Preparation and Characterization of Poly(arylenevinylene) Copolymers and Their Blends

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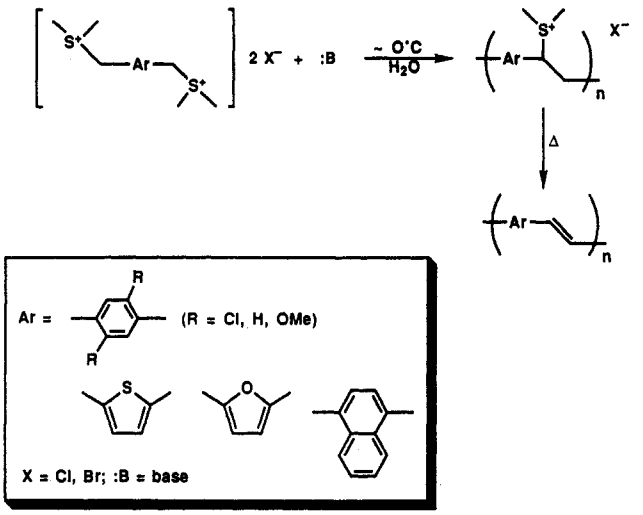
ABSTRACT: The preparation of the poly(arylenevinylene) (PAV) copolymers poly(1,4-phenylenevinylene-*co*-2,5-thienylenevinylene) (PPV-*co*-PTV) and poly[(2,5-dichloro-1,4-phenylene)vinylene-*co*-2,5-thienylenevinylene] (PdiClPV-*co*-PTV) is reported. Infrared spectroscopic analysis of the *trans*-vinylene wagging in the PAV homopolymers, copolymers, and blends showed that the PPV-*co*-PTV and PdiClPV-*co*-PTV copolymers could be readily distinguished from their equivalent homopolymer blends. The relative reactivity ratios at short reaction times in aqueous methanol of the monomeric species leading to poly(1,4-phenylenevinylene) (PPV) and poly(2,5-thienylenevinylene) (PTV) were found to be 0.67 and 6.8, respectively. Efforts to synthesize the copolymer poly(2,5-dimethoxy-1,4-phenylenevinylene-*co*-2,5-thienylenevinylene) led to material that was either very blocky or a homopolymer blend.

Introduction

The advantages of the synthesis of π-conjugated, organic, dopable, conducting polymers via processible precursors or intermediate polymers have been well established. Several π-conjugated polymers of the poly(arylenevinylene) (PAV) type[1-6] have been synthesized via the so-called Wessling precursor polymer route shown in Scheme I.[7] The precursor polymers for many of these π-conjugated polymers have been shown to have good film- and fiber-forming capabilities and to form uniaxially oriented films and fibers at relatively small draw ratios.[8-11] These polymers have variable susceptibility to oxidizing and reducing agents. Thus poly(1,4-phenylenevinylene) (PPV), with a reported redox potential of 0.76 V (against a SCE),[12] is oxidized by arsenic pentafluoride, and the doped polymer displays high conductivities ($\sim 10^3$ S·cm^{-1})[13] in highly drawn films. However, PPV is not readily oxidized by iodine, and the resulting doped polymer displays low conductivities[14] ($\sim 10^{-2}$ S·cm^{-1}). Further, the electron-rich analogues poly(2,5-dimethoxy-1,4-phenylenevinylene) (PdiMeOPV) and poly(2,5-thienylenevinylene) (PTV) are oxidized by iodine, with the doped polymers displaying high conductivities[4,15] (260 and 200 S·cm^{-1}, respectively). We have investigated the correlation of substituent electron donor ability and oxidation potential with the conductivity and processibility of these materials. This work has been hindered by the finding that syntheses of the more electronegative systems, PdiMeOPV and PTV, have a tendency to produce gels and powders in an aqueous system,[16,17] a characteristic that limits their utilization as conductors.

