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Synthesis and Electrical Conductivities of Poly(1,4-phenylenevinylene-co-2,3,5,6-tetramethyl-1,4-phenylenevinylene)s

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A series of copolymers of poly(1,4-phenylenevinylene-co-2,3,5,6-tetramethyl-1,4-phenylenevinylene), poly(PV-co-TMPV), were prepared in film forms from the precursor polymer films. The sulfonium salt precursor polymers were synthesized by copolymerization of the mixtures of the respective bis(sulfonium salt) monomers. All of the copolymer films could be doped with $FeCl_3$ to have high electrical conductivities and they showed good air stability. The maximum conductivity of the $FeCl_3$-doped films ranged 10^{-3} to $10^2 Scm^{-1}$ depending on the composition of the copolymer films. However, these copolymer films could not be doped with iodine. The coplanarity of PV and TMPV units in the main chain appears to be affected by steric effect of the methyl groups in the TMPV units.

Introduction

The synthesis of poly(1,4-phenylenevinylene), PPV, and its derivatives and copolymers through the water-soluble precursor route[1-7] is one of the most promising methods to obtain the polymers with extended π-conjugated structures. The PPV derivatives are attracting much interest as new conductive materials and materials for non-linear optics[8-11] because they can be obtained as dense, tough and flexible films and show superior chemical stability. The precursor route has been applied to the preparations of poly(2,5-dimethoxy-1,4-phenylenevinylene)(PDMPV)[4], poly(2,5-thienylenevinylene)(RTV)[5] and their copolymers.[6]

The PPV films obtained in this manner can be easily doped with strong oxidizing agents such as AsF_5 to produce highly conducting materials, but they can not be effectively doped with I_2.[2] Doping PPV films with AsF_5 results in conductivities of 10-40 Scm^{-1} for unstretched samples and 500-3000 Scm^{-1} for uniaxially stretched ones.[2,3,12] In contrast, the PPV derivatives such as PDMPV and its copolymers show easy dopability to I_2 leading to high conductivities. For example, the I_2-doped PDMPV exhibits an electrical conductivity in the order of 10^2 Scm^{-1} at room temperature. The high conductivities observed for doped PDMPV can be attributed to the electron-donating capacity of the methoxy groups on the phenylene group. They lower the oxidation potential of the conjugated polymers.[13]

In the preparation of these polymer films, water-soluble sulfonium salt precursor polymers of high molecular weight are first prepared and cast into films. They are then subjected to thermal elimination to the final polyconjugated polymers. If desired, the precursor films can be uniaxially drawn before or during the thermal elimination reaction. Oriented films show a significantly enhanced conductivity on doping along stretched direction.[14,15,20]

Recently, we prepared poly(2-methoxy-5-methythio-1,4-phenylenevinylene)(PMMPV) and its copolymers,[14] and poly(2-*n*-butoxy-5-methoxy-1,4-phenylenevinylene) (PBMPV)[15] via the corresponding water-soluble precursor polymers. These polyconjugated polymers could be readily doped with oxidizing dopants such as I_2, $FeCl_3$ and $Fe(ClO_4)_3$ to produce materials having a wide range of conductivities depending on the nature of substituents and dopants. In the case of PBMPV, I_2-doped films exhibited conductivities as high as 590 Scm^{-1} and $FeCl_3$-doped ones as high as 2160 Scm^{-1}. The films could be stretched up to a draw ratio of 4-8 before the final elimination.

