. This copolymer can be synthesized using variations on the previously described polymerization schemes^{22, 23} and allows for a clear description of its copolymeric nature. Furthermore, by choosing a system that is composed of two moieties with distinct ionization potentials and therefore, having a varied susceptibility to doping agents, it becomes possible to investigate the effect of doping only one component in a two component system.

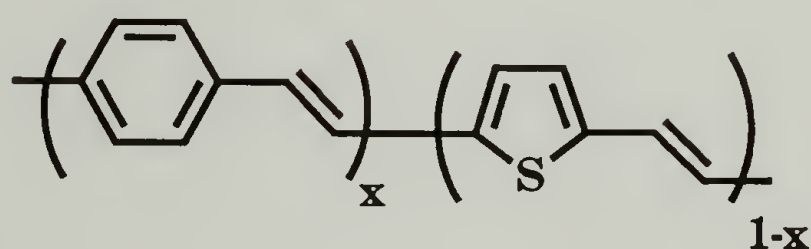


Fig. 1.2. Poly(*p*-phenylene vinylene-co-thienylene vinylene) (PPV-co-PTV).

Previous attempts at studying copolymeric systems of polyarylene vinylenes²⁴⁻²⁸ have been hampered by the inherent difficulty in verifying the copolymeric nature of such materials. The PPV-co-PTV system allows for a full verification of its copolymeric nature so that comparison

of the physical properties with molar equivalent blends may be achieved with confidence.

The dissertation is subdivided into four objectives:

- a) synthesis - to develop the techniques and procedures for a systematic synthesis of compositionally verifiable polyarylene vinylene copolymers.
- b) conductivity - to investigate the effects of copolymeric composition on the conductivity of polyarylene vinylenes, specifically, of PPV-co-PTV which have two components of distinct ionization potentials and to see how this may differ from blends of equivalent molar composition.
- c) orientation - to apply a particular stretching procedure on both copolymers and blends of the PPV-co-PTV system and to examine how this stretching technique produces orientation within the samples and how this orientation differs from theoretical predictions and from orientation achieved by other techniques.
- d) conductivity and orientation - finally, to probe the effects of orientation on the conductivity of PPV-co-PTV.

1.3. Dissertation Organization

Chapter 2 of this dissertation gives an over-all review of conducting polymers in general and polyarylene vinylenes in particular. The conduction mechanism, synthetic pathways, physical measurements previously described and which are pertinent to this work will be considered. Chapter 3 describes the methods and

procedures used in this investigation. Chapter 4 discusses the data, results and conclusions obtained from this investigation. Chapter 5 is a summary of the conclusions derived from the investigation and a description of the possible work that could be done in the future to further the investigation described herein.

1.4. References

1. Scrosati, B., Selvegi, A. and Owens, B. *Prog. Batteries Sol. Cells.*, **8**, 135 (1989).
2. Yoshino, K., Onada, M. and Kawai, T. *Optoelectron.-Devices Technol.*, **5**, 1 (1990).
3. Lupinski, J.H. and Moore, R.S. *ACS Symp. Ser. 407 (Polym. Mater. Electron. Packag. Interconnect.)*, 1 (1989).
4. Nigrey, P.J., MacInnes, D., Nairnes, D.P. and MacDiarmid, A.G. *J. Electrochem. Soc.*, **128**, 1651 (1981).
5. Passiniemi, P. and Österholm, J.E. *Synth. Met.*, **18**, 637 (1987).
6. Chiang, C.K. *Polymer*, **22**, 1454 (1981).
7. Shacklette, L.W., Maxfield, M., Gould, S., Wolf, J.F., Jow, T.R. and Baughman, R.H. *Synth. Met.*, **18**, 611 (1987).
8. Münstedt, H., Köhler, G., Möhwald, H., Naegele, D., Bitthin, R., Ely, G. and Meissner, E. *Synth. Met.*, **18**, 259 (1987).
9. Inganäs, O. and Lundström, I. *Synth. Met.*, **21**, 13 (1987).
10. Geneis, E.M., Lapkowski, M., Santier, C. and Vieil, E. *Synth. Met.*, **18**, 631 (1987).
11. Koezuka, H., Tsumura, A. and Ando, T. *Synth. Met.*, **18**, 699 (1987).
12. Chien, J.C.W. "Polyacetylene: Chemistry, Physics and Materials Science." (Academic, New York, 1984).
13. Yoneyama, H., Wakamoto, K. and Tamura, H. *J. Electrochem. Soc.*, **132**, 2414 (1985).

14. Potember, R.S., Hoffman, R.C., Hu, H.S., Cocchiaro, J.E., Viands, C.A., Murphy, R.A. and Poehler, T.O. *Polymer*, **28**, 574 (1987).
15. Lahti, P.M., Modarelli, D.A., Denton, F.R., Lenz, R.W. and Karasz, F. E. *J. Am. Chem. Soc.*, **110**, 7258 (1988).
16. Wessling, R. A. *J. Polym. Sci., Polym. Symp.*, **72**, 55 (1985).
17. Masse, M.A. PhD Thesis, University of Massachusetts, 1989.
18. Machado, J.M. PhD Thesis, University of Massachusetts, 1988.
19. Brédas, J.L., Chance, R.R. and Silbey, R. *Mol. Cryst. Liq. Cryst.*, **77**, 319 (1981).
20. Brazovski, S.A. and Kirova, N. *J. E. T. P. Lett.*, **33**, 4 (1981).
21. Bishop, A.R., Campbell, D.K. and Fesser, K. *Mol. Cryst. Liq. Cryst.*, **77**, 253 (1981).
22. Gagnon, D.R., Capistran, J., Karasz, F.E. and Lenz, R.W. *Polym. Bull.*, **12**, 293 (1984).
23. Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Polym. Commun.*, **25**, 327 (1984).
24. Han, C-C., Lenz, R.W. and Karasz, F.E. *Polym Commun.*, **28**, 26 (1987).
25. Lenz, R.W., Han, C-C. and Lux, M. *Polymer*, **30**, 1041 (1989).
26. Jin, J-I., Shim, H-K. and Lenz, R.W. *Synth. Met.*, **29**, E53 (1989).
27. Shim, H-K., Lenz, R.W. and Jin, J.I. *Makromol. Chem.*, **190**, 389 (1989).
28. Jin, J-I., Park, C-K. and Shim, H-K. *J. Polym. Sci., Polym. Chem.*, **29**, 93 (1991).

CHAPTER 2

LITERATURE REVIEW

2.1. Conduction Mechanism

Commensurate to the rich variety of conducting polymer systems there exists a large number of variations to the theory of conductivity in organic systems. This section will outline the basic ideas on the theory of conducting polymers and consider the issues regarding the theory of conducting polymers and how it relates to the current investigation.

2.1.1. General Case

The simplest description of the conduction mechanism of conjugated systems states that the charge, induced by the dopant or charge-transfer complex, is propagated along the π -conjugated backbone *via* delocalization. This is then modified to allow for the fact that a single polymer chain does not extend along the full macroscopic dimensions of the sample. An inter-chain hopping mechanism must be invoked. This can be applied to a system such as polyacetylene for which the resonance structures are degenerate¹. Such a definition allows the electrical conductivity (σ) to be macroscopically defined as:

$$\sigma = ne \mu \quad (2.1)$$

where (n) is the carrier density (carrier/unit volume), (μ) is the carrier mobility and (e) is the electronic charge. The carrier mobility (μ) is likewise defined as:

$$\mu = e\tau / m^* \quad (2.2)$$

where (τ) is the scattering time and (m^*) is the carrier effective mass.

An estimation of the conductivity values for a typical conducting system show that the carrier densities are in the order of 10^{21} or greater and thus by Pauli's Exclusion Principle would form a degenerate Fermi gas². Such a Fermi gas would exhibit a typical carrier velocity equivalent to the Fermi velocity, v_F , of the order of 10^8 cm/s. The mean distance between scattering events (λ) is then given by:

$$\lambda = v_F \tau \quad (2.3)$$

where the shortest possible mean free path is one lattice constant (a). In this case, the transport is better described as due to hopping of localized charge carriers, so that: $\lambda \approx 10^{-8}$ cm, $\tau \approx 2 \times 10^{-16}$ s, $\mu \approx 0.2$ cm²V⁻¹s⁻¹ and for $\sigma < 30$ S/cm, $n \approx 10^{21}$ cm⁻³.

The above calculations show that there can be two distinct classes of polymeric conductors. The first is of the type where all that is required is a moderately high density of charge carriers. Charge delocalization is not required. This class of heavily doped polymers are highly disordered systems where π -conjugation is not needed to achieve the exhibited low levels of conductivity³. These polymers may be considered as examples of the "Fermi glass" concept^{4, 5} and the main transport mechanism is described by the phonon-assisted variable-range hopping mechanism⁶.

The second class of conducting polymers is what may be considered as true metals. The intrinsic electrical conductivities (if these are experimentally available) for these types of conductors are usually in excess of several hundreds of siemens per centimeter. As molecular weight goes up, the inter-chain order of these species remain good and defect densities remain low. Delocalization within the system

leads to free metallic carriers with mean free paths that are much greater than the carbon-carbon repeat units and approximate that of the entire chain length⁷.

It is important to note that the same polymer could appear to be a member of either class under different conditions. Unoriented poly(*p*-phenylene vinylene) (PPV) highly doped with sulfuric acid would show non-metallic, low conductivity properties whereas oriented (PPV) doped with arsenic pentafluoride (AsF₅) would show very high conductivities and extensive delocalization⁸.

2.1.2. Polaron and Bipolaron Models

Dopant activity, the introduction of charge-transfer between the polymer and a reactive moiety, is a function of the redox energy of the system. The introduction of an oxidizing agent such as I₂ or AsF₅ to a polymer with a high redox energy, such as polyacetylene, will produce a "hole", that is, remove an electron from the valence band, in the polymer. This will result in local reorganization of the matrix in response to the induced charge and the charge-interaction within the polymer system. Reorganization serves to change the energy of the charged state and restrict the motion of the charge. This self-trapping or polaron mechanism is the key in determining charge-transport in degenerate species like poly(acetylene)⁹; the degree of localization is particularly dependent on the one-dimensionality of the system. A polaron is nothing more than a radical-ion, having a spin of 1/2 with an associated lattice distortion and localized electronic states. In this situation, the valence band remains full and the conduction band remains empty. There is no appearance of metallic character¹⁰.

Systems of non-degenerate resonance structures, however, require a description of the energetics, or the charge structures, involved in creating a charged unit along the backbone of the polymer.

* The concept of the bipolaron was introduced to take into account such considerations¹¹⁻¹³. Simply stated, when charge-transfer, *via* a redox type reaction, occurs between the polymer and the dopant/charge-transfer complexing agent the chain becomes ionized. This results in the appearance of a hole in the top of the valence band or an electron in the bottom of the conduction band depending on whether the polymer is acting as a donor or an acceptor respectively. This may manifest itself in a complete charge delocalization and is unaccompanied by any lattice distortion or geometry relaxation. The doped polymer will have a metallic character. Two possibilities arise when two charges become present on the polymeric chain. The first is the appearance of two separate polarons and the second is the coupling of these two polarons to form a bipolaron. A bipolaron is a pair of like charges (di-ion) associated with a strong lattice distortion (fig. 2.1).

In this scheme, the removal or insertion of a charge onto the ground-state of a conjugated polymer, and the subsequent gain in energy, E_1 , results in the excited or ionized state where the organic equilibrium geometry of the excited and ground states are not equivalent. The ionized state relaxes into an optimal geometry and the energy of relaxation, E_2 , is released. Conversely, the system can be described as a distortion of the ground-state geometry into the optimal ionized geometry coupled with the concurrent gain in energy (E_3),

followed by the ionization into the excited state coupled with the concurrent gain in energy (E_4).

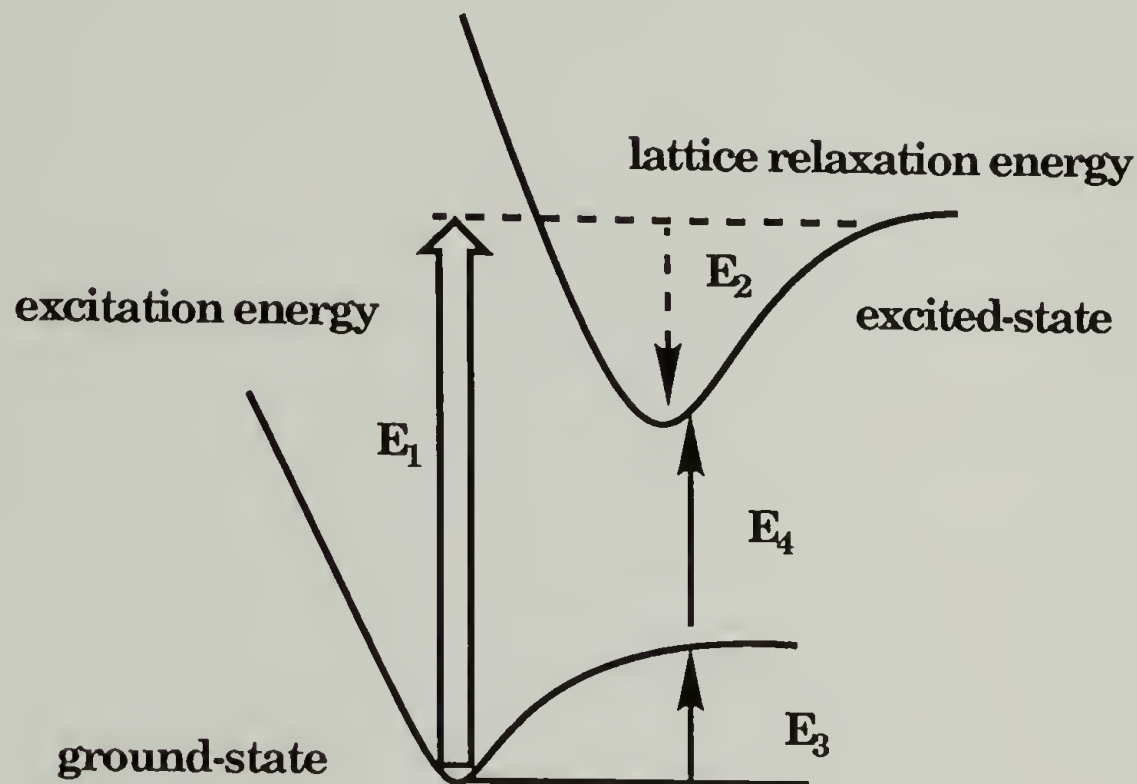


Fig. 2.1. Schematic Description of Molecular Excitation to a Conductive State.

It has been estimated ¹³⁻¹⁵ that the elastic energy, E_1 , to form a bipolaron is roughly equivalent to two polarons. The gain in relaxation energy due to the lattice relaxation about a bipolaron is large however, and is therefore energetically favored. The validity of these calculations can be easily determined since bipolarons are coupled spins that do should not show any absorption under electron spin resonance (ESR) investigation. Brédas¹⁶ has shown that this is in fact the case with poly(2,5-pyrrole) where the ESR signal grows at low doping levels, concurrent with the appearance of polarons and then vanishes at high

doping levels, concurrent with the coupling of polarons to form bipolarons.

2.1.3. Charge-transport and Ideal Conductors

Applying an electric field to a doped polymeric sample will induce a distortion of the localized potentials and cause a displacement of both the hole and dopant ion (in the case where the dopant is acting as an oxidizing agent). In a very fundamental sense, conducting polymers may be considered as self-organizing systems. The stiff conjugated chains force the dopant counter-ions into separate channels or planes within the lattice¹⁷, so that the dopant-ions are spatially separated from the quasi-one dimensional conduction path formed by the conjugated polymer⁷. This should suppress the resistive back-scattering effect. Band transport will be modified by adverse chain morphology, however. Imperfections such as chain kinks, chain termini, pinning action of unscreened ionized dopant molecules, back-scattering caused by lattice interactions will reduce the over-all conductivity of the sample. This implies that the measured conductivity is still limited by material imperfection. Attempting to reduce morphological imperfections and increasing the molecular weight should allow the experimentalist to approach an intrinsic conductivity that is limited solely by the phonon-assisted variable-range hopping mechanism only. The electron mean free path in this case will be determined only by the deviations from the regular atomic spacings due to thermal excitations.

There have been suggestions that the intrinsic electrical conductivity of conjugated systems like poly(acetylene) are significantly higher than copper¹⁸. Kivelson and Heeger⁷ have estimated that the

room temperature value of the intrinsic conductivity of metallic *trans*-(CH)_x is approximately $2 \times 10^6 \text{ Scm}^{-1}$ or four times that of copper.

Moreover, the conductivity of an ideal system will show an inverse exponential dependence on temperature so that as temperature decreases, and the consequent atomic vibrations approach equilibrium spacing, conductivity should increase dramatically. A decrease to 150K is estimated² to produce an increase in the conductivity in the parallel direction ($\sigma_{||}$) of greater than a factor of 50 to 100. Currently, the best materials show a conductivity of 0.2 to $1 \times 10^5 \text{ Scm}^{-1}$ with no temperature dependence. Doped-conjugated polymer conductivity is then still severely limited by sample quality.

2.1.4. Over-all Picture of Conduction Mechanism

The conduction mechanism postulated for π -conjugated polymers suggested that charge-transport occurred as a result of an injection of electrons or holes into the polymer matrix *via* a redox reaction between the polymer and the dopant. The appearance of a charge-carrier in the polymer would be accompanied by a lattice distortion to accommodate both the physical dopant and the added energy due to the imbedded electron or hole. This electron or hole would then be propagated along the chains according to a potential difference applied on the sample. The propagation would be mitigated by defects and coulombic forces.

The different conduction mechanisms have been shown to agree, as a first approximation, with the experimental data observed. However, the polymers currently available did not approximate the ideal conditions presented in theory. This was found to be especially true for complex non-degenerate and multivalent systems like PPV and its

myriad morphological structures and charge-transfer complexes. The need for well-defined and controlled systems that better approximate the descriptions of theoretical studies is apparent (see for example Bradley *et al.*¹⁹).

2.2. Preparation of Conducting Systems

The preceding description concerning the activity of donors and acceptors, the elementary excitation of ideal, isolated polymer chains with regard to polarons and bipolarons (see also Heeger²⁰) help to clarify the concept of electron transport in polymeric materials. On the other hand, those who are constantly wrestling with experimental data - particularly synthetic chemists and polymer scientists - often find that the chemical composition and morphological complexity²¹ often do not approach the ideal systems that theoretical scientists describe. A review by Bloor *et al.*²² concerning the poly(2,5-pyrrole) and polyaniline systems clearly indicate that the microscopic structure of a given sample has a very marked effect on the physical properties of the system. It should therefore be one of the more important priorities among experimental polymer scientists to consider how a π -conjugated polymeric conductor can be made so that variation from sample to sample is minimal.

In the succeeding sections, consideration will be given to synthetic pathways, film preparation and orientation and other morphological questions.

2.2.1. Synthesis of π -conjugated Systems

There are myriad approaches to organic conducting systems. Currently, the main areas of conductivity research based on organic molecules include the family of tetrathiafulvalene-

tetracyanoquinodimethane charge-transfer complexes (fig. 2.2), metallomacrocycles (fig. 2.3) and that of organic polymers with π -conjugated systems (fig. 2.4).

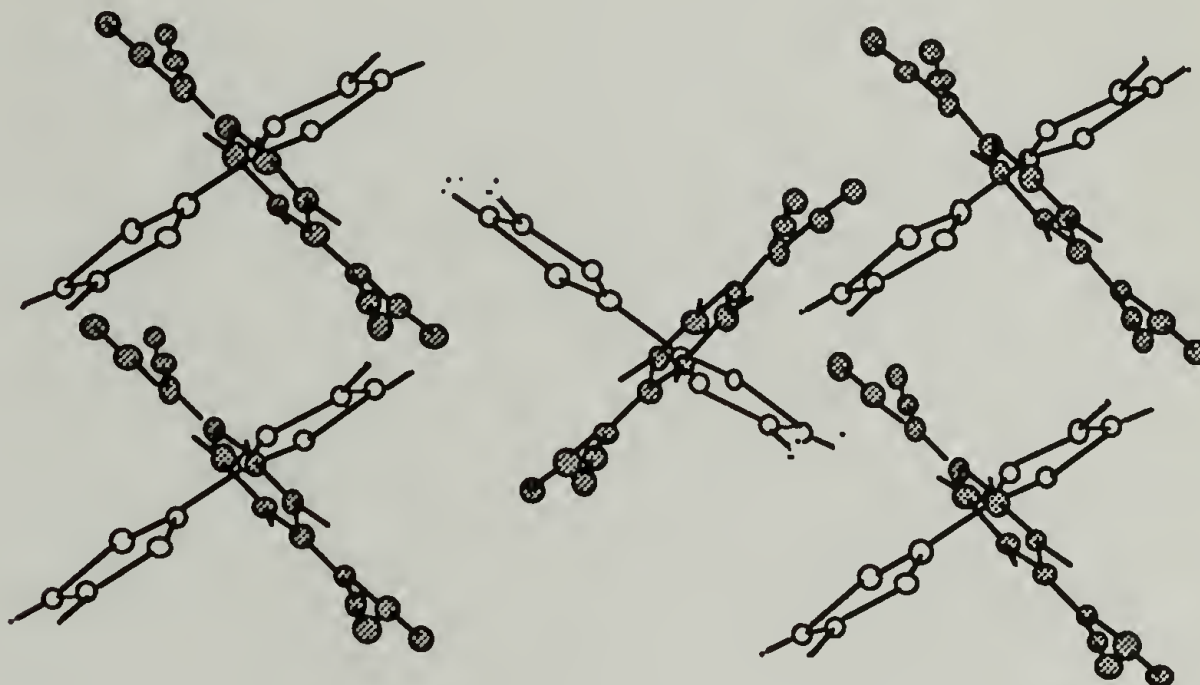


Fig. 2.2. Tetrathiafulvalene (o)-tetracyanoquinodimethane (•) Charge-transfer Stacking.

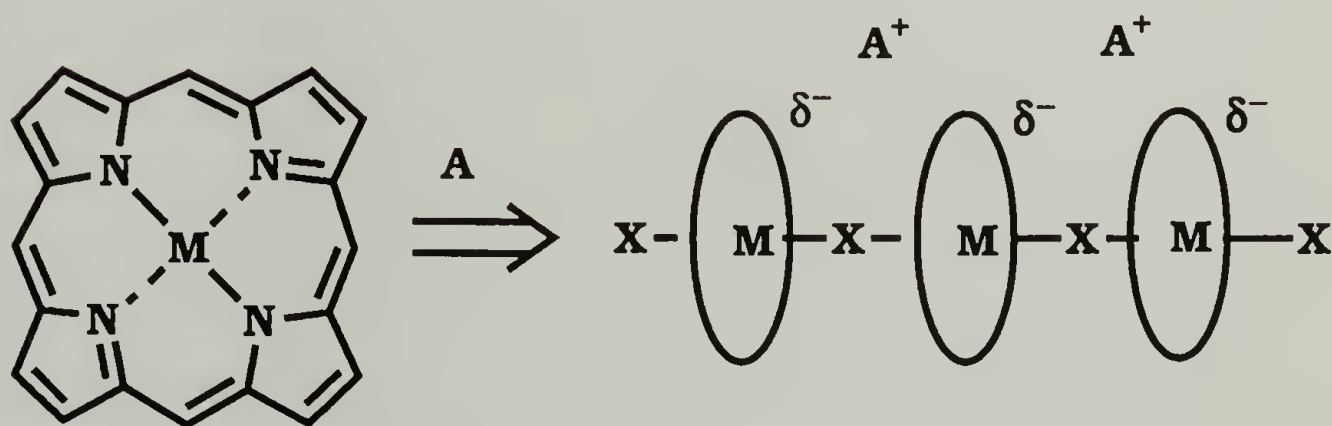


Fig. 2.3. General Description of Organometallic Macrocycles.

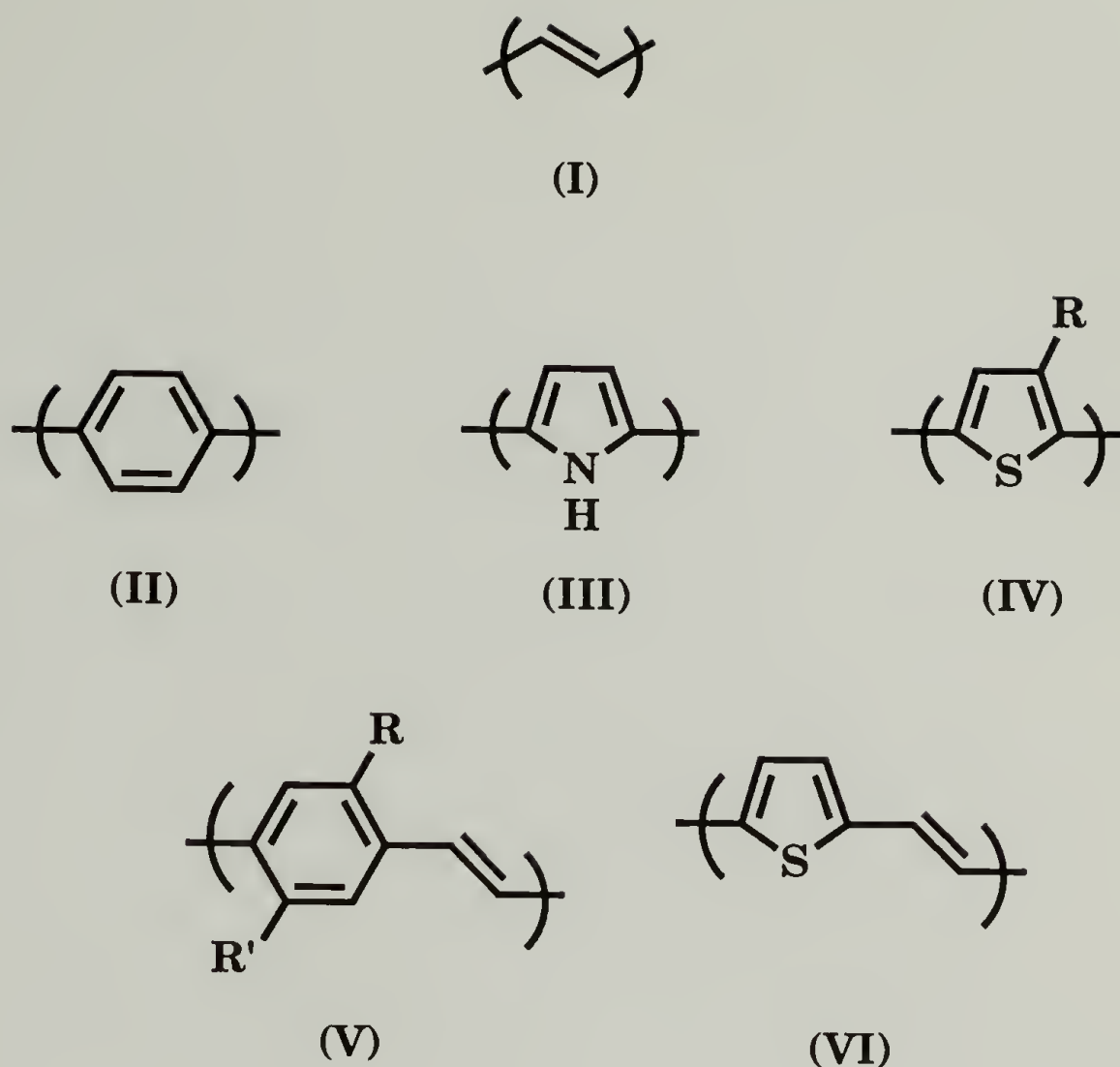
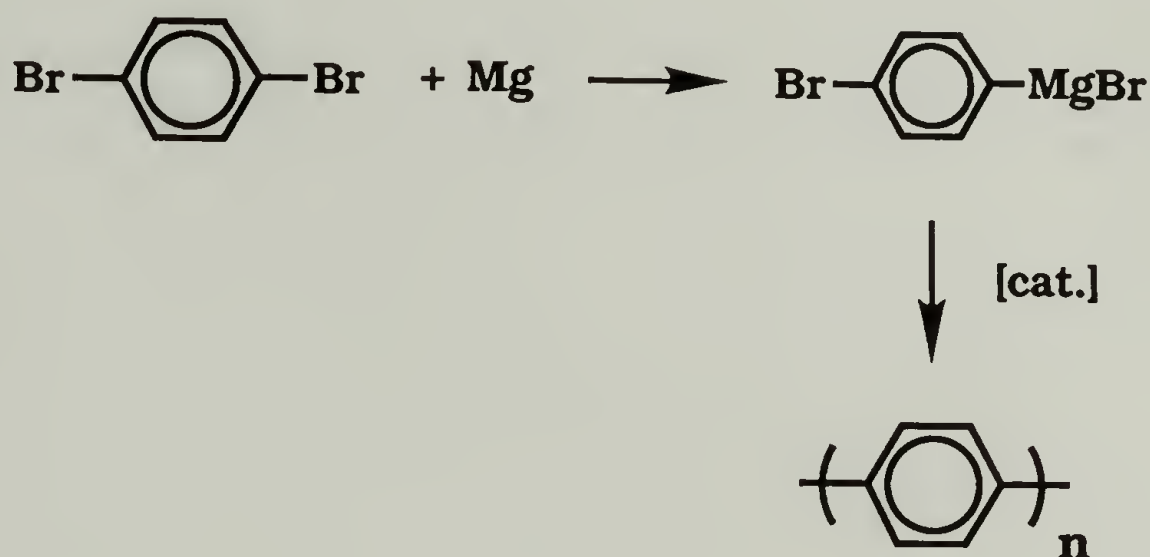


Fig. 2.4. Typical Organic π -conjugated Conducting Polymers.

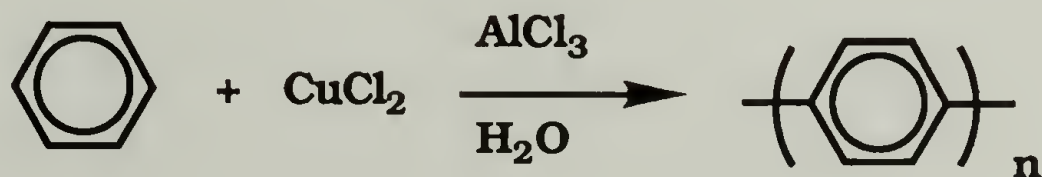
Early developments in conducting polymers based on π -electron delocalization were inhibited by the fact that the requirements of conjugated π -bonds also resulted in extreme intractability so that most of the early conjugated polymers produced were infusible, insoluble, low molecular weight, black powders which did not lend themselves to physical measurements or practical applications. Shirakawa and Ikeda^{23, 24} demonstrated that polyacetylene (I, fig. 2.4), polymerized directly from acetylene, could be made as strong, self-supporting films. It was shown that the treatment of this polymer with Lewis acids or bases increased the conductivity by up to 13 orders of magnitude²⁵. It

was found that exposure of acetylene gas to high concentrations (10mM) of catalyst in a non-stirred reactor led to the production of films of polyacetylene on the walls of the reaction vessel. This process was extensively reviewed by Chien¹.



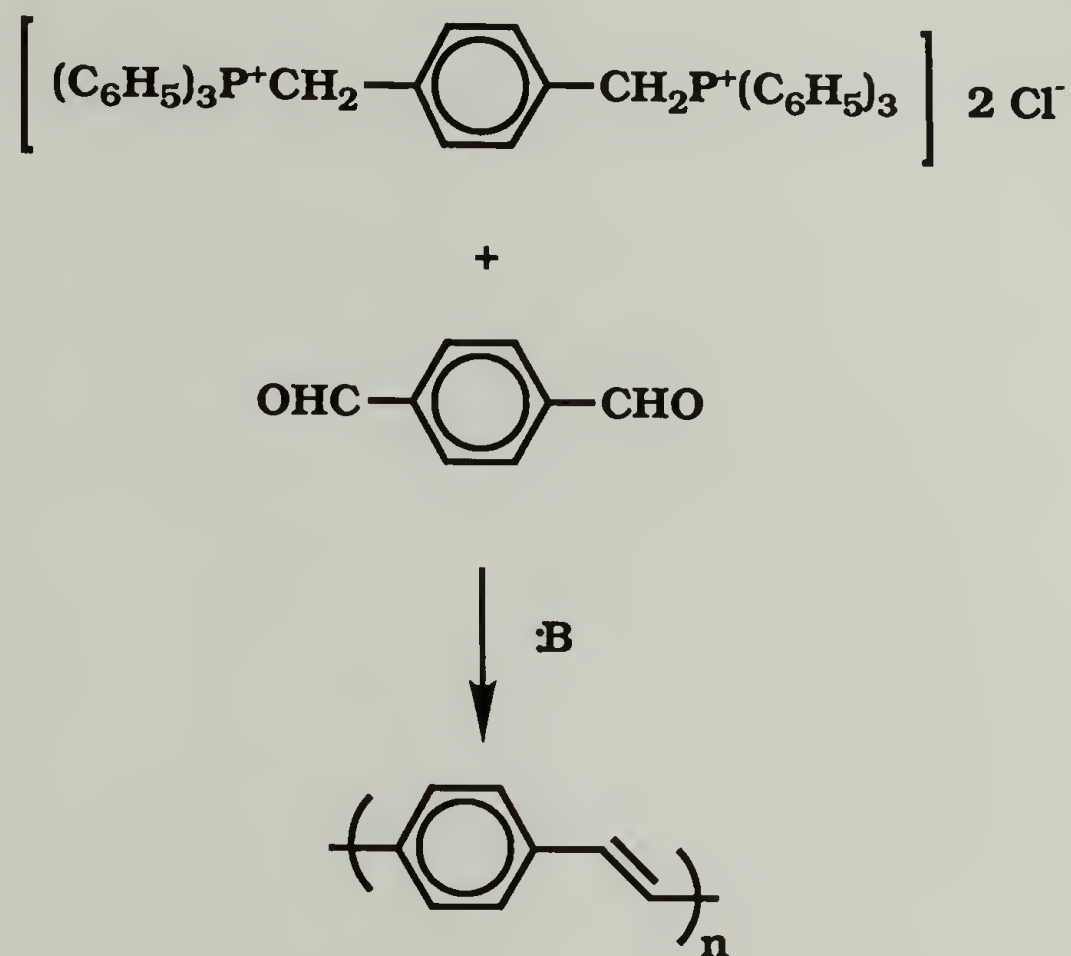
Scheme 2.1. Poly(*p*-phenylene) *via* Grignard Reaction.

A series of conjugated, conducting polymers were produced by varied, essentially step-reactions. Poly(*p*-phenylene) (II, fig. 2.4) was typically made *via* the decomposition of the corresponding Grignard reagent²⁶ (scheme 2.1) or by Friedel-Crafts addition²⁷ (scheme 2.2). Likewise, poly(2,5-pyrrole) (III, fig. 2.4) and poly(2,5-thiophene) (IV, fig. 2.4) have been synthesized using this process.



Scheme 2.2. Poly(*p*-phenylene) *via* Friedel-Crafts Addition.

Wittig and Schiff's Base reactions have also been used to produce step-growth conjugated polymers. This was typified by the condensation of *bis*-triphenylphosphonium chloride salts with dialdehydes in the presence of a strong base²⁸ (scheme 2.3).



Scheme 2.3. Poly(*p*-phenylene vinylene) *via* the Wittig Reaction.

Electrochemical polymerization techniques have been applied to synthesize the above mentioned polymers. Chandler and Pletcher have reviewed this technique²⁹.

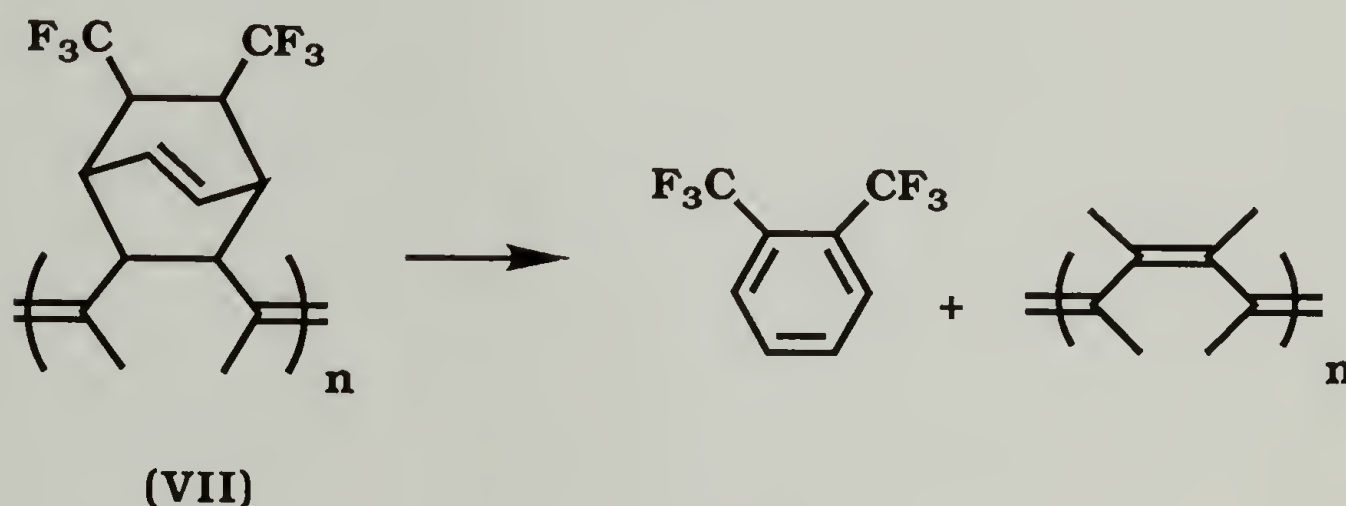
2.2.2. Synthesis of Conducting Polymers *via* Precursor Route

A special class of the conducting polymers based on conjugated π -bonds and dependent on extensive π -electron delocalization, are those produced *via* a precursor polymer. The infusibility and insolubility,

implicit in such π - conjugated structures, found in most conducting polymers, placed a tremendous emphasis on polymers that can be made *via* a processible precursor-polymer route.

2.2.2.1. Polyacetylene

Polyacetylene has been prepared through a polymer-precursor using the "Durham" route³⁰. The precursor (VII) (scheme 2.4), essentially the Diels-Alder adduct of an aromatic residue across alternate double bonds of polyacetylene - although the Diels-Alder reaction itself can not be used to synthesize the precursor, was obtained by a metathesis polymerization of the appropriate monomer.