The lower ionization potential of these more electron-rich π-conjugated systems and the ease of processing the parent PPV precursor has led to several attempts to combine their properties by copolymerization.[18-22] The copolymeric nature of the materials synthesized was difficult to establish definitively, however. Indeed, several "copolymers" showed physical properties that were not readily distinguishable from the equivalent homopolymer blends.[20,21] A troublesome uncertainty thus remains as to whether the materials synthesized were indeed copolymers or homopolymer blends.

Scheme I



This difficulty in verifying the copolymeric nature of certain copolymeric PAVs has led us to seek model systems for which copolymeric nature could be unambiguously differentiated from the corresponding homopolymer blends by means of their respective physical properties. Kossmehl et al.[23,24] have shown that the *trans*-vinylene wagging IR absorption of arylenevinylene oligomers—synthesized via the Wittig reaction—was sensitive to the surrounding environment of the arylene units. Moreover, the *trans*-vinylene wagging IR absorption maxima of homooligomeric phenylenevinylene (PV) and thienylenevinylene (TV) were found to be 40 cm^{-1} apart (970 and 930 cm^{-1}, respectively). We aimed to utilize this finding to probe copolymerization by Wessling methodology of PPV and PTV, with the expectation that any copolymeric system synthesized could be distinguished from its molar equivalent homopolymer blends.

Experimental Section

Materials and Equipment. All reactions, unless otherwise stated, were carried out under nitrogen (prepurified, Merriam Graves) that was passed through a drying column of 3-Å molecular sieves and activated calcium sulfate (Drierite). The water used for the aqueous solutions was passed through a demineralizing column (Barnstead) and glass distilled. Organic solvents were all HPLC grade (Aldrich).

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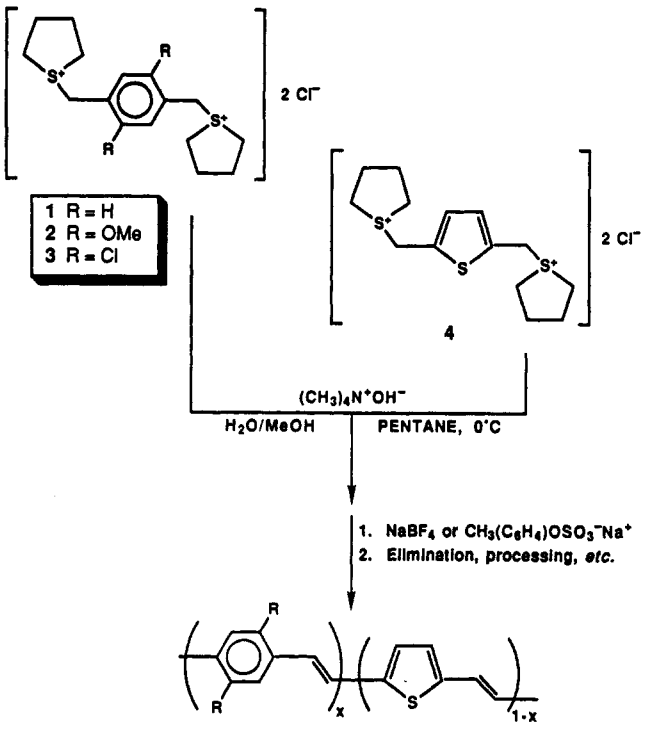
Scheme II



Elemental analyses were obtained from the University of Massachusetts Microanalysis Laboratory. The IR spectra were obtained with an IBM 9000 IR spectrophotometer.

Monomer Preparation. The α,α'-bis(tetrahydrothiophenio)-*p*-xylene dichloride (1 in Scheme II) was prepared from α,α'-dichloro-*p*-xylene (Eastman) and tetrahydrothiophene (Aldrich) as described by Gagnon et al.[25] The α,α'-bis(tetrahydrothiophenio)-2,5-dimethoxy-*p*-xylene dichloride (2 in Scheme II) was prepared from 1,4-dimethoxybenzene (Aldrich) by chloromethylation according to the procedure described by Wood and Gibson,[26] followed by reaction with tetrahydrothiophene.[27] The α,α'-bis(tetrahydrothiophenio)-2,5-dichloro-*p*-xylene dichloride (3 in Scheme II) was prepared from 2,5-dichloro-*p*-xylene as described by McCoy et al.[28] The 2,5-bis((tetrahydrothiophenio)methyl)thiophene dichloride (4 in Scheme II) was prepared by chloromethylation of thiophene using the method described by Griffing and Salisbury[29] and followed by reaction with tetrahydrothiophene.