In this paper, we describe the synthesis of a series of poly(1,4-phenylenevinylene-co-2,3,5,6-tetramethyl-1,4-phenylenevinylene)s, poly(PV-co-TMPV), using different mole ratios of the two respective sulfonium salt monomers in polymerization. The copolymers in film forms were doped with $FeCl_3$ and their electrical conductivities were measured. It was our purpose to learn more about the substituent effect on the electrical properties of PPV derivatives. The synthetic route and the structure of poly(PV-co-TMPV)s prepared and characterized in this investigation are shown below;

1   **2**

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Prepolymer
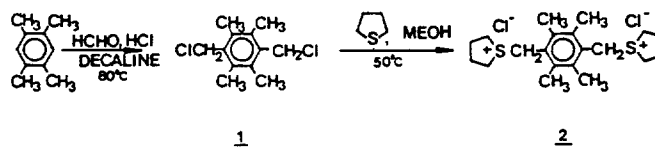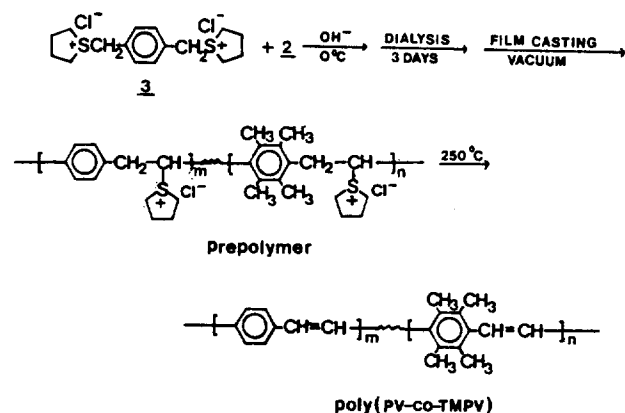
poly(PV-co-TMPV)

For simplicity the copolymers are described as X–poly (PV–co–TMPV) for the composition containing X–mole% of TMPV units. For example, 7–poly(PV–co–TMPV) contains 7 mole% of TMPV units.

Experimental

Synthesis of Monomers. 1,4–Bis(chloromethyl)benzene and 1,2,4,5–tetramethylbenzene, durene, were purchased from Aldrich Chemical Co. and were used as received. 1,4–Bis(chloromethyl)–2,3,5,6–tetramethyl benzene, 1, was prepared by chloromethylation of 1,2,4,5–tetramethylbenzene following literature method.[16]

The compound 1(5.0g; 0.022 mole) and tetrahydrothiophene (7.5 ml; 0.086 mole) were reacted for 20 hrs at 50 °C in 20 ml of methanol.[17] The solution was concentrated by distilling out a part of the solvent and exess tetrahydrothiophene, and was poured into acetone at 0 °C. The precipitate was washed with acetone and dried. The yield of 2,3,5,6–tetramethyl–1,4–phenylenedimethylene bis(tetramethylene sulfonium chloride), 2, was 5.2g (60%). ^{1}H–NMR (D$_2$O); δ 4.9 and 4.8 (d, 4H), 3.6 and 3.4 (m, 8H), 2.6 (m, 8H), 2.4 (S, 12H).

Polymerization. Two sulfonium salt monomers, 2 and 3, were copolymerized at 0 °C for 10 min under a N$_2$ atmosphere in a 0.22M aqueous NaOH solution containing equivalent weight of NaOH. The total molar concentration (0.455M) of the two monomers were kept constant, but their molar ratio was varied. The reaction was quenched by neutralization with 1M–HCl standard solution. The precursor polymer solutions were dialyzed against deionized water using a dialysis tube (Sigma, molecular weight cut–off; 12,000) to remove low molecular weight species. The films obtained by casting from aqueous solutions of precursor polymers were subjected to thermal elimination in vacuo (10^{-2} torr) at 250 °C for 10h to transform them into the final polyconjugated polymer films. If desired, the precursor polymer films were uniaxially drawn at 120 °C using a zone–heating apparatus before the final thermal elimination process.