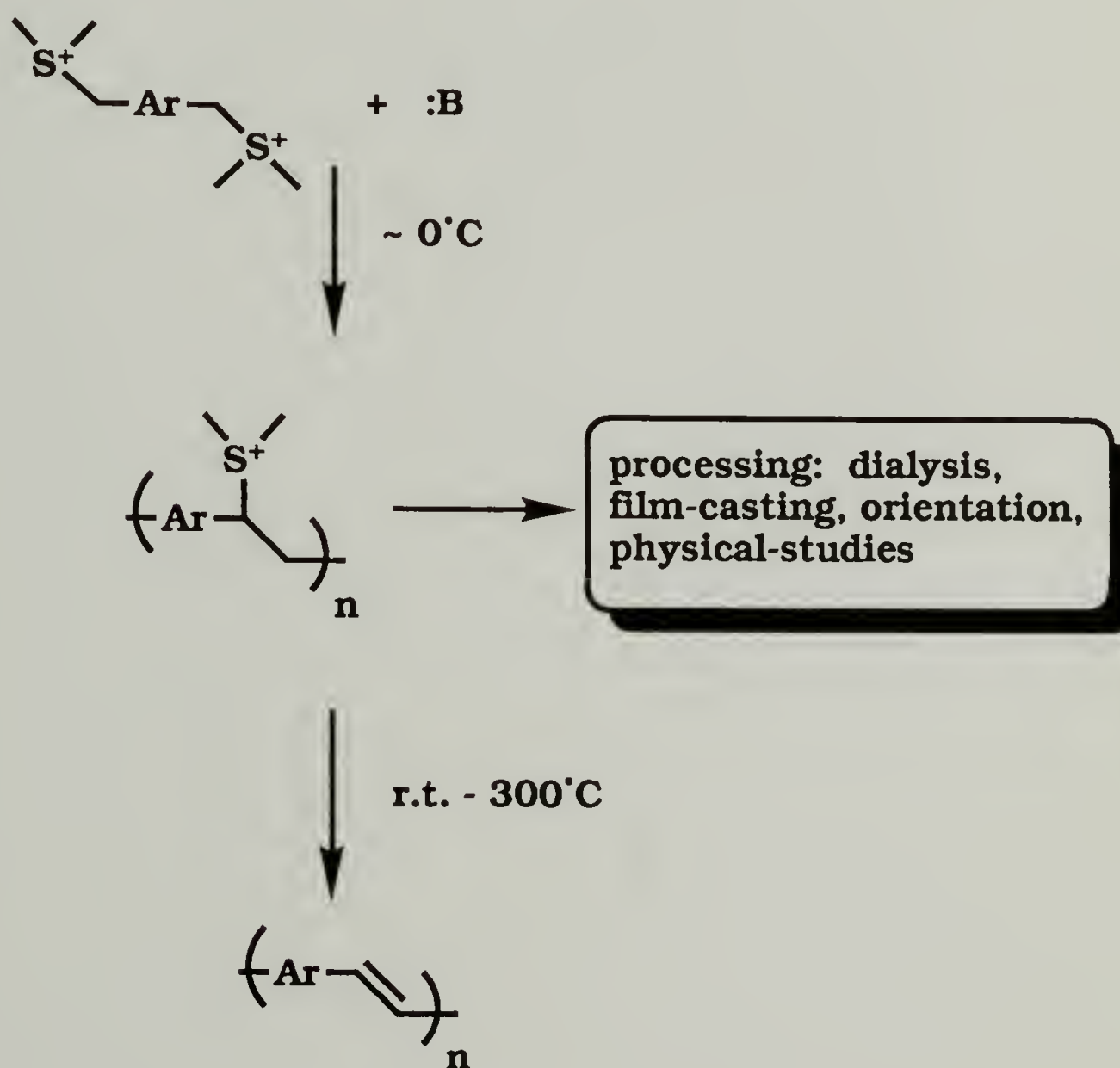


Scheme 2.4. "Durham" Precursor Route to Polyacetylene.

2.2.2.2. Poly(*p*-phenylene vinylene)

Poly(*p*-phenylene vinylene) (PPV) (V, fig. 2.4) has been known to exist for some time³¹. However, a route to an easily processible polymer was needed since the polymers produced by older methods were infusible and insoluble³². PPV has been synthesized *via* numerous step-growth type polymerizations, typically: Wittig reaction²⁸,

dehydrochlorination³³, and other modifications on condensation schemes³⁴. These procedures resulted in oligomeric powders with conductivities of up to 3 Scm^{-1} at best. A more convenient way of synthesizing PPV which allowed for facile variation of the monomer and easy processability *via* a precursor polymer was first described by Wessling and Zimmerman³⁵. This procedure was later properly described, more or less simultaneously, by Gagnon *et al.*³⁶⁻³⁸ and by Murase *et al.*^{39, 40}. The reaction (scheme 2.5)



Scheme 2.5. General Pathway to Polyarylene Vinylenes *via* Polymeric Precursor.

was typified by the treatment of the dialkylsulfonium salt of a *bis*(chloromethyl)-arylene, prepared by mixing both components in a polar solvent, with an equimolar amount of base at 0°C and produced a water-soluble polymeric precursor. The solution was dialyzed to remove starting materials, salts and oligomers and was then cast under vacuum into thin, self-supporting films. The films thus obtained were processable and eliminated HCl and the dialkylsulfide at room temperature through 300°C to form red, translucent films which were the conjugated polymer, PPV. The PPV film could then be doped with arsenic pentafluoride to high conductivities⁴¹. A table summarizing the progress in polyarylene vinylene synthesis is presented here (table 2.1).

Subsequent research in the variation of the PPV monomer and the synthetic pathway revealed certain trends. Murase *et al.*^{42, 43} showed that substitution of alkoxy groups into the phenylene ring resulted in polymers that could be easily doped to higher conductivities than PPV. This was possible since PPV was not dopable by such mild doping agents as iodine. Similarly, Antoun *et al.*⁴⁴⁻⁴⁶ showed that substitution on the phenylene ring with groups of different electronegativity changed the electron density of the polymer backbone and altered the reactivity of the conjugated polymer to dopants. The stability of the precursor polymer was likewise dependent on the electron density of the backbone. For example, it was shown that increasing the electron-donating properties of the substituents (**V**, fig. 2.4, R,R'=Me and R,R'=OMe) led to a decrease in the oxidation potential of the polymer such that the polymer could now be doped with milder doping agents such as iodine as opposed to

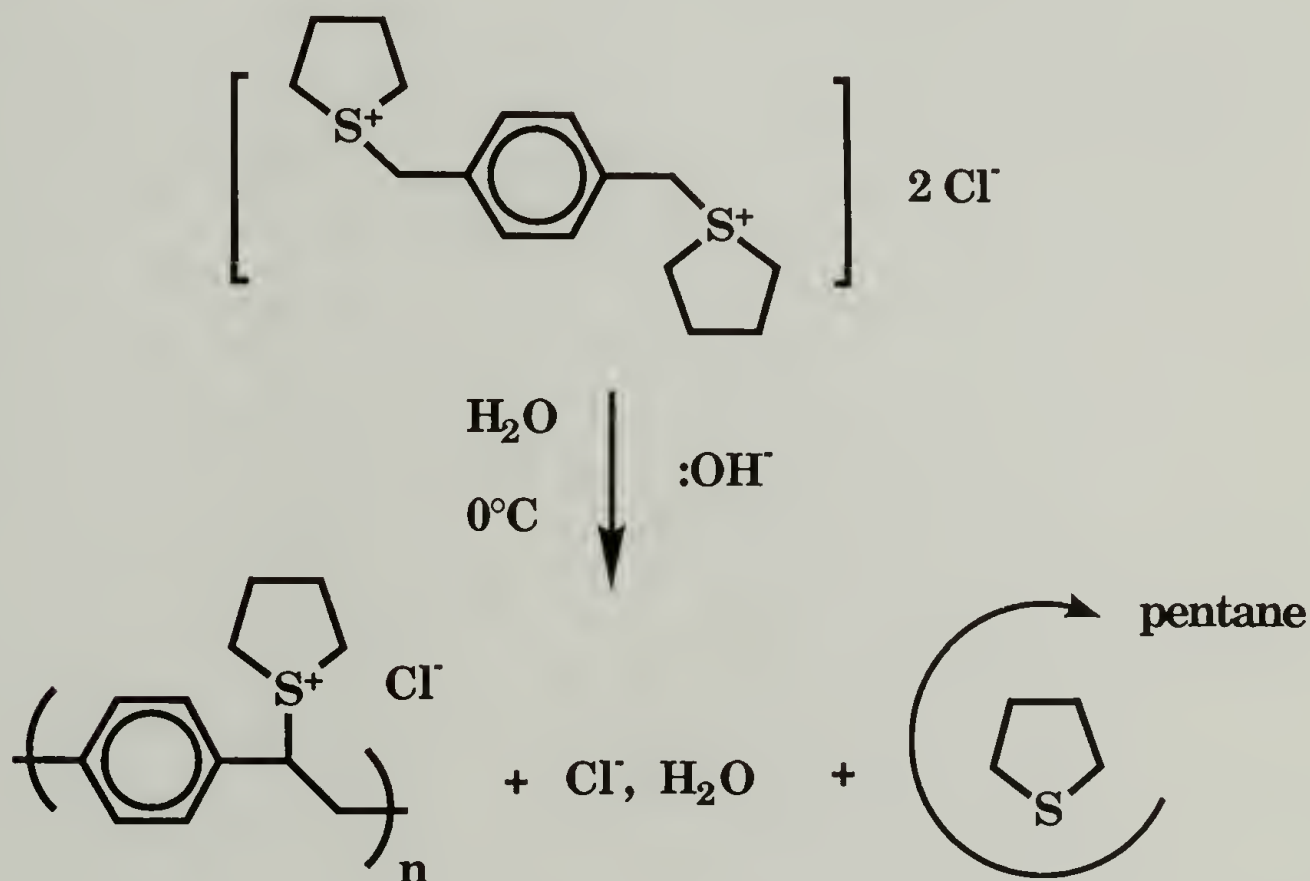
**Table 2.1. Significant Developments in the Synthesis of Polyarylene
Vinylenes.**

YEAR	DEVELOPMENTS	Principal Researchers
1984	First reported synthesis of PPV using a precursor polymer.	Gagnon, Capistran, Karasz, Lenz; Murase, Ohnishi, Noguchi, Hirooka
1985	poly(2,5-dimethoxy-1,4-phenylene vinylene).	Murase, Ohnishi, Noguchi, Hirooka
1986	poly(2-methyl-1,4-phenylene vinylene). First mono-substituted PPV derivative.	Antoun, Gagnon, Karasz, Lenz
1987	poly(2,5-dichloro-1,4-phenylene vinylene)	Murase, Ohnishi, Noguchi, Hirooka
1987	poly(2,5-furylene vinylene).	Jen, Jow, Elsenbaumer
1987	poly(2,5-thienylene vinylene).	Murase, Ohnishi, Noguchi, Hirooka; Yamada, Tokito, Tsutsui, Saito
1988	poly(2- (1-sodium sulfonate-3-propanoxy-) 1,4-phenylene vinylene) and the acid form. First application of the self-doping principle to PPV.	Shi, Wudl
1988	poly(2,5-di- <i>n</i> -hexyloxy-1,4-phenylene vinylene). First soluble form of the eliminated PPV.	Askari, Rughooputh, Wudl
1988	First reported use of NaBF ₄ to make an organic-soluble PPV precursor.	Momii, Tokito, Tsutsui, Saito

AsF₅. Higher conductivities were obtained from methoxy substituted PPV.

On the other hand, the stability of the precursor polymer decreased with increasing electronegativity in the phenylene ring. In many cases the poly(2,5-dimethoxy-*p*-phenylene vinylene) was reported to gel within hours of purification or during dialysis^{47, 48}.

Several improvements to the synthetic pathway were developed. Notably, Lenz *et al.*⁴⁹ suggested that cyclic sulfonium salts were better than their dialkyl counterparts. They reported higher yields, higher molecular weights and more efficient elimination of the sulfide in the formation of the conjugated PPV then when the equivalent dialkyl sulfide precursor salt was used.



Scheme 2.6. The Use of Pentane to Drive the PAV Reaction Forward.

Garay and Lenz⁵⁰ proposed to take advantage of the fact that one mole of the sulfide was released during the reaction. It was suggested that the addition of pentane or heptane to the reaction mixture should drive the reaction forward by extracting the sulfide from the water-layer (scheme. 2.6). They reported increased yields and higher molecular weights when this was implemented.

2.2.2.3. Other Arylene Vinylene Polymers

In terms of the effort employed in the investigation, two other important sub-groups of arylene vinylene polymers produced through the alkylsulphonium salt precursor polymer were: poly(2,5-dimethoxy-*p*-phenylene vinylene) (here PdMeOPV, **VIII**, fig. 2.5) and poly(2,5-thienylene vinylene) (PTV) (**IX**, fig. 2.5).

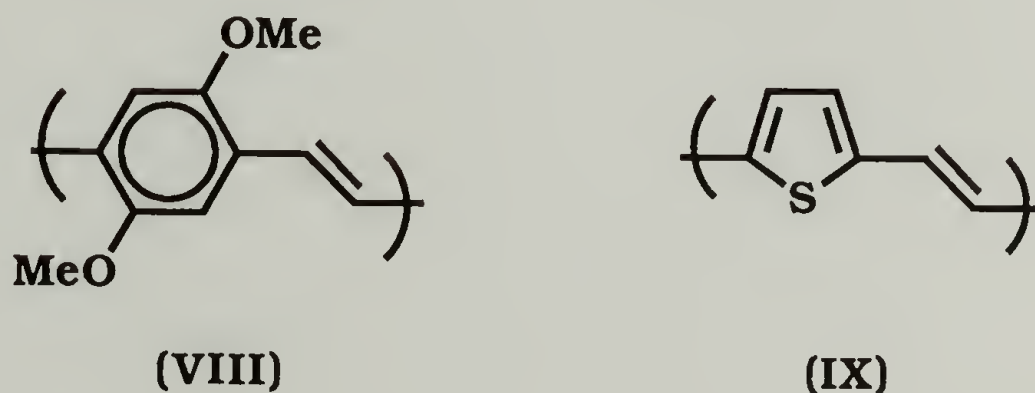
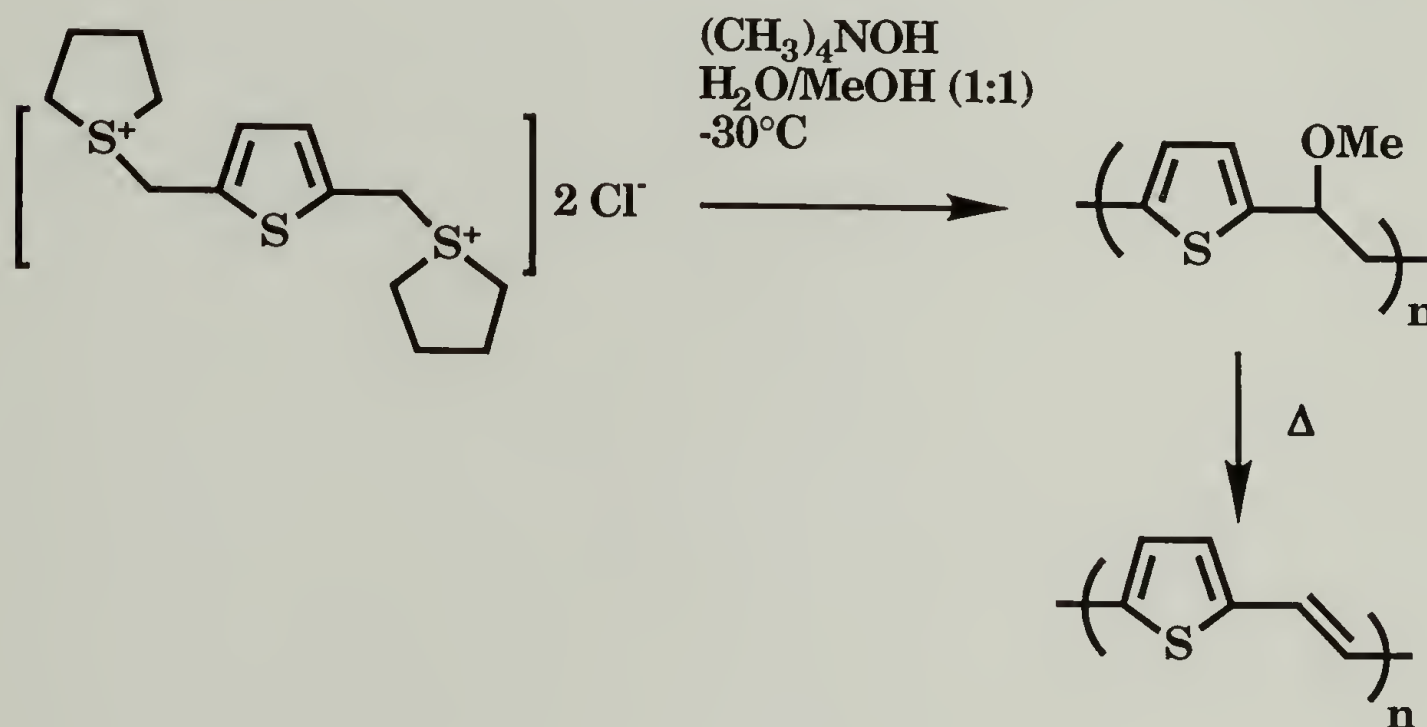


Fig. 2.5. Other Polyarylene Vinylenes.

Until recently, the difficulty in processability, attributed to side-reactions and inherent sensitivity of these arylene rings have inhibited their study. It was found however, that PTV could be synthesized at lower temperatures, with the inclusion of methanol in the solvent system and the use of tetramethylammonium hydroxide as base^{51, 52} (scheme 2.7). The investigation revealed that the resulting precursor

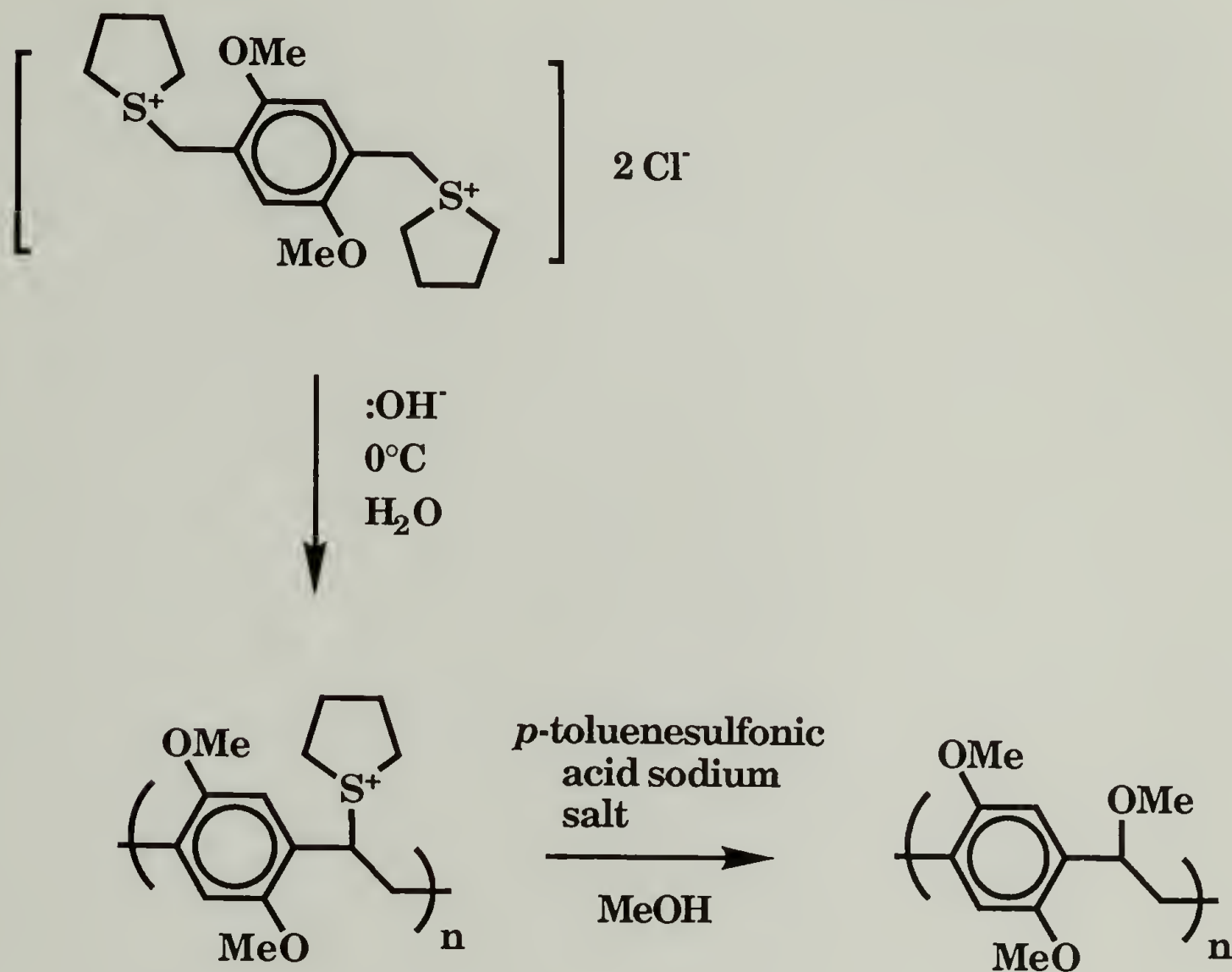
polymer was no longer the sulfide salt like that of PPV, nor was it the eliminated form as was normally obtained from the polymerization of α,α' -bis(tetrahydrothiophenium chloride)-2,5-dimethyl thiophene. Infrared data showed a strong ether absorption and it was suggested that the methylether moiety had replaced the THT-salt during the warm-up of the reaction. The precursor produced was found to be insoluble in water/methanol but soluble in DMF and THF.



Scheme 2.7. Novel Approach to the Synthesis of PTV.

PdMeOPV synthesis was equally improved when it was found that treatment of the precursor polymer solution with sodium *p*-toluenesulfonate not long after the reaction reached completion resulted in the precipitation of the precursor polymer as a sticky gum. This gum-like material was then dissolved and allowed to react with methanol to produce a methoxy-pendant precursor polymer. The precursor was no longer soluble in water but was soluble in organic

solvents such as THF, chloroform and DMF⁵³ (scheme 2.8). As with PTV, it was found that exchanges had occurred producing the final organically soluble precursor polymer with methyl ether functionalities.



Scheme 2.8. Novel Approach to the Synthesis of PdMeOPV.

Another important class of polyarylene vinylene materials synthesized from precursor polymers were those of the fully or partially eliminated systems which were soluble in a variety of solvents. This class of polymers, pioneered by Wudl and co-workers⁵⁴⁻⁵⁶, was based on long alkyl chains that disrupt the crystalline-packing of unmodified PPV chains and cause a higher solvent-chain interaction. Several

variations on this theme have been attempted. Using monomers with hexyloxy substituents on the the 2,5 positions on the phenylene ring produced poly(2,5-dihexyloxy-1,4-phenylene vinylene) which has been shown to be soluble to varying degrees in organic solvents. A water-soluble equivalent where the side-chains are terminated by neutralized acids - poly(2- (1-sodium sulfonate-3-propaneoxy)-*p*-phenylene vinylene) - has been shown not only to allow the stiff chains of PPV to be soluble in water but also to be self-doping⁵⁷⁻⁵⁹.

2.2.3. Copolymeric Systems of Polyarylene Vinylenes

Table 2.2. Significant Developments in the Synthesis of Polyarylene Vinylene Copolymers.

YEAR	DEVELOPMENTS	Principal Researchers
1987	Series of copolymers of PPV with 2,5-dialkyl-derivatives of PPV (n=1,2,4).	Han, Lenz, Karasz
1989	poly(1,4-phenylene vinylene-co-2,5-dimethoxy-1,4-phenylene vinylene).	Lenz, Han, Lux
1989	poly(1,4-phenylene vinylene-co-2,5-thienylene vinylene).	Jin, Shim, Lenz
1989	poly(2,5-dimethoxy-1,4-phenylene vinylene-co-2,5-thienylene vinylene).	Shim, Lenz, Jin
1991	poly(2-methoxy-5-methylthio-1,4-phenylene vinylene-co-2,5-thienylene vinylene).	Jin, Park, Shim

Copolymeric systems based on π -conjugation have been studied (table 2.2). Copolymeric materials produced *via* synthetic pathways

other than the polymer precursor route outlined by Wessling³⁵ have consistently produced intractable polymers that were difficult to process and which contained a lot of defects^{60, 61}. Understandably then, the research effort on copolymeric systems was limited to copolymers of PPV-like monomers using a precursor polymer route. All the monomers investigated to date have been shown to undergo homopolymerization under the conditions outlined by the precursor route synthesis of PPV. It is not yet known if the synthetic pathway or the polymerization mechanism^{62, 63} will allow for a more varied monomer type other than derivatives of *bis*(methylenethiophenium halide) arylenes. A special emphasis has been given to this section due to its direct relationship to this dissertation.

Table. 2.3. Table of PPV-co-PdMeOPV Synthesized by Han *et al.*

Run	PPV/PdMeOPV	mole% PdMeOPV	conductivity (S/cm)
PdMeOPV		100	51
C1	1/4	53	28
C2	1/10	19	18
C3	1/20	13	27
PPV		0	<10 ⁻⁵

In a short report, Han *et al.*⁶⁴ reported the synthesis and conductivity measurement of copolymers of PPV and alkoxy-substituted PPV. It is interesting to note that in their table, a section of which is

In a short report, Han *et al.*⁶⁴ reported the synthesis and conductivity measurement of copolymers of PPV and alkoxy-substituted PPV. It is interesting to note that in their table, a section of which is reproduced here (table 2.3), the feed ratio, copolymer composition and conductivity do not show any strong correlation apart from the fact that all the copolymers show a marked increase in conductivity over PPV. In a later publication, Lenz *et al.*⁴⁷ reported the synthesis of poly(2,5-dialkoxyphenylene vinylene-co-*p*-phenylene vinylene). The reactivity ratio showed no apparent preference in the inclusion of either PdMeOPV and PPV segments (fig. 2.6). An almost ideal ratio was observed. It was also indicated that the conductivity of the system was very dependent on PdMeOPV, such that any degree of insertion of PdMeOPV increases the conductivity over that observed for iodine-doped PPV (fig. 2.7). The significances of these results will be discussed in the light of the results obtained in this dissertation (ch 4).

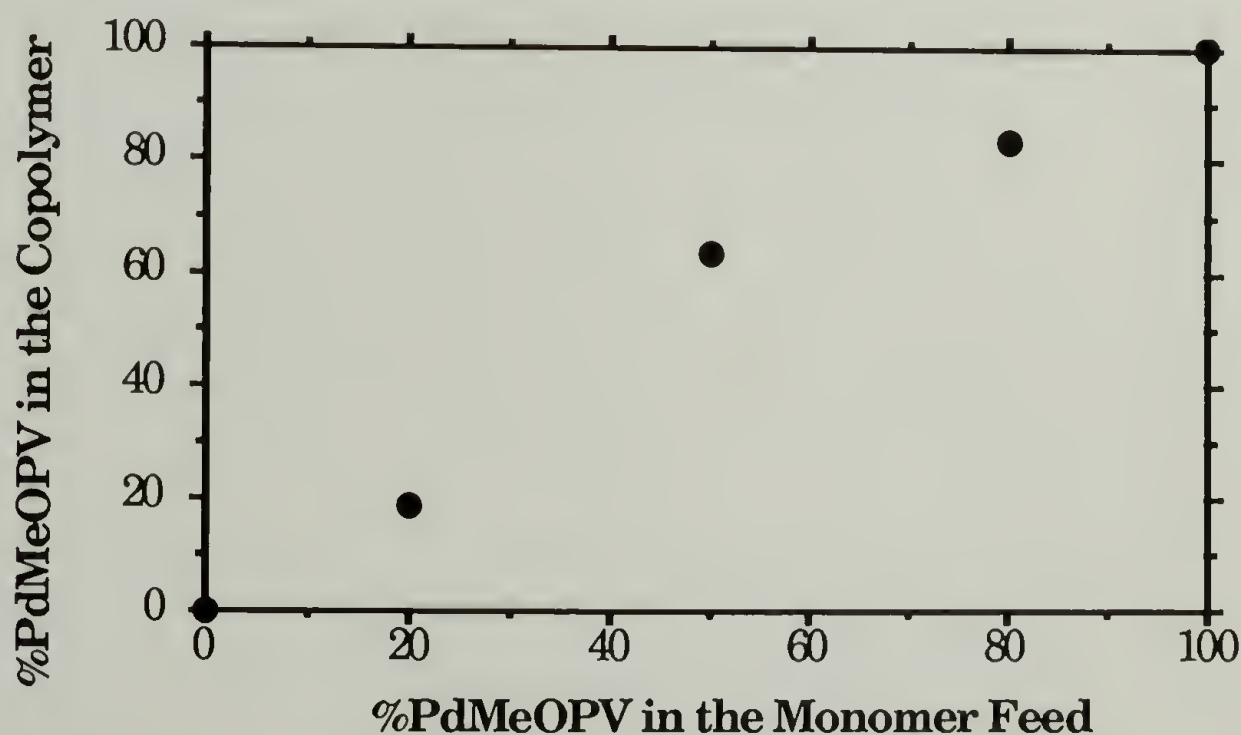


Fig. 2.6. PPV-PdMeOPV Copolymer Composition as a Function of Monomer Feed.

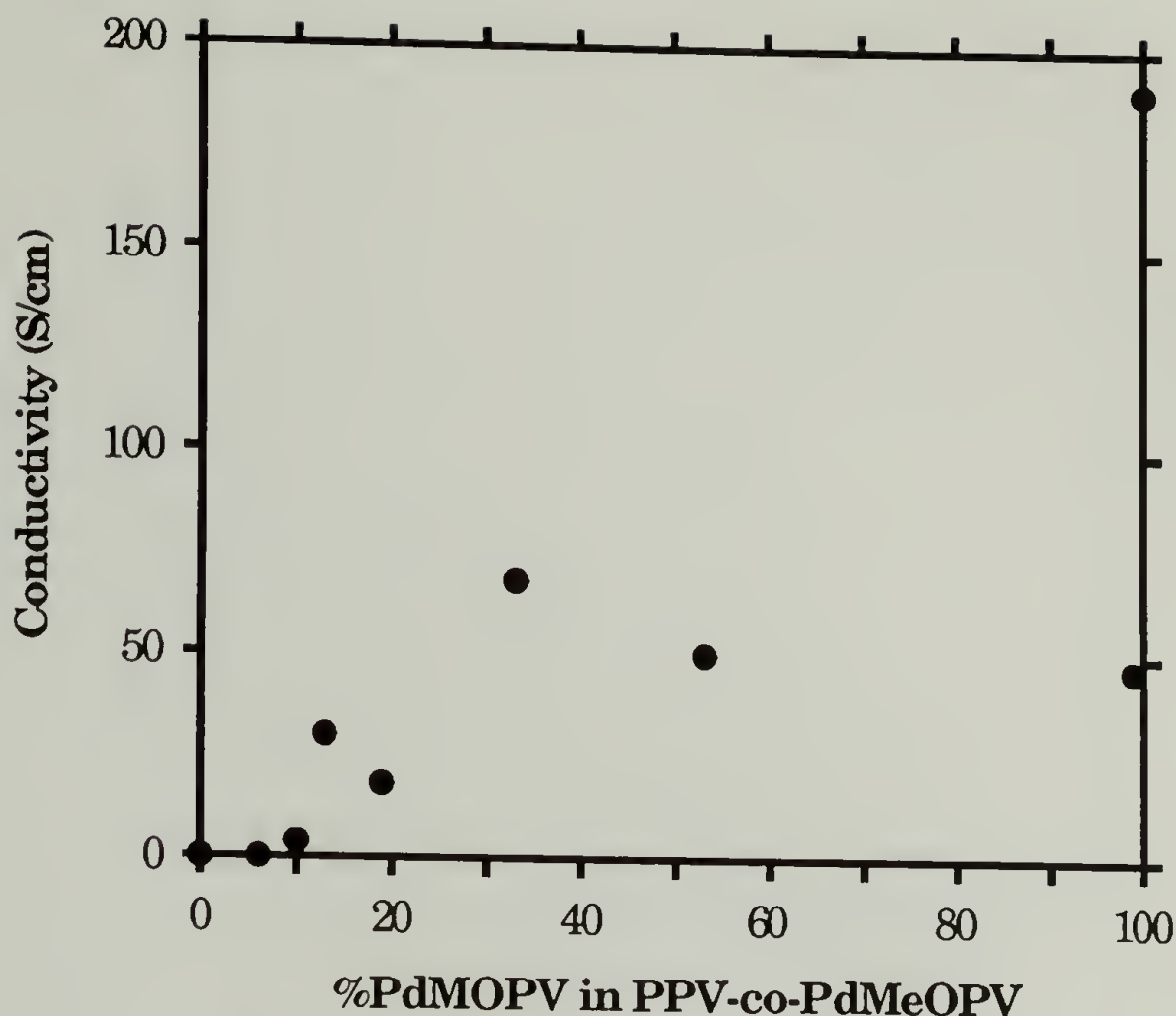


Fig. 2.7. Conductivity of PPV-co-PdMeOPV.

Jin *et al.*^{65, 66} reported two separate copolymeric systems, poly(1,4-phenylene vinylene-co-2,5-thienylene vinylene) (PPV-co-PTV) and poly(2-methoxy-5-methylthio-1,4-phenylene) copolymers with PPV and PdMeOPV. The results they reported for the PPV-PTV system are reproduced in fig. 2.8 and 2.9. The significance of these results will be discussed in chapter 4.

In the case of poly(2-methoxy-5-methylthio-1,4-phenylene vinylene) copolymers with PPV and PdMeOPV, the researchers admitted that the IR spectra of the copolymers (which was not presented in their publication) showed all the corresponding absorption peaks of both homopolymers. The *trans*-vinylene absorption maxima for the 2-

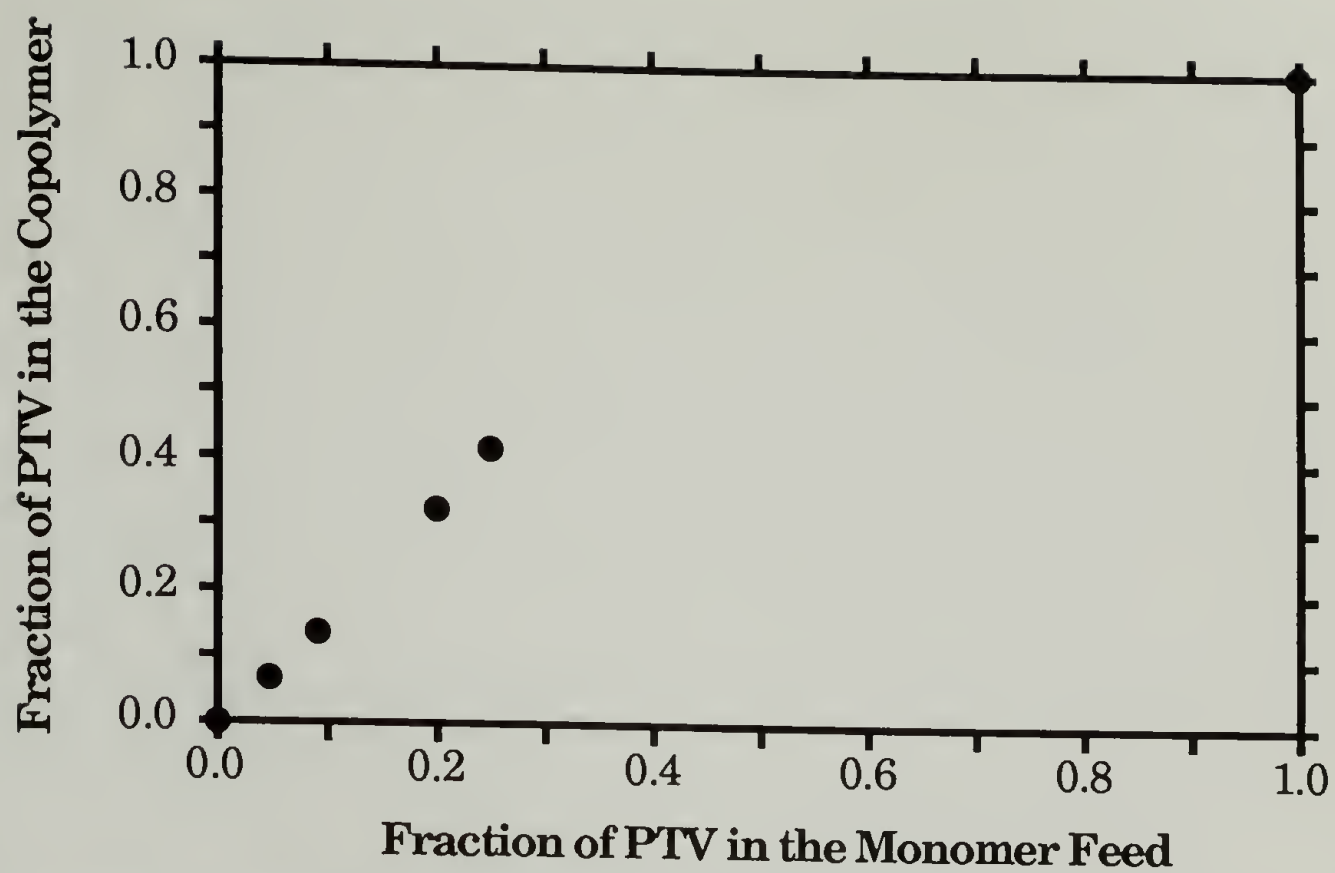


Fig. 2.8. PPV-co-PTV Copolymer Composition as a Function of Monomer Feed.

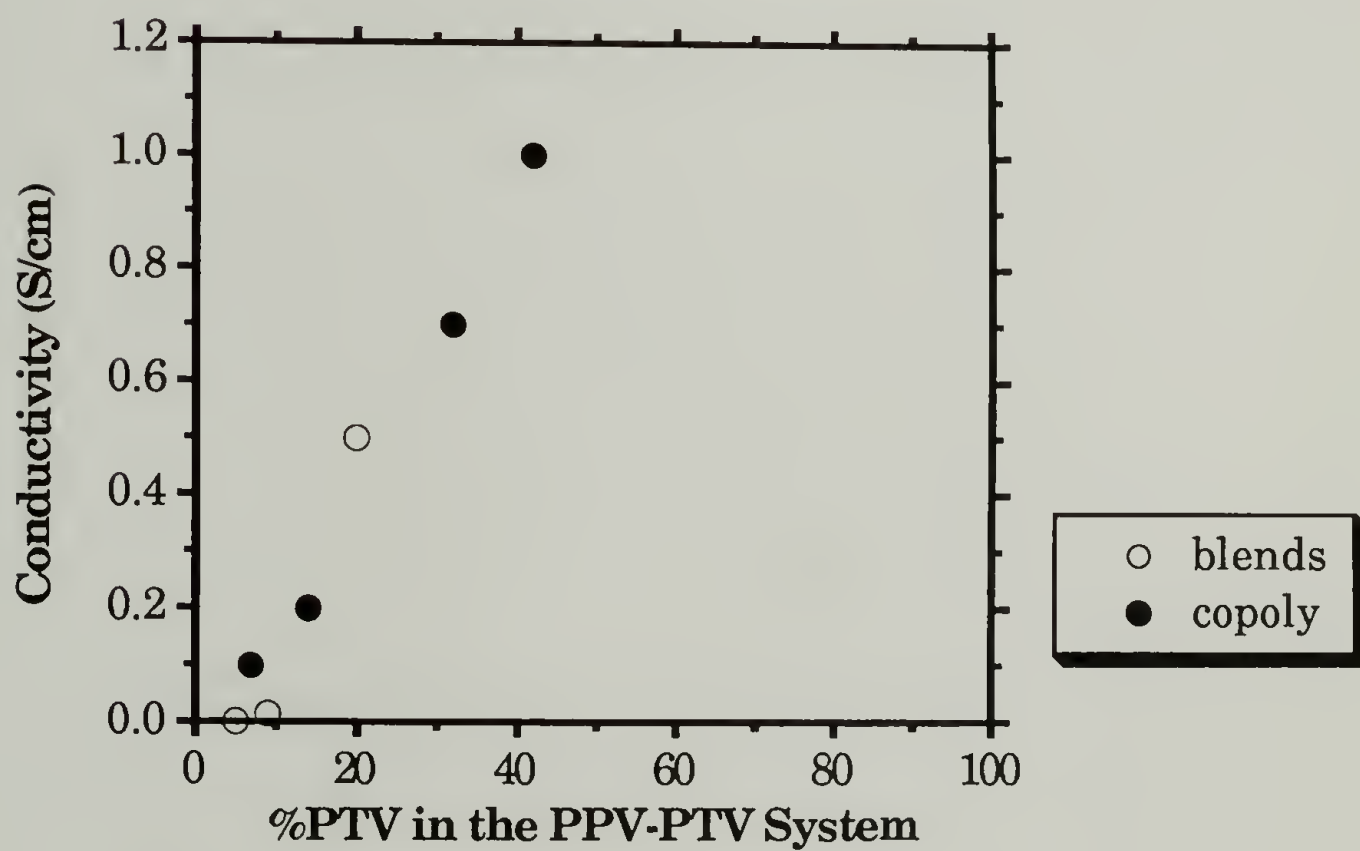


Fig. 2.9. Conductivity of Copolymers and Blends in the PPV-PTV System.

methoxy-5-methylthio-phenylene vinylene moiety was not discussed. There was no indication that that this particular *trans*-vinylene absorption was distinct from the equivalent *trans*-vinylene absorptions of PPV and PdMeOPV with which it was copolymerized. The copolymeric nature of this system was taken for granted given that the monomers underwent the same homopolymerization reaction scheme described for PAVs.

