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An Investigation of Polymerization via Reductive Coupling of Carbonyls

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ABSTRACT: The viability of carbonyl coupling in the presence of low-valent titanium has been investigated as a step propagation, condensation type polymerization mechanism to create polyvinylene and polypinacol polymers. Although it has been reported by Feast that 4,4′-dibenzoylbiphenyl can be polymerized to number-average degree of polymerization of 100, this study showed that, while oligomers and low molecular weight polymers can be formed, polymers with molecular weights exceeding 6000 could not be synthesized. Polymerization stiffness is a factor; solubility and mechanistic explanations for these results are presented. A threefold increase in molecular weight was observed when the more flexible polypinacol rather than the polyvinylene structures were synthesized, corroborating previous evidence regarding the influence of chain flexibility.

Introduction

In any step polymerization the propagation chemistry must be clean and essentially complete for high polymer to form, and in spite of the breadth of organic chemistry, only a dozen or so reactions satisfy the demands of step polymerization. The coupling of carbonyl functional groups in the presence of low-valent titanium appears to be a candidate step polymerization reaction, since so much research had been done to improve reaction yields. Baumstark was the first to couple dialdehydes and diketones,[1] yielding rings, followed by the extensive research of McMurry and co-workers.[2-9] Mukaiyama[10] demonstrated that aromatic aldehydes and ketones could be coupled in near-quantitative yields to the corresponding olefins and diols using a $TiCl_4$ and Zn combination, as illustrated in Figure 1 for benzaldehyde. Since the introduction of this low-valent titanium coupling chemistry by Mukaiyama, a great deal of work has been performed in the evaluation and improvement of this procedure. Surprisingly, no one has ever reported yields equivalent to those obtained by Mukaiyama with the $TiCl_4$–Zn system.

Extending this chemistry to step polymerization requires the coupling of aromatic compounds possessing two carbonyl functionalities per molecule, and once such a monomer is exposed to the $TiCl_4$–Zn complex, the polymeric pinacolate intermediate could be converted either to a polyvinylene (reflux) or to a polypinacol (hydrolysis; see Figure 2). Until now, only one such attempt had been reported, where Feast's[11] communication reported the polymerization of 4,4′-dibenzoylbiphenyl; M_{GPC} molecular weights suggested a number-average degree of polymerization of 100 had been achieved. Thus, on the basis of Feast's, Mukaiyuma's, and McMurry's work, it appeared that a thorough study of the low-valent titanium induced polymerization of carbonyls would be worthwhile.

Polyvinylenes are of interest due to the potential conjugated nature of their polymer backbones, creating the possibility of conductivity.[12] Conductive polymers synthesized by other methods often are low in molecular weight, which has generated interest in the elucidation of improved methods for their synthesis. Polypinacols would be of interest because they are a novel class of polymers which have not been synthesized by any other method of polymerization.

Since Mukaiyama and co-workers[10] demonstrated that only aromatic aldehydes and ketones could be coupled in near-quantitative yields, all monomers polymerized in this study possessed aromatic moieties. An earlier model compound study involving 2-furfural and 2-thiophenecarboxaldehyde, however, shows that high-yield reactions can be extended to heteroaromatics,[13] thereby allowing polymerization of a heterocyclic dialdehyde.

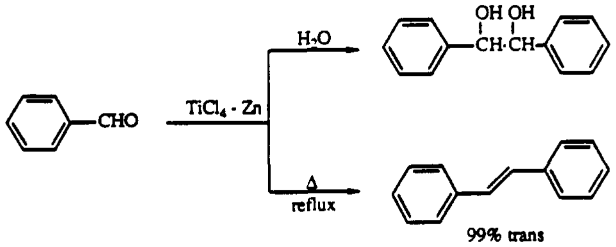

Figure 1. Reductive coupling of benzaldehyde using Mukaiyama's reagent.