Characterization. The compositions of copolymers were determined through ^{1}H–NMR spectroscopic analyses of the corresponding precursor polymers. Since precursor polymers are highly hygroscopic, water had to be removed by a specially deviced process; the aqueous solution of a dialyzed precursor polymer was poured into acetone–d$_6$ precipitating the polymer. The precipitate was collected on a filter paper and washed with acetone–d$_6$. And the polymer was

Table 1. Synthesis, Composition and Inherent Viscosities of Precursor Polymers

Copolymers	Monomer Conversion, mole %	Molar Ratio in Feed, 3:2	Molar Ratio of m:n in Polymer*	Inherent Viscosities, dl/g
3–poly(PV–co–TMPV)	61	90:10	97.4:2.6	2.59
7–poly(PV–co–TMPV)	52	80:20	92.6:7.4	2.16
18–poly(PV–co–TMPV)	52	50:50	82.5:17.5	2.97
30–poly(PV–co–TMPV)	41	20:80	70.0:30.0	2.02
42–poly(PV–co–TMPV)	33	15:85	58.3:41.7	2.38

*Here, the values of *m* and *n* simply describe the overall compositions, but not the lengths of each segments.

redissolved in D$_2$O and then reprecipitated into acetone–d$_6$. And the polymer was redissolved in D$_2$O and then reprecipitated into acetone–d$_6$. This procedure was repeated twice more. Finally, the polymer was dissolved in D$_2$O for ^{1}H–NMR spectral analysis. Elemental analysis of the final, polyconjugated copolymers was also attempted to find their compositions. But we found that contents of carbon and hydrogen are rather insensitive to compositional variation. Therefore, determination of copolymer compositions was relied soley on the ^{1}H–NMR spectroscopic analysis of precursor polymers. The inherent viscosity values of the dialyzed precursor polymers were measured at 30 °C for aqueous solutions containing 0.05M Na$_2$SO$_4$. The concentration of the precursor polymers were 0.20 to 0.30 g/dl.

^{1}H–NMR spectra were recorded on a Brucker AM 300 spectrometer. IR spectra were obtained on a Mattson Alpha Centauri FT–IR spectrometer. The differential scanning calorimetric (DSC) thermograms were recorded on a DuPont's DSC 910 instrument and thermogravimetry was performed on a Mettler 3000 thermal analyzer. UV–VIS spectra of the final polymer films were obtained on a Hewlett Packard 8452 A spectrometer. Doping with FeCl$_3$ was carried out at room temperature in nitromethane solution of the dopant (0.1M) under a nitrogen atmosphere. Electrical conductivities were measured by the four–probe method by evacuating the doping chamber to a pressure of 10^{-5} torr. Carbon paste was employed for electrical contact.

Results and Discussion

Polymerization to Precursor Polymers. Table 1 summarizes the data for monomer conversions to precursor polymers and their compositions. Conversions were estimated by titration of the final polymerization mixture with 1.0N–HCl. The degrees of monomer conversions (33–61%) to precursor polymers are comparable to or slightly lower than those reported for other similar polymerization systems.[18,19] One interesting phenomenon noted from the data in Table 1 is the gradual decrease in conversion with content of the tetramethyl substituted monomer in feed. Since the reaction time for all of the polymerization reactions was the same, 10 minutes,
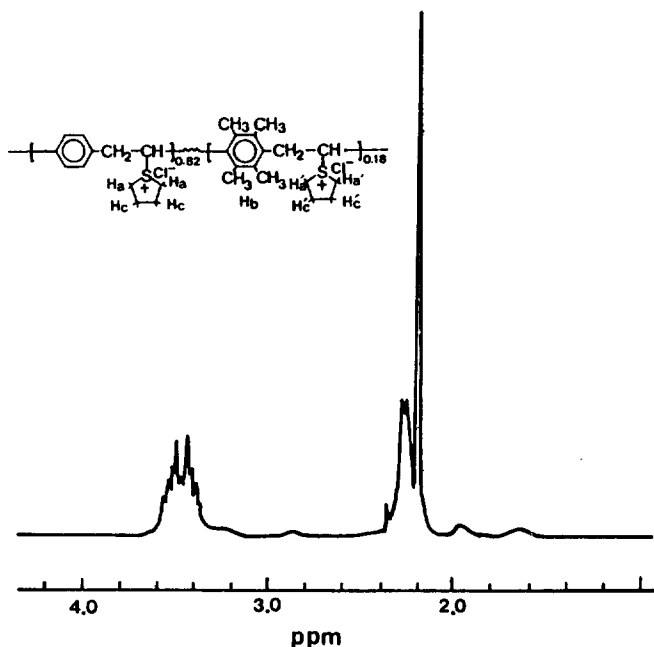
Conductivities of Poly(tetramethylphenylene vinylenes) Copolymers

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Figure 1. The Characteristic ^{1}H-NMR peaks of the precursor polymer of 18-poly(PV-co-TMPV) in D_2O.