2.2.4. Over-all Picture of PAV Synthesis

A careful reading of the available literature, revealed that certain morphological issues were better addressed by first designing a synthetic procedure that allowed for a finer control over the polymer handling with regard to purification and processing. The synthetic pathway to polyarylene vinylenes through a precursor polymer allowed such ease. Most precursor polymers could be tailored to be soluble in either aqueous or organic media and even the final conjugated species could be modified to allow for partial solubility. The polymerization scheme allowed for a wide variety of monomers which produced polymers of varying physical properties. The precursor polymer could undergo physical characterization which gave information about the more intractable π -conjugated counterpart, information which would otherwise be inaccessible from the π -conjugated material.

The copolymers of such π -conjugated homopolymers proved to be a little bit more difficult. In general, difficulties were encountered in providing proof for the copolymeric nature of the system studied. In the case of PPV-co-PdMeOPV⁴⁷, the only available proof was the inconsistent UV absorption of the copolymeric material that mimics the absorption

pattern of PPV rather than being a combination of the individual homopolymer components. In the case of PPV-co-PTV^{65, 66}, the comparison with the blend system was made in the hope of differentiating the copolymeric system from the blend, no IR comparisons were given. Unfortunately, in this case the conductivities obtained for the blends and "copolymers" were indistinct within the experimental error of the measurement (fig. 2.9). Clearly, an experimental procedure must be determined which will allow the researcher to investigate the copolymeric nature of the system studied. The scale of this investigation must not only be concerned with macroscopic features, such as conductance of the bulk, but should also be especially concerned with the chemical composition and with the chemical regularity of the copolymeric nature in order to safeguard against systems that turn out to be homopolymer blends. Such systems have been addressed directly in this dissertation (ch. 4).

2.3. Morphology and Processing

2.3.1. Inquiries into Poly(*p*-phenylene vinylene) Morphology

A study on unoriented samples of the PPV precursor using x-ray diffraction techniques revealed that the poly(α -[dimethyl thiophenium chloride]-1,4-dimethyl phenylene) to be essentially an amorphous polymer⁶⁷. Initial studies on partially eliminated PPV showed the structure to have some nematic-like order³⁶. A subsequent study on fully oriented PPV samples having varying levels of elimination showed that crystallinity increased with elimination and resulted in the formation and growth of microcrystalline domains of PPV oriented along the stretch axis⁶⁸. More importantly, it was observed that the

interchain length decreased and the longitudinal unit cell dimensions increased with conversion and that the already fully oriented precursor polymer developed an increase in orientational ordering with increased elimination. Electron diffraction patterns of both isotropic and axially oriented PPV showed that PPV occurred as a semicrystalline polymer which crystallized in the monoclinic form. The stretching of the precursor polymer during the elimination process only serves to orient the *c*-axis of the crystallites with the draw direction^{69, 70}. The data suggested that in oriented PPV, the molecules were perfectly aligned to the stretch axis but exhibited partial axial translation. Quantitative evaluation of the crystallinity could not be obtained, however, since the rigidity and the occurrence of the melting transition beyond the decomposition temperature of PPV prevents the preparation of a fully amorphous sample.

The crystalline structure of doped-PPV has likewise been investigated^{71, 72}. The varied interactions between PPV and differing dopants produced a variety of structural phases and transformations. Several general conclusions were suggested however. It was shown that the introduction of a dopant into the crystalline lattice of PPV induced a reorganization of the chains into a new lateral packing. The chains and the dopant molecules were shown to form mutually exclusive layers (either lamellar or columnar) within a unit cell. The crystallites did not show any spatial reorganization.

2.3.2. Processing Methods

Polyarylene vinylene (PAV) processing has always been motivated by the need to obtain high or, at the very least, uniform quality

materials. Several issues regarding technological use of PAVs have spurred materials research into PAV processing.

The fact that the doping of PAVs produced what were essentially delocalized carbonium ions which were stabilized but nevertheless still underwent chemical reactions⁷³ required a means of preventing reactions of the doped species with oxygen. Doped PAVs that were not shielded from ambient oxygen generally resulted in reduced conductivity of the materials. Such requirements resulted in several processing solutions such as: protective barrier coatings⁷⁴ and stabilization of the carbonium ion by the introduction of electron donating substituents⁷⁵.

Similarly, several methods for uniaxially orienting PAVs were investigated⁷⁶⁻⁷⁸ when it was shown that the conductivities of these materials increased by orders of magnitude upon orientation. The aqueous solution of the PPV precursor was spun into a non-solvent such as acetonitrile to obtain fibers. Alternatively, fibers could also be obtained by first causing ion exchange to produce a PPV precursor which was soluble in an organic solvent followed by gel-spinning the organically dissolved precursor into a non-solvent. Uniaxially oriented PPVs were obtained with varying degrees of order and draw ratios by hanging a weighted sample over steam, immersing a weighted film into a hot-oil bath or continuous hot-press stretchers. Langmuir-Blodgett films were also investigated. Biaxially oriented materials were also prepared by taking advantage of the film shrinkage during elimination and by blowing a bubble into a circularly clamped film.

2.3.3. Over-all Picture of PAV Processing

All the previously mentioned processes were shown to produce unexpectedly highly ordered materials. The orientations were even higher than the Kratky model⁷⁹. The picture that emerges is an orientation that is driven more by the morphological changes in the conversion from the precursor polymer to the conjugated species rather than the reorientation in a drawing process. The change from an amorphous polymer to a semicrystalline material induces a tremendous change in the volume and organizes the material into crystallites which are then oriented along the c-axis (as evidenced by the investigation by Masse⁷²). It is the unusual combination of drawing an amorphous material and the driving force to form a semicrystalline material from the concurrent elimination process which gives the PAV system synthesized *via* a precursor polymer its tremendous advantage in the preparation of highly ordered materials.

2.4. References

1. Chien, J.C.W. "Polyacetylene: Chemistry, Physics and Materials Science." (Academic, New York, 1984).
2. Heeger, A.J. *Faraday Discuss. Chem. Soc.*, **88**, 203 (1989).
3. Thakur, M. *Macromolecules*, **21**, 1379 (1988).
4. Anderson, P.W. *Commun. Solid State Phys.*, **2**, 193 (1970).
5. Fleischman, L. and Anderson, P.W. *Phys. Rev. B*, **21**, 2366 (1980).
6. Mott, N.F. and Davies, E.A. "Electronic Processes in Non-crystalline Materials." (Clarendon Press, Oxford, 1979).
7. Kivelson, S. and Heeger, A.J. *Synth. Met.*, **22**, 371 (1988).
8. Gagnon, D.R. PhD Thesis, University of Massachusetts, 1986.

9. Emin, D. in *Electronic and Structural Properties of Amorphous Semiconductors* (eds. LeComber, P.G. & Mort, J.) 261 (Academic Press, London, 1973).
10. Heeger, A.J., Kivelson, S., Schrieffer, J.R. and Su, W.P. *Rev. Mod. Phys.*, **60**, 781 (1988).
11. Brédas, J.L., Chance, R.R. and Silbey, R. *Mol. Cryst. Liq. Cryst.*, **77**, 319 (1981).
12. Brazovski, S.A. and Kirova, N. *J. E. T. P. Lett.*, **33**, 4 (1981).
13. Bishop, A.R., Campbell, D.K. and Fesser, K. *Mol. Cryst. Liq. Cryst.*, **77**, 253 (1981).
14. Brédas, J.L., Chance, R.R. and Silbey, R. *Phys. Rev.*, **B26**, 5843 (1982).
15. Brédas, J.L., Scott, J.C., Yakushi, K. and Street, G.B. *Phys. Rev.*, **30**, 1023 (1984).
16. Brédas, J.L. *Mol. Cryst. Liq. Cryst.*, **118**, 49 (1985).
17. Winokur, M., Moon, Y.B. and Heeger, A.J. *Phys. Rev. Lett.*, **58**, 2329 (1987).
18. Naarman, H. and Theophilou, N. *Synth. Met.*, **22**, 1 (1987).
19. Bradley, D.D.C., Colaneri, N.F. and Friend, R.H. *Synth. Met.*, **29**, E121 (1989).
20. Heeger, A.J. *Phil. Trans. Roy. Soc. Lond.*, **A314**, 17 (1985).
21. Wegner, G. *Makromol. Chem., Macromol. Symp.*, **1**, 151 (1986).
22. Bloor, D., Monkman, A.P., Stevens, G.C., Cheung, K.M. and Pugh, S. *Mol. Cryst. Liq. Cryst.*, **187**, 231 (1990).
23. Shirakawa, H. and Ikeda, S. *Polym. J.*, **2**, 231 (1971).
24. Shirakawa, H. and Ikeda, S., *Chem. Polymer Sci.*, **12**, 929 (1974).
25. Shirakawa, H., Louis, E.J., MacDiarmid, A.G., Chiang, C.K. and Heeger, A.J. *J. Chem. Soc., Chem. Commun.*, 578 (1977).
26. Yamamoto, T., Hayashi, Y. and Yamamoto, A. *Bull. Chem. Soc. Japan.*, **51**, 2091 (1978).

27. Kovacic, P. and Kyriakis, A. *Tetrahedron Lett.*, 467 (1962).
28. Wnek, G.E., Chien, J.C.W., Karasz, F.E. and Lillya, C.P. *Polymer*, **20**, 1441 (1979).
29. Chandler, G.K. and Pletcher, D. *Spec. Period. Report Electrochem.*, **10**, 117 (1985).
30. Edwards, J.H. and Feast, W.J. *Polymer*, **21**, 595 (1980).
31. McDonald, R. and Cambell, T. *J. Am. Chem. Soc.*, **82**, 4669 (1960).
32. Kanbe, M. and Okawara, M. *J. Polym. Sci., (A-1)*, **6**, 1058 (1968).
33. Gourley, K., Lillya, C., Reynolds, J. and Chien, C. *Macromolecules*, **17**, 1025 (1984).
34. Koßmehl, G. and Yaridjanian, A. *Makromol. Chem.*, **182**, 3419 (1981).
35. Wessling, R. and Zimmerman, R. *U. S. Patents 3,401,152* (1968).
- ✓36. Gagnon, D.R., Capistran, J., Karasz, F.E. and Lenz, R.W. *Polym. Bull.*, **12**, 293 (1984).
- ✓37. Gagnon, D.R., Capistran, J., Karasz, F.E. and Lenz, R.W. *Polym. Prepr.*, **25**, 284 (1984).
38. Gagnon, D.R., Capistran, J., Karasz, F.E. and Lenz, R.W. *Mol. Cryst. Liq. Cryst.*, **118**, 327 (1985).
- ✓39. Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Polym. Commun.*, **25**, 327 (1984).
- ✓40. Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Polym. Commun.*, **26**, 362 (1985).
41. Gagnon, D.R., Capistran, J., Karasz, F.E., Lenz, R.W. and Antoun, S. *Polymer*, **28**, 567 (1987).
42. Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Mol. Cryst. Liq. Cryst.*, **118**, 333 (1985).
43. Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Synth. Met.*, **17**, 639 (1987).
44. Antoun, S., Gagnon, D.R., Karasz, F.E. and Lenz, R.W. *J. Polym. Sci., Polym. Lett.*, **24**, 503 (1986).

45. Antoun, S., Gagnon, D.R., Karasz, F.E. and Lenz, R.W. *Polym. Bull.*, **15**, 181 (1986).
46. Antoun, S., Gagnon, D.R., Karasz, F.E. and Lenz, R.W. *Polym. Prepr.*, **27**, 116 (1986).
47. Lenz, R.W., Han, C-C. and Lux, M. *Polymer*, **30**, 1041 (1989).
48. Lux, M. personal communications.
49. Lenz, R.W., Han, C-C., Stenger-Smith, J. and Karasz, F.E. *J. Polym. Sci., Polym. Chem.*, **26**, 3241 (1988).
50. Garay, R. and Lenz, R.W. *Makromol. Chem. Suppl.*, **15**, 1 (1989).
51. Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Polym. Commun.*, **28**, 229 (1987).
52. Yamada, S., Tokito, S., Tsutsui, T. and Saito, S. *J. Chem. Soc., Chem. Commun.*, 1448 (1987).
53. Momii, T., Tokito, S., Tsutsui, T. and Saito, S. *Chem. Lett.*, 1201 (1988).
54. Patil, A.O., Rughooputh, S.D.D.V., Patil, A., Heeger, A.J. and Wudl, F. *ACS Preprints, [Polymeric Materials Science and Engineering]*, **59**, 1071 (1988).
55. Askari, S.H., Rughooputh, S., D. D. V. and Wudl, F. *Preprints, [ACS Division of Polymeric Materials Science and Engineering]*, **59**, 1068 (1988).
56. Askari, S.H., Rughooputh, S.D. and Wudl, F. *Synth. Met.*, **29**, E129 (1989).
57. Shi, S. and Wudl, F. *Preprints, [ACS Division of Polymeric Materials Science and Engineering]*, **59**, 1164 (1988).
58. Ikenoue, Y., Uotani, N., Patil, A.O., Wudl, F. and Heeger, A.J. *Synth. Met.*, **30**, 305 (1989).
59. Shi, S. and Wudl, F. *Macromolecules*, **23**, 2119 (1990).
60. Zhong, X.F. and Francois, B. *Synth. Met.*, **29**, E35 (1989).
61. Jin, J.-I., Lee, Y.-H., Lee, K.-S., Kim, S.-K. and Park, Y.-W. *Synth. Met.*, **29**, E47 (1989).

62. Lahti, P., Modarelli, D., Denton, F., Lenz, R.W. and Karasz, F.E. *J. Am. Chem. Soc.*, **110**, 7258 (1988).
63. Wessling, R. *J. Polym. Sci., Polym. Symp.*, **72**, 55 (1985).
64. Han, C-C., Lenz, R.W. and Karasz, F.E. *Polym Commun.*, **28**, 26 (1987).
65. Jin, J.I., Shim, H.K. and Lenz, R.W. *Synth. Met.*, **29**, E53 (1989).
66. Jin, J.I., Park, C.K. and Shim, H.K. *J. Polym. Sci., Polym. Chem.*, **29**, 93 (1991).
67. Bradley, D.D.C. *J. Phys. D.*, **20**, 1389 (1987).
68. Moon, Y.B., Rughooputh, S.D.D.V., Heeger, A.J., Patil, A.O. and Wudl, F. *Synth. Met.*, **29**, E79 (1989).
69. Granier, T., Thomas, E.L., Gagnon, D.R., Karasz, F.E. and Lenz, R.W. *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 2793 (1986).
70. Masse, M.A., Schlenoff, J.B., Karasz, F.E. and Thomas, E.L. *J. Polym. Sci., Polym. Phys.*, **27**, 1 (1989).
71. Chen, D., Winokur, M.J., Masse, M.A. and Karasz, F.E. *Phys. Rev. B.*, **41**, 6759 (1990).
72. Masse, M.A. PhD Thesis, University of Massachusetts, 1989.
73. Whitney, D.H. and Wnek, G.E. *Macromolecules*, **21**, 266 (1988).
74. Österholm, J.E., Yasuda, H.K. and Levenson, L.L. *J. Appl. Polym. Sci.*, **27**, 931 (1982).
75. Druy, M.A., Rubner, M.F. and Walsh, S.P. *Synth. Met.*, **13**, 207 (1986).
76. Patil, A.O. *Polymer News*, **14**, 234 (1989).
77. Machado, J.M., Karasz, F.E., Kovar, R.F., Burnett, J.M. and Druy, M.A. *New Polym. Mater.*, **1**, 189 (1989).
78. Era, M., Kamiyama, K., Yoshiura, K., Momii, T., Murata, H., Tokito, S., Tsutsui, T. and Saito, S. *Thin Solid Films*, **179**, 1 (1989).
80. Kratky, O. *Kolloid-Z.*, **64**, 213 (1933).

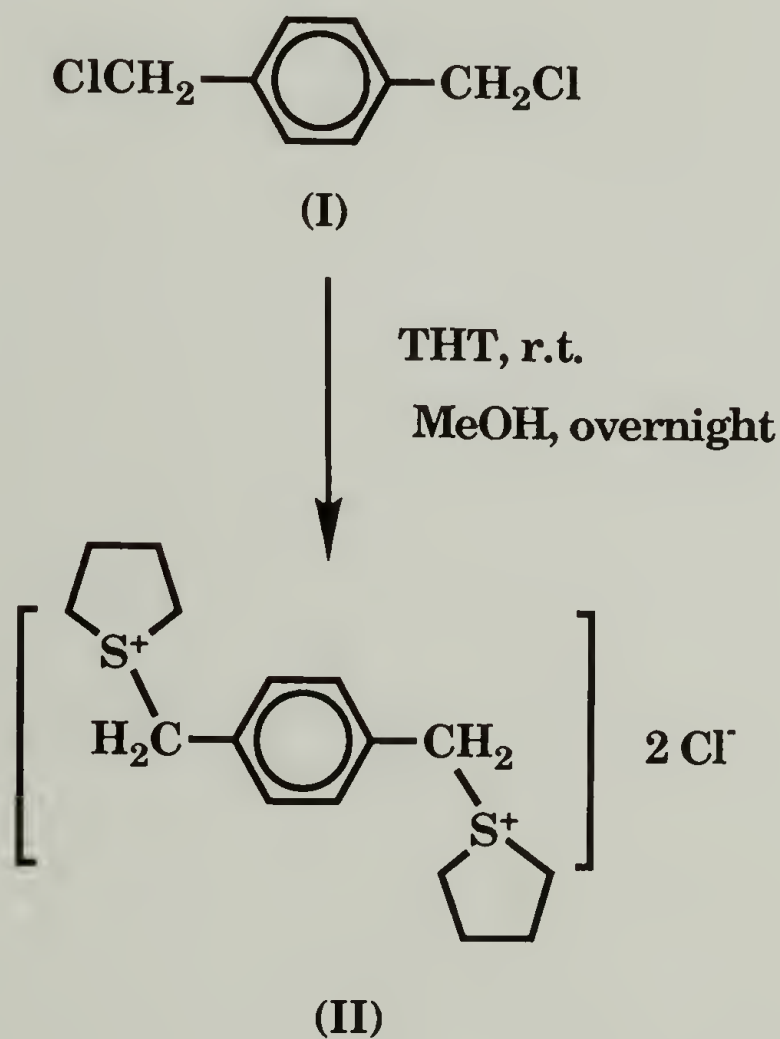
CHAPTER 3

EXPERIMENTAL METHODS

3.1. Copolymer Synthesis and Composition Analysis

3.1.1. Monomer Preparation

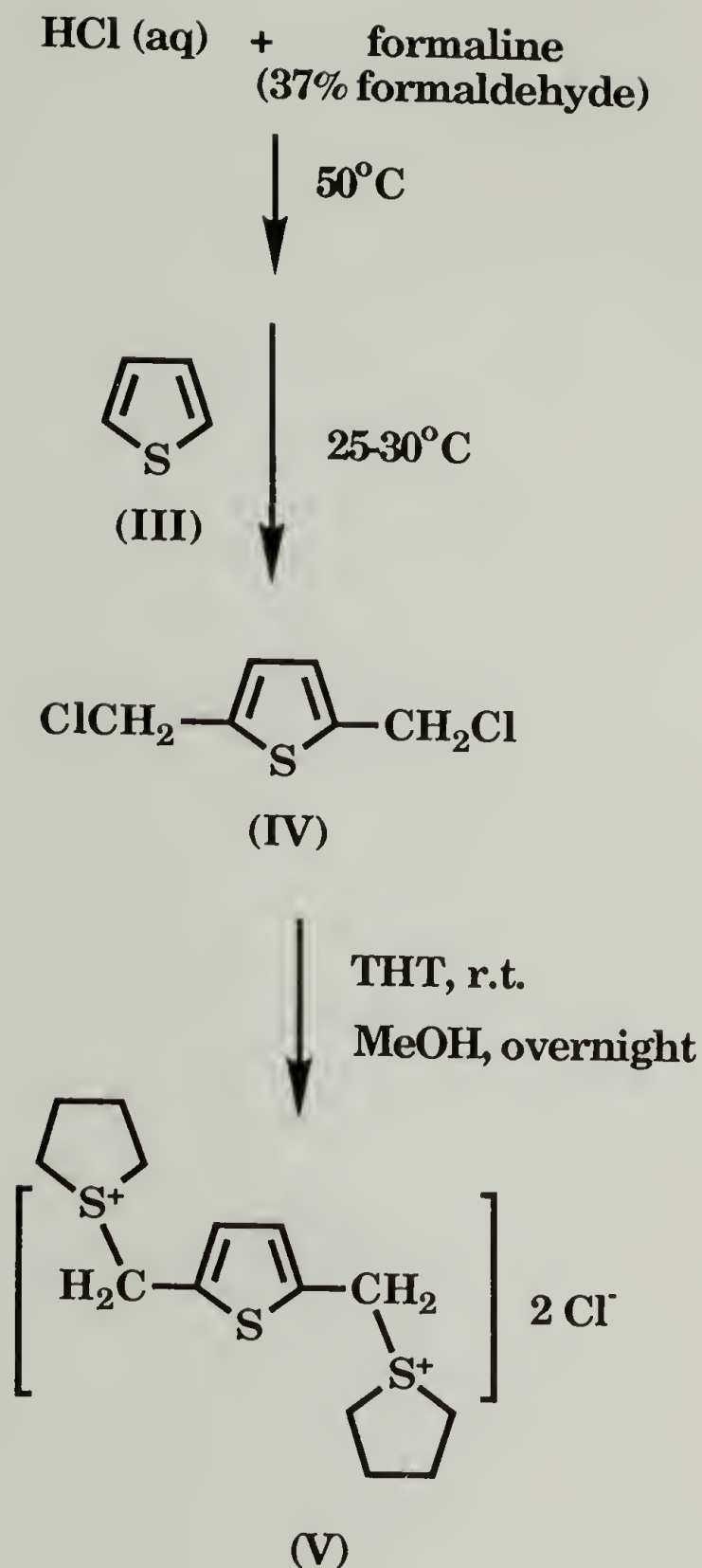
Monomers for homopolymerization and copolymerization were obtained by preparations described below and from Lark Enterprises. These monomers were prepared using the methods outlined by Griffing and Salisbury¹, Wood and Gibson² and Gagnon *et al.*³.



Scheme 3.1. PPV Monomer Preparation.

The α,α' -bis(tetrahydrothiophenium chloride)-*p*-xylene (**II**) was prepared from α,α' -dichloro-*p*-xylene (**I**) by swirling **I** in a saturated solution of methanol and 2.5x mole excess of tetrahydrothiophene at 50°C. The solution was stirred overnight (scheme 3.1). The fine needles which formed were collected and washed with cold acetone and purified following the steps described below³. More crystals could be collected by concentrating the methanol solution and precipitating in cold-acetone.

The α,α' -bis(tetrahydrothiophenium chloride)-2,5-dimethylene-thiophene (**V**) was prepared by chloromethylation of the thiophene (**III**) to form α,α' -dichloro-2,5-dimethylene-thiophene (**IV**) (scheme 3.2) followed by the THT salt formation. This is as described by Griffing and Salisbury¹. A stream of dried HCl gas (Merriam-Graves) is bubbled into a stirred solution of formaline (37% water solution of formaldehyde) and concentrated HCl(aq), allowing the temperature to rise to and remain at 50°C, until an acid-saturated solution is formed. The solution was considered saturated when the gases coming out of the reaction vessel rapidly reacted with an extremely saturated NaOH-base solution generating enough heat in the base solution to cause steam formation. Thiophene is added dropwise into this solution, carefully maintaining the temperature to be in between 25-35°C. Allowing the temperature to increase to 40°C for extended periods produced a black tar. Allowing the reaction to cool to below 20°C produced the spontaneously combustible mono-substituted thiophene. The reaction was stirred for an additional 30 min and the black-oily layer was siphoned off and washed repeatedly with water. The material was then treated with aqueous sodium carbonate until no appreciable CO₂ was formed. The organic layer was

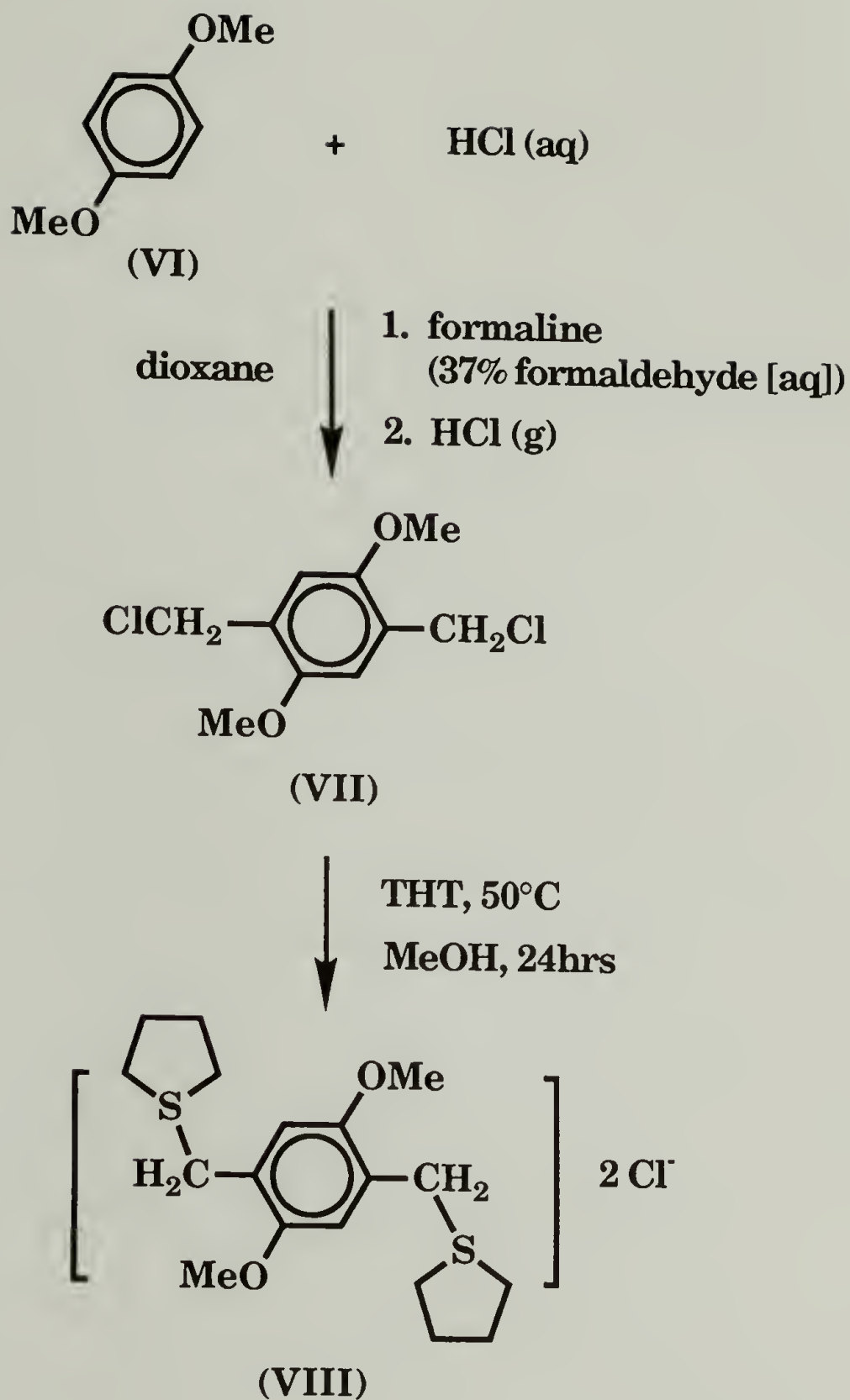


Scheme 3.2. PTV Monomer Preparation.

distilled under vacuum (250 μ m Hg) and the forerun produced at 30°C, the 2-chloromethyl thiophene, was collected and immediately destroyed by addition of dilute acid to prevent combustion. The second portion, the 2,5-dichloromethyl thiophene, distilling at 70-90°C was collected and

immediately reacted with tetrahydrothiophene (THT) in methanol to prevent further decomposition. The attempt to store the 2,5-dichloromethyl thiophene overnight at low (-30°C) temperatures produced a black tar. The distillate, 2,5-dichloromethyl thiophene, which tended to form crystals at room temperature was dissolved in a minimum amount of methanol and 2.4x mole excess of tetrahydrothiophene and stirred for 12 hours without heating. The white crystals that formed were purified by the methods described below. It is useful to note that the black-tar produced during the distillation must be washed with warm acetone right after the distillation is complete to prevent polymer formation which makes the glassware very difficult to clean. Also, the 2-chloromethyl thiophene has been reported⁴ to combust spontaneously even when kept under cool (-15°C) conditions. Similarly, **IV** must be converted to the thiophene salt **V** to prevent further decomposition. **IV** will form a dark-brown to black decomposition product even when kept at cold (-30°C) temperatures.

Similarly, the 2,5-dimethoxy- α,α' -bis(tetrahydrothiophenium chloride)-1,4-dimethyl benzene (**VIII**) was formed from the chloromethylation of 2,5-dimethoxy benzene (**VI**) to form the 2,5-dimethoxy- α,α' -dichloro-1,4-dimethyl benzene (**VII**)² (scheme 3.3). **VI** was added to a stirred solution of dioxane and concentrated HCl(aq) (6:1), through which a stream of HCl gas was being bubbled. Formaline (2.5x excess) was added in three portions. Stirring was continued for 3 hours and then 4.5x more of concentrated HCl was added. The solid that formed upon cooling was collected, washed with cold sodium carbonate and dried. The compound was recrystallized twice from acetone. The



Scheme 3.3. PdMeOPV Monomer Preparation.

purified material, **VII**, was converted to the thiophene salt, **VIII**, by dissolving **VII** in a minimum amount of methanol and 2.5x mole excess of tetrahydrothiophene. The resulting slurry was stirred at 50°C for 24 h. The solution was concentrated until crystals began to form and

was slowly added to very cold (-70°C) acetone. The crystals which formed were collected and purified by the methods described below.

The monomers were purified whenever degradation was suspected. **II**, **V** and **VIII** were all purified by repeatedly dissolving the compounds in a minimum amount of water, filtering the non-soluble impurities and precipitating in cold acetone. The white powder obtained was then filtered under nitrogen. All the monomers, especially **V**, were found to be extremely hygroscopic. It was necessary to keep the crystals under dried nitrogen gas during filtration. This was achieved by attaching a cap to a fritted glass filter that could be fed alternately by nitrogen gas and washing solvent. In the cases of **II** and **VIII**, drying was facilitated by swirling the acetone-wet powder in anhydrous ether before filtration or, alternatively, ether can be used to wash the filtrate. This procedure could not be used with **V** since it was partially soluble in ether at this stage. The monomers were dried overnight under $100\mu\text{m}$ Hg. Monomer **V** tended to turn a slight tan color during this drying process. This did not seem to adversely affect the synthesis.

The monomers slowly degraded even when kept under nitrogen and low (-30°C) temperatures. Compounds **II** and **VIII** produced degradation products that were not soluble in water and had to be repurified after a period of four and eight weeks, respectively. Compound **V**, within two weeks, produced a dark red or brown degradation product that was oily at room temperature. These materials could be repurified using the previously described process and used without adverse effects. Homopolymers and copolymers could be prepared with good yields even from the unrepurified monomers.

Repurification was only necessary to prevent errors in the calculation of starting monomer feed ratios.

3.1.2. Copolymer Preparation

The copolymers were prepared by adding an equimolar amount of base solution (0.2M) to an ice-cold, stirred solution of mixed monomers. The desired amount of monomers were weighed and dissolved in an amount of water such that the combined water and methanol, in a 1:4 ratio, produced a 0.2M solution of mixed monomers. The water solution was filtered (to remove any water-insoluble materials that may have formed during the weighing process) and added to methanol. Pentane was added in a proportion equal to the combined water and methanol volume. The base, tetramethyl ammonium hydroxide, was similarly diluted to 0.2M into a 1:4 - water:methanol solution from a 25%-methanol solution obtained from Aldrich. Both solutions were cooled separately with stirring in an ice-bath, and purged with a steady stream of pre-purified nitrogen gas (Merriam-Graves) passed through a drying column of molecular sieves and calcium sulfate. After one to two hours of purging, the base was cannulated, or simply poured into the monomer solution. The reaction was allowed to run for a minimum of two hours under a steady atmosphere of nitrogen before the reaction was quenched with enough dilute HCl acid solution to obtain a neutral pH by pH paper (S&S Panpeha pH-indicator strips). The reaction-flask was then allowed to warm to room temperature, in some cases, a green to yellow to orange precipitate formed. This was found to most likely occur in systems of high PTV content in the copolymer. It was often found

that exposure to light and stopping the stirring of the solution accelerated the formation of the precipitate.

A saturated solution of sodium tetrafluoroborate in water was added dropwise to the swirled solution of the polymeric precursor until a cloudy solution persisted. After a few minutes of standing, the precipitate could be collected as a powder or a gum-like precipitate. This precipitate was washed with copious amounts of water and methanol to remove unreacted materials. Similarly, the poly(2,5-dimethoxy-*p*-phenylene vinylene-co-thienylene vinylene) (PdMeOPV-co-PTV) precursor copolymers were treated with a saturated solution of sodium *p*-toluene sulfonate (Aldrich). The sticky ball which formed was collected, washed and stirred for 24 hours in methanol after which a fine powder could be collected and washed with water and methanol.

A typical calculation for preparing PPV-co20-PTV which was found to be equivalent to a 5% PTV monomer feed (see results section, table 4.2), is described below. The monomer feed mole fraction (f) was first calculated where:

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \quad (3.1)$$

and when (where the subscript 1 \equiv PTV), $f_1 = 0.05$ and $[M_1] + [M_2] = 0.2M$ then $[M_1] = 0.01M$ and $[M_2] = 0.19M$ which is equivalent to 1.7871g₁ and 33.3821g₂ for a 500mL solution. This was dissolved in 100mL deionized water, filtered and mixed with 400mL methanol. 42.10mL of 25% base (tetramethylammonium hydroxide in methanol) was mixed with 100mL deionized water and enough methanol to make a 500mL solution of 0.2M

solution concentration. The reaction, after purification, yielded typically 5g of precursor copolymer (~22%).

3.2. Film Preparation and Processing

3.2.1. Film Casting

The PPV-co-PTV copolymers were dissolved in DMF, filtered to remove undissolved gels and dust and cast on dichloro-dimethyl silane-treated flat glass dishes that were set inside desiccators and dried under 100 μ m of pressure.

The flat dishes were first immersed for two days in a base bath (KOH in water/ethanol). After rinsing thoroughly with water, the release agent, dichloro-dimethyl silane, was swirled in the dish followed by washing with THF, water and the solvent used for dissolving the copolymer or blend. This ensured that the glass had a fresh coat of siloxanes (glass) and a layer of methyl groups which would have a very low surface-activity.

It was found in certain instances of dissolving the PPV based systems that a green gel resisted dissolution. Addition of a small amount of water to the DMF solution and continued stirring often dissolved these materials. The greenish gel was believed to be PPV segments that escaped treatment of sodium tetrafluoroborate. This was often unavoidable since it was necessary not to add too much NaBF₄ since the excess was difficult to wash off the gummy materials that formed and would later cause large crystal formation during film casting. These crystals of NaBF₄ would make the over-all films brittle and unusable. The solutions of PPV-co-PTV were cast onto the pre-treated flat-bottomed dishes and set inside a desiccator. The vessel was

evacuated down to 100 μ m Hg. It would take 3-4 days of evacuation to complete cast and dry a film from 400mL of solvent.

Equivalently, the PdMeOPV-co-PTV copolymers were dissolved in CHCl₃/THF in an equivalent ratio to the PdMeOPV/PTV content of the copolymer. The solutions were filtered and cast on dichloro-dimethyl silane treated flat-bottom dishes, set inside desiccators, evacuated overnight using a water-aspirator to remove volatiles and fully dried under 100 μ m Hg for a day.

The blend solutions of homopolymers were cast into films using the same technique as described above except that the homopolymer solutions were prepared, filtered and gravimetrically assigned concentrations before mixing to form the blend solutions. This was done to avoid changes in concentration that would have resulted if the homopolymer solids were mixed, dissolved and then filtered.

A minimum of 0.6 g of sample was needed to form a coherent film covering an area of $\pi(14.5\text{cm})^2$. Consequently, a gravimetric test was often applied on a 10mL aliquote of the solutions to obtain an approximate concentration before casting. In the case of the blends, the gravimetric test provided information to allow appropriate ratios of solution mixtures that would give the proper molar ratios of blend films and to satisfy the minimum weight-sample requirements to give coherent films.

A typical calculation is presented here. The concentrations (g/mL) of the PPV and PTV solutions in DMF after filtration were obtained using the procedure described previously. Typical values were

$\sim 2.9 \times 10^{-3}$ g/mL for PPV and $\sim 8.4 \times 10^{-4}$ g/mL for PTV. The volumes used for each solution were calculated using:

$$V_1 = \frac{\frac{g_0}{Mw_1(f_1) + Mw_2(f_2)} f_1 Mw_1}{[M_1]} \quad (3.2)$$

where V_x is the volume needed from solution "x", g_0 is the needed number of grams to produce a coherent film, f_x is the fraction of the component in the sample to be made, Mw_x is the molecular weight of the precursor polymer and $[M_x]$ is the concentration of the solution used.

3.2.2. Film Orientation

The cast films were stretched and oriented in a hot-oil immersion stretcher (fig. 3.3).

Roughly 1.5×1 to 2×1 cm² sections were cut and clamped in place using a combination of magnetic bars and metal clips. Weight (constant stress) and temperatures were varied to ascertain the conditions that would give varying stretches (l/l_0). Typically, a 1×1 cm² sample stretched to 5×2 cm² when a 25g weight was applied at 120°C. The initial length, width and thickness of the films were compared to those of the stretched film to ascertain the degree of stretching (l/l_0) and any volume change. Unfortunately, this could not be considered reliable since the thickness of the samples were in the range of 10-30µm and necking of the film prevented proper measurements of the dimensions.