The chloromethylation of thiophene was carried out in formalin (37% w/w solution in water, Aldrich) and with gaseous HCl (Merriam Graves) or concentrated HCl (Aldrich) used as received. The resultant 2,5-bis(chloromethyl)thiophene was purified by using methods described elsewhere[29] and was immediately treated with a 2.5-fold excess of tetrahydrothiophene in a stirred methanol solution for a minimum of 6 h. The solution was concentrated, whereupon fine, white needles of 4 formed. The crystals were collected and purified by dissolving them in a minimum amount of water, removing the undissolved particles by filtration, and precipitating in acetone at 0 °C. The precipitate was collected on a nitrogen-flushed fritted glass funnel, washed with cold acetone, and dried under vacuum (0.1 mmHg) overnight to give a product with properties consistent with those described previously.[15] The crystals sometimes turned slightly tan during this drying process, but this color change did not affect subsequent reactions. The yields of 4 were quantitative with respect to the 2,5-bis(chloromethyl)thiophene starting compound.

All sulfonium salt monomers were stored under nitrogen at −30 °C, for no longer than 2 weeks in the case of 4 and 6 weeks in the cases of 1 and 2. Eventually, monomer 4 produced a dark red degradation product that was oily at room temperature, and monomers 1 and 2 produced white degradation compounds that did not dissolve in water. All the monomers could be repurified by the methods described herein and used without adverse effects in subsequent polymerizations. The homopolymerizations and copolymerizations could be carried out with good yields even from unrepurified materials, but repurification was necessary for the quantitative calculations of feed versus composition in the copolymer preparation.

Organic-Soluble Precursor Homopolymer Preparation. The precursor homopolymers to PTV and PdiMeOPV were prepared as described by Tokito et al.,[30] who presented procedures for preparing organically soluble PAV precursor polymers. Typical yields were ~35–45%. The PPV polyelectrolyte precursor polymer was prepared and precipitated as the organic-soluble tetrafluoroborate salt by the method of Machado et al.[31]

Organic-Soluble Precursor Copolymer Preparation. The precursor form of the poly(1,4-phenylenevinylene-*co*-2,5-thienylenevinylene) (PPV-*co*-PTV) copolymers were prepared (Scheme II) by using the procedure described below, adjusting the molar feed ratios as necessary and keeping the total monomer concentration at 0.2 M.

In a typical procedure using a 5:95 (4:1) monomer molar feed ratio, a 0.2 M solution of mixed monomers was prepared by dissolving 1.78 g (0.004 98 mol) of 4 and 33.38 g (0.0950 mol) of 1 in 100 mL of water. The solution was filtered and then added to 400 mL of methanol and 500 mL of pentane to form a bilayer solvent system as described by Garay and Lenz.[32] Tetramethylammonium hydroxide (42.1 mL of a 25% w/w solution in methanol, Aldrich) was mixed with 100 mL of water and sufficient methanol added to make 500 mL of a 0.2 M solution. Both solutions were cooled to 0 °C and purged, with stirring, by a steady stream of nitrogen for a minimum of 1 h. The base solution was cannulated under nitrogen pressure into the monomer solution of 1 plus 4, and the reaction mixture was stirred for 2 h, keeping the temperature at 0 °C. The reaction was quenched with dilute hydrochloric acid solution until the solution was neutral to pH paper. The reaction mixture was then stirred continuously and allowed to warm to room temperature with the mixture shielded from light. A saturated solution of sodium tetrafluoroborate ($NaBF_4$) (Aldrich) was next added dropwise until a cloudy solution persisted with stirring. At this point, a fibrous or gumlike precipitate formed, which was collected and washed with copious amounts of water and then methanol. The yield of this material was typically ~5 g (~20%). For the reactivity ratio experiments described below, the reaction was typically halted by addition of acid at a stage that yielded 5–10% of polymer.