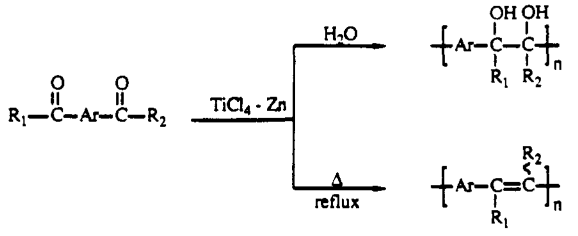

Figure 2. Extension of low-valent titanium chemistry to step polymerization.

Experimental Section

Formation of $TiCl_4$–Zn Reductive Complex for Coupling Reactions. All coupling reactions involved the formation of the Mukaiyama reductive complex before addition of the aldehyde or ketone. This procedure incorporated methods reported in the literature,[7,10] as well as new modifications which increased the reactivity and overall efficiency of the reductive complex.

Into a 200-mL, three-necked, round-bottomed flask which had been evacuated, flame dried, and flushed with argon was place high-purity, 100-mesh zinc powder (2.36 g, 36 mmol). Argon gas was dried by bubbling through concentrated sulfuric acid, followed by a column of sodium hydroxide pellets, and finally a column of anhydrous calcium sulfate (Drierite). A rubber septum was placed in the center neck, a condenser with a drying tube was placed in a side neck, and a slow stream of argon was maintained through the third neck. THF (50 mL), which had been dried by reflux with calcium hydride and distilled before each reaction, was syringed through the septum and cooled to -10 °C with a dry ice/CCl_4 bath. The $TiCl_4$ (2 mL, 18 mmol) was carefully injected into the THF with stirring, resulting in a clear green-yellow solution. $TiCl_4$ was purchased in 200-g quantities in a Sure/

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Seal bottle with a purity of 99.9%, and once the septum on the Sure/Seal bottle showed signs of deterioration (after four or five uses), a new bottle was purchased. The mixture was refluxed 1 h, causing the color to darken to blue and then to black. The complex was allowed to cool before addition of the carbonyl compound.

Polymerization of Dialdehydes with $TiCl_4$–Zn: Polymerization of Terephthaldehyde to Poly(1,4-phenylenevinylene). A solution of freshly sublimated terephthaldehyde (0.8 g, 6 mmol) in 10 mL of dry THF was injected into the reductive complex and refluxed for 10 h. After the reaction was allowed to cool, 100 mL of 10% potassium carbonate solution was added to the reaction and stirred for 30 min. After filtration, the water/THF layer and filter cake were washed with several fractions of diethyl ether. The ether was dried over magnesium sulfate and removed by a rotary evaporator, leaving behind trace amounts of a yellow oil. No starting compound was isolated.

The solid filter cake was placed in a flask with 100 mL of DMSO and refluxed for several hours, causing the solution to become fluorescent yellow. After filtration, the solution was slowly dripped into several hundred milliliters of water, resulting in precipitation of a yellow solid, highly contaminated with inorganic salts. Purification of the polymer was accomplished by refluxing in DMF followed by reprecipitation in water, yielding a yellow brittle film after filtration. The polymer was still found to be contaminated based on elemental analysis results. An adequate ^{13}C NMR spectrum was not obtained due to the low solubility of the polymer. Solid-state ^{13}C NMR was performed with a solid-state probe manufactured by Doty Scientific Inc., but line widths of the resulting spectrum were too broad to be of use. Mp: dec >200 °C. Anal. Calcd for C_8H_6: C, 94.12; H, 5.88. Found: C, 90.65; H, 5.71. ^1H NMR: δ 6.2–8.7 (m). IR (KBr): 3100 (strong, C–H stretch), 1650 (strong, C=C stretch), 1000 (weak), 825 (weak) cm^{-1}. Molecular weight ($\bar{M}_n$): 1050 (end-group analysis).