The oil was heated and stirred under a steady stream of nitrogen and as soon as the appropriate temperature stabilized, the whole sample was immersed in the high-temperature silicon oil (Aldrich). It was necessary to keep the films within the hot-oil bath for as much as thirty

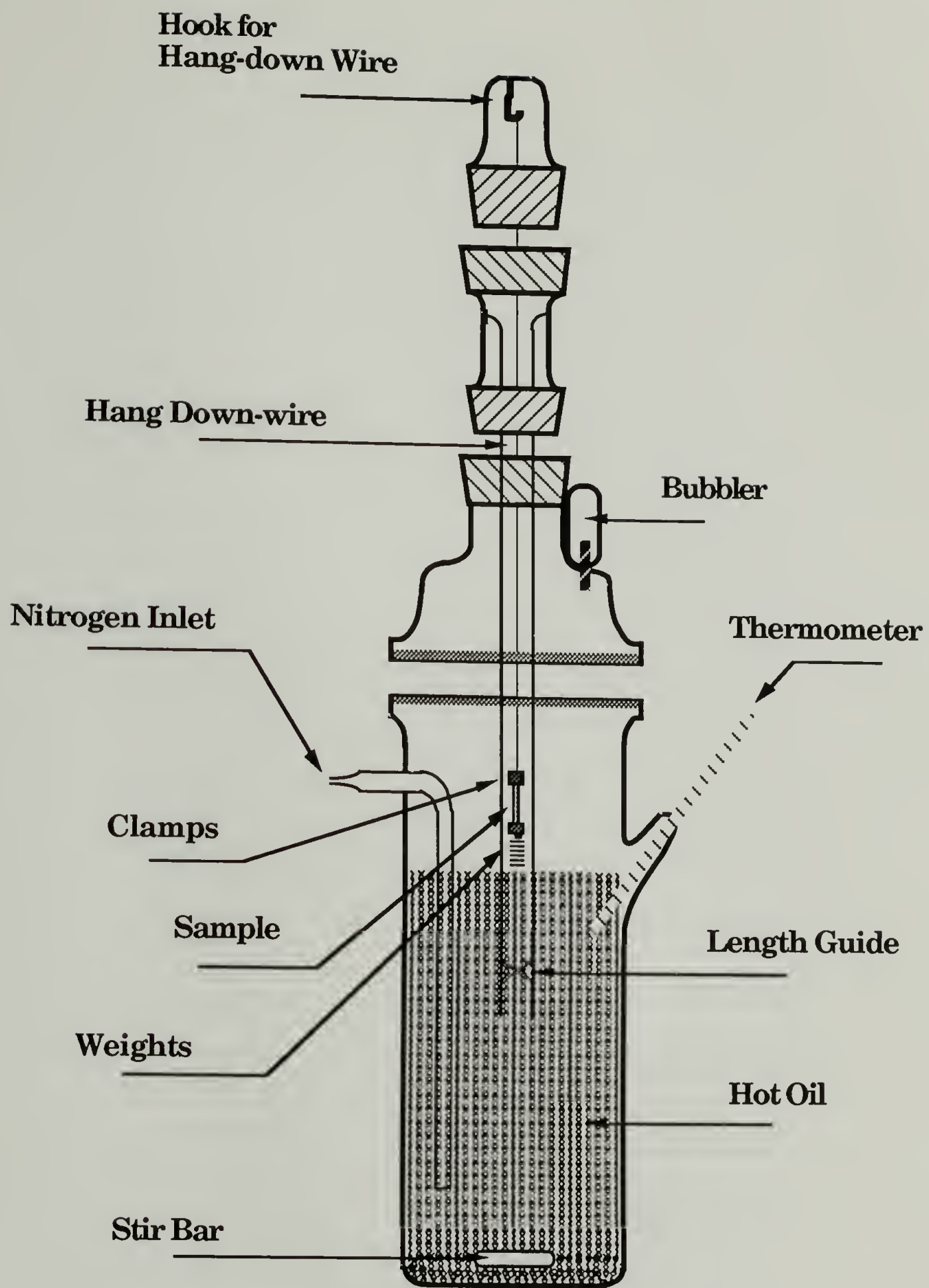


Fig. 3.1. Hot-oil Stretching Apparatus.

minutes to allow enough elimination to take place under weight-tension. This prevented film shrinkage during the final elimination step. The bath was maintained at the optimum stretching temperature (typically 120°C), and continuously purged with dry nitrogen gas to avoid ramp-up times.

3.2.3. Elimination Procedure

Both oriented and unoriented films were made into the fully conjugated polymer during the final elimination step. Strips of film were sandwiched between thick (0.125 in.) sheets of teflon (obtained from Small Parts Inc.), clamped tightly with metal clips and inserted into pyrex tubes equipped with nichrome wire heaters and thermocouple sensors. The vessel was brought to a vacuum of less than 10 μ m Hg and then heated to 250 \pm 20°C for six hours. The resulting conjugated polymers were self-supporting films with a metallic gold luster on one side and a black sheen on the other.

3.3. Physical Measurements

3.3.1. IR Dichroism Experiments

The IR dichroism for each oriented sample was obtained using the IBM system 9000 FTIR Spectrophotometer and a Harrick gold-wire polarizer. An IR baseline through the polarizer set at 0° was obtained followed by a measurement of the film held in place and oriented horizontally with magnetic clamps. A second spectrum was obtained after taking a baseline for the 90° polarizer setting. The setting at 90° was taken to be the stretch direction. The baseline for each band was adjusted using the IBM FTIR's baseline adjustment facility and the absorbance was noted using the peak picking function. The calculations

employed followed that of Zbinden⁵ as modified by Bradley⁶. This will be detailed in the discussion section.

3.3.2. Conductivity Measurements

The thickness of the fully eliminated films were measured before mounting onto the four-probe cell (figs. 3.2 and 3.3) using electrodag (conducting graphite suspended in methyl ethyl ketone). The distance between the innermost sections of the electrodag were measured along with the average width of the film. Both the controlled-atmosphere chamber and the dopant cell were evacuated to 100 μ m Hg. The dopant cell was intermittently cooled with liquid nitrogen to prevent excessive release of iodine vapor into the vacuum pump. The controlled atmosphere chamber was isolated from the pump and exposed to iodine vapor from the chamber holding iodine crystals kept at room temperature. The resistance was measured every 12 hours using a Kiethley 197 autoranging multimeter adapted for four probe measurements and the minimum resistance was obtained. This value was converted to conductivity using the dimensions that were determined and the equation:

$$\sigma = \frac{l}{wt} \left(\frac{1}{\Omega} \right) \quad (3.1)$$

where l is the length of the film in cm, w is the width of the film in cm and t the thickness of the film in cm. Ω is the measured resistance from the four-probe in ohms and σ is the conductivity in Scm^{-1} .

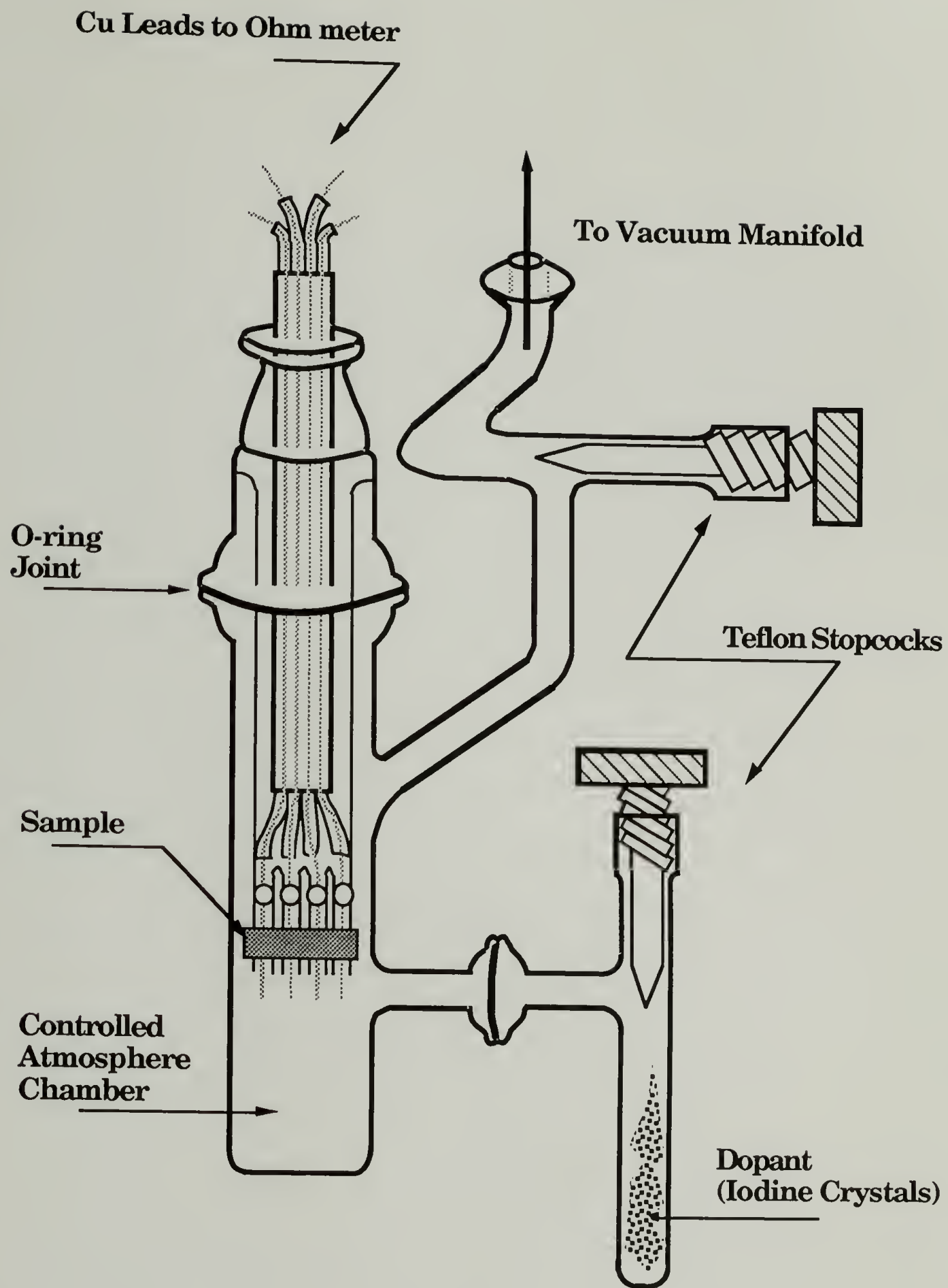


Fig. 3.2. Four-Probe and Doping Vessel.

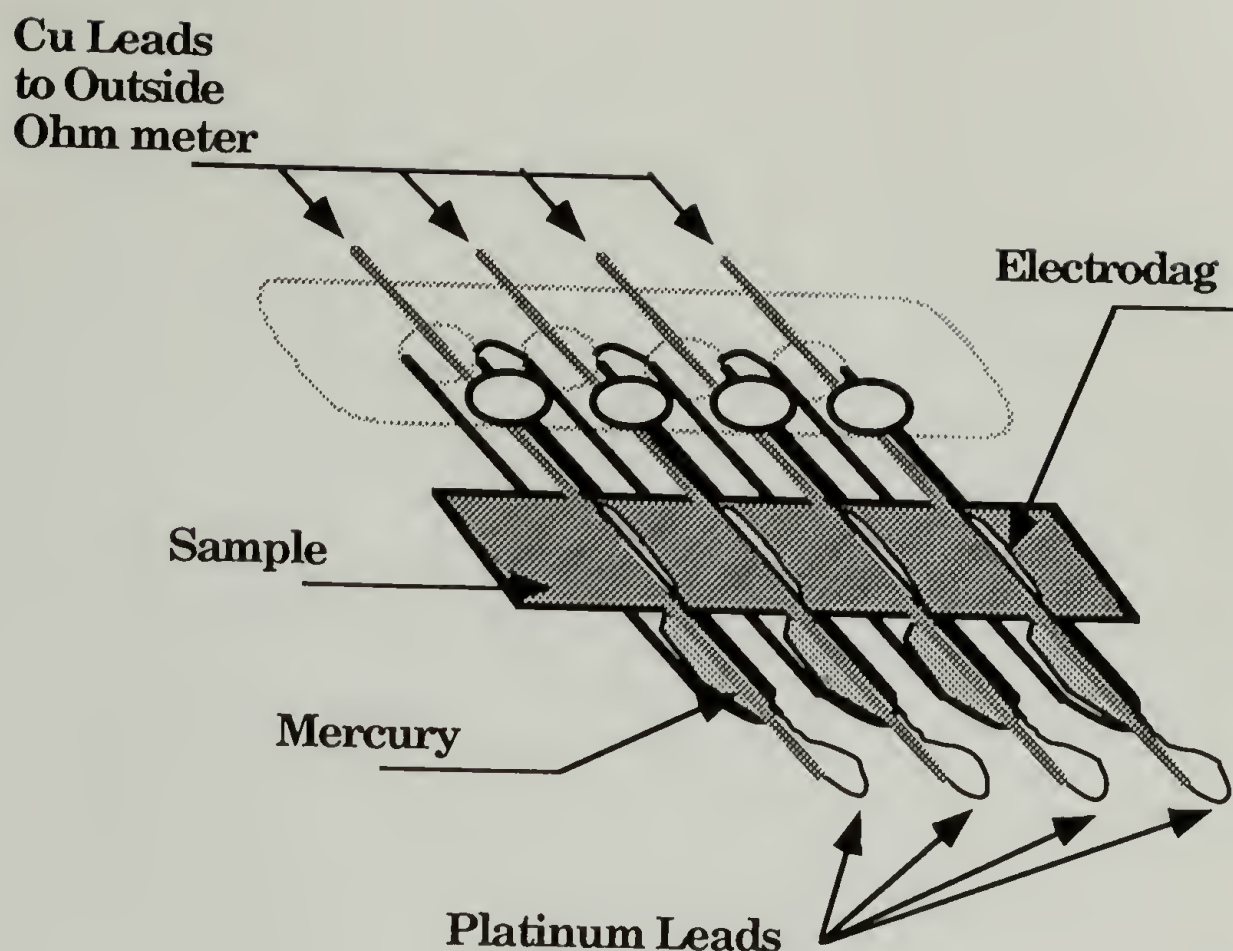


Fig. 3.3. Close-view of the Four-probe System.

3.4. References

1. Griffing, J.M. and Salisbury, L.F. *J. Am. Chem. Soc.*, **70**, 3416 (1948).
2. Wood, J.H. and Gibson, E. *J. Am. Chem. Soc.*, **71**, 393 (1949).
3. Gagnon, D.R., Capistran, J., Karasz, F.E., and Lenz, R.W. *Polym. Prepr.*, **25**, 284 (1984).
4. Franke, L. personal communications.
5. Zbinden, R. "Infrared Spectroscopy of High Polymers." (Academic Press, New York and London, 1964).
6. Bradley, D., Friend, R., Lindenberger, H. and Roth, S. *Polymer*, **27**, 1709 (1986).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Synthesis of Polyarylene Vinylene Copolymers

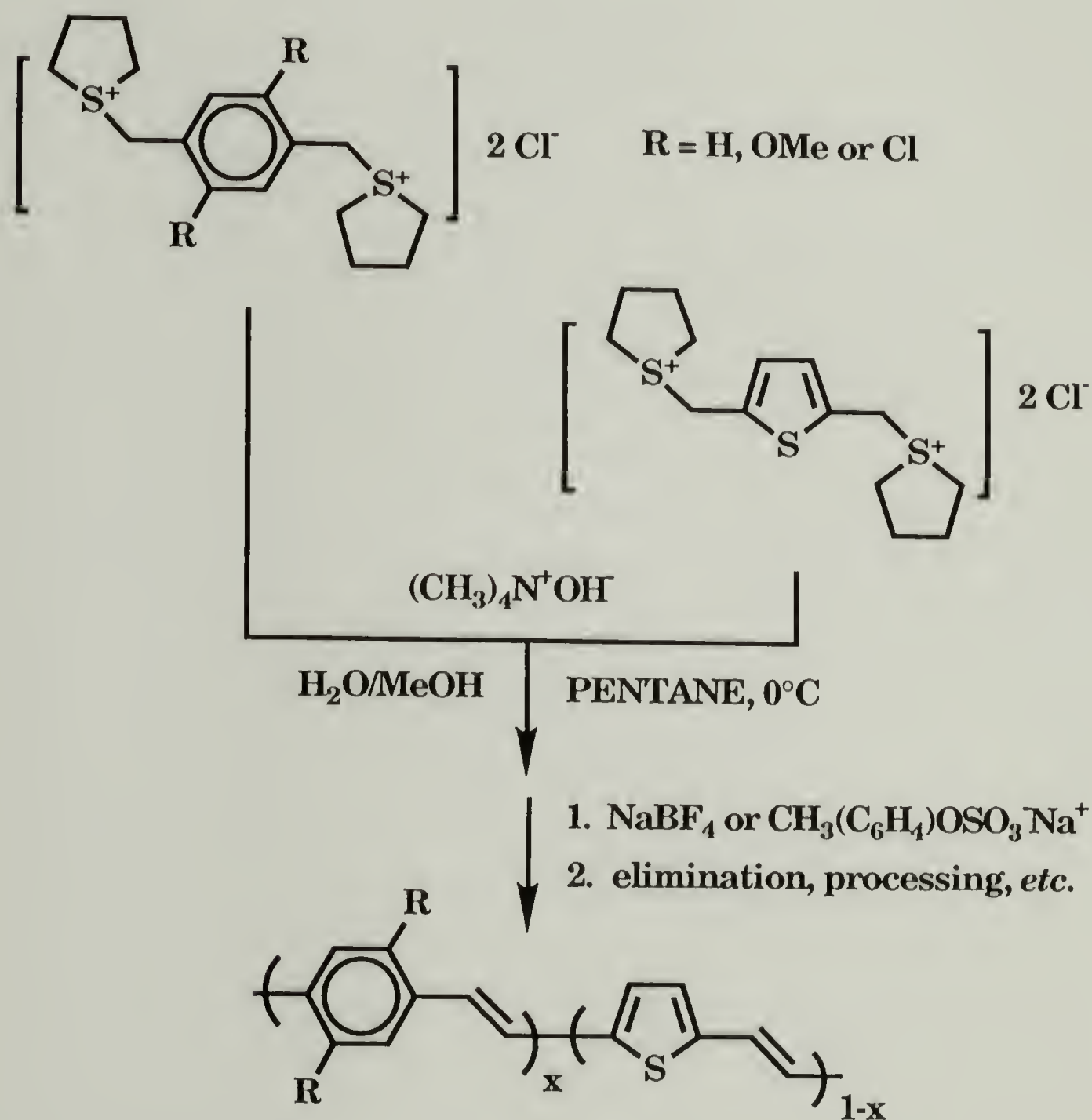
This section presents the data and results concerning the synthesis of poly(*p*-phenylene vinylene-*co*-2,5-thienylene vinylene) (PPV-*co*-PTV) and other related copolymers. The studies on the molar-equivalent homopolymer blends (denoted by PPV/PTV) are also reported.

4.1.1. Reaction Scheme

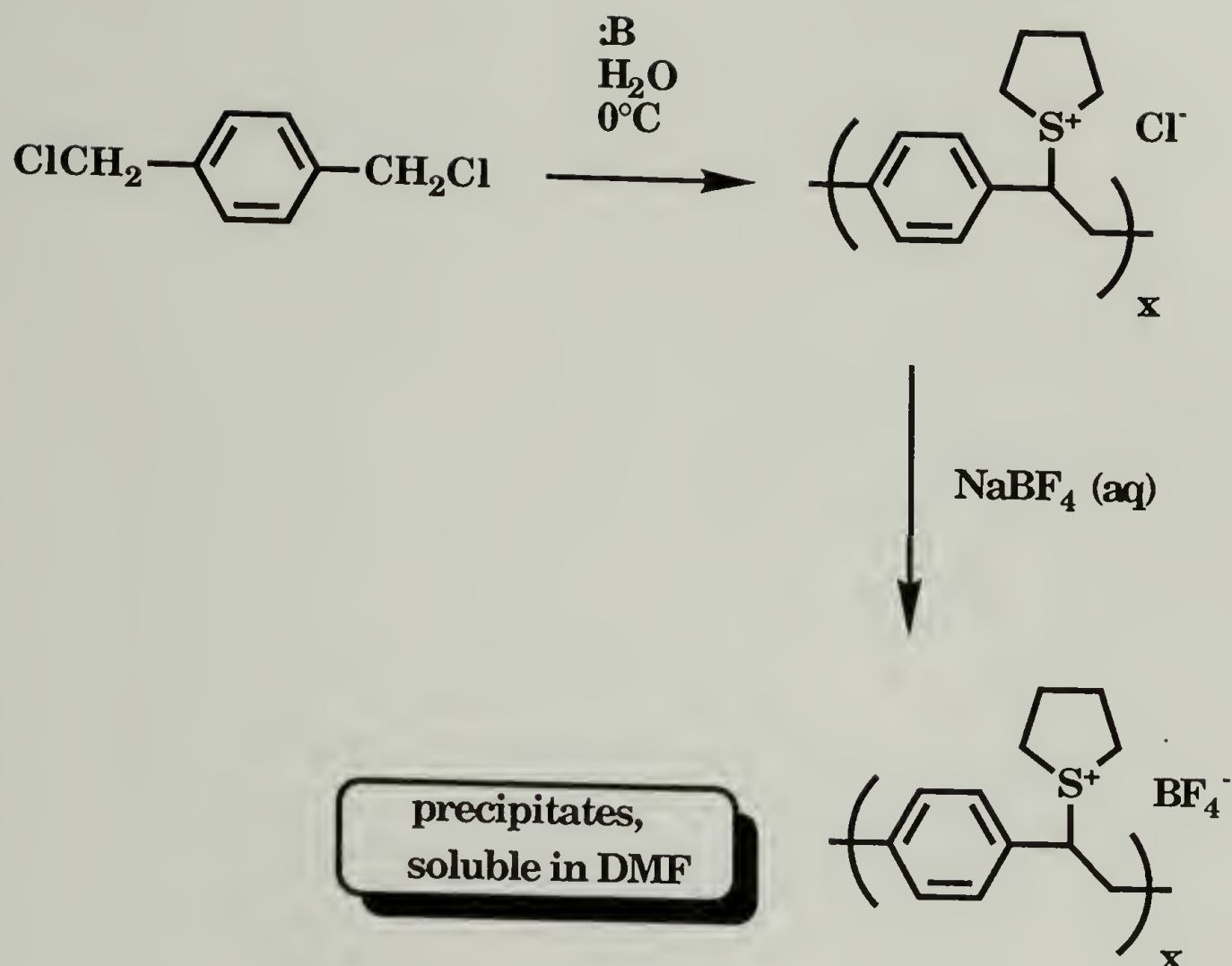
The reaction scheme used for the synthesis of PPV-*co*-PTV (scheme 4.1) is a combination of the procedures reported earlier¹⁻⁸ for poly(*p*-phenylene vinylene) (PPV), poly(2,5-thienylene vinylene) (PTV) and poly(2,5-dimethoxy-1,4-phenylene vinylene) (PdMeOPV) which were designed to improve the preparation of polyarylene vinylenes. The standard procedure^{1, 2} which involved the addition of an equimolar amount of base to the bis(methylene-dialkylsulfide)-arylene monomers dissolved in water and cooled to 0°C was modified to produce better yields, higher molecular weights and organic solubility.

Cyclic thiophenes, such as tetrahydrothiophene, were used to provide a more stable, sterically hindered, precursor polymer³ resulting in higher yields and higher molecular weights than those produced from their dialkylsulfide counterparts. Pentane was used to provide an organic layer which would extract the sulfides produced in the reaction⁴ and drive the reaction forward producing higher yields and higher molecular weights. The strong base, tetramethylammonium hydroxide ([CH₃]₄NOH) was used instead of sodium hydroxide (NaOH) to allow for

greater solubility of the base in the organic reaction medium and ease of removal of the unreacted base and salts during the π -conjugation formation. $(\text{CH}_3)_4\text{NOH}$ was found to decompose to trimethylamine and methanol⁹ and these decomposition products were easily removed in the elimination step.

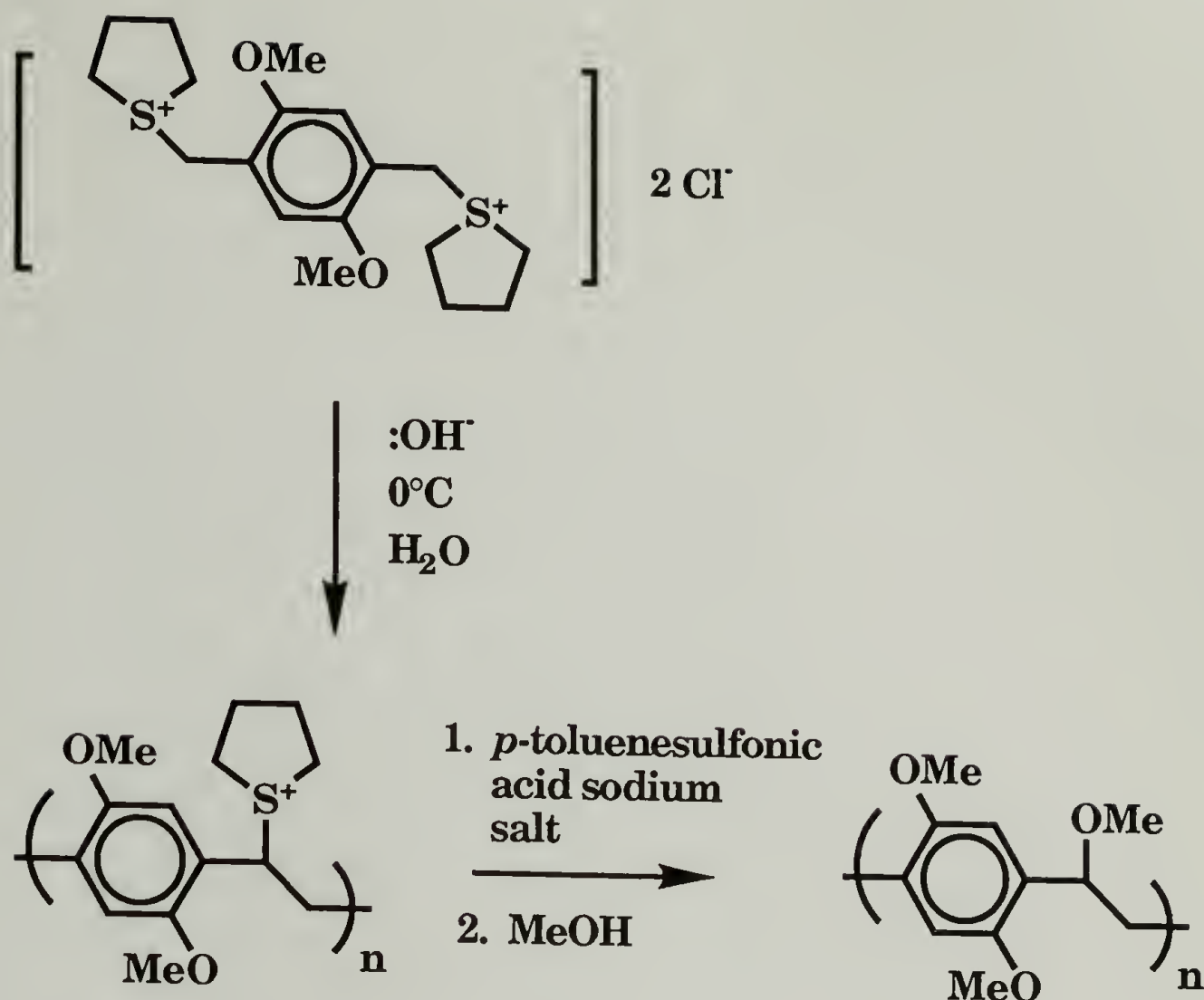


Scheme 4.1. The Synthetic Pathway to PPV-co-PIV and Other Related Copolymers.



Scheme 4.2. Preparation of an Organic-soluble PPV Precursor.

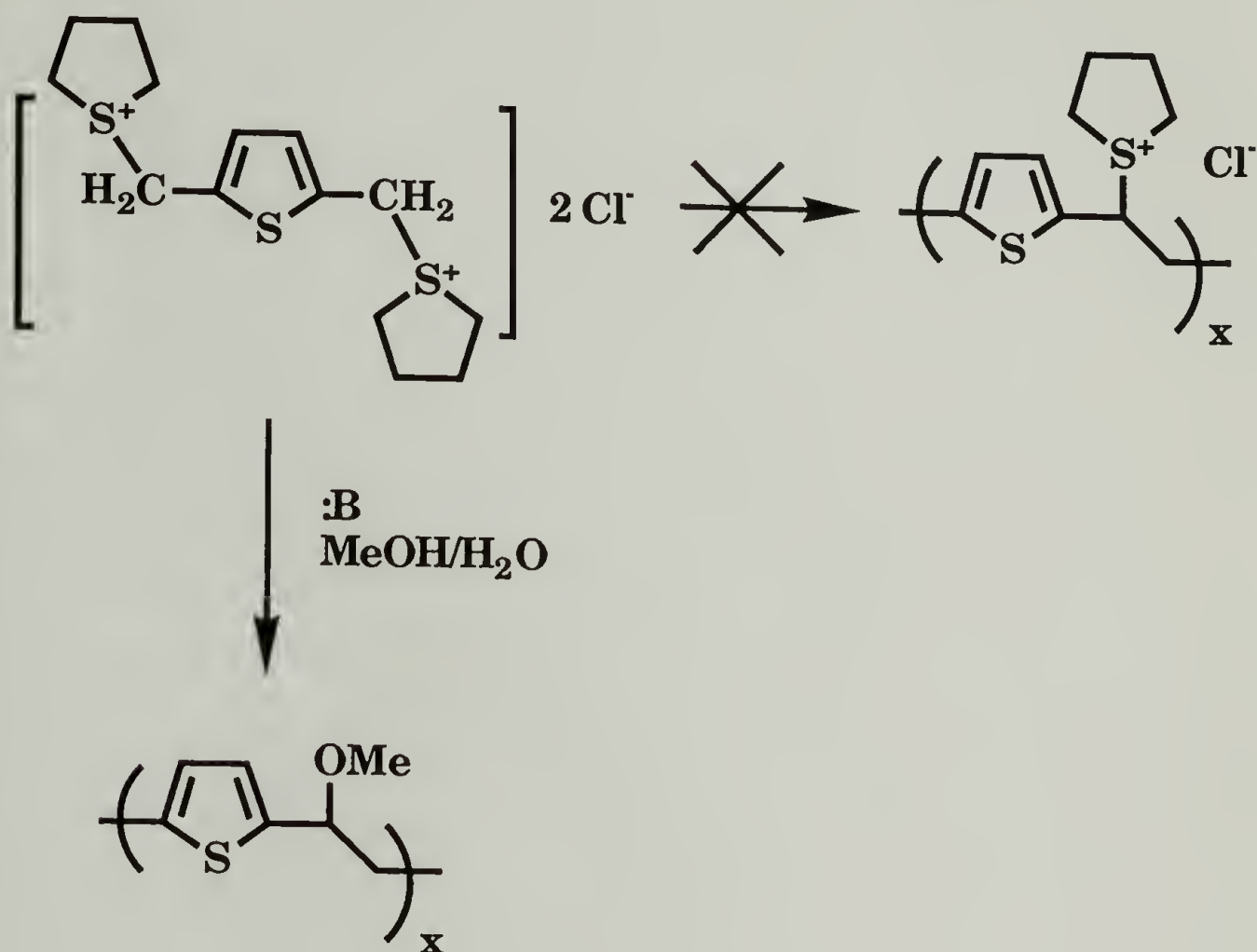
Sodium tetrafluoroborate (NaBF_4) was used to exchange the halide counter-ion (usually Cl^-) of the PPV precursor polymer to a fluoroborate (BF_4^-) and produce an organically soluble PPV precursor polymer⁵ (scheme 4.2). The fluoroborate salt of the PPV precursor polymer was found to be soluble in DMF. Similarly, the sodium salt of *p*-toluene sulfonic acid [$(\text{CH}_3)\text{---}p\text{---C}_6\text{H}_4(\text{SO}_3^-\text{Na}^+)$] was added to the reaction mixture containing the PdMeOPV precursor polymer and followed by a treatment of methanol to produce an organically soluble PdMeOPV precursor polymer⁶ (scheme 4.3). The resulting PdMeOPV precursor polymer was found to contain methoxy- functionalities and was soluble in organic solvents such as methylene chloride, THF and chloroform.



Scheme 4.3. Preparation of an Organic-soluble PdMeOPV Precursor.

Methanol was added to the solvent system since this was found to aid in the conversion of the PTV precursor polymer thiophene-salt to a methyl-ether functionality^{7, 8}. The resulting PTV precursor with a methyl ether functionality was found to be more stable against thermal elimination than the equivalent sulfonium salt precursor (scheme 4.4). Note that in the case of the PTV precursor, as opposed to the PdMeOPV precursor, the exchange to a methyl-ether functionality was not observed to go through an isolable intermediate counter-ion exchange product. The thiophene moiety activates the α -carbon to allow a nucleophilic displacement of the tetrahydrothiophene unit by the methyl ether-functionality. The dimethoxy benzene moiety in the PdMeOPV

precursor, which was eventually converted to the precursor having methylether functionality *via* a different route, proved not to be electronegative enough to allow a conversion during the synthesis step.



Scheme 4.4. PTV Precursor Preparation.

The molar-equivalent homopolymer blends used for the purpose of comparing physical properties with those of the copolymers were prepared in the same manner as discussed above and in the methods and procedures section. The homopolymer blends were prepared in the same solvent systems and treated with the same counter-ion exchange compounds as those used in the copolymer reactions. The PTV homopolymer precursor was treated with NaBF_4 or $(\text{CH}_3)\text{-}p\text{-C}_6\text{H}_4\text{-(SO}_3^-$

Na⁺), depending on whether they were to be codissolved with the PPV precursor or the PdMeOPV precursor, even though there was no apparent effect of these compounds on the PTV precursor. DMF was used to dissolve the PPV/PTV blends although PTV dissolved better in THF. Equivalent THF/CHCl₃ solvent systems were used for the blends of PdMeOPV/PTV just as in the samples obtained from the copolymerization reactions.

4.1.2. The Copolymeric Nature of PPV-co-PTV

Table 4.1. IR Absorption Data from Koßmehl *et al.*

(* P ≡ PPV repeat unit; T ≡ PTV repeat unit)

Model*	<i>Trans</i> -vinylene Wagging (cm ⁻¹)	Aromatic-Ring Breathing (cm ⁻¹)
PPPPP	970	830
PPTPP	960	820/800
polyP	970	835
polyT	930	810
polyPTPT	945	860(m)/810

Koßmehl *et al.*^{10, 11} showed that PPV has a C-H out-of-plane bending *trans*-vinylene infrared (IR) absorption maximum at 970 cm⁻¹ and that the equivalent absorption maximum of PTV was at 930 cm⁻¹ (table 4.1). Model compounds of known repeat-unit sequence were prepared *via* Wittig reactions, and they showed that insertion of PTV units into a PPV chain caused the *trans*-vinylene absorbance maximum of the compound to shift from 970 cm⁻¹ down to 930 cm⁻¹ as more and

more PTV units replaced the PPV units in the chain. It was, therefore, expected that the PPV-co-PTV prepared *via* the Wessling method, if it were not composed of large blocks of PPV and PTV, should show the same shift in maxima.

The studies in this Wessling-copolymerization work on the FTIR absorbance for this region (fig. 4.1) did show such a shifting of absorbance maxima for the PPV-co-PTV as those observed in the oligomers prepared by Koßmehl *et al.* The clear shift in maxima towards shorter wavelengths as the composition of the copolymer became heavier in PTV showed that there was an increasing insertion of PTV units within the copolymer chain. Moreover, there was no evidence for contiguous repeat units greater than 5, except in the extreme ratios of monomer feed where it was expected. Such a number of contiguous repeat units would have manifested itself as an IR absorption maximum at either 970 cm^{-1} or 930 cm^{-1} as found by Koßmehl *et al.* This indicated that there was very little "blockiness" to the copolymer, that is, the PPV-co-PTV existed as a random copolymer. Note for example that the PPV-co42-PTV (fig. 4.1) showed an IR absorption maximum at 975 cm^{-1} , some minor absorption maxima elsewhere, but no significant absorption at 970 cm^{-1} or 930 cm^{-1} . The fact that the absorbance pattern showed discrete maxima rather than a smooth curve suggested that the measurement discriminated between different pentads or even smaller units. There was no reason to suspect that there were distinct groups of more probable repeat units rather than a continuum of all possible repeat unit combinations. Rather, it

was more likely that the IR spectra showed distinct maxima due to the wide (40 cm^{-1}) gap between the observed maxima of PPV and PTV.

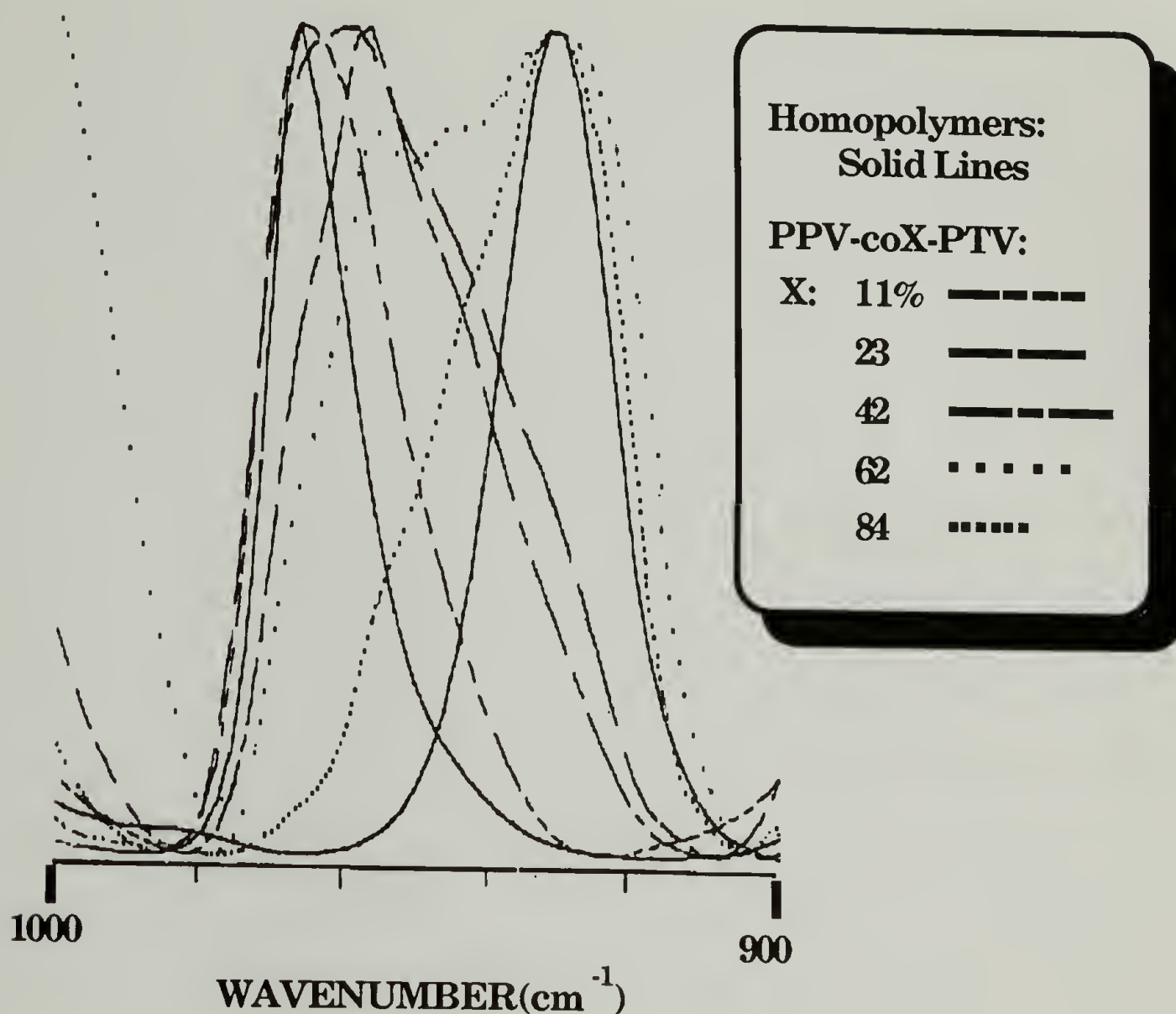


Fig. 4.1. *Trans*-vinylene IR Absorption for PPV, PTV and PPV-co-PTV of Varying Composition.

A comparison with the IR absorbance patterns (fig. 4.2) of the molar equivalent blends of PPV and PTV emphasized the distinction of the copolymers from blends. There was *no* shift of the IR maxima from the 970 cm^{-1} maximum of PPV to the maximum at 930 cm^{-1} of PTV, rather, both maxima at 970 cm^{-1} and 930 cm^{-1} existed throughout the

whole range of blending composition. This revealed that independent PPV and PTV units existed and that the interactions between the blend components was not sufficient to produce the shifts observed in the copolymeric counterparts.