Figure 2. IR spectra of (a) the precursor polymer and (b) final vinylene copolymer of 18-poly(PV-co-TMPV).

it appears that the tetramethyl substituted monomer retards the reaction.

The inherent viscosity values of the dialyzed polymers range from 2 to 3 dl/g. This suggests that the molecular weights of the present polymers are rather high. The solution viscosities of these precursor polymers were determined in the presence of Na_2SO_4 in order to avoid the possible artefact arising from the extended conformation in dilute solutions of polyelectrolytic polymer chains.[6,20]

We tried to determine the compositions of precursor polymers through elemental analysis, but we found that reproducibility was rather poor. Complete and selective removal of water from the precursor polymers could not be achieved without premature, partial elimination of tetrahydrothiophene and HCl during drying, which is believed to be the reason for the unsatisfactory results of elemental analyses. Therefore, we tried to estimate the contents of the two repeating units by ^{1}H-NMR spectroscopic analysis. Water (H_2O) was removed by repeated dissolution and precipitation of the precursor polymers using the D_2O-acetone-d_6 solvent-nonsolvent pair. A portion of a representative ^{1}H-NMR spectrum is given in Figure 1 for the precursor polymer prepared from 1:1 mole ratio of 2 and 3 in feed. The protons labeled Ha, Ha', Hc and Hc' appear as multiplets at δ 3.3–3.7 and δ 2.1–2.4, respectively. We could estimate the mole ratio of the two structural units from the areas of these two peaks. The results thus obtained are included in Table 1. According to the results, the amount of 2 moiety incorporated in copolymers is consistently much lower than the amount of 2 taken in feed suggesting that the monomer 2 is significantly less reactive than the monomer 3.

We tried to synthesize a precursor polymer solely from the monomer 2. The polymer, however, precipitated out of the reaction mixture as it was formed. The presence of four methyl substituents attached to the benzene ring certainly reduces the solubility of the resulting polyelectrolyte poly-
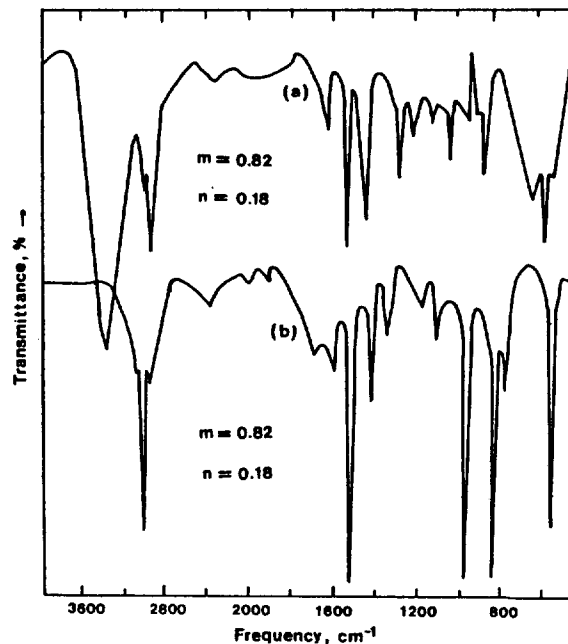
mer in water and causes precipitation. Although it may be possible to convert the precursor polymer to an organic soluble composition from which films can be obtained,[21,22] we did not pursue it any further and have left it for a future task.