Polymerization of Furan-2,5-dicarboxaldehyde to Poly(2,5-furylenevinylene). The monomer for this reaction was synthesized by the oxidation of 5-(hydroxymethyl)furfural with lead tetraacetate.[14] Mp: 108–109 °C (lit.[14] mp 100–112 °C). ^1H NMR: δ 7.35 (s), 9.9 (s) (lit.[13] ^1H NMR δ 7.56 (s), 9.88 (s)). ^{13}C NMR: δ 119.2, 154.3, 179.2.

The furan 2,5-dicarboxaldehyde (0.62 g, 5 mmol) was then reacted with the reductive complex in the same manner as above, yielding a crimson oil from the diethyl ether filtrate. Visual inspection of the filter cake revealed the presence of small crimson-colored flakes which were believed to be polymer, but every attempt to separate them from the inorganic salts proved unsuccessful.

Polymerization of Terephthaldehyde to Poly(1,4-phenylene-1,2-ethylenediol). A solution of freshly sublimated terephthaldehyde (0.8 g, 6 mmol) in 10 mL of dry THF was injected into the reductive complex, which had been cooled to 0 °C with an ice bath. The temperature was carefully maintained at 0 °C while the mixture stirred for 10 h, after which it was hydrolyzed with a 10% potassium carbonate solution, stirred for an additional 5 h, and filtered. The lower molecular weight fraction of the polymer was isolated by removal of the water/THF solvent mixture. The higher molecular weight fraction was isolated by refluxing the filter cake in THF for 4 h, followed by filtration and solvent removal. The off-white polymer was purified by reprecipitation in hexane. Mp: softens 90–110 °C, dec >180 °C. Anal. Calcd for $C_8H_8O_2$: C, 70.59; H, 5.88. Found: C, 70.64; H, 6.65. ^1H NMR: δ 4.3–5.3 (m), 5.3–5.8 (m), 6.5–8.0 (m), 9.9 (m). ^{13}C NMR: δ 76.5, 78.0, 125.0, 126.0, 127.0, 141.0. IR (KBr): 3400 (strong, O–H stretch?), 1200 (strong), 1080 (strong) cm^{-1}. Molecular weight ($\bar{M}_n$): 2850 (end-group analysis): 2650 (VPO).

Polymerization of Furan-2,5-dicarboxaldehyde to Poly(2,5-difurylene-1,2-ethylenediol). The furan-2,5-dicarboxaldehyde (0.62 g, 5 mmol) was reacted with the reductive complex in the same manner as above. The lower molecular weight fraction of the polymer was isolated as a crimson oil by removal of the water/THF solvent mixture. The higher molecular weight fraction was isolated as a brittle dark red solid. Mp: dec >220 °C. Anal. Calcd for $C_6H_6O_3$: C, 57.14; H, 4.76. Found: C, 57.35; H, 4.78. ^1H NMR: δ 4.0–4.7 (m), 4.7–5.9 (m), 6.0–6.9 (m), 7.4 (s), 10.0 (m). IR (KBr): 3400 (strong, O–H stretch), 2900 (strong, C–H stretch), 1710 (weak, C=O), 1510 (weak), 1010 (strong) cm^{-1}. Molecular weight ($\bar{M}_n$): 5540 (end-group analysis).

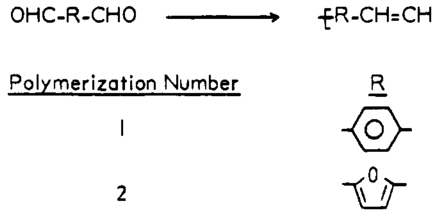

Figure 3. Polymerization of terephthaldehyde to poly(1,4-phenylenevinylene).