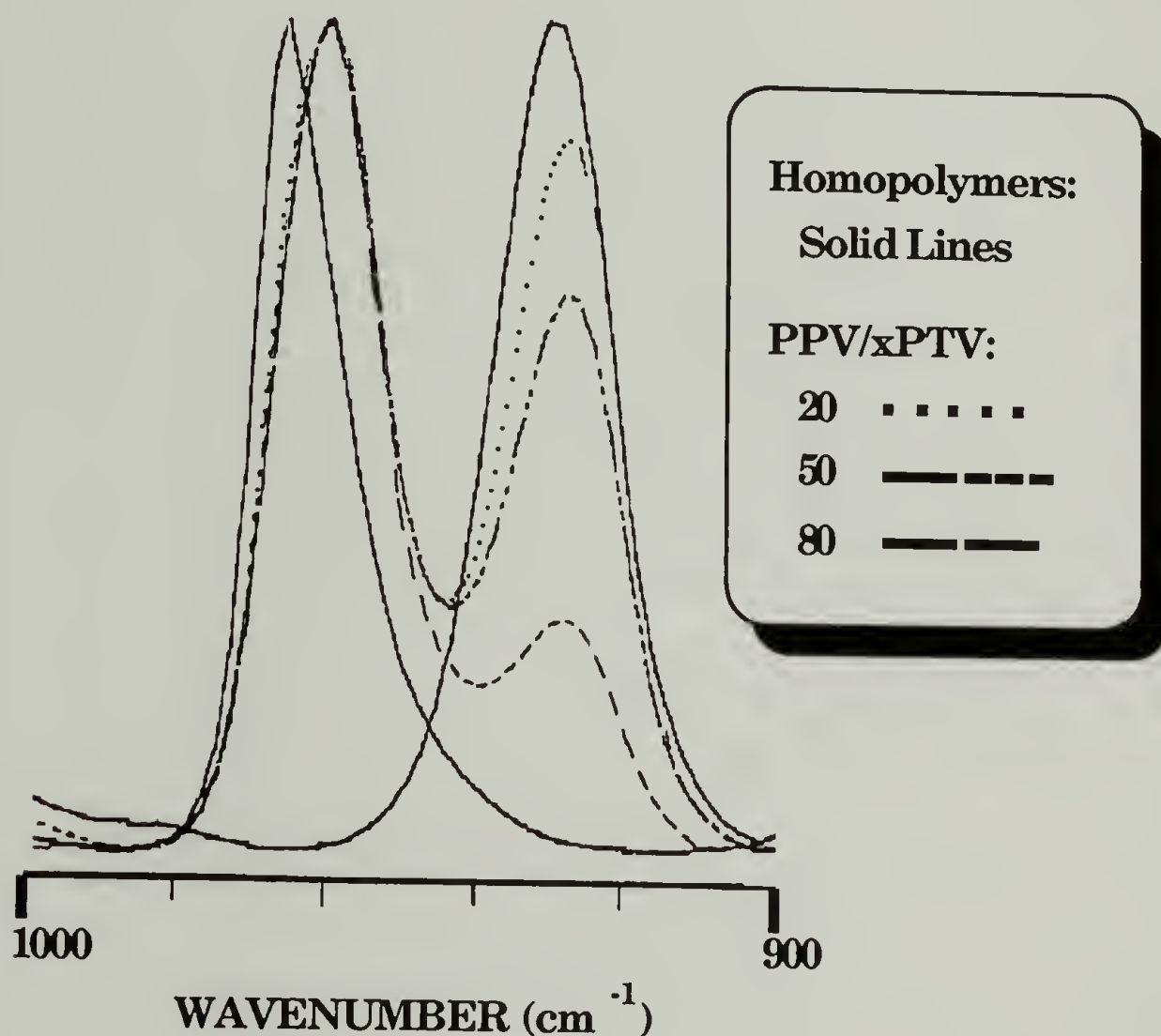


Fig. 4.2. *Trans*-vinylene IR Absorption for PPV, PTV and PPV/PTV of Varying Composition.

The slight shift in absorption maxima of the blend components from their homopolymer counterparts, especially noticeable for the PPV component, may be due to polymer-polymer interactions such as charge-transfer complexation. This has been observed in other systems¹².

4.1.3. Reactivity of the Monomers

A general description relating the rates of copolymerization with monomer feeds is given by¹³:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \quad (4.1)$$

where:

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}} \quad (4.2)$$

and k_{ab} is the rate constant for a propagating chain ending in M_a adding to a monomer M_b . Defining f_1 and f_2 as the mole fractions of M_1 and M_2 in the feed, respectively, and F_1 and F_2 the equivalent mole fractions in the copolymer then:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (4.3)$$

and this can be rearranged¹⁴ to:

$$\frac{f_1(1 - 2F_1)}{F_1(1 - f_1)} = r_2 + \left[\frac{f_1^2(F_1 - 1)}{F_1(1 - f_1)^2} \right] r_1 \quad (4.4)$$

this can then be applied to the experimental data of "instantaneous" monomer feed mole fractions and copolymer mole fraction composition.

The relationship of the monomer feed mole fraction (f_1) and copolymer mole fraction composition (F_1) in terms of PTV (compound 1) for a two-hour reaction was obtained (table 4.2, fig. 4.3). The yields for these reactions were low (ca. 15-35%). However, in order to obtain experimental data that were nearly "instantaneous" as the equations demanded, reactions were quenched by the addition of acid within two minutes of initiation. These reactions resulted in yields of 5-10% and are

summarized here (table 4.3). Equation 4.4 was applied to the data on the PPV-co-PTV reported here and the reactivity ratios r_1 and r_2 were calculated to be 6.9 and 0.088, respectively, with a correlation coefficient of 0.89 (fig. 4.4). The higher reactivity of the PTV monomer was clearly indicated.

Table 4.2. Elemental Analysis Results for PPV-co-PTV in a Two-hour Reaction.

%PTV Monomer in the Feed	Elemental Analysis Data			% PTV in the Co-polymer	% Error in the Fitting Calculation
	C	H	S		
2	85.80	5.83	3.50	11.4	-0.7
5	80.75	5.47	6.78	22.7	-0.8
10	74.99	5.07	12.41	42.1	-1.2
15	72.37	4.52	18.27	62.2	-0.9
18	62.75	5.32	18.60	63.4	-5.9
25	62.63	4.76	20.64	71.4	-5.4
30	67.5	4.01	25.84	87.8	-1.8
40	67.73	4.09	24.55	83.8	-1.7
	65.15	4.63	24.62	81.7	-6.5
60	65.33	4.17	24.52	84.4	-3.8

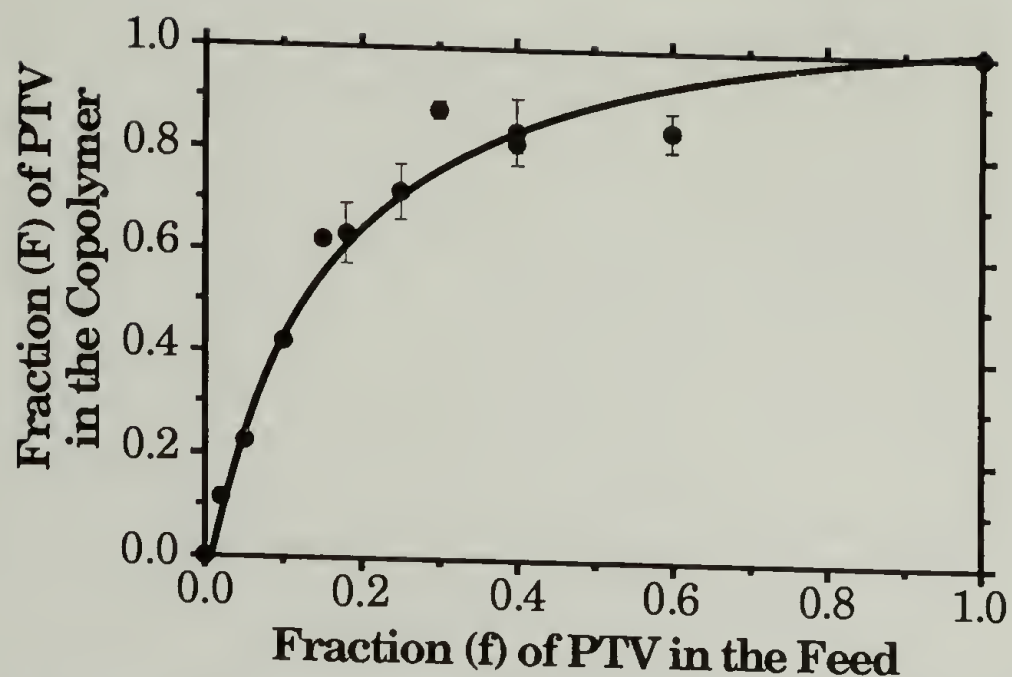


Fig. 4.3. PTV Mole Fraction in the Copolymer (F_1) as a Function of the Mole Fraction in the Feed (f_1) in a Two-hour Reaction.

Table 4.3. Elemental Analysis Results for the Synthesis of PPV-co-PTV in a Two-minute Reaction.

%PTV Monomer in the Feed	Elemental Analysis Data			% PTV in the Co-polymer	% Error in the Fit Calc.
	C	H	S		
5	70.74	5.57	9.10	31.6	-2.4
	73.72	4.83	11.92	41.8	-0.9
10	69.12	4.52	16.47	58.3	-1.4
15	66.27	4.74	20.55	69.8	-3.9
	67.41	4.29	16.01	58.7	-1.0
20	67.34	4.05	18.86	68.7	-0.5
25	65.19	4.30	24.56	83.7	-4.7
30	58.59	4.91	18.12	65.9	-6.1
	65.24	3.78	18.65	70.8	0.7
40	65.49	3.94	25.13	42.9	-9.3
45	65.8	4.27	25.31	85.5	-4.8

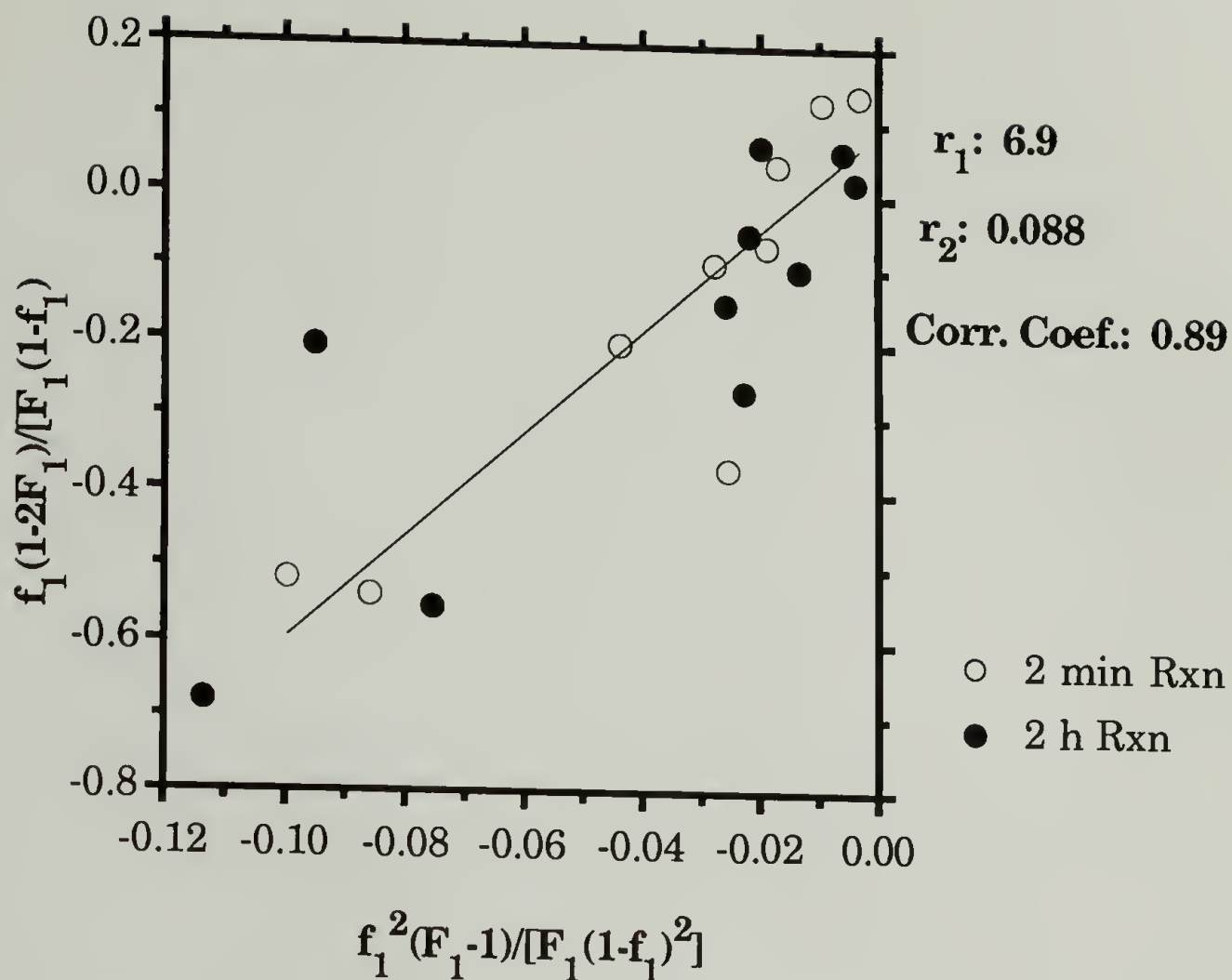


Fig. 4.4. Calculation of the Reactivity Ratios (r_1 and r_2) for PPV-co-PTV.

Note that in figure 4.4 both the two-minute reaction data (•) and the two-hour reaction data (o) were shown. The two-hour reaction approximated the calculated linear fit for the two-minute reaction to about the same degree. This was also shown when the monomer fractions of the feed and the copolymer fractions for both two-minute and two-hour reactions were compared (fig. 4.5). There was no apparent distinction between the resulting compositions for the copolymer from those obtained for the two-minute and the two-hour reactions. The dissimilarities in elemental composition between the two-minute and two-hour reactions was within experimental error, and a consideration of the data scatter showed that the results may be equivalent. This

suggested that the reaction was not sensitive enough to monomer concentration changes, between a 5% (two-minute) yield and a 35% (two-hour) yield, to reflect compositional changes in the copolymer bulk sample. There was no drift in copolymer composition to accompany the drift in monomer concentrations expected from the marked difference in monomer reactivity.

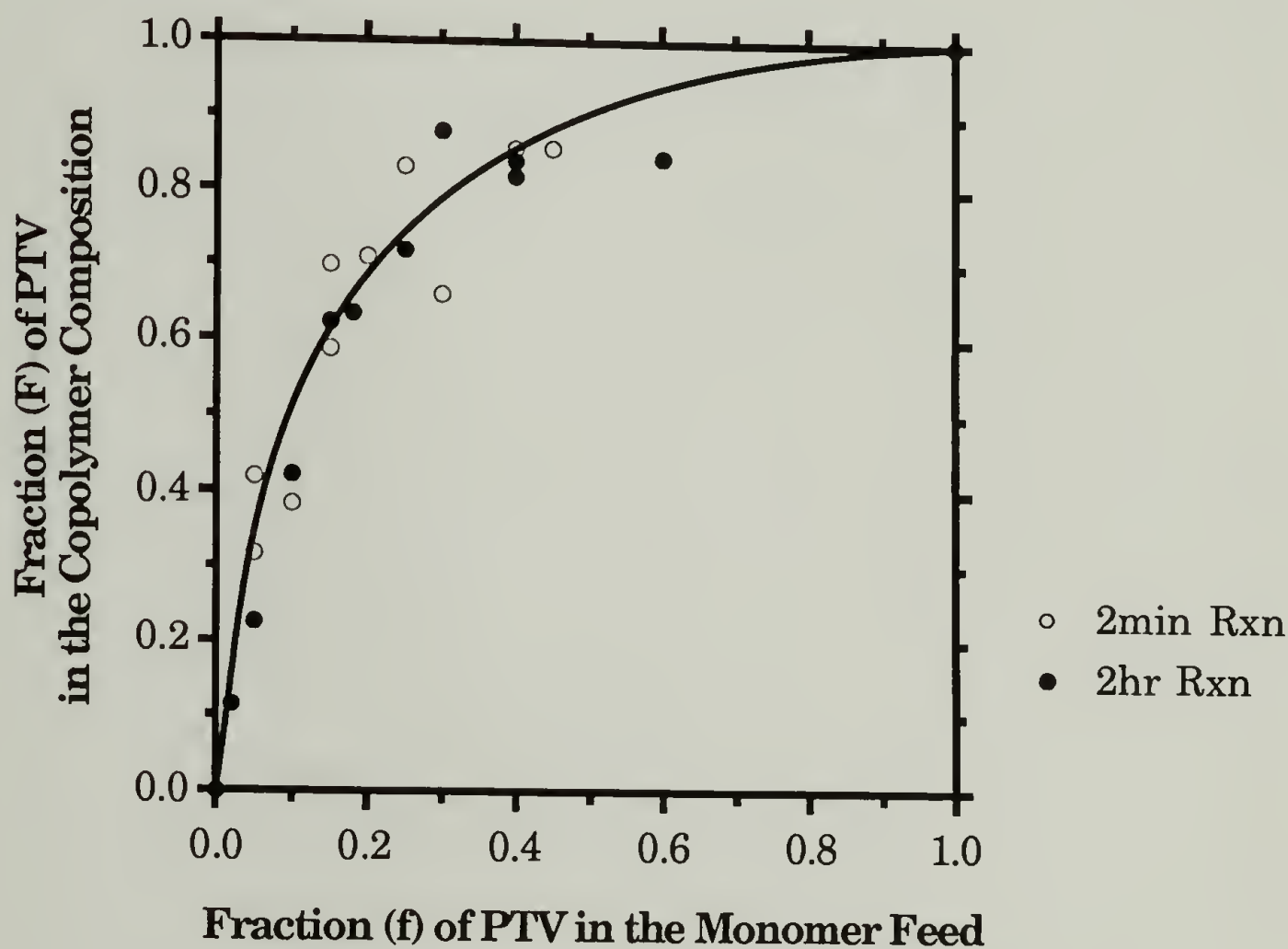


Fig. 4.5. F vs. f for Two-minute and Two-hour Reactions in the PPV-co-PTV System.

There are, at least, two reasons to explain this particular behavior. The first is simply that the measurements (elemental analysis, IR spectra, monomer concentration calculations) were not

sensitive enough to observe the drift that was expected. The other possibility is that the reaction has two distinct steps: rapid initiation, propagation and chain-termination (within two minutes), which could be sensitive to monomer concentrations but which is difficult to determine without sophisticated kinetic measurements for fast time scales; followed by macromer linking-reactions, which are essentially independent of the monomer concentrations. A copolymerization kinetic scheme that is zeroth order in the monomer concentration was found to be inapplicable to the conditions of this synthesis since varying copolymer compositions were obtained from varying monomer concentrations. This would not have been the case if the copolymerization kinetics were independent of the monomer concentration.

The macromer reaction hypothesis takes into account the difference in yields, copolymer film forming abilities (only powders are obtained at two minutes) or difference in molecular weights and the similarities in IR spectra. Greater yields are to be expected when such macromer reaction take place since more materials would precipitate or be captured during dialysis. Lower molecular weights are to be expected from the first stage of the macromer-type reaction and therefore would not be expected to form films, as was observed. Both systems would produce the same distributions of arylene₁-vinylene-arylene₂ IR absorptions since this would not be disrupted by the macromer linking reaction. Similarly, the elemental analysis at both stages of the macromer reaction would not show any significant difference since the

macromer linking step would not significantly change the chemical composition of the polymer.

Investigations regarding the possibility of end-homopolymerization, that is, the continued chain-growth after the depletion of one of the monomer species showed that such end-capping does not occur. The reaction mixtures were continually stirred at 0°C for in excess of 18 h and the resulting films were inspected using IR after elimination. The *trans*-vinylene IR absorption spectra for the samples in extended runs showed no significant differences from those obtained from the two-hour experiments.

However, when the experimental runs were extended to 24 h after being allowed to warm to room temperature, without quenching, subsequent to the standard reaction at 0°C for two hours, the *trans*-vinylene spectra obtained showed homopolymers or blocks of the PTV moiety (fig. 4.6). This was contrary to expectations since the PTV monomer concentrations should be very low compared to that of the PPV monomer.

PPV-co-PTV copolymerization at 0°C was not observed to form any PTV homopolymers - as observed by IR - even over extended periods. Moreover, the %-conversions or %-yields were not observed to increase appreciably beyond 2-4 h reaction times. This indicated that some chain-termination steps were induced by the decrease in the base concentration or some fortuitous reaction with adventitious elements in the reaction system. However, the reaction was apparently reinitiated by an increase in temperature even at low base concentrations and especially for the more electronegative species. This particular piece of

PPV-co-PTV in a water solvent system rather than the water/methanol system used here. Attempts to duplicate these preparations produced samples that tended to precipitate out of solution during the reaction. Moreover, comparison of TGA runs for the precursor polymers produced in water versus those in water/methanol showed a much higher %-weight loss due to elimination products from samples prepared in the water/methanol system as opposed to just water alone. The discrepancy was more substantial at higher PTV contents. This led us to conclude that copolymers produced in water resulted in PTV units that were already substantially eliminated which resulted in the precipitation out of solution of the growing polymer chain. Indeed, attempts to synthesize the PTV homopolymer in water yielded a dark red powder which did not produce as large a %-mole-weight loss of elimination products in a TGA run (*ca.* 40%) compared to those synthesized in water/methanol (*ca.* 50-60%).

The elimination reaction and subsequent precipitation during the polymerization in water also had adverse effects on the reactivity ratio of PPV to PTV (fig. 4.7). Altered reactivity ratios of the kind shown here has been observed in other systems¹⁷⁻¹⁹. Deviations in reactivity ratios were often observed in systems where the copolymers being produced were poorly soluble in the solvent system. Under such conditions, altered reactivity ratios were observed when one of the monomers was preferentially adsorbed onto the precipitating copolymer.

The difference in the reactivity ratios for this investigation, compared to those reported previously¹⁶, could be rationalized by taking the precipitation of PTV in aqueous systems into account. Should the

PPV monomer be preferentially adsorbed onto the precipitating, growing PPV-co-PTV precursor copolymeric chain, the resulting material would artificially show a higher PPV inclusion than those prepared from a non-precipitating scheme. However, such a preferential adsorption has not been verified for this particular system.

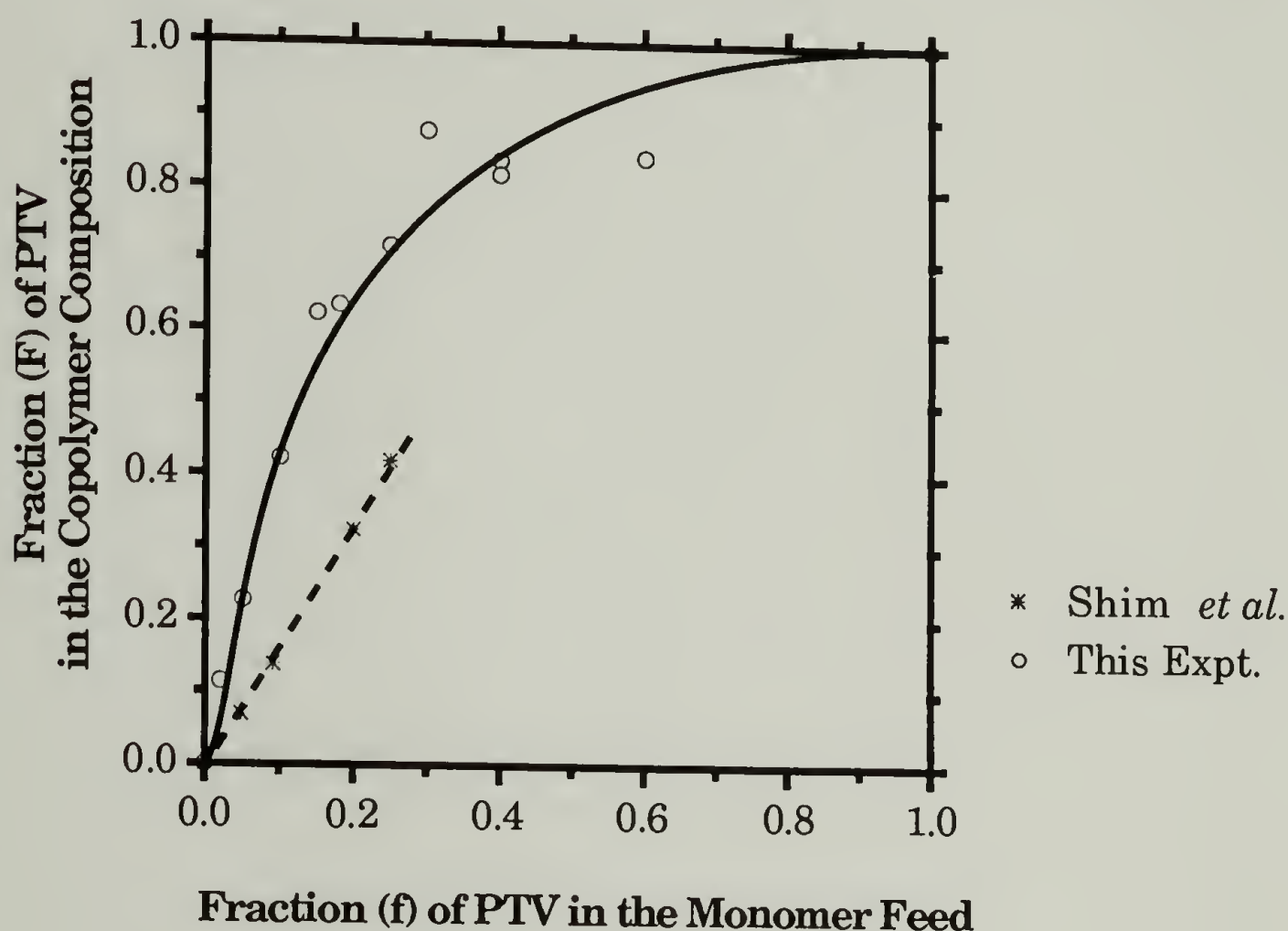


Fig. 4.7. Reactivities of PPV and PTV Monomers in Water and Water/Methanol Systems.

Attempts to synthesize a series of copolymers based on PdMeOPV and PTV in a water/methanol system apparently produced only blends. Moreover, the rate of homopolymerization of PTV and PdMeOPV appeared equivalent, that is, for the range of monomer feeds tested, the elemental analysis of the blend showed an equal molar amount of PTV

and PdMeOPV produced (fig. 4.8). The *trans*-vinylene IR absorption did not show any shift in maxima from the 970 cm^{-1} maximum of PdMeOPV to the 930 cm^{-1} of PTV (fig. 4.9). There have been no reports on model compounds of oligomeric PdMeOPV-*co*-PTV. However, it is highly unlikely that the *trans*-vinylene unit surrounded by 2,5-dimethoxy benzene and thiophene to show a C-H out-of-plane bending IR absorption maxima at both 970 cm^{-1} and 930 cm^{-1} .

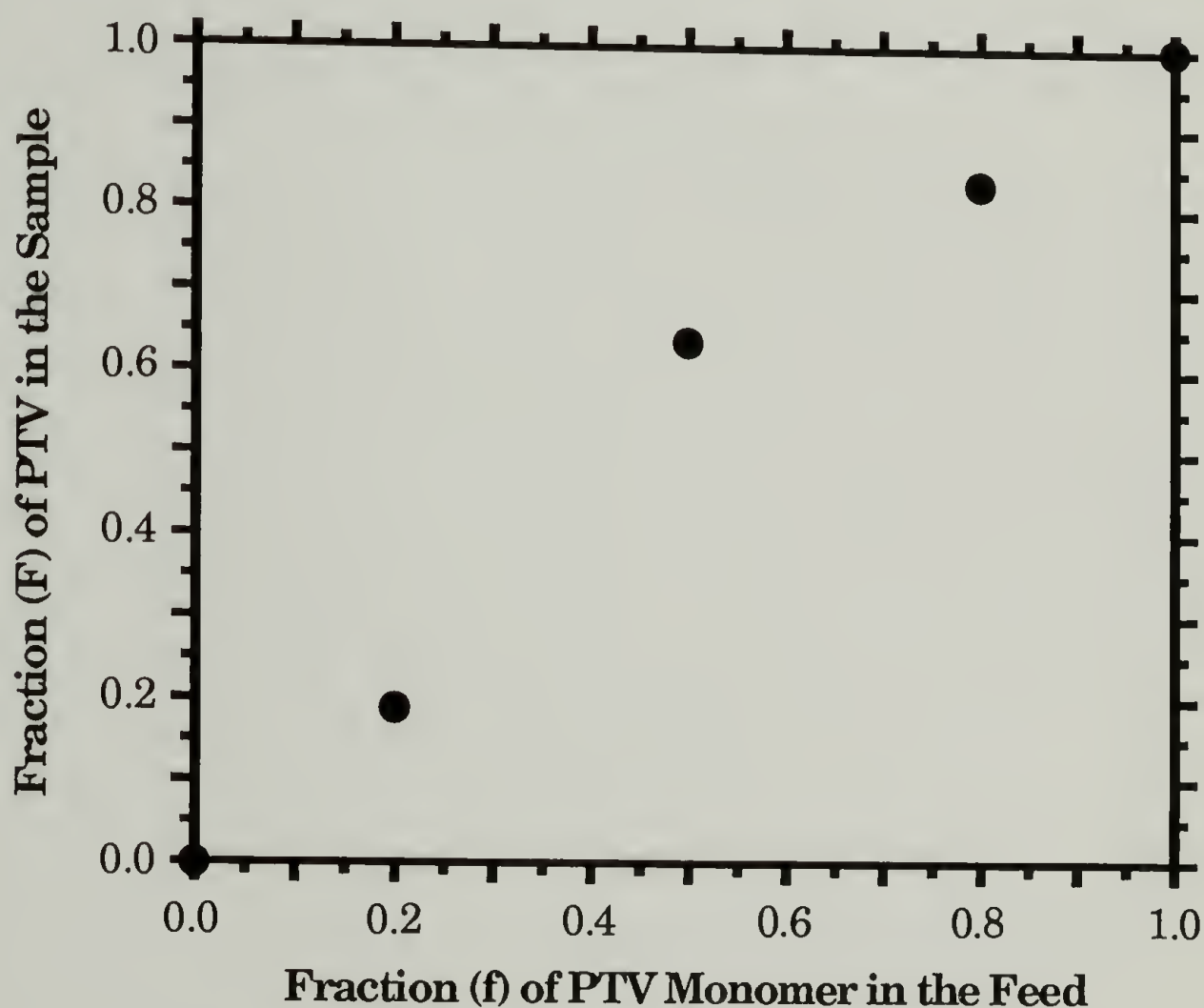


Fig. 4.8. Relative Reactivity of PTV and PdMeOPV Homopolymerization under Copolymerization Conditions.

The possibility of A-B block formation was investigated. A series of reactions were quenched within two minutes of initiation to decrease the molecular weights and increase the ratio of the postulated A-B

linkage to that of pure A-A and B-B. The *trans*-vinylene IR absorption pattern was as shown in figure 4.9. There was no evidence for A-B block formation. The A and B components in the postulated A-B block copolymers could have very high molecular weights even at the low conversions (5-10%) obtained in the two-minute reactions. However, it was not possible to limit the reaction time below two-minutes since the inherent inhomogeneity during the initial stages of the mixing resulted in oligomers that were extremely difficult to collect and purify.

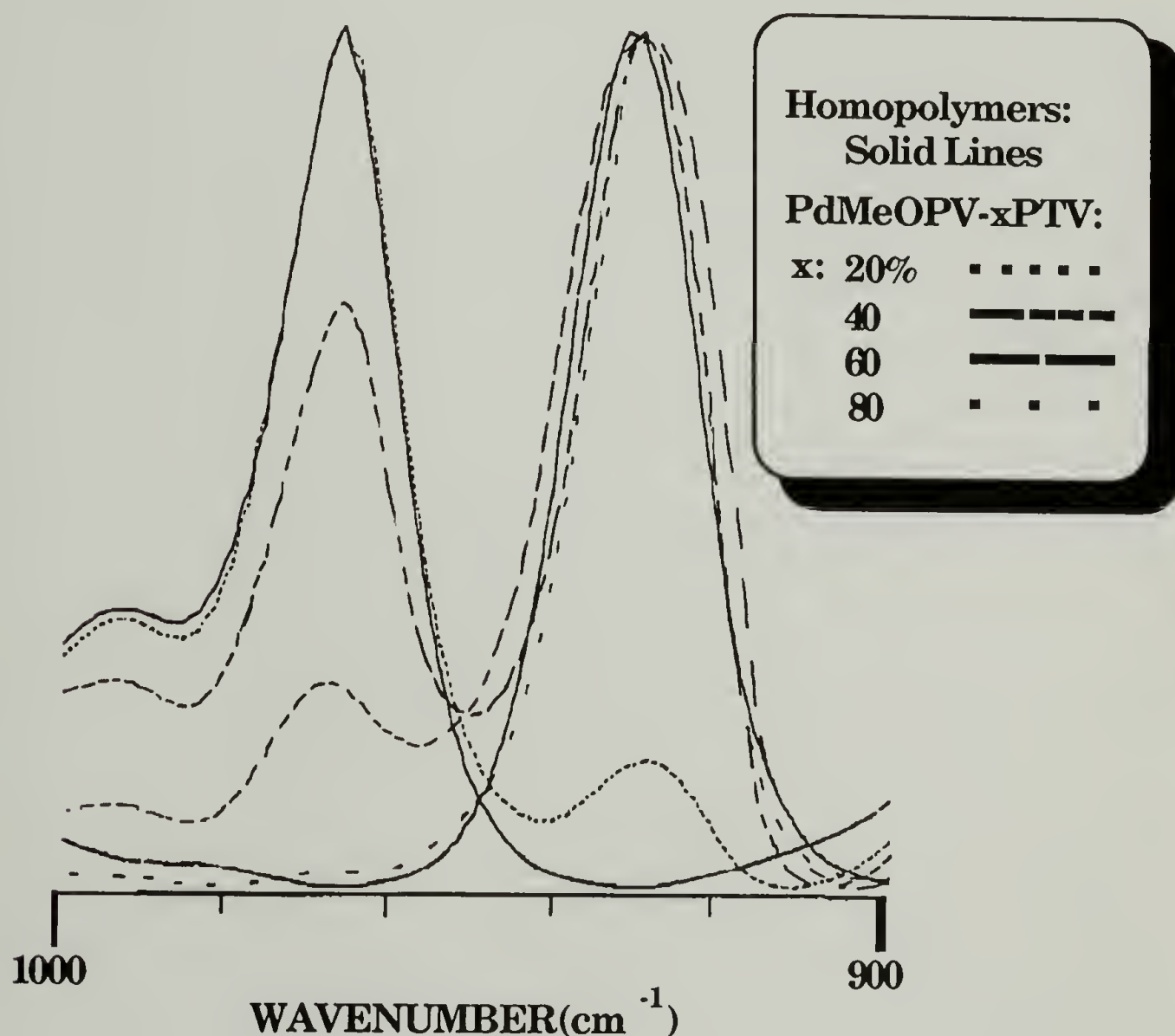


Fig. 4.9. *Trans*-vinylene IR Absorptions for PdMeOPV, PTV and the Results of the PdMeOPV-*co*-PTV Synthesis.

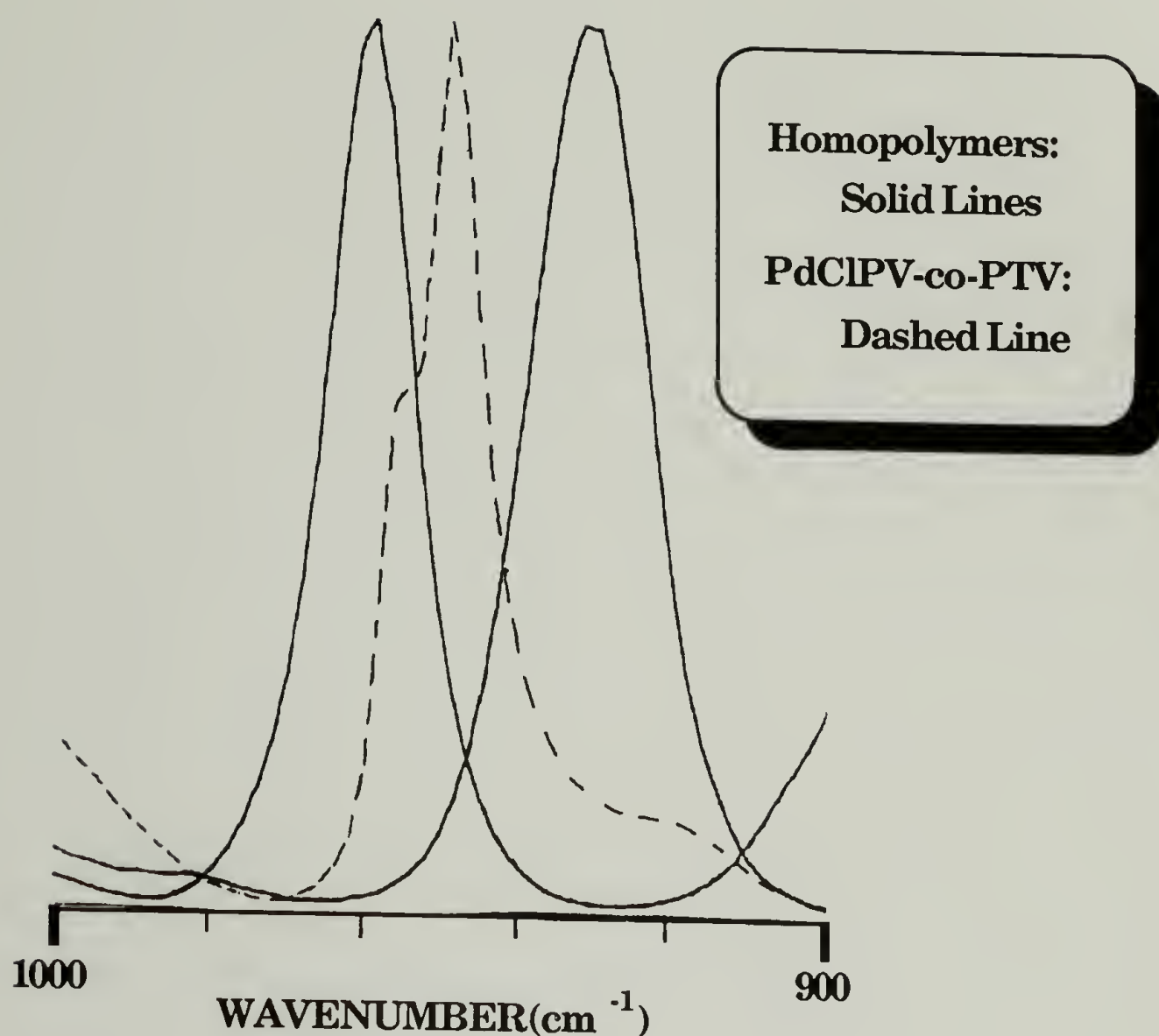


Fig. 4.10. *Trans*-vinylene IR Absorptions for PdClPV, PTV and PdClPV-co-PTV.

A test of the feasibility of copolymerizing poly(2,5-dichloro-1,4-phenylene vinylene) (PdClPV) - also known to homopolymerize through the Wessling synthetic route²⁰ - with PTV was made. A series of 2, 5 and 10% PTV monomer to PdClPV monomer feed ratios were prepared under two-minute reaction conditions. The resulting gels tended to produce ashing by-products either during the elimination step (300°C, 6 h) or elemental testing. The use of lower elimination temperatures (250 °C) and longer elimination times (10-12 h) resulted in incomplete

elimination that was reported by the elemental analysis service to yield samples which "exploded" during testing. This was understood to mean that severe outgassing of elimination by-products during pyrolysis occurred. Samples for IR analyses were obtained by carefully heating a small amount of sample (5mg) in a thermogravimetric analysis cell (TGA) and stopping the heating as soon as 280°C was reached. Samples obtained in this way were still unreliable for elemental analysis but showed no methoxy or THT IR absorption and could be reliably analyzed under IR for sequence distribution. The *trans*-vinylene IR absorption of the PdClPV-*co*-PTV obtained from the two-minute reactions (fig. 4.10) indicated that copolymers made were distinct from the equivalent blends and formed random copolymers similar to those obtained in the preparation of PPV-*co*-PTV rather than blocky-type copolymers.

4.2. Conductivity of Unoriented PAV Copolymers and Blends

PPV has been shown not to form redox products with iodine, its oxidation potential being a little bit too high (0.76 V *vs.* standard calomel electrode (SCE)²¹). PTV on the other hand, has been shown to be oxidized by iodine^{6, 22, 23} to give high (as much as 200 S cm⁻¹) conductivities⁷. The conductivity experiment on PPV-*co*-PTV is, therefore, an indication of the susceptibility of varying lengths of PTV segments to iodine doping, the intramolecular correlation of PTV repeat units, the intermolecular proximity of the PTV charge-carriers and the charge-density or charge-transport capacity of PTV within a random copolymeric system.