The preparation of the precursor form of poly[(2,5-dichloro-1,4-phenylene)vinylene-*co*-2,5-thienylenevinylene] was essentially the same as above, except that often the polymerized solutions would form precipitates even before the addition of $NaBF_4$. These solutions would still become cloudy with the addition of $NaBF_4$, however, and the process was carried out as before to give yields of ~10%. The procedure for the preparation of the precursor form of poly[(2,5-dimethoxy-1,4-phenylene)-vinylene-*co*-2,5-thienylenevinylene] (PdiMeOPV-*co*-PTV) was the same as that described for the PPV-*co*-PTV precursor except that a saturated solution of *p*-toluenesulfonic acid sodium salt was used instead of $NaBF_4$ for the precipitation step. The copolymeric material precipitated at once into a very sticky, gumlike material, which was stirred in a solution of methanol for 24 h at room temperature, after which a fine powder was collected. Typical yields of PdiMeOPV-*co*-PTV precursor were approximately 30%.

Preparation of Eliminated PAV Films. The BF_4 salt of the PPV precursor polymer as well as the corresponding PPV-*co*-PTV and PdiClPV-*co*-PTV precursor copolymers, were dissolved in *N,N*-dimethylformamide (DMF). The PdiMeOPV-*co*-PTV precursor copolymers were dissolved in chloroform/tetrahydrofuran ($CHCl_3$/THF) in a ratio equivalent to the ratio of the corresponding monomer units in the feed. The PTV precursor polymer was dissolved in DMF or THF, depending on whether the solution was intended for use with the PPV or PdiMeOPV, respectively. The PdiMeOPV precursor was dissolved in $CHCl_3$.

The respective solutions were poured into dichlorodimethylsilane-treated flat-bottomed dishes and cast by evacuation to 0.1 mmHg. The homopolymer blend films were prepared from precursor solutions of equal concentration that were filtered and weighed out in appropriate proportions before mixing. Typically, 0.6 g of precursor polymer was used to form a coherent film covering an area of about 600 cm^2.

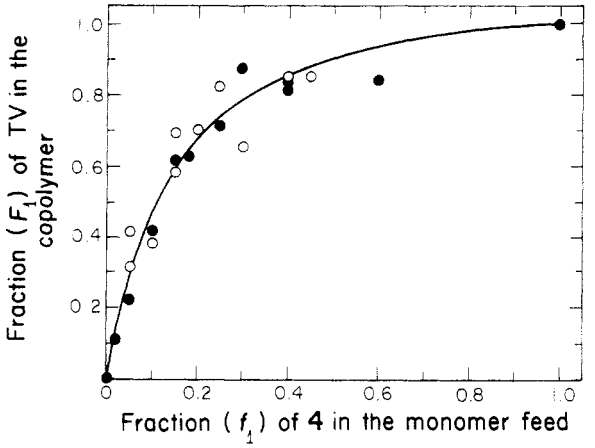


Figure 1. Reactivity plot of the composition F_1 of TV in PPV-*co*-PTV formed as a function of fraction f_1 in monomer (4; Scheme II) feed solution, for 2-min (○) and 2-h (●) reaction times.

The cast precursor films were placed between Teflon sheets and inserted into a Pyrex tube wrapped with heating elements and then heated at 250 °C for a minimum of 6 h under a vacuum of 0.01 mmHg. The resulting eliminated PAV films had a metallic gold luster. The homopolymers of PPV and PdiMeOPV showed negligible amounts of residual sulfur (<0.01% w/w) by elemental analysis. The TV-containing copolymers and homopolymers showed no residual methoxy functionalities using IR after elimination.