Results and Discussion

Synthesis of Polyvinylenes. Initial elemental analysis of the isolated poly(1,4-phenylenevinylene) (Figure 3, polymerization 1) revealed the polymer to be impure, with the experimental carbon value being slightly more than half of its theoretical value. Such a discrepancy could only be caused by a large amount of titanium salt combined with or incorporated in the polymer. The yellow color, however, indicates possible formation of poly(phenylenevinylene).[15]

Infrared spectroscopy of the product supported this explanation with a broad absorption from 800 to 600 cm^{-1}, which is representative of a Ti–O absorption.[16] This absorption is also visible in the IR spectrum of the inorganic filter cake.

Inorganic contamination can partly be explained by an ESR investigation performed by Dams and co-workers on a $TiCl_3$–$LiAlH_4$ reaction mixture,[17] where they found that immediately after deoxygenation to the olefin, a Ti(III) species is π bonded to the product olefin until the reaction is worked up. Therefore, it is feasible that π bonding allows titanium to become incorporated into the polymer matrix, making it difficult to separate from the product, even after hydrolysis workup.

Elemental analysis of a reprecipitated film showed a dramatic improvement in the purity of the polymer, even though contamination was still evident. Likewise, the corresponding IR spectrum showed little evidence of titanium incorporation into the polymer.

NMR analysis of the yellow polymer was very difficult due to its low solubility. Using DMSO-d_6 and allowing a long acquisition time, we obtained a proton spectrum showing a broad signal from δ 6.2 to δ 8.7 for the aromatic protons and a narrower signal at δ 7.9 for the vinyl protons. In addition, a signal peak at δ 9.9 was visible, representing unreacted aldehyde end groups. The latter signal suggests that the reaction is not complete, since aldehyde functional groups are still present. Extending the reaction times had little or no effect on the outcome of the polymerization.

A heteroaromatic monomer, furan-2,5-dicarboxaldehyde, was reacted with the $TiCl_4$–Zn complex in an attempt to make a high molecular weight polyvinylene where a successful polymerization would yield poly(2,5-furylenevinylene) (Figure 3, polymerization 2). With the same procedures as before, little more than a small quantity of a crimson oil could be isolated.

On the basis of the color of the polymerization product during workup (lemon yellow for poly(phenylenevinylene)),[15] coupling of the carbonyls appears to have taken place. The polymer in each case, however, apparently reaches a limiting molecular weight, after which it becomes insoluble and precipitates, and only a low molecular weight oil was isolated. When higher molecular weight fractions were isolated, they were contaminated with inorganic salts. These results suggest that the attachment of solubilizing groups may induce further polymerization by this method, which in fact may explain

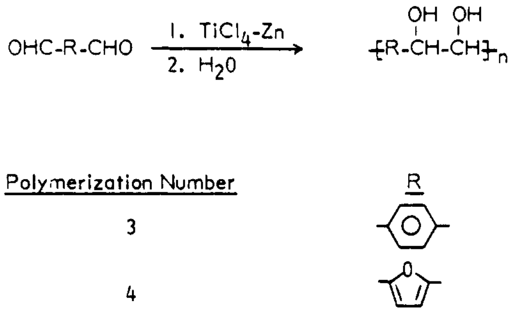

Figure 4. Polymerization of dialdehydes to their respective polypinacols.

Table I
Degrees of Polymerization and Molecular Weights for Polymers Synthesized

polymer and polymn no.	polymer/aldehyde	$\bar{X}_n$	$\bar{M}_n$
poly(phenylenevinylene), 1	96.67/3.33	9	1050
poly(phenyleneethylenediol), 3	98.79/1.21	20	2850
poly(furylenethylenediol), 4	99.05/0.95	43	5540

the higher molecular weights observed by Feast.[11] In his case, the solubilizing groups are the pendant aromatic rings.

Synthesis of Polypinacols. The investigation into possible formation of polymers with McMurry's chemistry was extended to the synthesis of polypinacols, where the presence of hydroxy functional groups would make the polymers more soluble. Two monomers were investigated, terephthaldehyde and furan-2,5-dicarboxaldehyde, which, if successfully polymerized, would yield poly(1,4-phenylene-1,2-ethylenediol) and poly(2,5-furyl-1,2-ethylenediol), respectively (Figure 4, polymerizations 3 and 4, respectively).