The four-probe d.c. conductivities of the unoriented PPV-*co*-PTV film samples doped with iodine vapor were investigated (fig. 4.11). The conductivities for samples ranging from 11% to 63% in PTV content

showed very little change in conductivity ($[1.16 \pm 0.57] \times 10^{-4} \text{ Scm}^{-1}$). A dramatic increase of 3 orders of magnitude occurred between 75%-80% PTV incorporation in the copolymer chain.

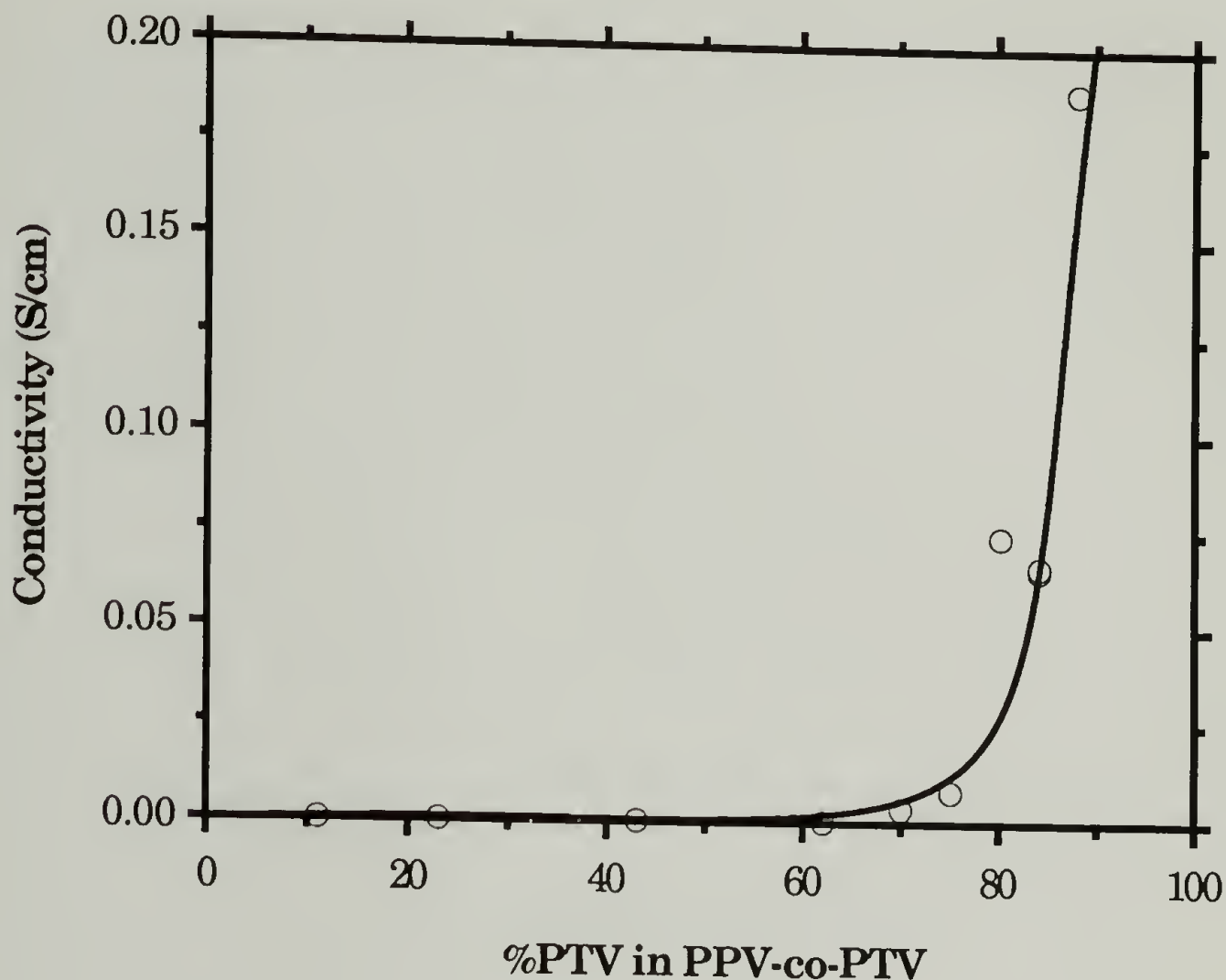


Fig. 4.11. Four-Probe d.c. Conductivities of Iodine-doped PPV-co-PTV.

This dramatic increase in conductivity suggested that the conductivity for the PPV-co-PTV system was strongly dependent on the intramolecular correlation of the PTV repeat units, that is, each increment of contiguous PTV repeat units successively lowered the oxidation energy until the point where iodine was able to oxidize the material. The previously described IR results suggested that PPV-co-PTV was a random copolymer, in which case, at 80% PTV copolymer

composition, there would be four contiguous PTV repeat units on average. It was therefore postulated that the threshold for PTV ionization by iodine must be at four repeat units. There was every reason to suppose that ionization energies of conjugated systems continually diminished with each addition of a contiguous repeat unit, that is, ionization energy lowering was an effect of conjugation and that the threshold for PTV was at four repeat units. A similar suggestion was made for PPV²⁴⁻²⁶. It was pointed out that a so-called "stilbene dimer" (two stilbene molecules connected by a *trans*-vinylene linkage) showed practically the same UV spectrum as that of a high-molecular weight PPV, allowing for thermal perturbation. Similarly the PPV X-ray photoelectron spectroscopic data showed a material that acted more as a disordered molecular solid rather than a one-dimensional metal that could be modeled against 4 repeat units of PPV. Thus, the suggestion was made that only 4 repeat units were needed to show conduction patterns similar to high molecular weight materials.

Similar conductivity measurements obtained for PPV/PTV blend samples showed a markedly different trend (fig. 4.12). The blends showed a transition at approximately 20% PTV composition. The first section - from 0-20% PTV - showed conductivities that were independent of the change in the PTV content of the blend, that is, the conductivity was constant within this range of compositions. This was followed by a linear dependence on the PTV content for compositions greater than 20% in PTV. This conductivity behavior was markedly different from the conductivity trends obtained for the copolymeric system where the change was very dramatic, as was discussed previously.

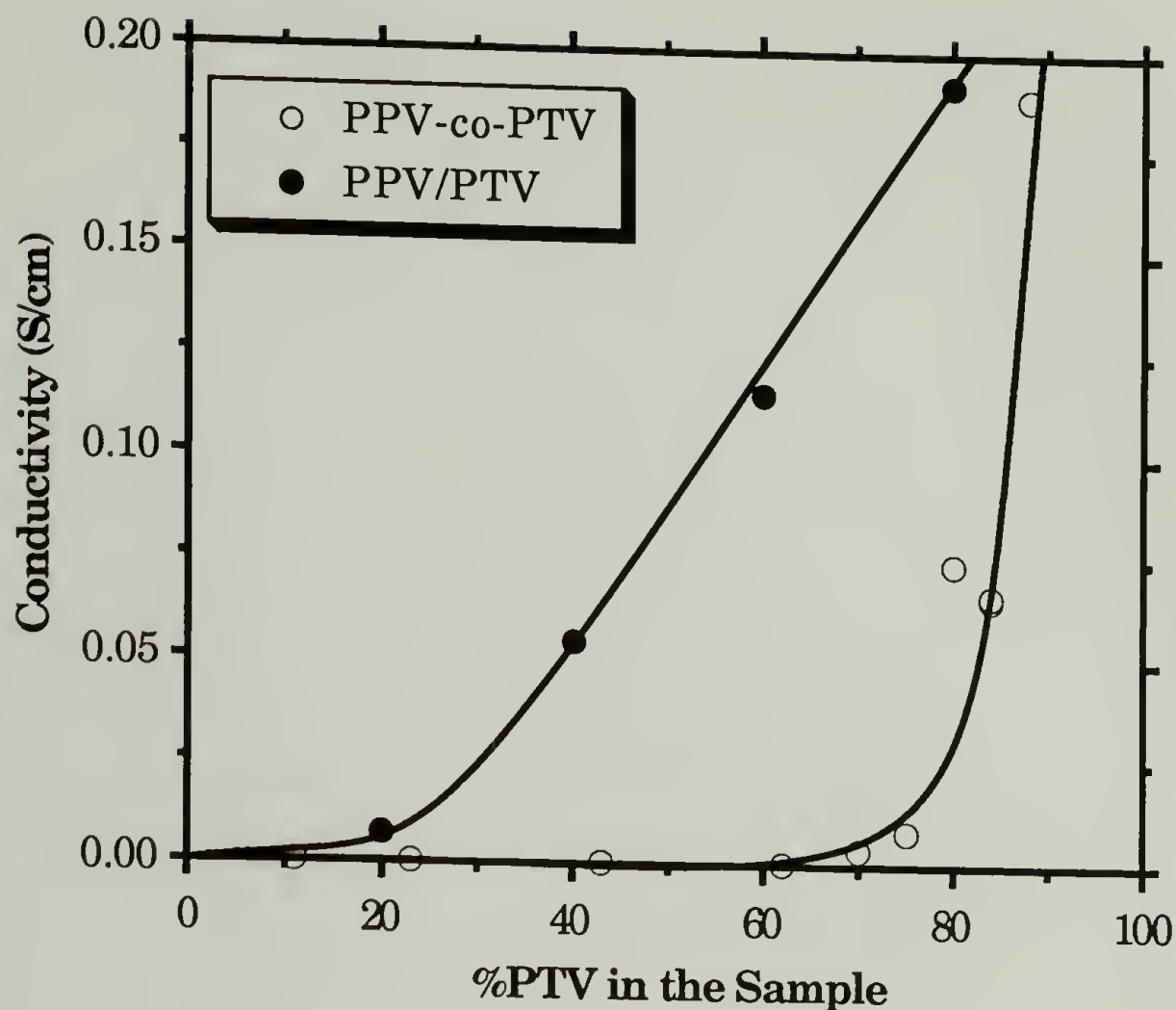


Fig. 4.12. Conductivities of the Iodine-doped Samples in the PPV-PTV System.

In the homopolymer blends of PPV/PTV, the average number of PTV repeat units per chain remained constant and uninterrupted by PPV segments so that the inherent charge-transport capacity of the PTV chain remained constant with varying PTV content in the blend. The only limiting factors in the measured conductivities of the blends were the charge-density of the bulk sample and the intermolecular proximity of the PTV chains. The charge-density of the bulk sample should be linearly proportional to the PTV content within the sample. The chain-proximity of PTV chains should manifest itself as a critical limit of

concentration below which the conductivity of the sample would be negligible having no mechanism to transfer electrons from chain to chain. This was what was found in the samples of PPV/PTV and also PdMeOPV/PTV (fig. 4.13). Both blend systems' conductivities showed a negligible effect in conductivity at 0-20% PTV content. Twenty mole-percent PTV was taken to be the upper limit to the morphological barrier between PTV chains below which chain-segments were sufficiently separated to prevent intermolecular electron-hopping. Beyond this upper-limit, the blend systems showed a linear relationship between conductivity and PTV content - a manifestation of the charge-density of the bulk sample.

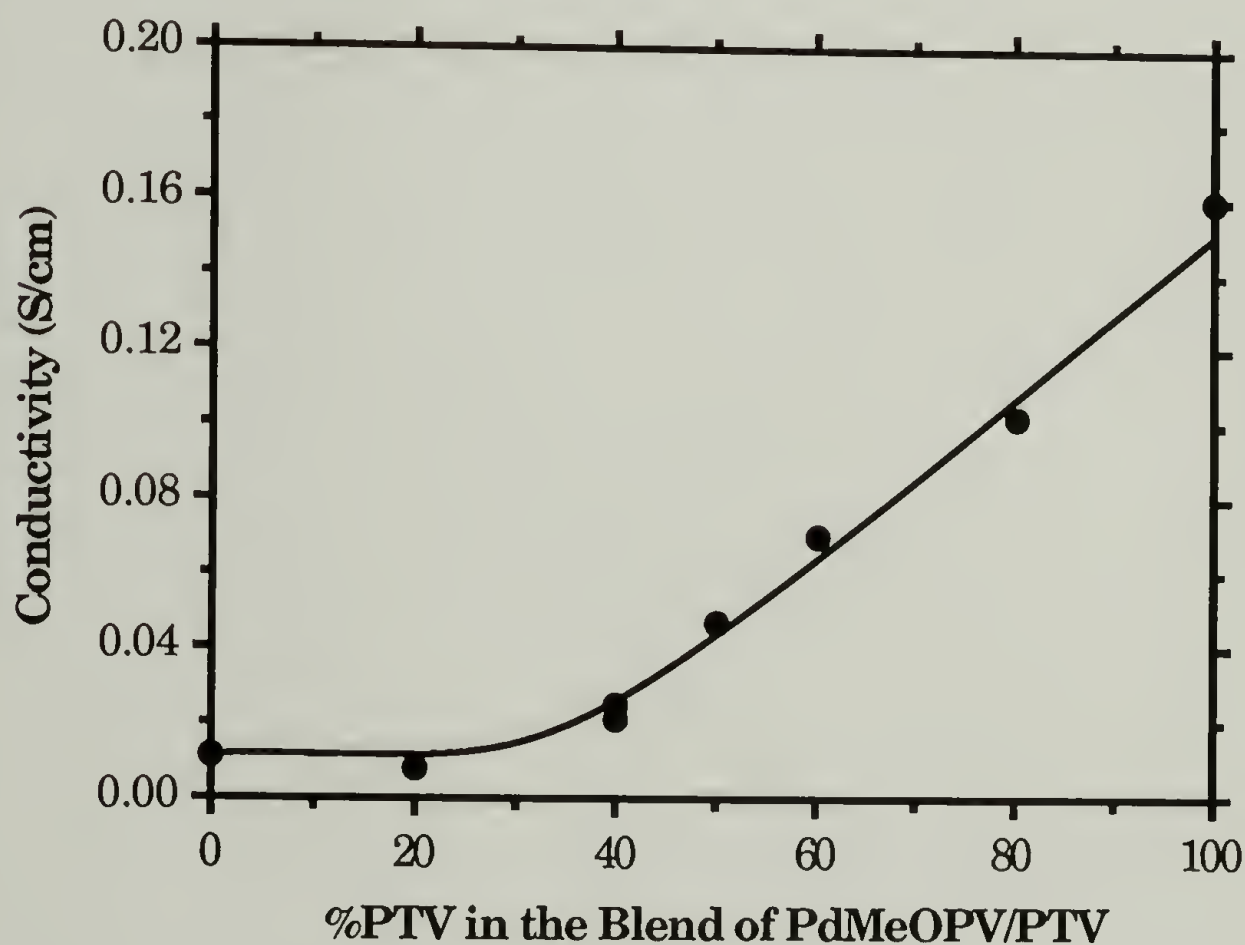


Fig. 4.13. Four-probe d.c. Conductivities of PdMeOPV/PTV Blends.

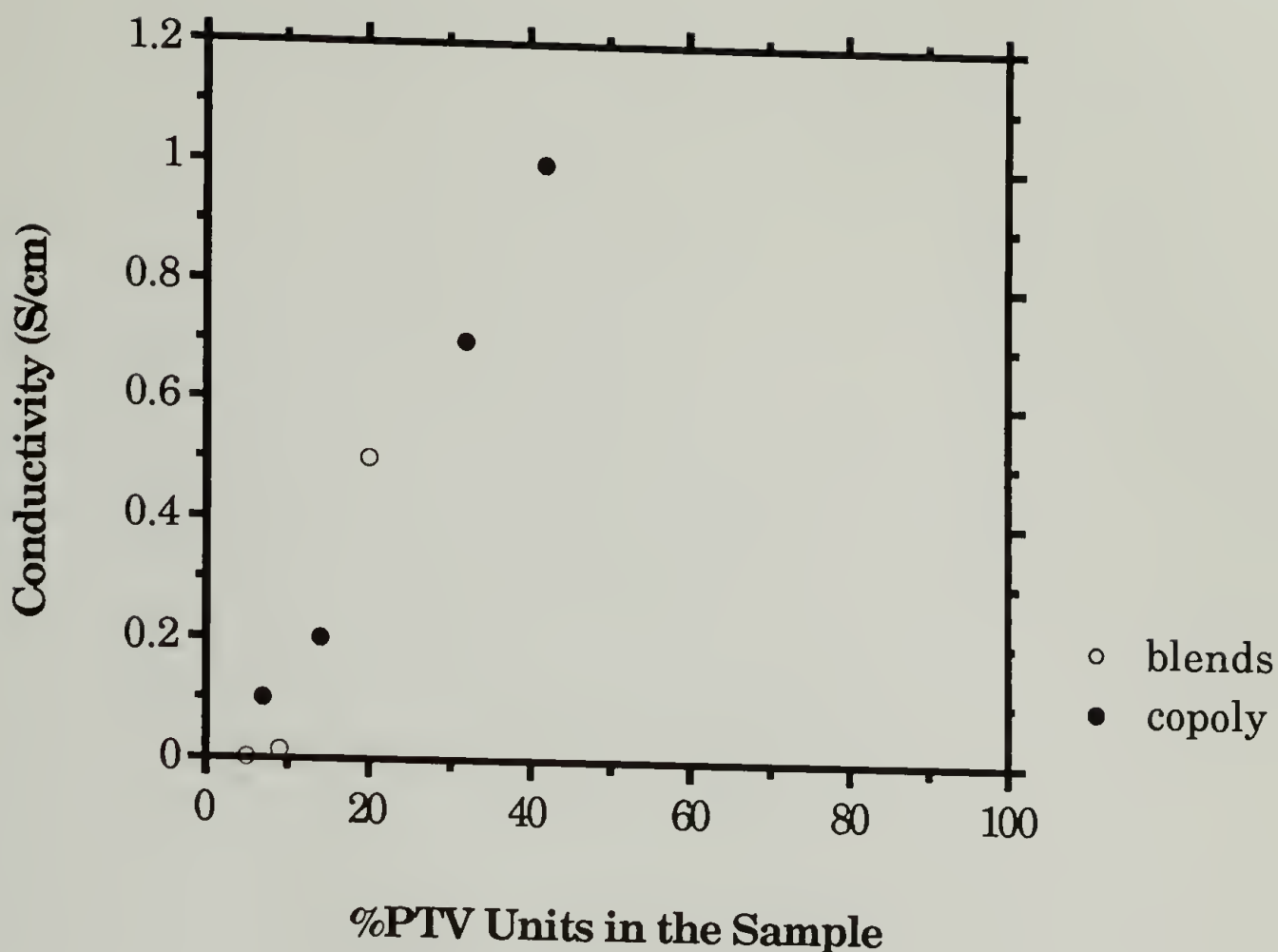


Fig. 4.14. Conductivities of PPV/PTV Samples Obtained from Water Solvent Systems (from Jin *et al.*).

Comparison of the conductivities obtained here to those reported by Jin *et al.*^{15, 16} (fig. 4.14) suggested that PPV-co-PTV produced from a water solvent system was either a homopolymer blend of PPV and PTV or a very blocky copolymer. The results presented in that work did not show any distinction between blend and copolymer conductivities. Moreover, there was no apparent manifestation of any effects of PTV repeat unit sequence. If blends had been formed, that would also explain the apparently linear incorporation of PTV in the attempt to synthesize PPV-co-PTV in a water system by Shim *et al.*¹⁶ as shown in figure 4.7 and as found with PdMeOPV-PTV (fig. 4.8). Unfortunately, IR absorptions for PPV-co-PTV produced in water were not reported in

that work. Attempts here to produce some PPV-co-PTV samples from an aqueous medium that would be suitable for an IR study resulted in materials that tended to produce ash during elimination (250°C, 3 h) preventing proper elemental analysis or IR analysis. Lower temperatures (200°C) and longer heating times (8 h) produced materials that were insufficiently eliminated making any analysis unreliable.

4.3. Orientation Studies on PPV-co-PTV

4.3.1. Background Theory and Analysis Methods

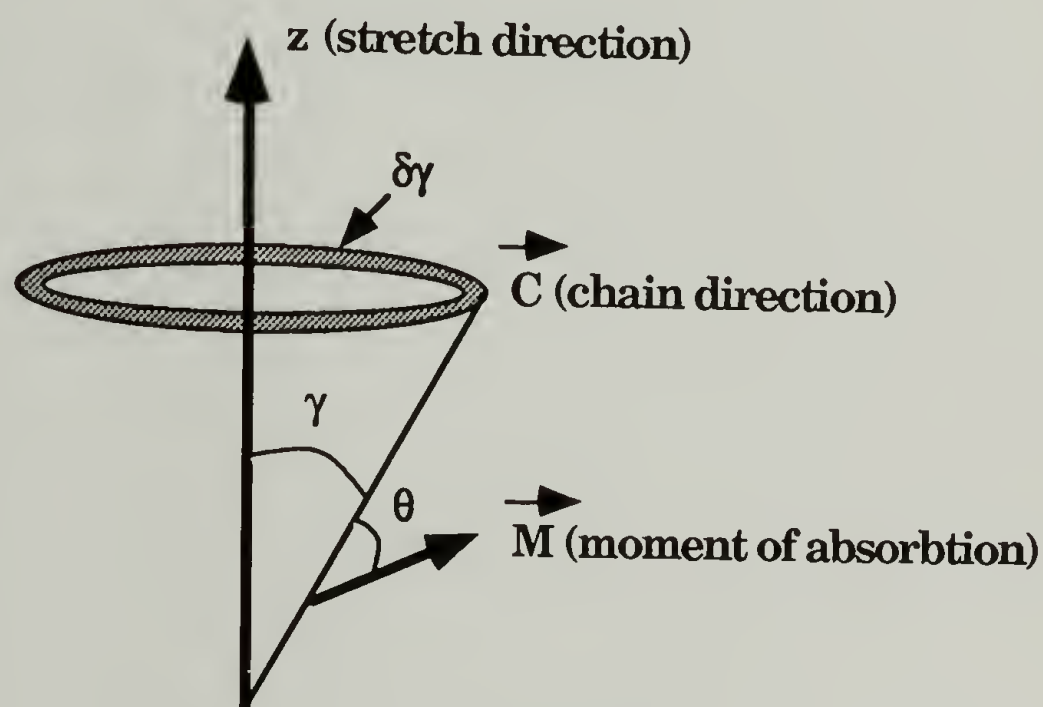


Fig. 4.15. Representation of a Stretched Sample and Orientation.

Orientational order can be quantified by relating the stretch ratio (λ) to the IR dichroic ratio (R). Zbinden²⁷ and Fraser²⁸ derived the general equations which are presented here and Bradley *et al.*²⁹ showed that they can be applied to the PPV system. The main statements are that for a given stretch direction (z), the oriented sample will have its chains aligned in a particular direction (C), producing an angle (γ) over

a distribution function $f(\gamma)$ with the stretch direction (fig. 4.15).

Chemical bonds active in IR will have a moment of absorption (**M**) forming an angle (θ) with the chain axis.

It has been shown that the relationship of the IR dichroic ratio ($R=A_x/A_z$; where A_x is the absorbance perpendicular to the stretch direction and A_z is the absorbance parallel to the stretch direction) can be related to the moment angle θ by the order parameter (S), such that:

$$R_{xz} = \frac{A_x}{A_z} = \frac{\sin^2 \theta + S}{2 \cos^2 \theta + S} \quad (4.5)$$

where S is defined by:

$$S = \frac{F}{N - \frac{3}{2}F} \quad (4.6)$$

and:

$$F = \int_0^{\pi/2} \sin^2 \gamma f(\gamma) \partial \gamma \quad \text{and} \quad N = \int_0^{\pi/2} f(\gamma) \partial \gamma \quad (4.7)$$

so that for a perfectly uniaxial-oriented sample: $f(\gamma) = \delta \gamma$ and $S = 0$. A perfectly planar-oriented sample gives $f(\gamma) = \delta(90^\circ - \gamma)$ and $S = -2$. A randomly oriented sample gives $f(\gamma) = \sin(\gamma)$ and $S = \infty$.

The order parameter (S) can be related²⁸ to the Hermans' orientation function³⁰. A sample can be defined as having a random fraction r and a perfectly aligned fraction $(1-r)$. In this case, $f(\gamma) = r \sin \gamma (r-1) \partial \gamma$ and $S = 2r / (3[1-r])$. It can then be shown that the fully aligned fraction is equivalent to the second order term in the expansion: $\langle p_n(\cos \gamma) \rangle$, that is,:

$$\langle p_2(\cos \gamma) \rangle \equiv \frac{2}{3S + 2} \quad (4.8)$$

or in Fraser's formulation^{31, 32}:

$$f = \frac{(R-1)(R_0+2)}{(R_0-1)(R+2)} \quad (4.9)$$

where f is equivalent to the second order term in the expansion of Hermans' orientation function $\langle p_2(\cos\gamma) \rangle$, and $R_0 = 2 \cot^2\theta$, the dichroic ratio for a perfectly aligned sample. IR dichroism ($R = A_{\parallel} / A_{\perp}$) can then be related to either the order parameter (S) or (f) (fig 4.16).

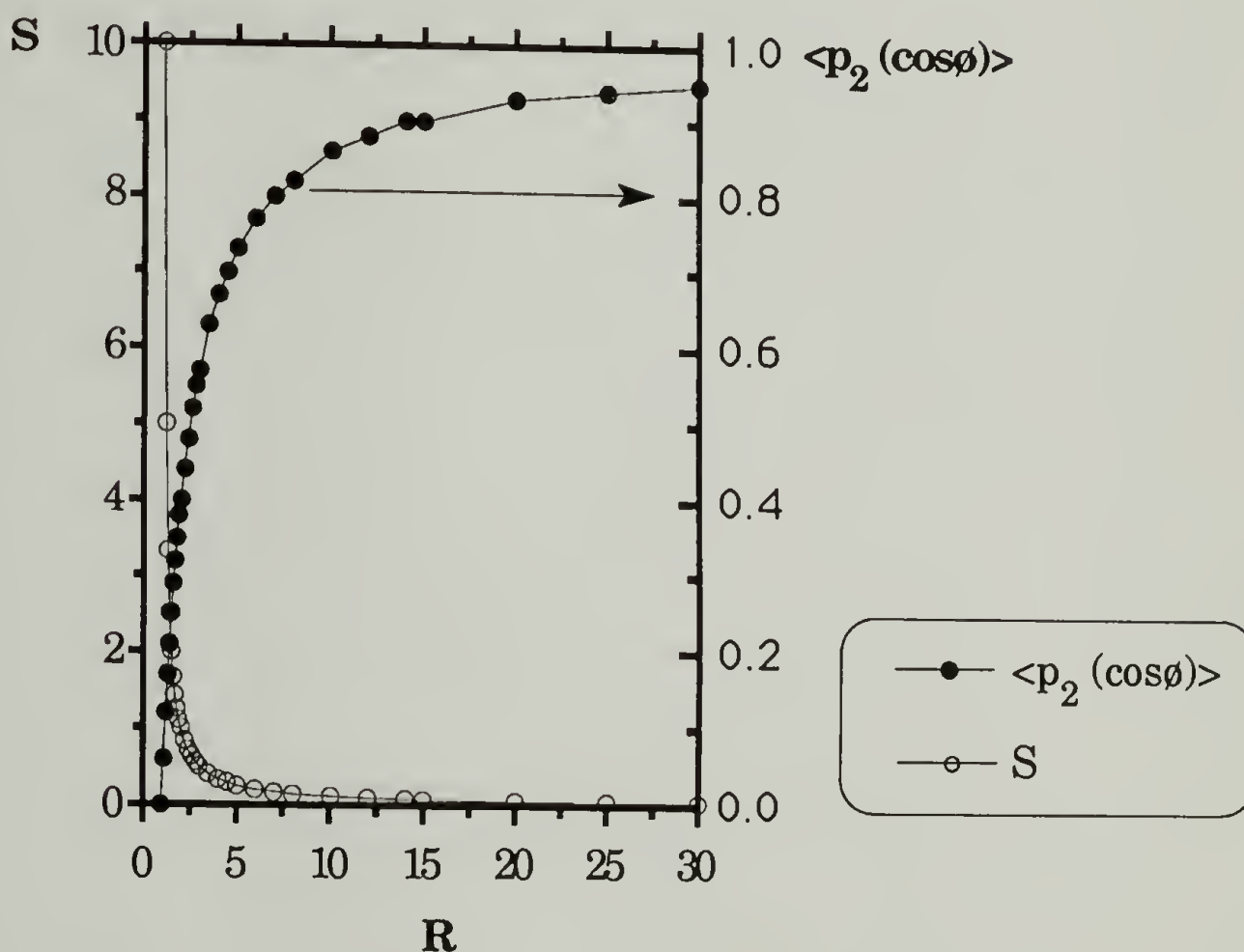


Fig. 4.16. Relationship of IR Dichroism to the Order Parameter and Orientation Function.

The equation (4.5) requires that two of the three variables R , S and θ be obtained experimentally. This is often not possible using only the IR

technique for which these equations were derived. The IR dichroic ratio (R) can be easily obtained experimentally as described in the previous chapter, however, θ must be obtained by some other method or be approximated.

Fraser³³ has suggested a means of obtaining the upper and lower limits of S or equivalently f even when θ is unknown but for which several dichroic ratios for different bands can be measured. Essentially, this method uses the highest dichroic ratio to obtain the lower limit (most disordered) value for f . Several angles can then be assigned an upper and lower limit assuming that f is constant for all the absorption bands, that is, the sample is homogeneous.

In the case of PPV-co-PTV, Bradley *et al.*²⁹ have assumed that the moment angle for the absorption band at 555 cm^{-1} , attributed to phenylene ring-breathing, to be at 90° and calculated the other moment angles using equation 4.5. The derived values were then compared, with some success, to those that might be expected from the molecular geometry suggested by Dugay and Fabre³⁴. In this discussion, the same assumptions will be made.

Zbinden²⁷ has also shown that the order parameter obtained from an analyses of IR dichroic ratios can be related to different polymer stretching models, particularly, the Kratky or psuedo-affine model^{35, 36}. The model describes a volume element of an unoriented sample where the chains are distributed randomly (fig.4.17a). The volume element is drawn (fig. 4.17b) by the draw ratio v defined by:

$$v = \frac{L}{L'} \quad (4.10)$$

and if the density does not change then:

$$W^2 L = W'^2 L' . \quad (4.11)$$

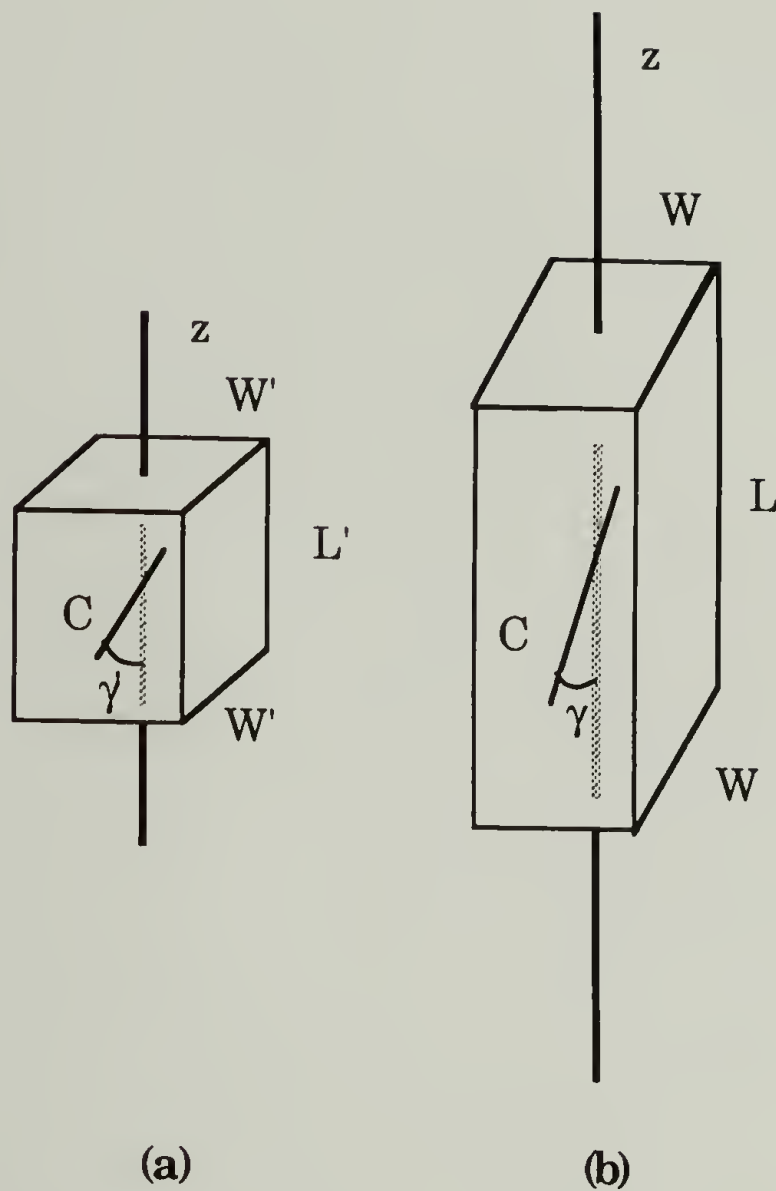


Fig. 4.17. Elongation of a Volume Element in the Kratky Model.

Furthermore, by assuming that the molecular orientation of the chain segment corresponds to the macroscopic deformation of the sample then:

$$\tan \gamma = \tan \gamma' v^{-3/2} \quad (4.12)$$

and the following distribution function can be derived:

$$f(\gamma) = \frac{v^{3/4} \sin \gamma}{(v^{-3/2} \cos^2 \gamma + v^{3/2} \sin^2 \gamma)^{3/2}} \quad (4.13)$$

and related to Hermans' orientation function thus:

$$f = \frac{3v^3}{2(v^3 - 1)} \left[\frac{2v^3 + 1}{3v^3} - \frac{\tan^{-1}(v^3 - 1)^{1/2}}{(v^3 - 1)^{1/2}} \right] \quad (4.14)$$

and figure 4.18 shows this relationship graphically. It is important to note that explicit in this derivation are the assumptions that the volume does not change during extension and that the orientation of the chains are primarily a function of sample elongation.

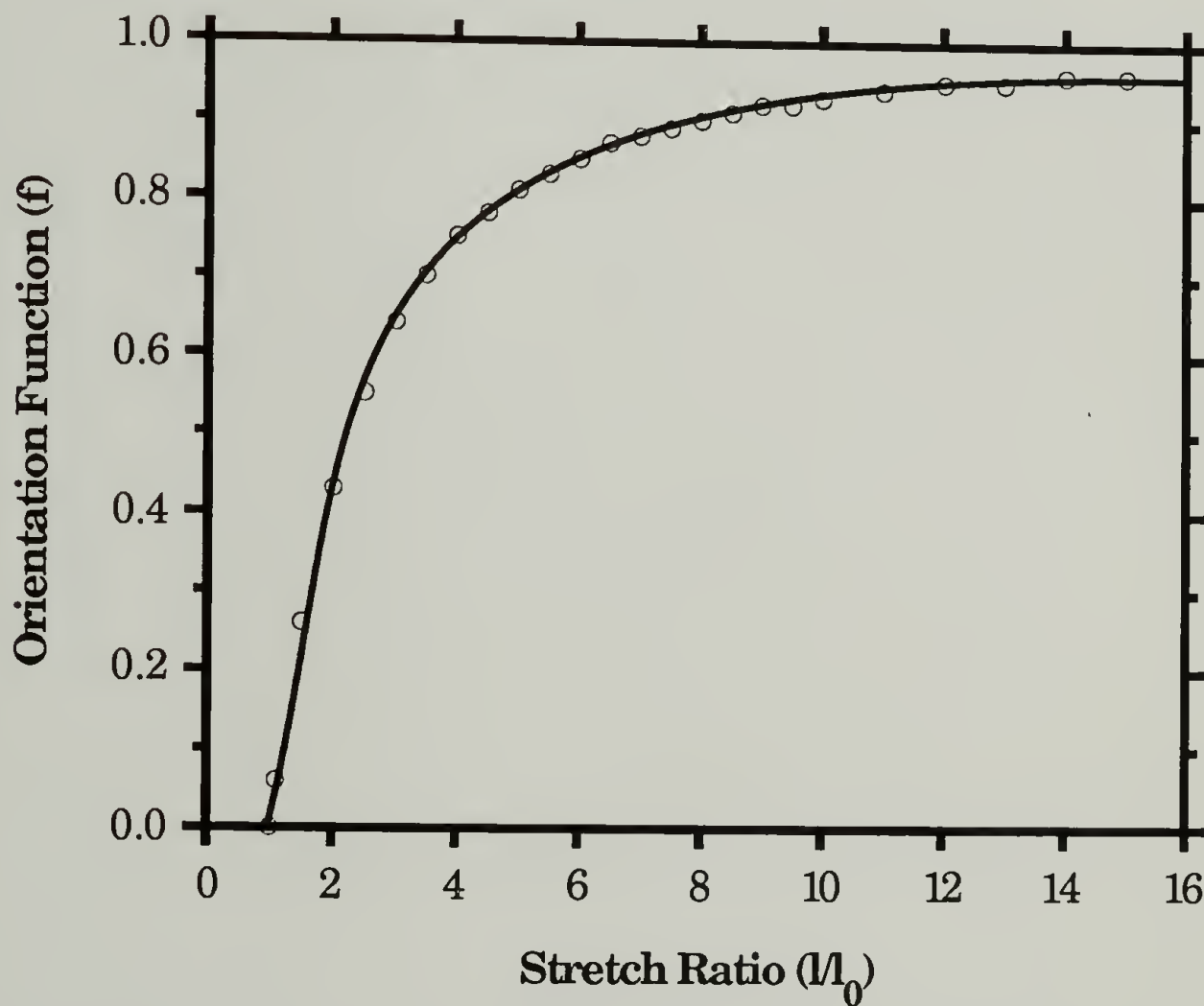


Fig. 4.18. Prediction by the Kratky Model for the Orientation of a Stretched Polymer.

The Kratky model was thought to describe an upper-limit for the orientational order found in polymers under elongational stretching since the model did not take into account the effects of entanglements, molecular weight, viscous flow and chain relaxation which would tend to reduce the orientational order of the sample. On the other hand, the basic assumption of the Kratky model - that no change in the volume of the sample occurred during the stretching process - allowed for polymeric materials that underwent a density change to produce an orientational order much higher than those expected from the model. Morphological changes which affect the density of the material, such as stretch-induced crystallization, would tend to increase the orientational order beyond the predictions of the Kratky model. Moreover, chemical changes, such as the loss of a small molecule, would also induce a change in the density by increasing the intermolecular interactions in the polymer product or by making the resultant volume smaller than the volume assumed by the Kratky model.

4.3.2. IR Analyses of the Degree of Orientation

Bradley²⁹ and Machado³⁷ observed that the PPV sulfonium salt precursor has the capacity for high orientational order when stretched and eliminated. Bradley reported an order parameter of $S = 0.04$ (equivalent to an f of 0.93) for a stretch ratio (λ) of 5. Machado reported a similar orientation function of $f = 0.9$ (equivalent to an S of .059) for a stretch ratio of $\lambda=4$. The higher orientational order found in PPV samples which have undergone uniaxial stretching has been interpreted to be a result of stress-induced crystallization and the increase in the driving force on orientation due to the concurrent

formation of conjugated species during the stretching process. Indeed, Machado³⁷ reported that the unoriented films of the PPV precursor showed both a decrease in the volume and an increase in the orientational order ($f = 0.17$) upon elimination at constant length to PPV.

The same was found of the PPV-co-PTV samples prepared in this investigation. Several samples that were taken out of the previously described hot-oil immersion stretcher (fig. 3.1) within a minute after immersion showed stretch ratios equivalent to those kept in the apparatus for at least thirty minutes. However, the samples that were taken out immediately after stretching all tended to break into fragments during the elimination step. This suggested that samples which were clamped tight within the Teflon sandwich experienced increasing stress as the samples eliminated and shrunk. The samples kept in the hot-oil, on the other hand, experienced constant stress since only one end of the samples were clamped while the other was held down by a constant weight. Unoriented samples did not fragment even without pre-elimination since the stress experienced during the elimination step could be relieved by orientation. Stretched samples, however, showed fragmentation since the chains in these samples were already highly oriented and partially eliminated so that stress can only be relieved by chain slippage which is not known to occur for stiff, partially eliminated, conjugated chains like PPV.