Results and Discussion

The procedures employed in the syntheses of PPV-*co*-PTV, PdiMeOPV-*co*-PTV, and PdiClPV-*co*-PTV incorporated recent improvements of the PAV Wessling-type scheme. Thus cyclic sulfonium salts of the xylene monomers were used to produce higher yields and higher molecular weights in the precursor polymers.[18] Pentane, as an immiscible cosolvent, was used to extract the sulfides produced in the polymerization reaction.[32] Tetramethylammonium hydroxide was used as base, instead of sodium hydroxide, because of its better solubility under reaction conditions and because its use eliminates the lengthy dialysis purification step required when sodium hydroxide is employed. Sodium tetrafluoroborate was used to produce an organically soluble PPV precursor polymer[31] by converting the polymer precursor sulfonium chloride salt into a sulfonium fluoroborate salt. Similarly, sodium *p*-toluene sulfonate in methanol was used to convert the 2,5-dimethoxy PPV sulfonium chloride precursor polymer into the organically soluble PdiMeOPV precursor polyether.[4,30,33]

The PPV-*co*-PTV copolymer compositions estimated by elemental analyses for both 2-min and 2-h reaction times are shown in Figure 1. We used a linear formulation[34] to relate the initial monomer (4) feed fraction (f_1) to the fraction of TV in the isolated copolymer (F_1) in eq 1, where

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

r_1 and r_2 are the ratios of homopolymerization (k_{nn}) to copolymerization (k_{mn}) reactivities for the monomers leading to PTV and PPV, respectively. The ratios

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}} \qquad (2)$$

yielded r_1 and r_2 of 6.8 and 0.67, respectively, for the 2-min reaction. This result suggests that the growing chain end, whether a PV or TV unit, preferentially adds TV units.

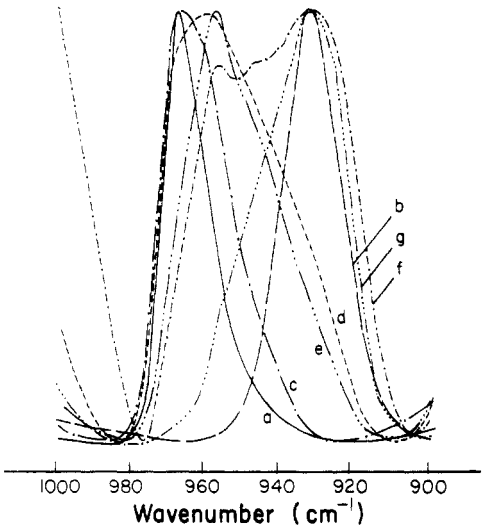


Figure 2. Vinylene out-of-plane infrared spectral region for PPV (a), PTV (b), and PPV-*co*-*N*% PTV polymers (*N* = 11% (c), 23% (d), 42% (e), 62% (f), 88% (g)). Spectra are normalized to the same ordinate scale.

Thus, in this reaction system monomer 4 was 1 order of magnitude more reactive than monomer 1. The 2-min reaction was used to approximate the "instantaneous" monomer concentrations required by eqs 1 and 2. A quicker quenching rate could not be achieved because the inherent inhomogeneity of the reaction mixture, even with rapid addition of the base, presented difficulties during purification. The monomers and oligomers at very short quenching times (15–45 s) were very difficult to separate. The large relative difference between the reactivity ratios of the monomers leveling to PPV and PTV suggests that end-homopolymerization of the less reactive monomer (1) is expected after all of 4 is consumed. We shall return to this point later.

The copolymeric nature of the systems was investigated by methods analogous to the oligomeric model studies of Kossmehl,[23,24] who observed the *trans*-vinylene wagging IR absorption band of the oligomeric PV at 970 cm^{-1} and that for oligomeric TV at 930 cm^{-1}. Insertion of TV segments within the oligomeric PV unit was found to cause a shift in absorption maxima from the value for PPV down to that of PTV. A PV pentad, in which the middle phenylene unit was replaced by a thienylene unit, showed a maximum at 960 cm^{-1}, and an alternating PV-*co*-TV oligomeric material was found to have a maximum at 945 cm^{-1}. We used these precedents in the interpretation of our infrared spectral data.