Comparisons of the proton NMR spectra of the polymers with the spectra of the analogous model compounds supported the formation of the expected diol repeat units, where hydroxy signals had shifted downfield in both cases. Previous characterization of the pinacol model compounds, 1,2-diphenyl-1,2-ethanediol and 1,2-dithienyl-1,2-ethanediol, with a chiral shift reagent demonstrated a predominant formation of the *dl* isomer over the meso isomer, supporting the speculation that the reaction mechanism proceeds through a cyclic intermediate involving a low-valent titanium surface. As in the case of the model compounds, representative peaks for the meso and *dl* isomers within the polymer chains are recognizable, confirming the projection of a stereochemically random polymer. A major element in the polymer spectra is the presence of an aldehyde signal at δ 9.9 for poly(phenyleneethylenediol) and δ 10.0 for poly(furyleneethylenediol), signifying that the reaction had not gone to completion.

Lengthening the reaction time past 10 h had little or no effect on the extent of reaction but instead increased the amount of polymer formed. Olefin signals were visible in the proton spectra for both poly(phenyleneethylenediol) and poly(furyleneethylenediol) at δ 7.2 and 7.4, respectively, as well as in the ^{13}C spectrum of PPED at δ 141.

Initial molecular weight assessments of poly(phenylenevinylene), poly(phenyleneethylenediol), and poly(furyleneethylenediol) were made by an end-group analysis using the integration data obtained from the proton NMR spectrum for each polymer. The aldehyde peaks in each case are representative of the unreacted end groups for the polymers, and by a comparison of their relative integration values with the rest of the molecule, a number-average degree of polymerization $\bar{X}_n$ was calculated, leading to number-average molecular weight $\bar{M}_n$ values of 1050, 2850, and 5540 for the three polymers, respectively (Table I).

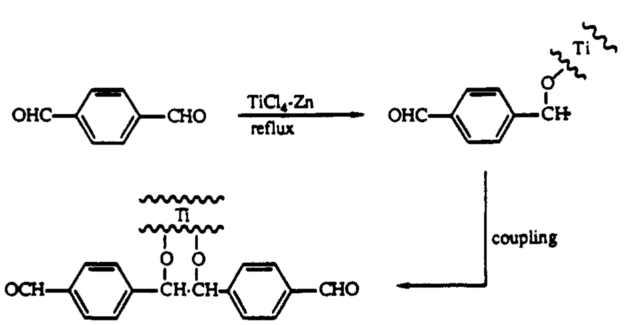

Figure 5. Formation of dimer complex during initial stage of polyvinylene and polypinacol polymerization.

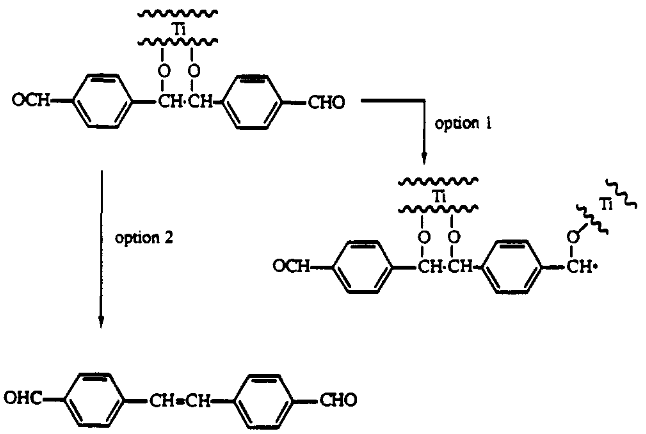

Figure 6. Second stage of polymerization involving one of two route options.