Similar experiments of eliminating the samples under constant length were attempted for the PPV-co-PTV samples but proved inconclusive. It was found that to deduce a value of $f = 0.17$ as Machado did, an IR dichroic ratio of 1.3 for the absorption at 555 cm^{-1} would have

to be obtained. Although such values were indeed found, a series of similar experiments revealed that the standard deviation (± 0.25) for such a small dichroic ratio, and a consideration of the poor signal to noise ratio experienced when factoring in the background correction, made these values to be at the limits of experimental error. The only strong evidence then for suggesting that PPV-co-PTV samples shrunk during elimination was the physical sample fragmentation described above. The values obtained through IR dichroic experiments supported such a suggestion but could not be taken as a quantitative description of such a shrinkage. The orientational effect during the elimination and the apparent second stage gain in orientational order after stretching indicated that the crystallization of these samples during elimination accounted for some of the orientational order observed.

The samples of PPV-co11-PTV (fig. 4.19) and PPV-co23-PTV (fig. 4.20) showed orientational orders that were higher than those predicted by the Kratky model. This was similar to those obtained for the PPV homopolymer. The samples of PPV-co70-PTV (fig. 4.21), however, showed orientational orders much lower than similarly drawn PPV-co-PTVs with low %PTV content. The similarity of the orientational order obtained for PPV-co70-PTV and those predicted by the Kratky model may likely have been fortuitous. The mechanism of orientation for the PPV-PTV system is known to be much too complex to be fully modeled against the assumptions of Kratky. The more important consideration was why the PTV-rich samples showed a poorer orientational order than those rich in the PPV component and what orientational mechanism accounts for this.

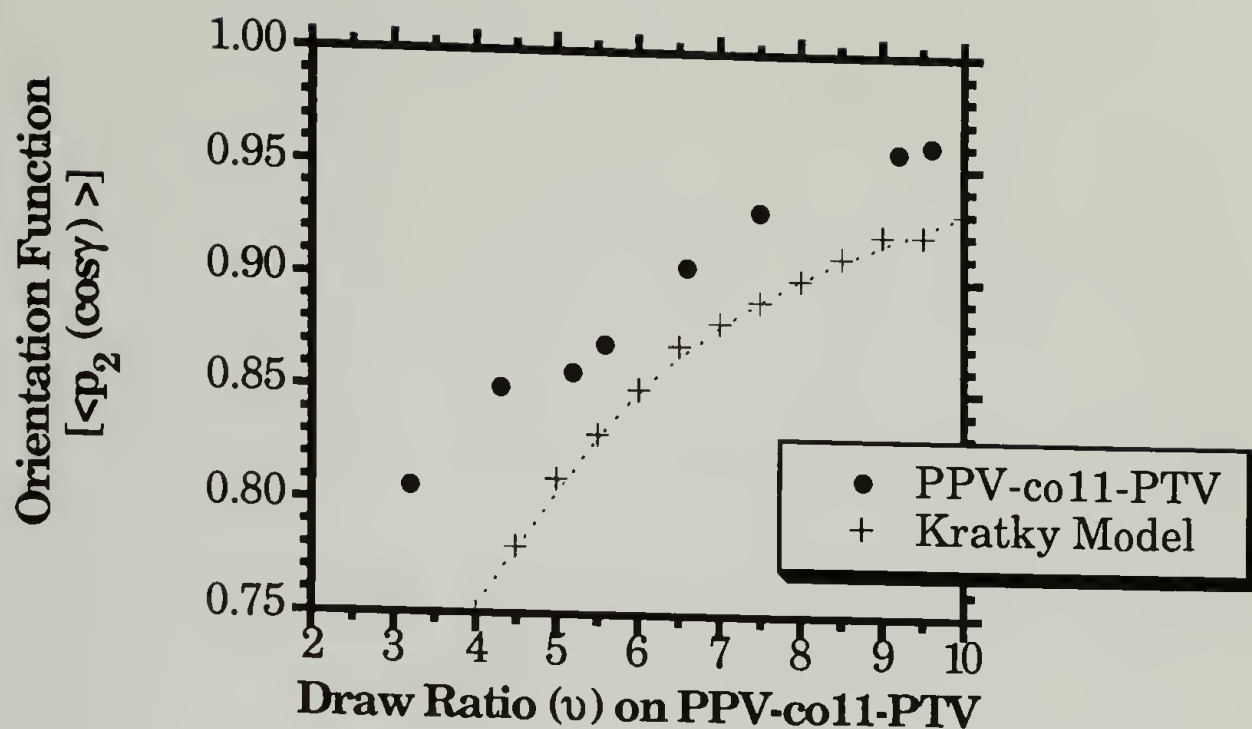


Fig. 4.19. Orientation of PPV-co11-PTV by Stretching Compared with the Prediction by the Kratky Model.

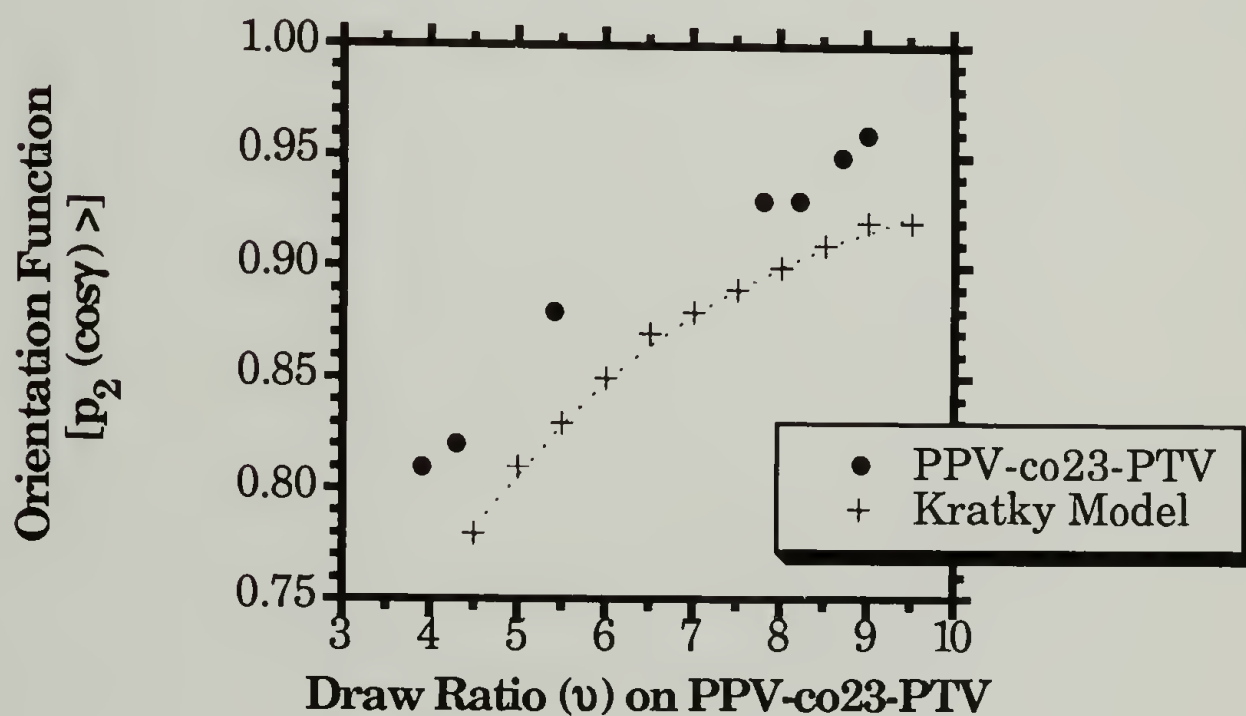


Fig. 4.20. Orientation of PPV-co23-PTV by Stretching Compared with the Prediction by the Kratky Model.

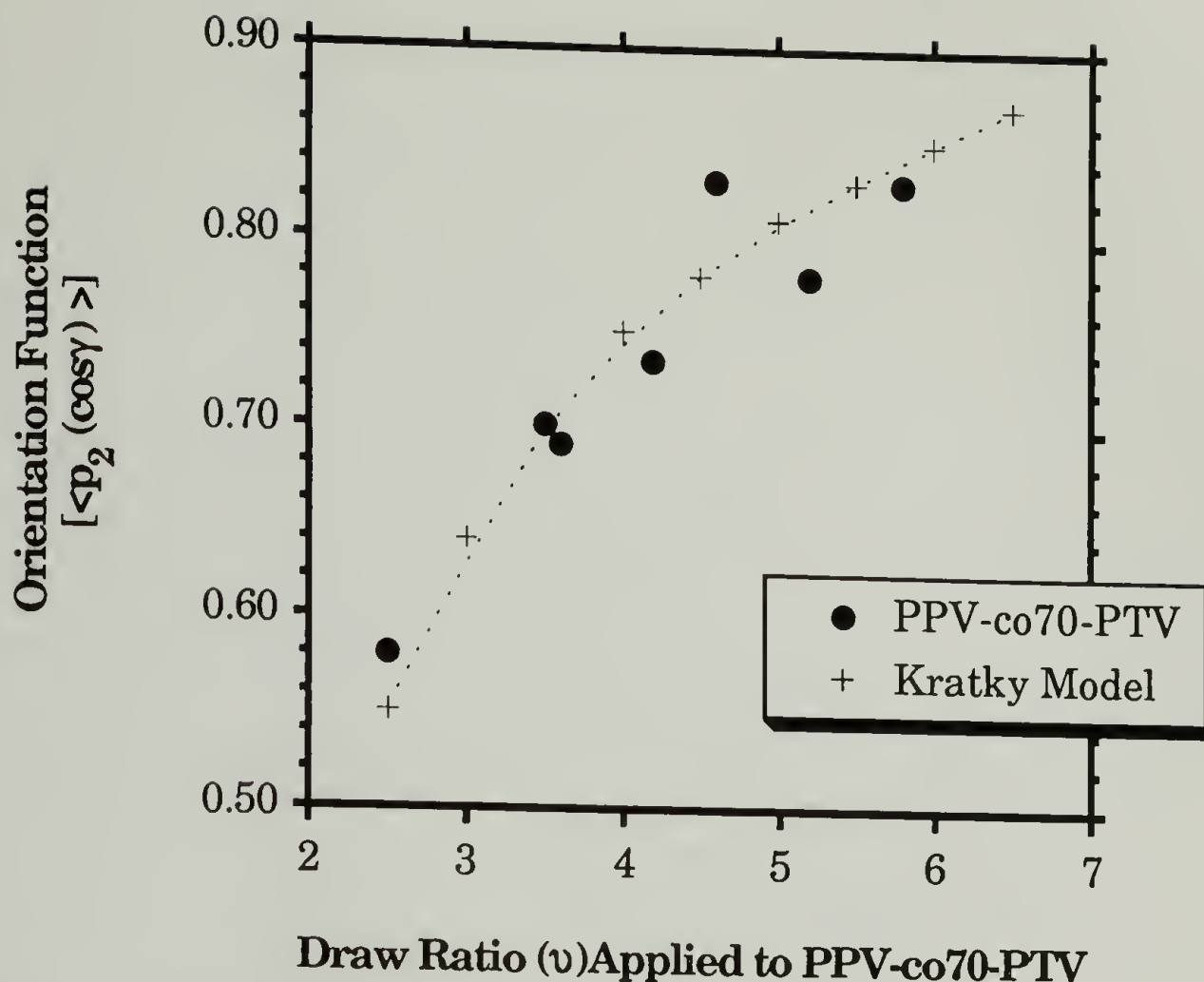


Fig. 4.21. Orientation of PPV-co70-PTV by Stretching Compared with the Prediction by the Kratky Model.

Previous studies on the orientation of polyarylene vinylenes^{29, 37} suggested that the higher degree of orientation attained for PPV samples than those predicted by the Kratky model was an effect of stress induced crystallinity coupled with a large volume change during the elimination that was concurrent to the orientation. An investigation of the morphology of the precursor polymer and the conjugated PPV³⁸ showed that the precursor was an amorphous polymer whereas the oriented PPV had a high crystalline order. Similar results were obtained for PTV²³ although the material reported had a draw ratio of 16 and no attempt was made to compare the orientation order obtained to those predicted by the Kratky model. No such analyses were available

for PPV-co-PTV although there was evidence of sample shrinkage and orientation of unstretched samples which must have resulted from crystallite formation and volume loss. This would account for an orientation order that is higher than that of the Kratky model prediction.

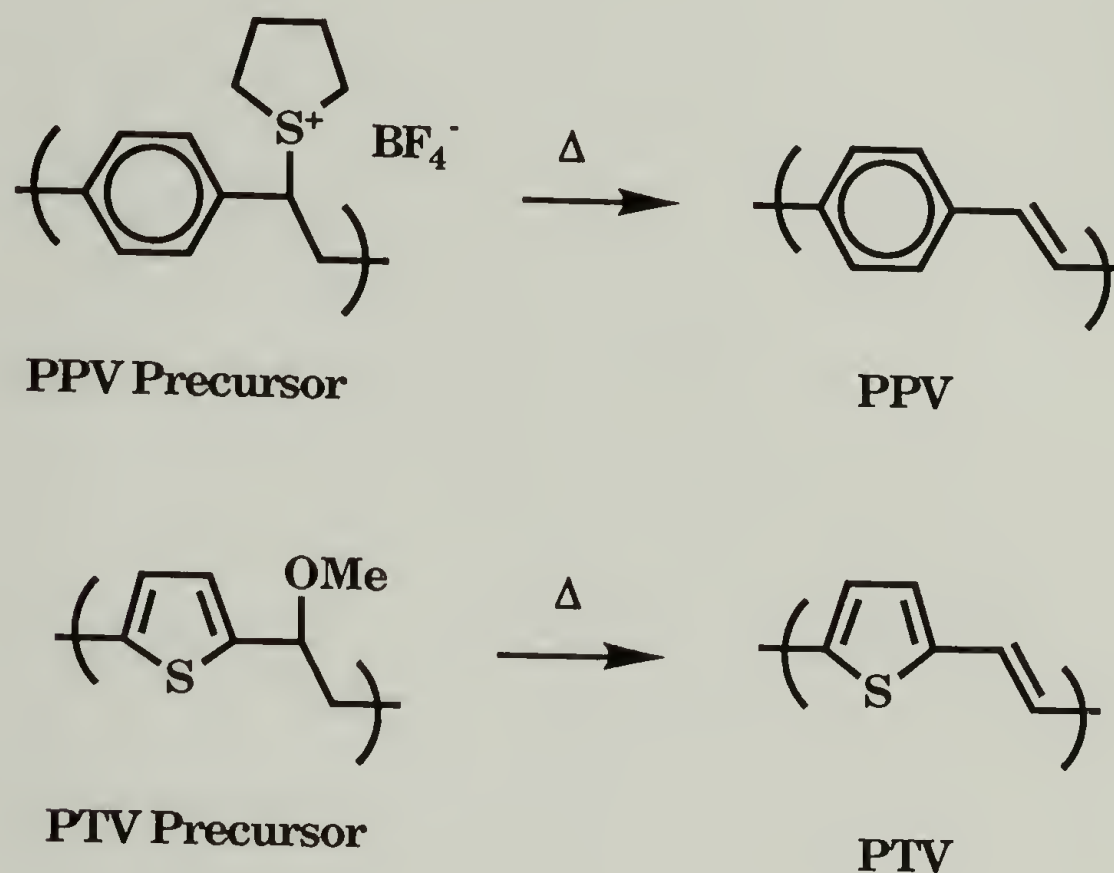


Fig. 4.22. Elimination Step in the Polyarylene Vinylene System.

The fact that the PPV-co70-PTV showed a lower degree of orientation than those achieved by PPV-co11-PTV and PPV-co23-PTV can be rationalized by a closer examination of the precursors (fig. 4.22). The precursor segment from which the PPV moiety developed contained the large pendant group - tetrahydrothiophenium fluoroborate. On the other hand, the precursor segment that produced the PTV moiety contained the relatively small and neutral methoxy group. This difference in terms of size of material eliminated during the stretching

and heating process could account for the difference in the orientational order between PPV-rich and PTV-rich copolymers. The larger size of the eliminated compound in the PPV precursor segment would develop a larger volume loss and subsequently a larger difference from the orientational order predicted by the Kratky model.

Alternatively, the difference in the orientational properties of a PPV-rich precursor system from a PTV-rich precursor system could be considered as the difference between polyelectrolytes and ionomers. Polyelectrolytes, containing near 1:1 charge units per repeat unit, have been shown to have free-volumes that were equivalent to their uncharged polymeric counterparts³⁹⁻⁴² since the ions were shielded from each other. Ionomers on the other hand, especially at very low (5-10%) ionization content, do not exhibit the shielding effects found in polyelectrolytes and thus show the formation of multiplets and aggregates⁴³. This difference in morphology could account, in part, for the larger volume loss in converting a polyelectrolyte such as the PPV-co11-PTV precursor, as compared to an ionomer, such as the PPV-co70-PTV precursor. Moreover, it could also explain why PTV has been shown to form highly ordered species but PPV-co70-PTV showed this to a lesser degree.

4.3.3. IR Analyses of PPV/PTV Blend Miscibility

In the previous discussion of orientational order as obtained by IR dichroism, there was an explicit assumption that the order parameter (S) or the orientation function (f) was constant throughout the chain and for all moment angles of absorption. This was true only for a homogeneous sample and would not be the case for an immiscible blend.

The average orientational order for the sample would not coincide with the orientational order of the matrix or the dispersed phase (fig. 4.23). The matrix may be expected to relieve the stress by conforming to the stretch direction. The dispersed phase, on the other hand, would experience a reduced stress and would manifest the stress-relaxation as a distortion of the phase-boundaries and a consequently lowered degree of orientation of the chains.

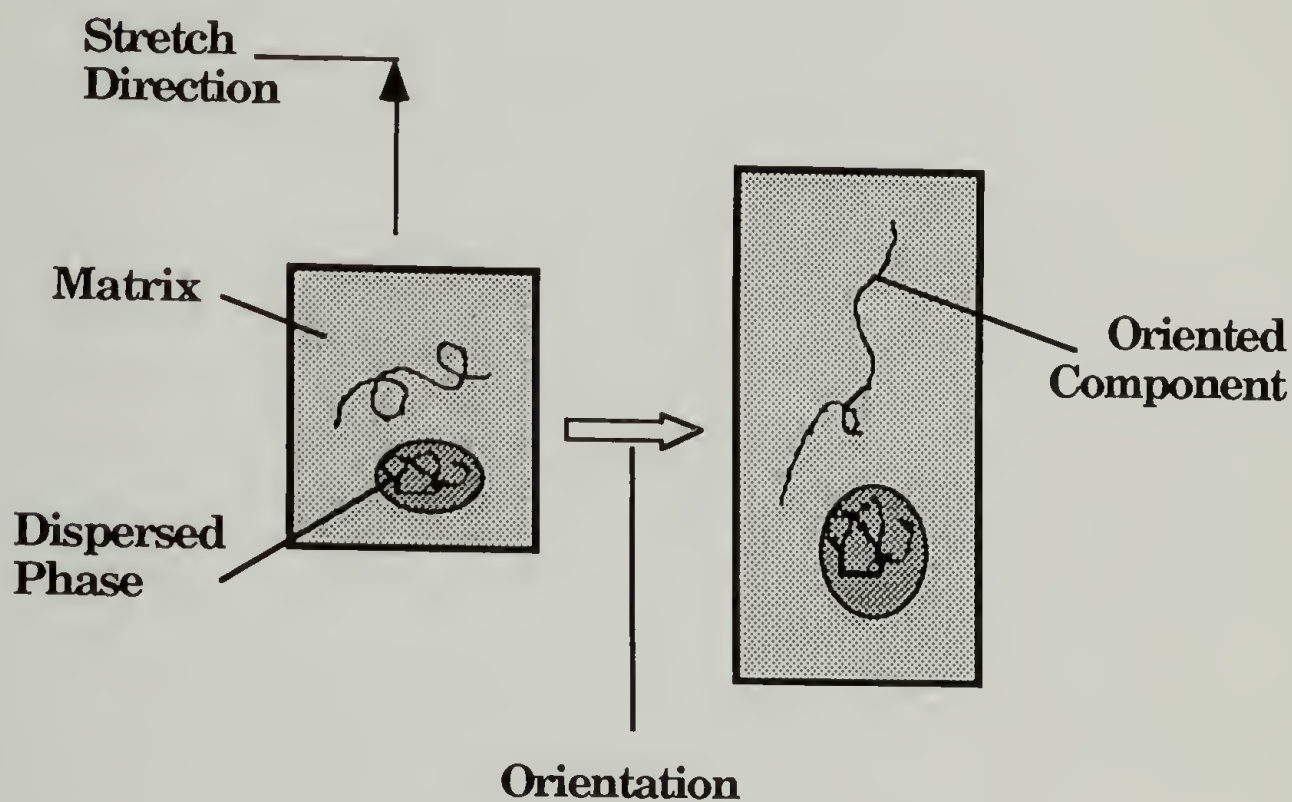


Fig. 4.23. Orientation of an Immiscible Blend.

The IR absorption spectra of PPV and PTV contained maxima that were unique to each homopolymer as well as those that were shared (fig. 4.24). The absorbance maximum at 555 cm^{-1} , equivalent to the aromatic ring-breathing to which a moment angle of 90° has been assigned, was shown by both PPV and PTV^{10, 11, 44}. The absorbance maxima at 970 cm^{-1} and 1520 cm^{-1} , equivalent to the *trans*-vinylene

wagging and the C-C valence stretching mode of the α -carbons respectively, for PPV was isolated from the equivalent absorbance maxima of PTV which were found to be at 930 cm^{-1} and 1600 cm^{-1} respectively⁴⁵.

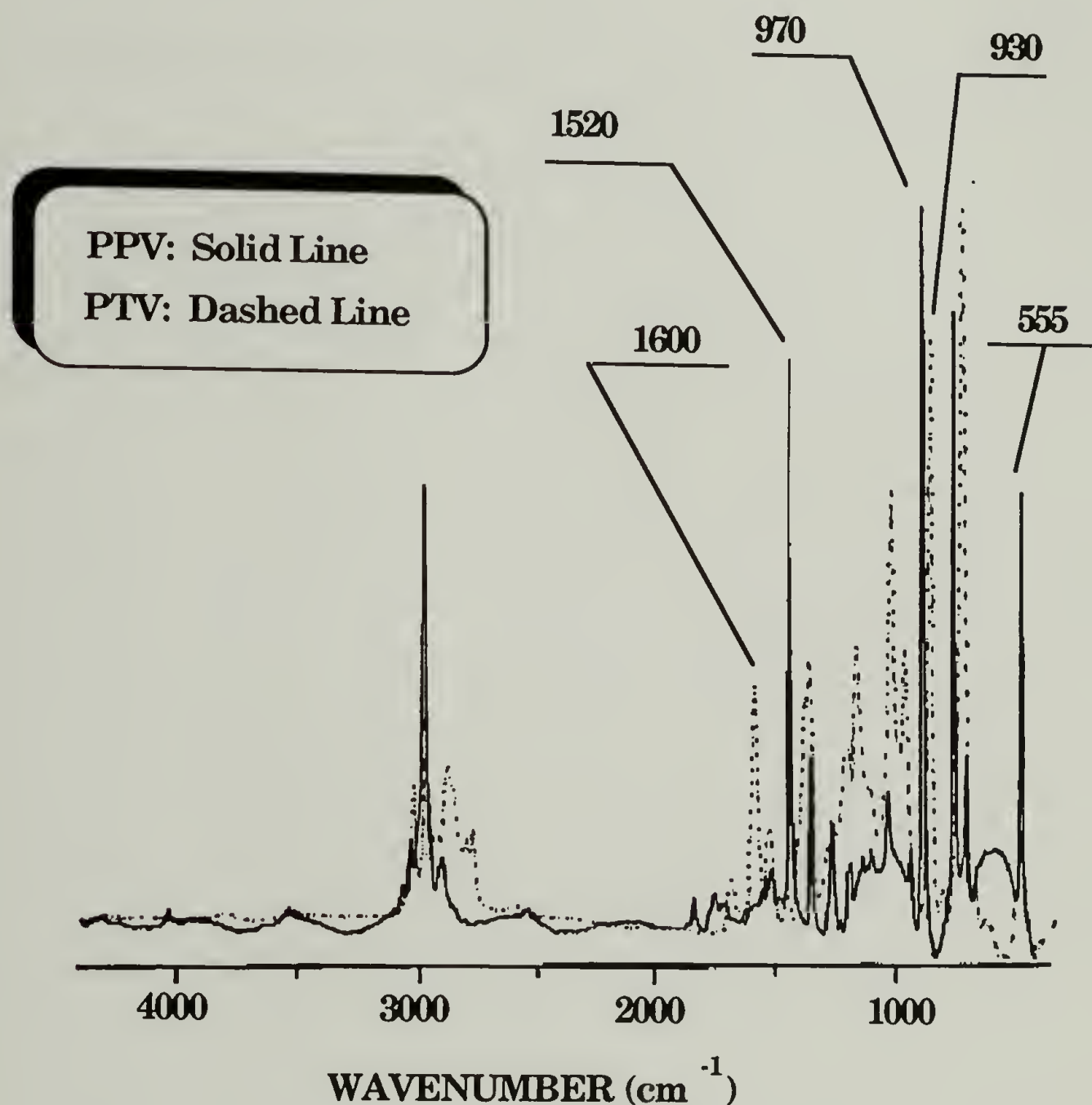


Fig. 4.24. IR Absorbance Spectra of PPV and PTV.

The moment angles of the IR absorbances for the unique bands were derived by calculating the order parameter (S) of several samples of oriented PPV and PTV on the assumption that the homopolymer

samples were homogeneous (table 4.4). The order parameters for the blend components were then obtained using these derived moment angles.

Table 4.4. Derived Moment Angles for PPV and PTV.

SAMPLE	DERIVED MOMENT ANGLES			
	930cm ⁻¹	1600cm ⁻¹	970cm ⁻¹	1520cm ⁻¹
PTV	75° ± 4	42° ± 1	-	-
PPV	-	-	87° ± 4	15° ± 2

Table 4.5. Orientation Function (S) for PPV and PTV in the Blend.

BLEND PPV/PTV (%PTV)	ORIENTATION FUNCTION (S)				
	Assumed (90°)	PTV Derived		PPV Derived	
	555cm ⁻¹	930cm ⁻¹	1600cm ⁻¹	970cm ⁻¹	1520cm ⁻¹
20	.11	.094	.11	.93	.13
40	.18	.13	.13	.11	.18
60	.13	.16	.090	.12	.16

The order parameters obtained, using the absorbance maxima at 930 cm⁻¹, 970 cm⁻¹, 1520 cm⁻¹ and 1600 cm⁻¹ showed little distinction from those obtained using the absorbance maximum at 555 cm⁻¹. The differences shown were more a reflection of the sensitivity of the

differences shown were more a reflection of the sensitivity of the analyses and did not show any particular trend (table 4.5). The investigation suggested that the PPV/PTV precursor blend did not exist in a phase separated form that manifested varying degrees of orientation for each separate component under low uniaxial draws. The precursor polymers of PPV and PTV were miscible to the degree that the IR dichroic ratio for oriented systems could determine.

4.4. Orientation and Conductivity

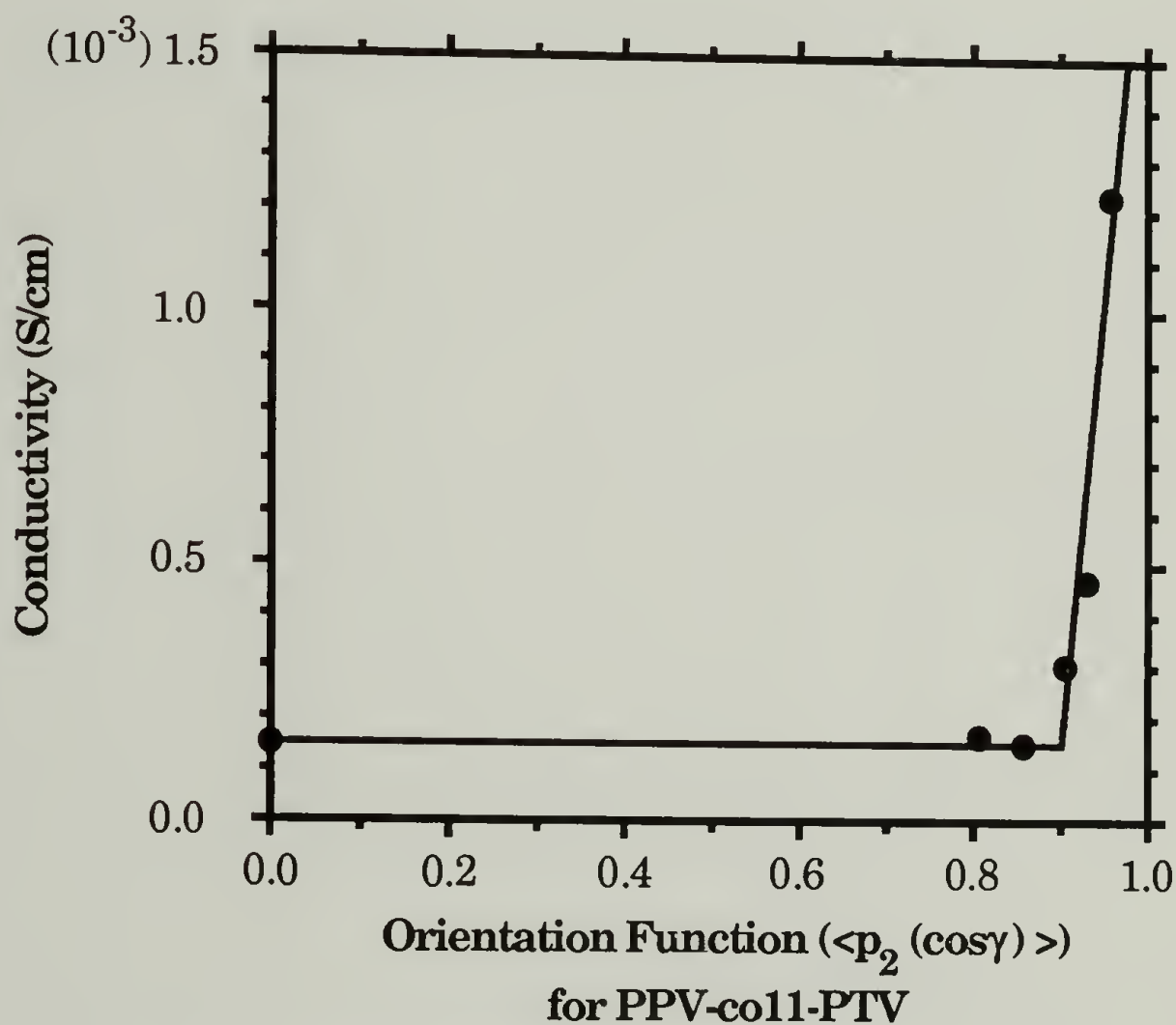


Fig. 4.25. Conductivity of Oriented PPV-co11-PTV.

The conductivity of oriented samples increased markedly with orientation, as expected. The conductivity of PPV-co11-PTV increased by an order of magnitude (1.5×10^{-4} to 1.2×10^{-3} S/cm) in going from an

orientation function of $f = 0$ to $f = 0.96$ (fig. 4.25). A more dramatic increase is shown by PPV-co70-PTV in going from an orientation function $f = 0$ to $f = 0.82$ with a concurrent increase of 3 orders of magnitude from 3.6×10^{-3} S/cm to 1.8 S/cm (fig. 4.26).

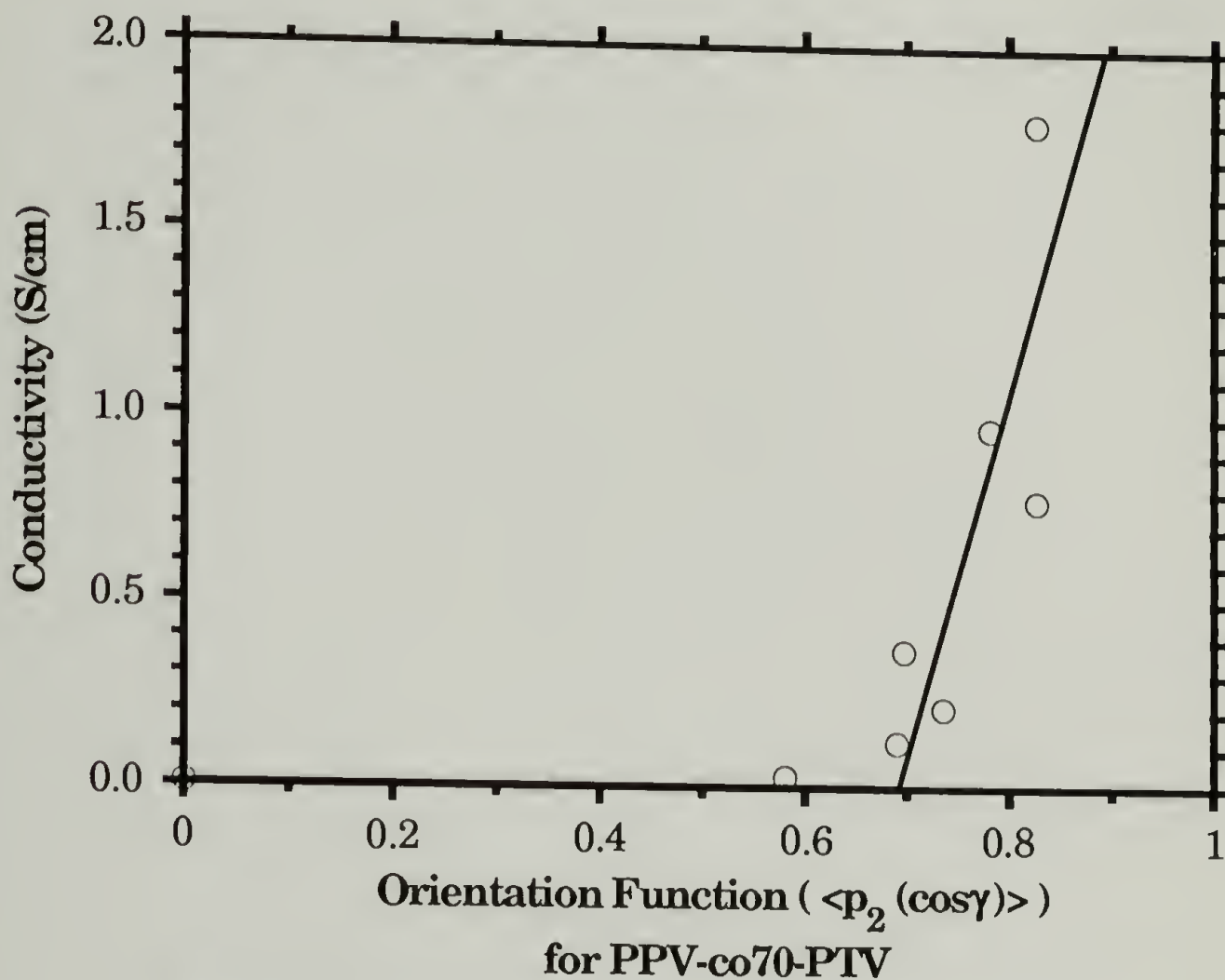


Fig. 4.26. Conductivity of Oriented PPV-co70-PTV.

This phenomenal increase in the conductivity was expected since similar reports of such increases in conductivity have been reported for PPV^{37, 46}. The difference in the increase in the conductivity for similarly ordered PPV-co11-PTV and PPV-co70-PTV could be understood as a manifestation of the number of contiguous repeat units of PTV within the copolymer. This chemical nature has already been shown to be manifested in the dramatic increase in conductivity for PPV-co-PTV

with increasing PTV contents (fig. 4.11). Such random PPV incorporation into the copolymer was shown likewise to mitigate the increase in conductivity for oriented species. Moreover, the morphological barrier to interchain electron hopping found in polyarylene blends (fig. 4.12 and 4.13) was shown in this experiment to affect the conductivity in the crystalline PPV-co-PTV also, such that the copolymers with lower PTV content have fewer low-energy paths for interchain electron hopping and therefore showed a lower increase in conductivity.

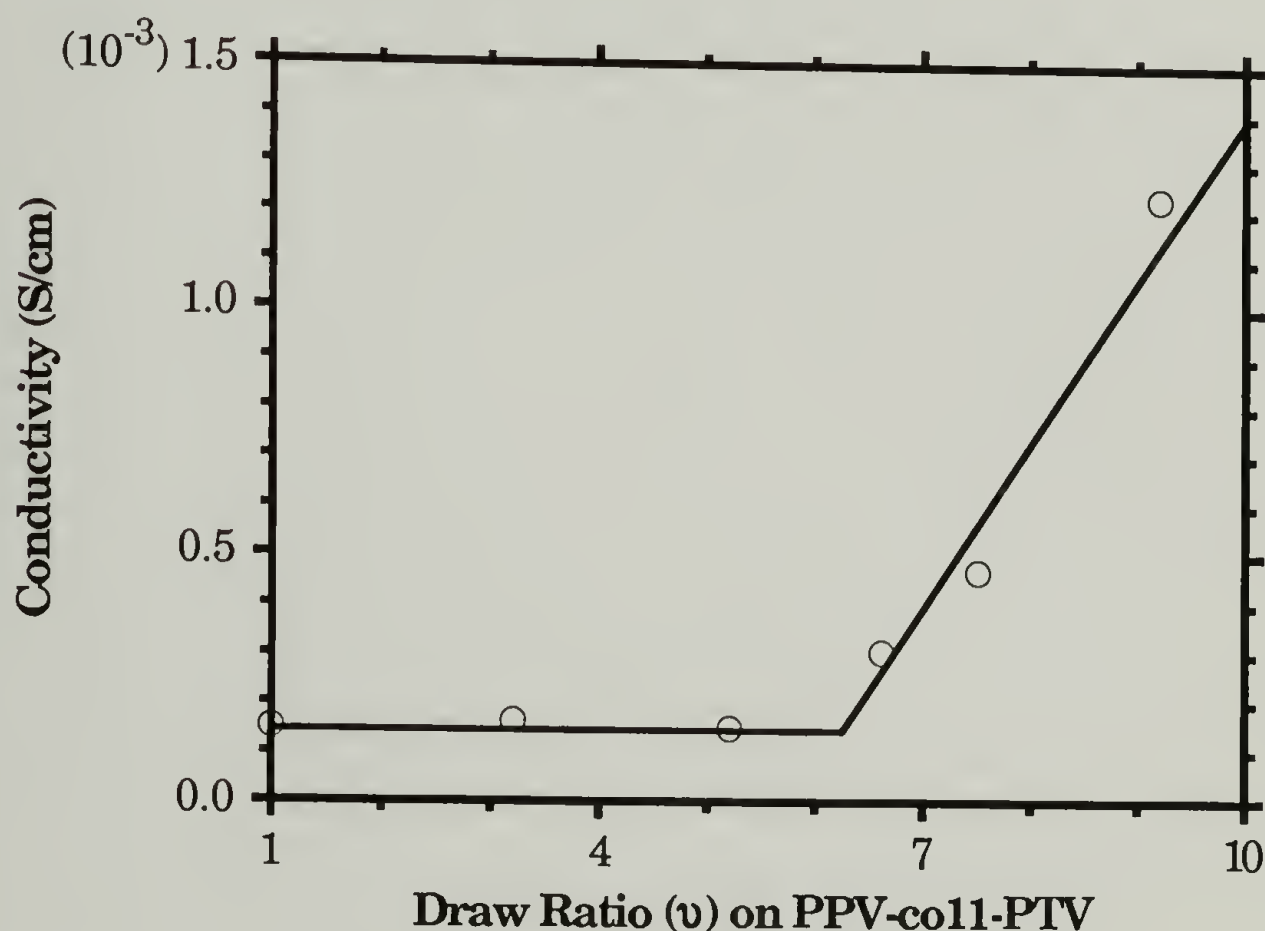


Fig. 4.27. Conductivity as a Function of Stretch Ratio on PPV-co11-PTV.