The IR spectra obtained for the putative PPV-*co*-PTV copolymer synthesized via the Wessling methodology in our study shows the phenomenon of shifting absorption maxima as the TV fraction in the copolymer composition increases (Figure 2). The shift in absorption maxima for the PPV-*co*-PTV compounds as the TV fraction increases shows that there was an increasing insertion of TV units into the copolymer chain. Moreover, the fact that there are no apparent absorption maxima at 970 and 930 cm^{-1} except for copolymers with extreme composition ratios suggests that "blocks" (meaning here sequences of contiguous TV units more than six units long) are not produced in the isolated material in most instances. The IR spectral data suggest that PPV-*co*-PTV isolated by our procedure in most cases has very little "blockiness" and that the arrangement of subunits is presumably random. The fact that the IR absorption pattern of some of the copolymers (notably PPV-*co*-62% PTV) showed discrete maxima at

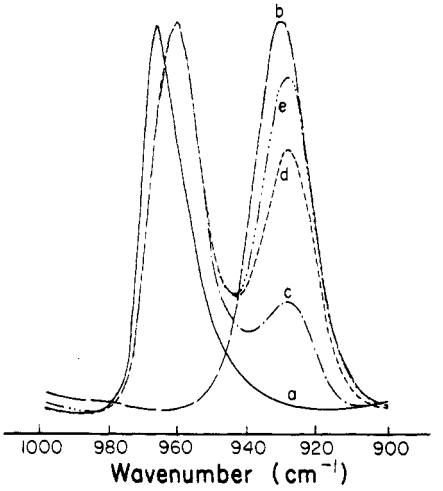


Figure 3. Vinylene out-of-plane infrared spectral region for PPV (a), PTV (b), and PPV/N% PTV blends (N = 20% (c), 50% (d), 80% (e)). Spectra are normalized to the same ordinate scale.

different wavelengths, rather than a single broad absorbance, was interpreted to mean that these measurements *can* discriminate between blocky sequences of each monomer and the copolymeric links, in the cases where blockiness may occur under a particular set of reaction conditions.

Comparison of the IR absorption pattern of the molar equivalent homopolymer blends of PPV and PTV (Figure 3) and of their copolymers emphasizes the distinction between the copolymers and the blends. In these blends the central absorption between 940 and 960 cm^{-1} similar to that of the copolymers in the *trans*-vinylene IR region was absent. Both homopolymeric absorption maxima were apparent throughout the entire range of blend compositions. This result shows that essentially noninteracting PV and TV units were present and that any interactions between the blend components were not sufficient to produce the shifts associated with the copolymeric counterparts. The slight shift in the absorption maxima for both the PPV and PTV components in the homopolymer blends relative to the locations of the maxima of the pure polymers (especially noticeable for the PPV component) are presumably due to the type of polymer–polymer interactions that have been observed for other systems.[35]

The copolymer synthesis runs were repeated and extended to 18 h to determine whether PV end-homopolymerization took place after the more active monomer 4 was consumed. The IR spectra for these materials were found to be very similar to those shown for copolymeric materials synthesized and quenched within 2 h. This result suggests that *in the isolated material* the reaction does not progress to any observable degree after the first 2 h. However, when the reactions were allowed to warm to room temperature—without quenching—*after* the standard 2-h reaction and stirred for another 24 h, the IR absorption pattern at 930 cm^{-1} showed homopolymeric blocks of the TV moiety (Figure 4). This puzzling finding suggests that when the temperature of the reaction is raised, equilibrium shifts or other related factors can further emphasize the superior reactivity of the PTV-forming pathway, thus leading to a reinitiation of the polymerization, essentially as a homopolymerization, to give PTV or long terminal TV blocks. The reinitiation of the reaction upon warming is consistent with our observation that the xylylene-like intermediate in PTV homopolymerization is readily observed by ultraviolet–visible spectroscopy for up to 1 h in solution, an observation implying that it takes some time to generate all of this