Vapor pressure osmometry (VPO) was used to confirm these data. Dimethyl sulfoxide at 102 °C was chosen as the solvent. An $\bar{M}_n$ value of 2650 for poly(phenyleneethylenediol) was determined, which is consistent with the value of 2850 obtained by end-group analysis. The molecular weights of poly(phenylenevinylene) and poly(furyleneethylenediol) could not be obtained by this method, since the corresponding solutions were apparently too dilute to create an effective (or reproducible) change in the relative vapor pressure of DMSO.

Different Polymerization Mechanisms for Polyvinylene and Polypinacol Formation. The two molecular weight values obtained for poly(phenyleneethylenediol) in this study correspond well enough to verify the assumption that the polymer's end groups are aldehydes. If the polymer chains still possess carbonyl functionalities, why did they not continue to couple and form higher molecular weight polymer? One possibility might be insufficient reaction times, yet it has already been shown that lengthening the reaction times had little or no effect on the molecular weight of the polymers. Answering this question, therefore, requires an understanding of the additional mechanistic features involved in the formation of polymers using McMurry's chemistry.

Although each monomer possesses two carbonyls per molecule, only one of them is reduced within a given time frame prior to coupling. Therefore, the rate of coupling is faster than the rate of reduction due to the reactivity of radical anions. The initial step in both polyvinylene and polypinacol polymerization therefore involves formation of a dimer complex possessing an unreacted carbonyl at each end (Figure 5).

In the case of polyvinylene formation, one of two processes can occur (Figure 6). Option 1 involves further reduction of another carbonyl to a radical anion, resulting in rapid coupling with monomer or another dimer. Option 2 involves the subsequent deoxygenation of the intermediate, causing olefin formation. There is some discrepancy

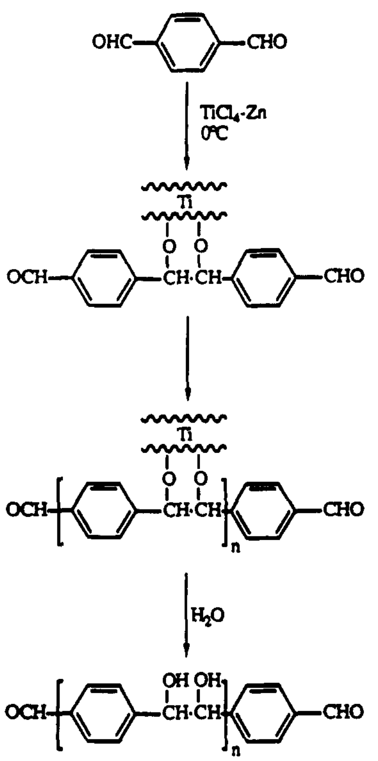

Figure 7. Polymerization mechanism leading to formation of a polypinacol.

in the literature, however, concerning which of these two processes occurs more rapidly. McMurry[7] reported that the rate-determining step in the coupling to olefins must involve loss of oxygen from the pinacolate intermediate but that deoxygenation should be easier in aromatic cases than in aliphatic cases since the C–O bond involved is benzylic. In the mechanistic study performed by Dams and co-workers,[17] however, the rate-determining step is said to be the dimerization and not the cleavage of the oxygens.

Considering this information as well as the molecular weight data obtained for poly(phenylenevinylene), the rate of deoxygenation during the polymerization must be faster than the rate of carbonyl reduction, and the result of this process is the slow formation of the polyvinylene while maintaining carbonyl end groups. When an aldehyde is reduced, coupling then occurs, extending the chain, followed by cleavage of the oxygens. The growth of the polymer chain continues in this fashion until it reaches the limiting molecular weight leading to precipitation. Once the polymer has precipitated, polymerization stops and the carbonyls are no longer susceptible to reduction; thus, the end groups remain intact.

The initial stages in the mechanism for polypinacol formation are the same as described for the polyvinylene case. A carbonyl on the monomer molecule is reduced to a radical anion and couples with another radical anion along a titanium surface, forming the intermediate dimer. However, since the temperature is maintained at 0 °C, deoxygenation does not occur and is therefore not a factor in the polymerization mechanism. Consequently, the polymer chain continues to lengthen while remaining complexed to the titanium (Figure 7).