Noteworthy, was the dampened effect of the orientation upon the conductivity. The data suggested that at orientation functions lower than $f = 0.8$ and $f = 0.5$, for PPV-co11-PTV and PPV-co70-PTV

respectively, the increase in the conductivity was negligible. An investigation of the effect of the stretch ratio (σ) on the conductivity revealed similar results (fig. 4.27, and 4.28).

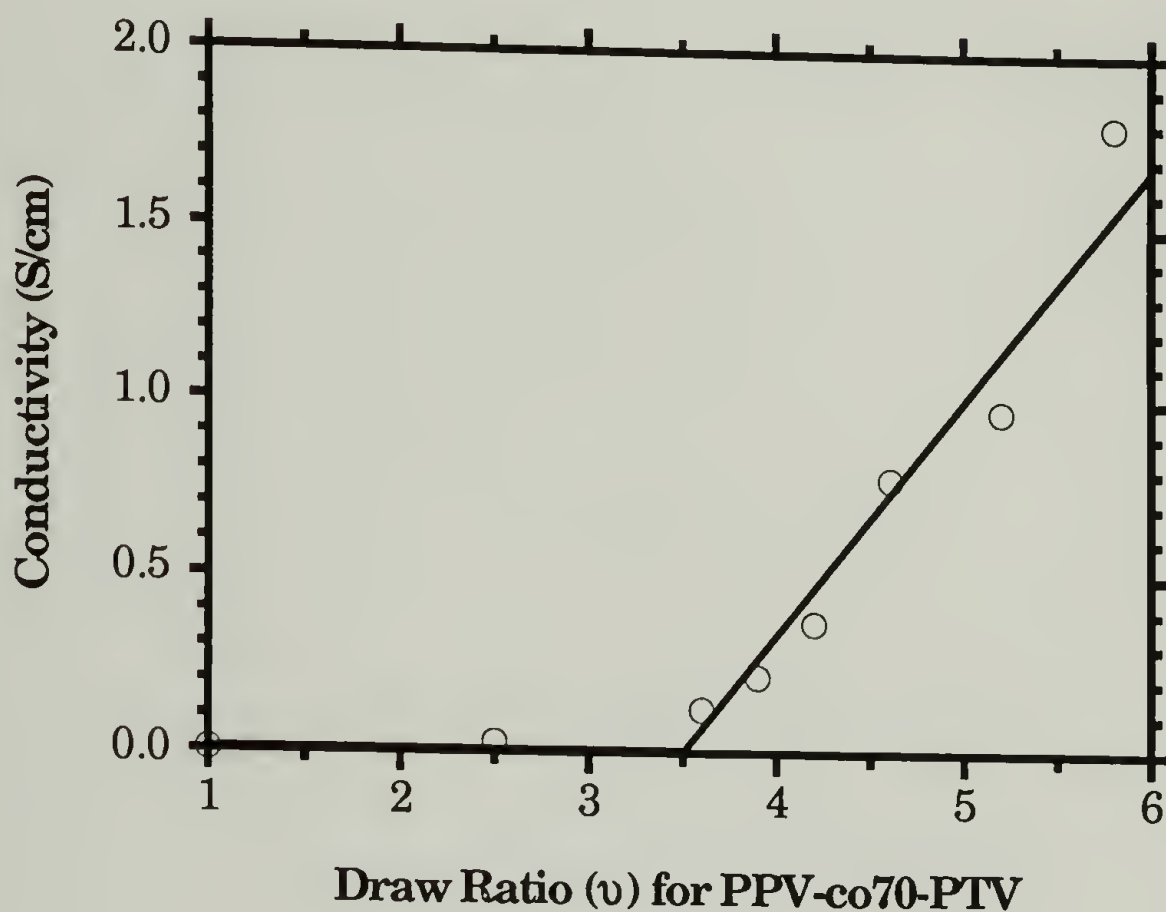


Fig. 4.28. Conductivity as a Function of Stretch Ratio on PPV-co23-PTV.

This effect was significantly different from those obtained for the homopolymers of PPV³⁷ and PTV²³. In both cases of the homopolymers, large increases in conductivity were obtained for relatively low draw ratios followed by a lessened effect of drawing due to the already high orientations achieved with low stretches. The large increases in the conductivities at low draw ratios were suggested to be correlated to the equivalent increases in the tensile strength and modulus of these materials. This was rationalized from the point of view that both the mechanical properties and the conductivity of oriented samples were a

function of crystallite formation during the orientation process. The picture that emerged was of a material that incurred a tremendous increase in axial orientation due to the elimination-induced and stress-induced crystallization coupled with large volume loss at even small draw ratios. This produced high orientational order which resulted in high tensile strength, Young's modulus and conductivity.

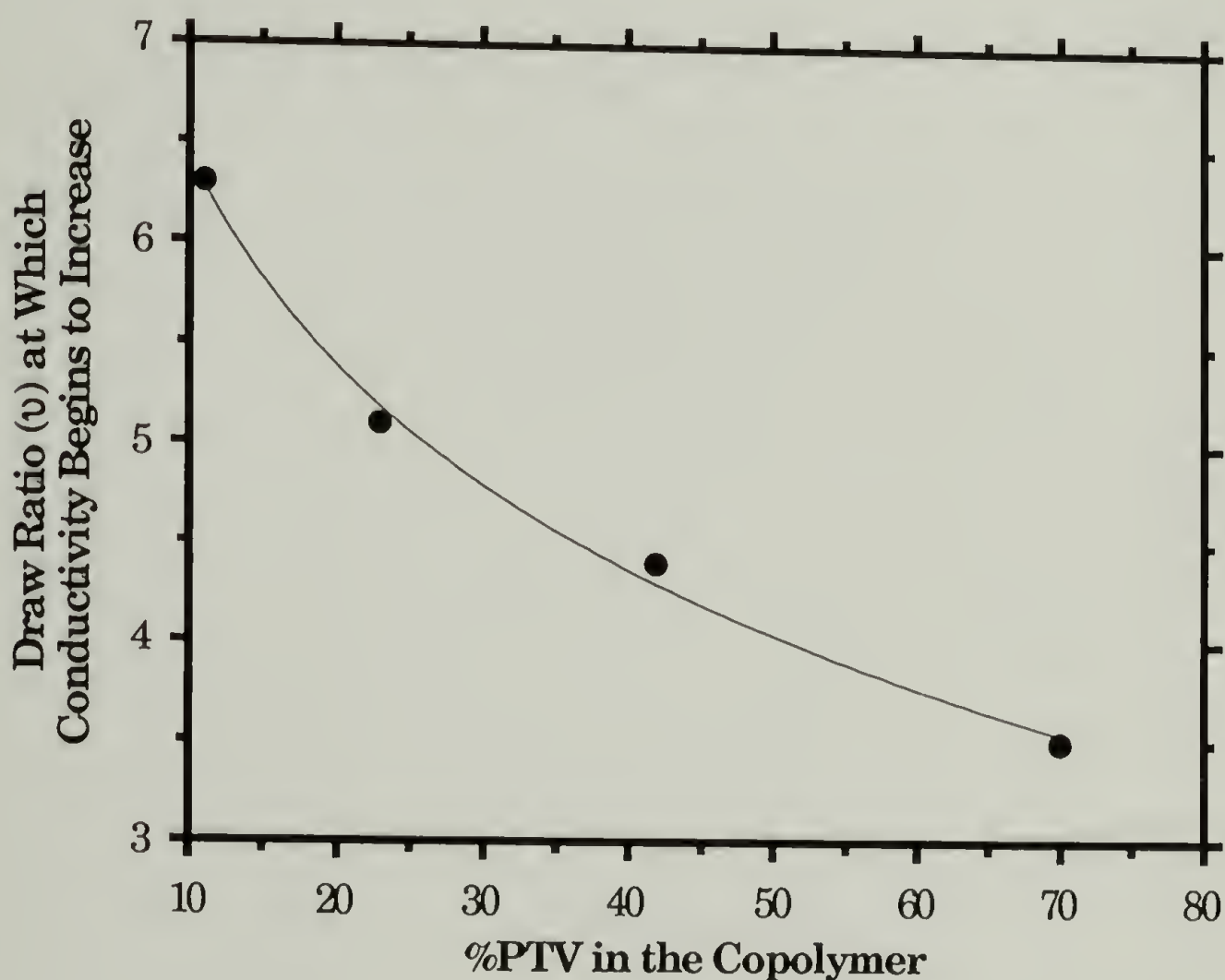


Fig. 4.29. Onset of Orientation Effects on Conductivity as a Function of %PTV Composition.

It is now apparent from this investigation that in random copolymers another parameter must be considered. It was shown that crystalline formation does occur in PPV-co-PTV as evidenced by the

high orientational order obtained at low draw ratios. Although this may result in high tensile strength and modulus (a fact which still has to be investigated) this did not necessarily result in high conductivities. The fact remained that the conduction behavior of iodine doped PPV-co-PTV was a function of the number of contiguous PTV repeat units (see section 4.2) and this was shown to be significantly lower for copolymers with PTV contents of less than 65%. The data presented here (fig. 4.29) has shown further that although the PTV-poor copolymers can exhibit conduction, the fact remained that the poor interchain lateral registry of the PTV segments, or limited electronic lattice perpendicular to the stretch direction of these materials, extremely limited the charge-transport capacity of the chains even at high orientation. Evidently, higher draw ratios and orientational order were required to achieve the increase in connectivity and conductivity, possibly by allowing the chains to slip by each other while the material was still in its precursor, amorphous form, and form properly registered PTV units.

Alternatively, the PPV-co-PTV chains may need much higher draw ratios - when the %PTV composition was low - in order to form crystallites which accommodated the PTV segments in proper registry to each other. It is assumed that the random placement of PTV segments within the copolymer disrupts the formation of unit cells and high draw ratios compensates for this disruption.

4.5. References

1. Gagnon, D.R., Capistran, J., Karasz, F.E. and Lenz, R.W. *Polym. Prepr.*, **25**, 284 (1984).
2. Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Polym. Commun.*, **25**, 327 (1984).

3. Lenz, R.W., Han, C.C., Stenger-Smith, J. and Karasz, F.E. *J. Polym. Sci., Polym. Chem.*, **26**, 3241 (1988).
4. Garay, R. and Lenz, R.W. *Makromol. Chem. Suppl.*, **15**, 1 (1989).
5. Momii, T., Tokito, S., Tsutsui, T. and Saito, S. *Chem. Lett.*, 1201 (1988).
6. Tokito, S., Momii, T., Murata, H., Tsutsui, T. and Saito, S. *Polymer*, **31**, 1137 (1990).
7. Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Polym. Commun.*, **28**, 229 (1987).
8. Yamada, S., Tokito, S., Tsutsui, T. and Saito, S. *J. Chem. Soc., Chem. Commun.*, 1448 (1987).
9. "The Merck Index." 10th. Windholz, M., ed. (Merck & Co., Inc., Rahway, N.J., 1983).
10. Koßmehl, G., Härtel, M. and Manecke, G. *Makromol. Chem.*, **131**, 15 (1970).
11. Koßmehl, G., Härtel, M. and Manecke, G. *Makromol. Chem.*, **131**, 37 (1970).
12. Ringsdorf, H., Wünstefeld, R., Zerta, E., Ebert, M. and Wendorf, J.H. *Angew. Chem. Int. Ed.*, **28**, 914 (1989).
13. Odian, G. "Principles of Polymerization." (John Wiley and Sons, New York, 1981).
14. Fineman, M. and Ross, S.D. *J. Polym. Sci.*, **5**, 259 (1950).
15. Jin, J-I., Shim, H-K. and Lenz, R.W. *Synth. Met.*, **29**, E53 (1989).
16. Shim, H-K., Lenz, R.W. and Jin, J-I. *Makromol. Chem.*, **190**, 389 (1989).
17. Suggate, J.R. *Makromol. Chem.*, **180**, 679 (1979).
18. Pichot, C., Guyot, A. and Strazielle, C. *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2269 (1979).
19. Ledwith, A., Galli, G., Chiellini, E. and Solaro, R. *Polym. Bull.*, **1**, 491 (1979).

20. McCoy, R.K. personal communications.
21. Horhold, H.-H. and Helbig, M. *Makromol. Chem., Macromol. Symp.*, **12**, 229 (1987).
22. Murata, H., Tokito, S., Tsutsui, T. and Saito, S. *Synth. Met.*, **36**, 95 (1990).
23. Tokito, S., Smith, P. and Heeger, A.J. *Synth. Met.*, **36**, 183 (1990).
24. Obrzut, J. and Karasz, F.E. *J. Chem. Phys.*, **87**, 2349 (1987).
25. Obrzut, J., Obrzut, M.J. and Karasz, F.E. *Synth. Met.*, **29**, E109 (1989).
26. Obrzut, M.J. and Karasz, F.E. *Macromolecules*, **22**, 458 (1989).
27. Zbinden, R. "Infrared Spectroscopy of High Polymers." (Academic Press, New York and London, 1964).
28. Fraser, R.D.B. *J. Chem. Phys.*, **28**, 1113 (1958).
29. Bradley, D., Friend, R., Lindenberger, H. and Roth, S. *Polymer*, **27**, 1709 (1986).
30. Hermans, J.J., Hermans, P.H., Vermaas, D. and Weidinger, A. *Rec. Trav. Chim. Pays-Bas*, **65**, 427 (1946).
31. Fraser, R.D.B. *J. Chem. Phys.*, **21**, 1511 (1953).
32. Fraser, R.D.B. *J. Chem. Phys.*, **24**, 89 (1956).
33. Fraser, R.D.B. *J. Chem. Phys.*, **29**, 1428 (1958).
34. Dugay, M. and Fabre, C. *Solid State. Commun.*, **47**, 965 (1983).
35. Kratky, O. *Kolloid-Z.*, **64**, 213 (1933).
36. Kuhn, W. and Grün, F. *Kolloid-Z.*, **101**, 248 (1942).
37. Machado, J.M. PhD Thesis, University of Massachusetts, 1988.
38. Masse, M.A. PhD Thesis, University of Massachusetts, 1989.
39. Vincent, C.A. *Chem. Br.*, **25**, 394 (1989).
40. Yang, H., Huq, R., Farrington, G.C. and Thomas, J.O. *Polym. Prepr.*, **30**, 412 (1989).

41. Wright, P.V. *Polym. Prepr.*, **30**, 402 (1989).
42. Wright, P.V. *J. Macromol. Sci. Chem.*, **A26**, 519 (1989).
43. "Multiphase Polymers: Blends and Ionomers." Utracki, L.A. and Weiss, R.A., ed. (American Chemical Society, Washington, D. C., 1989).
44. Jen, K., Jow, T. and Elsenbaumer, R. *J. Chem. Soc., Chem. Commun.*, 1113 (1987).
45. Foster, C.M., Kim, Y.H. and Heeger, A.J. *Synth. Met.*, **29**, E135 (1989).
46. Gagnon, D.R. PhD Thesis, University of Massachusetts, 1986.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

Previous attempts at synthesizing polyarylene vinylene (PAV) copolymers¹⁻⁵ have always been faced with the difficulty of verifying the copolymeric nature of the system. This investigation has shown that the copolymeric nature of the materials synthesized may be evaluated if a means of distinguishing the different *trans*-vinylene moieties can be found. In this particular case, the *trans*-vinylene IR absorption of the poly(2,5-thienylene vinylene) (PTV) was sufficiently distinct from the equivalent absorption spectra of the other PAV systems investigated. The reliability of this identification has allowed for the confidence in comparing copolymeric activity as opposed to those of molar-equivalent homopolymer blends.

Probing the chemical nature of the poly(1,4-phenylene vinylene-co-2,5-thienylene vinylene) (PPV-co-PTV) copolymeric system has revealed certain details that previously were unavailable. The relative reactivity of poly(1,4-phenylene vinylene) (PPV) and poly(2,5-thienylene vinylene) (PTV) monomers was shown to favor the addition of PTV monomers independent of the active terminus of the growing chain. Moreover, an unusual kinetic behavior was found that described a monomer addition that showed a preference to the addition of PTV monomers but which did not show - within experimental error - any drift in copolymer composition with the drift in monomer concentration. It was also shown that different solvent systems could dramatically change the

monomer activity of the PAV system. In the system investigated, PPV and PTV were shown to copolymerize in water/methanol but (from the data presented by others^{3, 4} in conjunction with the results obtained here) the materials produced in water were either very blocky copolymers or homopolymer blends.

Surprising was the fact that the poly(2,5-dimethoxy-1,4-phenylene vinylene) (PdMeOPV) monomer was found, apparently, not to cross-polymerize with the PTV monomer. Conversely, it was shown that the poly(2,5-dichloro-1,4-phenylene vinylene) (PdClPV) monomer does copolymerize with the PTV monomer to form the chemically distinguishable poly(2,5-dichloro-1,4-phenylene vinylene-co-2,5-thienylene vinylene) (PdClPV-co-PTV) from the equivalent homopolymer blends.

The conducting behavior of the PPV-co-PTV systems studied revealed a very strong dependence on the sequence distribution of the PPV and PTV moieties. The scheme where only the PTV units would be the charge-transfer carriers, showed that a critical conjugation coherence length, that spanned four to five PTV repeat units, was needed to sufficiently minimize the charge-transport energy barrier so that significant conductivities could be observed. It was also observed that a morphological parameter attenuated the conductivities for both the copolymer and the blend in unoriented systems. This was manifested in the blend system as a lower limit of conducting moiety concentration below which significant increases in conductivities would not be observed.

The effects of morphology were emphasized by the substantial increases in the conductivities with uniaxial orientation. This investigation has shown that uniaxial drawing is only one of the factors for the impressive increases in conductivity when the material was stretched. Others^{6, 7} have already hinted at the idea that it was the conversion from an amorphous precursor to a semicrystalline polymer that provided the driving force for the tremendous orientational order obtained from low draw ratios. It was shown here, that due to the random distribution of PTV moieties in the PPV-*co*-PTV chain, the expected dramatic increase in conductivity with orientation or draw ratios does not occur, especially for copolymers with low PTV content, until higher draw ratios and orientation were achieved. This emphasized the need for lateral coherence among crystallites, especially the lateral coherence of individual PTV segments. The drawing process only served to orient the chains, whereas it was necessary to obtain crystallites that accommodated unit cells with lateral PTV coherence in order to attain improved conductivities.

5.2. Recommendations for Future Work

5.2.1. Short Term

A direct extension of the PPV-*co*-PTV synthesis could be made to the PdClPV-*co*-PTV system. This might allow the investigation of reductive doping on copolymers. Similarly, the PPV-*co*-PTV system could be studied with arsenic pentafluoride (AsF₅) doping. In this case, both PPV and PTV segments would be dopable. This should reveal another facet of sequence distribution effects on conductivity.

The kinetics and the possibility of macrocyclic activity may be investigated by a quantitative analysis of the molecular weights of the PPV-co-PTV synthesized at varying reaction times or in conjunction with chain-growth trapping additives. A multiple distribution of molecular weights would clearly indicate such an activity. Similarly, it would be interesting to note whether increases in molecular weights could be obtained by secondary addition of monomers. Likewise, it would be interesting to see if blocky copolymers could be made by a delayed addition of the more reactive species, that is, by allowing the PPV chain to propagate before the addition of the PTV monomer.

The sequence distribution of such polyarylene vinylene copolymeric materials could also be investigated by selectively ^{13}C labeling the monomers used. Alternatively, solid state ^1H NMR studies of the copolymer precursor materials could provide sequence distribution information whenever the pendant units for the segments of the individual components turn out to be dissimilar such as in the case of PPV and PTV precursors having tetrahydrothiophenium fluoroborate salts as opposed to methanol.

5.2.2. Long Term

Hall⁸ has suggested that monomer specificity is a function of electronegativity. Their investigation revealed interactions between electron-rich and electron-poor monomers that resulted in apparently spontaneous initiation, copolymer alternation and bond-forming initiation. The fact that PPV-co-PTV and PdClPV-co-PTV can be formed but the PdMeOPV-PTV and apparently the PPV-PdMeOPV² homopolymerizes seems to suggest that electron-rich and electron-poor

species are needed for copolymerization to occur. A wider range of copolymers with clearly distinguishable *trans*-vinylene units must be investigated. Already, a number of monomers^{1, 8-12} with varying electronegativity have been shown to undergo PAV type polymerization. It should be interesting to see if the varying electronegativities of the monomers define the copolymerization activity of PAV type monomers.

The conductivity behavior of PTV copolymers and the related investigation on the UV spectroscopy and x-ray diffraction patterns of PPV and its oligomers¹³⁻¹⁵ have suggested that only 4 to 5 repeat units were needed in order to simulate the conductive behavior of the high molecular weight polymers. The morphological implications of the blend studies and the oriented PPV-co-PTV suggested that the required repeat units may be somewhat higher than 4 to 5 in order for proper PTV registry to take place. Thus, some method of synthesizing block copolymers must be investigated. The aqueous medium used by Shim *et al.*⁴, tuned properly, may yet reveal blocky materials rather than homopolymers. Some stepwise addition scheme may certainly be devised to provide blocky PTV units. This process would not have the advantage of having a precursor polymer but may show some processability if a flexible spacer were condensed with 5 to 6 repeat units of PTV.

Effort should also go into the investigation of the crystallinity of the range of PPV-co-PTV to further obtain information on the lateral interaction of segments along a random chain. The effect of drawing should be distinguished from the effect of crystallization. The PTV precursor polymer and the PPV-co-PTV copolymers are rubber-like at

room temperature. It should be possible to draw these materials and apply a controlled amount of heat to obtain limited conjugation at varying draw ratios. The tremendous effort in investigating the processing of PAV type materials should be guided by knowledge of which factors are more important to obtain high conductivities.

Finally, the easily regulated PPV-co-PTV composition should provide those who wish to study the complete range of physical behavior, from ionomers of 5-10% ionic content to polyelectrolytes of 100% ionic content, an easily produced and completely soluble system. The limitation would be that the precursors may not be studied under elevated temperatures, however, this should be offset by the availability of a completely soluble system with a 0-100% ionic content - currently not available¹⁶ - and which has been shown to easily exchange counter-ions¹⁷.

5.3. References

1. Han, C-C., Lenz, R.W. and Karasz, F.E. *Polym Commun.*, **28**, 26 (1987).
2. Lenz, R.W., Han, C-C. and Lux, M. *Polymer*, **30**, 1041 (1989).
3. Jin, J-I., Shim, H-K. and Lenz, R.W. *Synth. Met.*, **29**, E53 (1989).
4. Shim, H-K., Lenz, R-W. and Jin, J-I. *Makromol. Chem.*, **190**, 389 (1989).
5. Jin, J-I., Park, C.K. and Shim, H-K. *J. Polym. Sci., Polym. Chem.*, **29**, 93 (1991).
6. Tokito, S., Smith, P. and Heeger, A.J. *Synth. Met.*, **36**, 183 (1990).
7. Masse, M.A. PhD Thesis, University of Massachusetts, 1989.
8. Hall, H.K.J. and Padias, A.B. *Acc. Chem. Res.*, **23**, 3 (1990).

9. Jen, K., Jow, T. and Elsenbaumer, R. *J. Chem. Soc., Chem. Commun.*, 1113 (1987).
9. Yamada, S., Tokito, S., Tsutsui, T. and Saito, S. *J. Chem. Soc., Chem. Commun.*, 1448 (1987).
10. Antoun, S., Gagnon, D.R., Karasz, F.E. and Lenz, R.W. *Polym. Bull.*, **15**, 181 (1986).
11. Askari, S.H., Rughooputh, S.D. and Wudl, F. *Synth. Met.*, **29**, E129 (1989).
12. Ikenoue, Y., Uotani, N., Patil, A.O., Wudl, F. and Heeger, A.J. *Synth. Met.*, **30**, 305 (1989).
13. Obrzut, J. and Karasz, F.E. *J. Chem. Phys.*, **87**, 2349 (1987).
14. Obrzut, J., Obrzut, M.J. and Karasz, F.E. *Synth. Met.*, **29**, E109 (1989).
15. Obrzut, M.J. and Karasz, F.E. *Macromolecules*, **22**, 458 (1989).
16. "Multiphase Polymers: Blends and Ionomers." Utracki, L.A. and Weiss, R.A., ed. (American Chemical Society, Washington, D. C., 1989).
17. Rutt, S. personal communications.

BIBLIOGRAPHY

- Anderson, P.W. *Commun. Solid State Phys.*, **2**, 193 (1970).
- Antoun, S., Gagnon, D.R., Karasz, F.E. and Lenz, R.W. *J. Polym. Sci., Polym. Lett.*, **24**, 503 (1986).
- Antoun, S., Gagnon, D.R., Karasz, F.E. and Lenz, R.W. *Polym. Bull.*, **15**, 181 (1986).
- Antoun, S., Gagnon, D.R., Karasz, F.E. and Lenz, R.W. *Polym. Prepr.*, **27**, 116 (1986).
- Askari, S.H., Rughooputh, S., D. D. V. and Wudl, F. *Preprints, [ACS Division of Polymeric Materials Science and Engineering]*, **59**, 1068 (1988).
- Askari, S.H., Rughooputh, S.D. and Wudl, F. *Synth. Met.*, **29**, E129 (1989).
- Bishop, A.R., Campbell, D.K. and Fesser, K. *Mol. Cryst. Liq. Cryst.*, **77**, 253 (1981).
- Bloor, D., Monkman, A.P., Stevens, G.C., Cheung, K.M. and Pugh, S. *Mol. Cryst. Liq. Cryst.*, **187**, 231 (1990).
- Bradley, D., Friend, R., Lindenberger, H. and Roth, S. *Polymer*, **27**, 1709 (1986).
- Bradley, D.D.C. *J. Phys. D.*, **20**, 1389 (1987).
- Bradley, D.D.C., Colaneri, N.F. and Friend, R.H. *Synth. Met.*, **29**, E121 (1989).
- Brazovski, S.A. and Kirova, N. *J. E. T. P. Lett.*, **33**, 4 (1981).
- Brédas, J.L. *Mol. Cryst. Liq. Cryst.*, **118**, 49 (1985).
- Brédas, J.L., Chance, R.R. and Silbey, R. *Mol. Cryst. Liq. Cryst.*, **77**, 319 (1981).
- Brédas, J.L., Chance, R.R. and Silbey, R. *Phys. Rev.*, **B26**, 5843 (1982).
- Brédas, J.L., Scott, J.C., Yakushi, K. and Street, G.B. *Phys. Rev.*, **30**, 1023 (1984).

- Chandler, G.K. and Pletcher, D. *Spec. Period. Report Electrochem.*, **10**, 117 (1985).
- Chen, D., Winokur, M.J., Masse, M.A. and Karasz, F.E. *Phys. Rev. B.*, **41**, 6759 (1990).
- Chiang, C.K. *Polymer*, **22**, 1454 (1981).
- Chien, J.C.W. "Polyacetylene: Chemistry, Physics and Materials Science." (Academic, New York, 1984).
- Druy, M.A., Rubner, M.F. and Walsh, S.P. *Synth. Met.*, **13**, 207 (1986).
- Dugay, M. and Fabre, C. *Solid State. Commun.*, **47**, 965 (1983).
- Edwards, J.H. and Feast, W.J. *Polymer*, **21**, 595 (1980).
- Emin, D. in *Electronic and Structural Properties of Amorphous Semiconductors* (eds. LeComber, P.G. & Mort, J.) 261 (Academic Press, London, 1973).
- Era, M., Kamiyama, K., Yoshiura, K., Momii, T., Murata, H., Tokito, S., Tsutsui, T. and Saito, S. *Thin Solid Films*, **179**, 1 (1989).
- Fineman, M. and Ross, S.D. *J. Polym. Sci.*, **5**, 259 (1950).
- Fleischman, L. and Anderson, P.W. *Phys. Rev. B*, **21**, 2366 (1980).
- Foster, C.M., Kim, Y.H. and Heeger, A.J. *Synth. Met.*, **29**, E135 (1989).
- Franke, L. personal communications.
- Fraser, R.D.B. *J. Chem. Phys.*, **21**, 1511 (1953).
- Fraser, R.D.B. *J. Chem. Phys.*, **28**, 1113 (1958).
- Fraser, R.D.B. *J. Chem. Phys.*, **29**, 1428 (1958).
- Fraser, R.D.B. *J. Chem. Phys.*, **24**, 89 (1956).
- Gagnon, D.R., Capistran, J., Karasz, F.E. and Lenz, R.W. *Mol. Cryst. Liq. Cryst.*, **118**, 327 (1985).
- Gagnon, D.R., Capistran, J., Karasz, F.E. and Lenz, R.W. *Polym. Bull.*, **12**, 293 (1984).
- Gagnon, D.R., Capistran, J., Karasz, F.E. and Lenz, R.W. *Polym. Prepr.*, **25**, 284 (1984).

- Gagnon, D.R., Capistran, J., Karasz, F., Lenz, R.W. and Antoun, S. *Polymer*, **28**, 567 (1987).
- Gagnon, D.R. PhD Thesis, University of Massachusetts, 1986.
- Garay, R. and Lenz, R.W. *Makromol. Chem. Suppl.*, **15**, 1 (1989).
- Geneis, E.M., Lapkowski, M., Santier, C. and Vieil, E. *Synth. Met.*, **18**, 631 (1987).
- Gourley, K., Lillya, C., Reynolds, J. and Chien, C. *Macromolecules*, **17**, 1025 (1984).
- Granier, T., Thomas, E.L., Gagnon, D.R., Karasz, F.E. and Lenz, R.W. *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 2793 (1986).
- Griffing, J.M. and Salisbury, L.F. *J. Am. Chem. Soc.*, **70**, 3416 (1948).
- Hall, H.K.J. and Padias, A.B. *Acc. Chem. Res.*, **23**, 3 (1990).
- Han, C-C., Lenz, R.W. and Karasz, F.E. *Polym Commun.*, **28**, 26 (1987).
- Heeger, A.J. *Faraday Discuss. Chem. Soc.*, **88**, 203 (1989).
- Heeger, A.J. *Phil. Trans. Roy. Soc. Lond.*, **A314**, 17 (1985).
- Heeger, A.J., Kivelson, S., Schrieffer, J.R. and Su, W.P. *Rev. Mod. Phys.*, **60**, 781 (1988).
- Hermans, J.J., Hermans, P.H., Vermaas, D. and Weidinger, A. *Rec. Trav. Chim. Pays-Bas*, **65**, 427 (1946).
- Horhold, H.-H. and Helbig, M. *Makromol. Chem., Macromol. Symp.*, **12**, 229 (1987).
- Ikenoue, Y., Uotani, N., Patil, A.O., Wudl, F. and Heeger, A.J. *Synth. Met.*, **30**, 305 (1989).
- Inganäs, O. and Lundström, I. *Synth. Met.*, **21**, 13 (1987).
- Jen, K., Jow, T. and Elsenbaumer, R. *J. Chem. Soc., Chem. Commun.*, 1113 (1987).
- Jin, J.-I., Lee, Y.-H., Lee, K.-S., Kim, S.-K. and Park, Y.-W. *Synth. Met.*, **29**, E47 (1989).

- Jin, J-I., Park, C.K. and Shim, H-K. *J. Polym. Sci., Polym. Chem.*, **29**, 93 (1991).
- Jin, J-I., Shim, H-K. and Lenz, R.W. *Synth. Met.*, **29**, E53 (1989).
- Kanbe, M. and Okawara, M. *J. Polym. Sci., (A-1)*, **6**, 1058 (1968).
- Kivelson, S. and Heeger, A.J. *Synth. Met.*, **22**, 371 (1988).
- Koßmehl, G. and Yaridjanian, A. *Makromol. Chem.*, **182**, 3419 (1981).
- Koßmehl, G., Härtel, M. and Manecke, G. *Makromol. Chem.*, **131**, 15 (1970).
- Koßmehl, G., Härtel, M. and Manecke, G. *Makromol. Chem.*, **131**, 37 (1970).
- Koezuka, H., Tsumura, A. and Ando, T. *Synth. Met.*, **18**, 699 (1987).
- Kovacik, P. and Kyriakis, A. *Tetrahedron Lett.*, 467 (1962).
- Kratky, O. *Kolloid-Z.*, **64**, 213 (1933).
- Kuhn, W. and Grün, F. *Kolloid-Z.*, **101**, 248 (1942).
- Lahti, P.M., Modarelli, D.A., Denton, F.R., Lenz, R.W. and Karasz, F.E. *J. Am. Chem. Soc.*, **110**, 7258 (1988).
- Ledwith, A., Galli, G., Chiellini, E. and Solaro, R. *Polym. Bull.*, **1**, 491 (1979).
- Lenz, R., Han, C-C. and Lux, M. *Polymer*, **30**, 1041 (1989).
- Lenz, R.W., Han, C-C., Stenger-Smith, J. and Karasz, F.E. *J. Polym. Sci., Polym. Chem.*, **26**, 3241 (1988).
- Lupinski, J.H. and Moore, R.S. *ACS Symp. Ser. 407 (Polym. Mater. Electron. Packag. Interconnect.)*, 1 (1989).
- Lux, M. personal communications.
- Machado, J.M. PhD Thesis, University of Massachusetts, 1988.
- Machado, J.M., Karasz, F.E., Kovar, R.F., Burnett, J.M. and Druy, M.A. *New Polym. Mater.*, **1**, 189 (1989).
- Masse, M.A. PhD Thesis, University of Massachusetts, 1989.

- Masse, M.A., Schlenoff, J.B., Karasz, F.E. and Thomas, E.L. *J. Polym. Sci., Polym. Phys.*, **27**, 1 (1989).
- McCoy, R.K. personal communications.
- McDonald, R. and Cambell, T. *J. Am. Chem. Soc.*, **82**, 4669 (1960).
- Momii, T., Tokito, S., Tsutsui, T. and Saito, S. *Chem. Lett.*, 1201 (1988).
- Moon, Y.B., Rughooputh, S.D.D.V., Heeger, A.J., Patil, A.O. and Wudl, F. *Synth. Met.*, **29**, E79 (1989).
- Mott, N.F. and Davies, E.A. "Electronic Processes in Non-crystalline Materials." (Clarendon Press, Oxford, 1979).
- "Multiphase Polymers: Blends and Ionomers." Utracki, L.A. and Weiss, R.A., ed. (American Chemical Society, Washington, D. C., 1989).
- Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Mol. Cryst. Liq. Cryst.*, **118**, 333 (1985).
- Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Polym. Commun.*, **25**, 327 (1984).
- Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Polym. Commun.*, **26**, 362 (1985).
- Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Polym. Commun.*, **28**, 229 (1987).
- Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Synth. Met.*, **17**, 639 (1987).
- Murata, H., Tokito, S., Tsutsui, T. and Saito, S. *Synth. Met.*, **36**, 95 (1990).
- Münstedt, H., Köhler, G., Möhwald, H., Naegele, D., Bitthin, R., Ely, G. and Meissner, E. *Synth. Met.*, **18**, 259 (1987).
- Naarman, H. and Theophilou, N. *Synth. Met.*, **22**, 1 (1987).
- Nigrey, P.J., MacInnes, D., Nairnes, D.P. and MacDiarmid, A.G. *J. Electrochem. Soc.*, **128**, 1651 (1981).
- Obrzut, J. and Karasz, F.E. *J. Chem. Phys.*, **87**, 2349 (1987).
- Obrzut, J., Obrzut, M.J. and Karasz, F.E. *Synth. Met.*, **29**, E109 (1989).

- Obrzut, M.J. and Karasz, F.E. *Macromolecules*, **22**, 458 (1989).
- Odian, G. "Principles of Polymerization." (John Wiley and Sons, New York, 1981).
- Österholm, J.E., Yasuda, H.K. and Levenson, L.L. *J. Appl. Polym. Sci.*, **27**, 931 (1982).
- Passiniemi, P. and Österholm, J.E. *Synth. Met.*, **18**, 637 (1987).
- Patil, A.O. *Polymer News*, **14**, 234 (1989).
- Patil, A.O., Rughooputh, S.D.D.V., Patil, A., Heeger, A.J. and Wudl, F. *ACS Preprints, [Polymeric Materials Science and Engineering]*, **59**, 1071 (1988).
- Pichot, C., Guyot, A. and Strazielle, C. *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2269 (1979).
- Potember, R.S., Hoffman, R.C., Hu, H.S., Cocchiaro, J.E., Viands, C.A., Murphy, R.A. and Poehler, T.O. *Polymer*, **28**, 574 (1987).
- Ringsdorf, H., Wünstefeld, R., Zerta, E., Ebert, M. and Wendorf, J.H. *Angew. Chem. Int. Ed.*, **28**, 914 (1989).
- Rutt, S. personal communications.
- Scrosati, B., Selvegi, A. and Owens, B. *Prog. Batteries Sol. Cells.*, **8**, 135 (1989).
- Shacklette, L.W., Maxfield, M., Gould, S., Wolf, J.F., Jow, T.R. and Baughman, R.H. *Synth. Met.*, **18**, 611 (1987).
- Shi, S. and Wudl, F. *Macromolecules*, **23**, 2119 (1990).
- Shi, S. and Wudl, F. *Preprints, [ACS Division of Polymeric Materials Science and Engineering]*, **59**, 1164 (1988).
- Shim, H-K., Lenz, R.W. and Jin, J-I. *Makromol. Chem.*, **190**, 389 (1989).
- Shirakawa, H. and Ikeda, S. *Polym. J.*, **2**, 231 (1971).
- Shirakawa, H. and Ikeda, S., *Chem. Polymer Sci.*, **12**, 929 (1974).
- Shirakawa, H., Louis, E.J., MacDiarmid, A.G., Chiang, C.K. and Heeger, A.J. *J. Chem. Soc.; Chem. Commun.*, 578 (1977).

- Suggate, J.R. *Makromol. Chem.*, **180**, 679 (1979).
- Thakur, M. *Macromolecules*, **21**, 1379 (1988).
- "The Merck Index." 10th. Windholz, M., ed. (Merck & Co., Inc., Rahway, N.J., 1983).
- Tokito, S., Momii, T., Murata, H., Tsutsui, T. and Saito, S. *Polymer*, **31**, 1137 (1990).
- Tokito, S., Smith, P. and Heeger, A.J. *Synth. Met.*, **36**, 183 (1990).
- Vincent, C.A. *Chem. Br.*, **25**, 394 (1989).
- Wegner, G. *Makromol. Chem., Macromol. Symp.*, **1**, 151 (1986).
- Wessling, R. and Zimmerman, R. *U. S. Patents* 3,401,152 (1968).
- Wessling, R.A. *J. Polym. Sci., Polym. Symp.*, **72**, 55 (1985).
- Whitney, D.H. and Wnek, G.E. *Macromolecules*, **21**, 266 (1988).
- Winokur, M., Moon, Y.B. and Heeger, A.J. *Phys. Rev. Lett.*, **58**, 2329 (1987).
- Wnek, G.E., Chien, J.C.W., Karasz, F.E. and Lillya, C.P. *Polymer*, **20**, 1441 (1979).
- Wood, J.H. and Gibson, E. *J. Am. Chem. Soc.*, **71**, 393 (1949).
- Wright, P.V. *J. Macromol. Sci. Chem.*, **A26**, 519 (1989).
- Wright, P.V. *Polym. Prepr.*, **30**, 402 (1989).
- Yamada, S., Tokito, S., Tsutsui, T. and Saito, S. *J. Chem. Soc., Chem. Commun.*, 1448 (1987).
- Yamamoto, T., Hayashi, Y. and Yamamoto, A. *Bull. Chem. Soc. Japan.*, **51**, 2091 (1978).
- Yang, H., Huq, R., Farrington, G.C. and Thomas, J.O. *Polym. Prepr.*, **30**, 412 (1989).
- Yoneyama, H., Wakamoto, K. and Tamura, H. *J. Electrochem. Soc.*, **132**, 2414 (1985).
- Yoshino, K., Onada, M. and Kawai, T. *Optoelectron.-Devices Technol.*, **5**, 1 (1990).

Zbinden, R. "Infrared Spectroscopy of High Polymers." (Academic Press, New York and London, 1964).

Zhong, X.F. and Francois, B. *Synth. Met.*, **29**, E35 (1989).