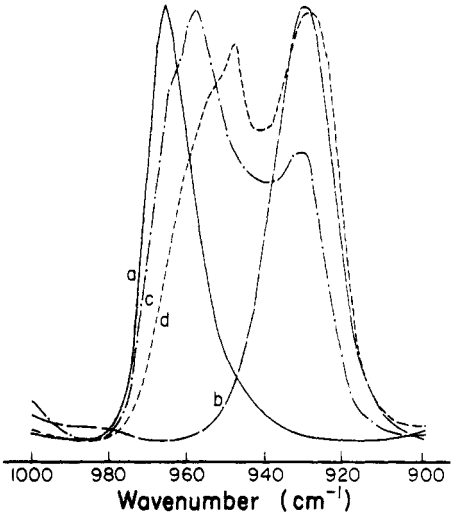


Figure 4. Vinylene out-of-plane infrared spectral region for PPV (a), PTV (b), PPV-*co*-5% PTV (c), and PPV-*co*-15% PTV (d). Copolymers were synthesized at room temperature with extended reaction times.

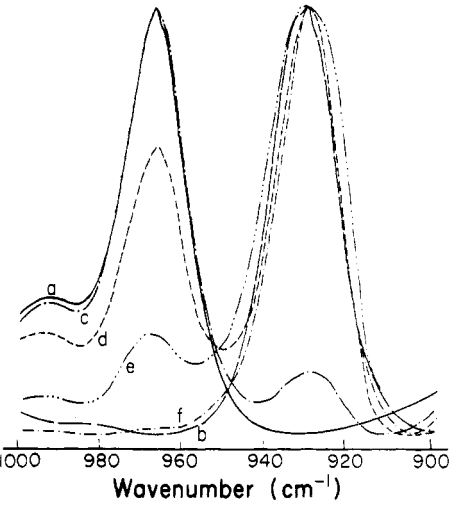


Figure 5. Vinylene out-of-plane infrared spectral region for PdiMeOPV (a), PTV (b), and PdiMeOPV-*co*-N% PTV polymers (N = 20% (c), 40% (d), 60% (e), 80% (f)). Spectra are normalized to the same ordinate scale.

possible reactive intermediate from the starting salt 4 after addition of base. The complex series of equilibria in the Wessling process[35] can plausibly give rise to a variety of more complicated effects such as that described above, in which polymer product compositions can vary considerably with reaction conditions and substitution effects.

The *trans*-vinylene wagging IR absorption maxima of PdiMeOPV[36] and PdiClPV[37] homopolymers were found to be at 970 and 959 cm^{-1}, respectively, so similar analyses for PdiMeOPV-*co*-PTV and PdiClPV-*co*-PTV synthesis could be obtained in principle. The IR spectra (Figure 5) for the materials obtained in the PdiMeOPV-*co*-PTV copolymerization attempts were most consistent with homopolymer blends. No transitional absorption maxima between 970 and 930 cm^{-1} were observed, even when the monomer feed ratio was varied. The possibility of finding diblocks (e.g., A···AB···B) was investigated by analyzing the materials obtained from reactions quenched within 2 min of initiation, in hopes of increasing the ratio of copolymeric linkage relative to that of homopolymeric linkage at early reaction times. The IR spectra obtained for materials from 2-min reactions were essentially identical to those of the 2-h reactions, with no indication of A–B moieties. Moreover, typical homopolymer blends of