Since the developing backbone is saturated and therefore more flexible than a polyvinylene, the polypinacol is more soluble and remains in solution longer, allowing a more complete reduction of the aldehydes present. This result explains the increase in extents of reaction from 0.89 for poly(phenylenevinylene) to 0.95 for poly(phenyleneethylenediol) and 0.98 for poly(phenyleneethylenediol). Even with the increased flexibility of the polymer backbone, however, there still exists a limiting chain length after which point reduction of the remaining carbonyl end groups ceases. Once this point has been reached, the length of the reaction time is no longer a factor. In fact, longer reaction times usually resulted in a higher amount of undesired olefin formation.

The final step of the reaction is the hydrolysis of the intermediate polymer to the corresponding polypinacol. Even though this step proceeds in a fashion similar to that for model compounds, longer reaction times were allowed to ensure complete hydrolysis.

Conclusion

It is obvious that chain stiffness plays an important role in the polymerization of aromatic diketones and that solubilizing groups can enhance the polymerizability of the monomer under study. Mechanistic considerations also suggest that polymerizability is influenced by the structure of the reaction intermediate. Also, it should be noted that the titanium complex is consumed on a molar basis, thereby limiting the viability of the polymerization scheme. Future research in this area should be directed at these points.

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References and Notes

(1) Baumstark, A. L.; Bechara, E. J. H.; Semigran, M. J. *Tetrahedron Lett.* **1976**, *37*, 3265.
(2) McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 4708.
(3) McMurry, J. E.; Fleming, M. P. *J. Org. Chem.* **1976**, *41*, 896.
(4) McMurry, J. E.; Fleming, M. P.; Silvestri, M. G.; Hoz, T.; Grayston, M. W. *J. Org. Chem.* **1978**, *43*, 3249.
(5) McMurry, J. E.; Krepski, L. R. *J. Org. Chem.* **1976**, *41* (24), 3929.
(6) McMurry, J. E. *Acc. Chem. Res.*, **1983**, *16*, 405.
(7) McMurry, J. E. *Acc. Chem. Res.* **1974**, *9*, 281.
(8) McMurry, J. E.; Fleming, M. P. *Org. Synth.* **1981**, *60*, 113.
(9) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43* (17), 3255.
(10) Mukaiyama, T.; Sato, T.; Harna, J. *Chem. Lett.* **1973**, 1041.
(11) Feast, W. J.; Millichamp, I. S. *Polym. Commun.* **1983**, *24*, 102.
(12) Kossmehl, G. A. *Semiconducting and Conducting Polymers with Aromatic and Heteroaromatic Units. Handbook of Conductive Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, p 351.
(13) Cooke, A. W. Ph.D. Dissertation, University of Florida, 1989, p 41
(14) van Reijendam, J. W.; Heeres, G. J.; Janssen, M. J. *Tetrahedron* 1970, *26*, 1291.
(15) McDonald, R. N.; Campbell, T. W. *J. Am. Chem. Soc.* **1966**, *82*, 4669.
(16) *Sadtler Standard Spectra*; Sadtler Research Laboratories, Inc.: Philadelphia, PA, 1976.
(17) Dams, R.; Malinowski, M.; Westdorp, I.; Geise, H. Y. *J. Org. Chem.* **1982**, *47*, 248.

Registry No. $TiCl_4$, 7550-45-0; Zn, 7440-66-6; terephthaldehyde, 623-27-8; 1,4-phenylenevinylene (homopolymer), 26009-24-5; furan-2,5-dicarboxaldehyde, 823-82-5; 2,5-furylenevinylene (SRU), 80833-84-7; terephthaldehyde (homopolymer), 27456-81-1; furan-2,5-dicarboxaldehyde (homopolymer), 131490-32-9.