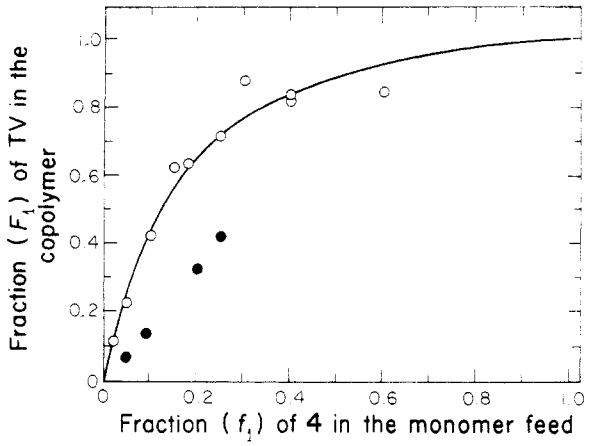


Figure 6. Reactivities of monomer 4 (Scheme II) in copolymerization with PPV in water (●) and in water/methanol (○) solvent systems. Data for copolymerization of PPV in water are from refs 20 and 21.

PdiMeOPV and PTV showed IR spectra virtually indistinguishable from those obtained for the "copolymerization" experiments. The reason for the preferential formation of homopolymers rather than copolymers in the PdiMeOPV–PTV system is still being investigated.

The *trans*-vinylene IR absorption spectra for PdiClPV-*co*-PTV obtained from 2-min reactions indicated that the materials obtained were copolymers rather than homopolymer blends. Transition patterns analogous to those shown by the PPV–PTV system were observed for PdiClPV-*co*-PTV copolymers with various TV contents. Therefore, our results suggest that the PdiClPV-*co*-PTV synthesized by us was a random copolymer rather than a heavily "blocky" material or a homopolymer blend.

A comparison of the present results with those reported by others[20,21] suggests that materials previously isolated were different from ours. The pattern for our copolymerization of PV and TV showed that the reactivity ratio of the monomer leading to PTV relative to the monomer for PPV was greater than that previously reported (Figure 6), but we also note that the materials previously reported were prepared in an aqueous solvent system rather than in the water/methanol system used here. Attempts to duplicate the synthesis of the aqueous reaction materials produced samples that tended to precipitate out of solution during the reaction, giving dark red powders rather than the yellow, gumlike materials precipitated from aqueous methanol. Moreover, thermogravimetric analysis (TGA) scans for the precursor polymers prepared from an aqueous medium produced fewer moles of elimination products than did those synthesized from a water/methanol system. The discrepancy was more substantial for materials with higher TV content. This result led us to conclude that the copolymers produced in water readily resulted in chains with partially eliminated TV precursor units, which caused the materials to precipitate out of solution.

Changed reactivity ratios of the kind shown here have been observed in other systems,[38-40] in which deviations in copolymeric reactivity ratios were observed when the product synthesized was poorly soluble in the reaction media. The deviations were caused by preferential adsorption of one of the monomers into the matrix of the precipitating copolymer. A possible reason for these changes is that 1 is preferentially adsorbed under aqueous conditions onto the still-growing and precipitating copolymer chain, a mechanism resulting in copolymers that appeared richer in PPV than those obtained from our nonprecipitating reaction scheme. Unfortunately, *trans*-vinylene IR absorptions for the materials previously produced in water were not reported, so direct comparison with our work is not presently possible. Thus the copolymeric nature of the materials produced in water is, in our opinion, still to be clearly defined.

Conclusions

This investigation has shown that the copolymeric nature of PAV copolymers may be investigated by using an IR analysis method that distinguishes the vinylene units linking various arylene units. In aqueous methanol, PPV/PTV and PdiClPV/PTV monomer systems formed copolymers. Using the same reaction scheme, we found that the monomer system expected to yield PdiMeOPV-*co*-PTV did not form copolymers. We suspect that the PAV copolymerization is governed by a balance between electron-rich and electron-poor coupling.[41] Moreover, the relative reactivity ratios of the PPV/PTV system were found to be heavily skewed toward TV incorporation. These reactivity ratios are assumed to be specific to the solvent system, although the copolymeric nature of the material produced from water is unclear. Clearly, protocols for verifying the copolymeric nature of PAV systems need to be further defined in order to study confidently the physical characteristics assigned to such putative copolymers.

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