All of the precursor polymer films cast from aqueous solutions after dialysis, appeared homogeneous and transparent. They could be stretched uniaxially at about 120 °C up to a draw ratio of 7. The IR spectra (Figure 2a) of the precursor polymers exhibit a very broad absorption at 3100–3650 cm^{-1} due to absorbed water, which disappears in the spectra (Figure 2b) of the final polyconjugated polymer films. Figure 2a shows absorptions at about 3040 and 1520 cm^{-1}, respectively, for aromatic C-H and C=C stretching vibration modes. The C-H bending absorption of CH_3 group appears at 1420 cm^{-1}.

Thermal Elimination of Polyconjugated Polymers. Thermal properties of the precursor polymers were studied by thermogravimetry (TG) and DSC with a heating rate of 10 °C/min. Representative TG and DSC thermograms are shown in Figure 3. The major weight loss occurred up to 200 °C according to TG thermogram. The rapid weight loss up to 100 °C is due to evaporation of absorbed water and partial elimination of HCl and tetrahydrothiophene. DSC analysis, however, reveals two major endothermic processes at about 100 °C and 140–230 °C. The low temperature endotherm corresponds mainly to the loss of water and the higher temperature one to the elimination of HCl and tetrahydrothiophene. The weight loss above 385 °C is attributed to the decomposition of the polyconjugated polymer. Based on such analysis, in order to insure complete elimination reaction, all of the precursor polymers were subjected to thermal elimination at 250 °C for 10 hours at the pressure of 10^{-2} torr.

The IR spectrum of a copolymer containing 17.5% of durene unit, 18-poly(PV-co-TMPV), shown in Figure 2b, exhibits a strong absorption at 970 cm^{-1} arising from the *trans* vinylene = C-H out-of-plane bending motion. This absorp-
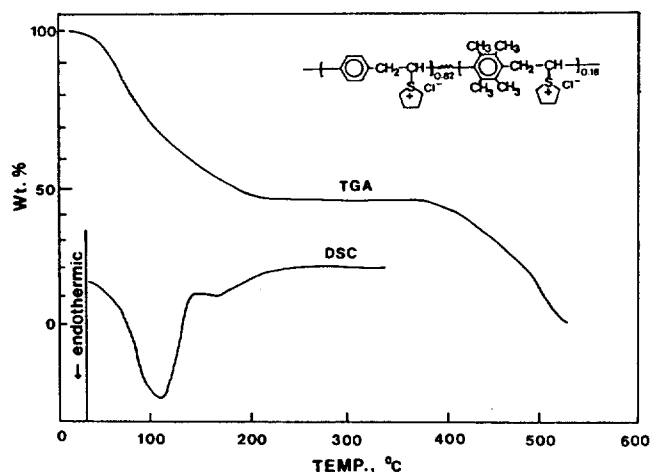
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Figure 3. TGA and DSC thermograms of the precursor of 18-poly (PV-co-TMPV).

Figure 4. UV-VIS spectra of PPV and poly(PV-co-TMPV)s, (a) PPV; (b) 3-poly(PV-co-TMPV); (c) 7-poly(PV-co-TMPV); (d) 18-poly(PV-co-TMPV) and (e) precursor polymer of 18-poly(PV-co-TMPV).

tion indicates that the vinylene C=C bonds formed are of *trans* configuration.[2,23,24]

Figure 4 shows UV-VIS spectra of thin films of a precursor copolymer and fully eliminated polyconjugated copolymers. For comparison purpose, a spectrum of a PPV film prepared separately by us also is included in the figure. The maxima of the longest wave length absorptions for $\pi-\pi^*$ transitions are 440, 430, 400 and 390 nm, respectively, for PPV, 3-poly(PV-co-TMPV), 7-poly(PV-co-TMPV) and 18-poly (PV-co-TMPV). The film of the precursor polymer for 18-poly(PV-co-TMPV) exhibits a weak absorption maximum at about 320 nm, which is ascribed to premature, partial elimination reactions occurred during film casting. As described above, we made a rather unexpected observation that the UV-VIS absorption maximum position gradually shifted toward shorter wave length (blue or hypsochromic shift) as the content of the TMPV unit in the copolymers increased.

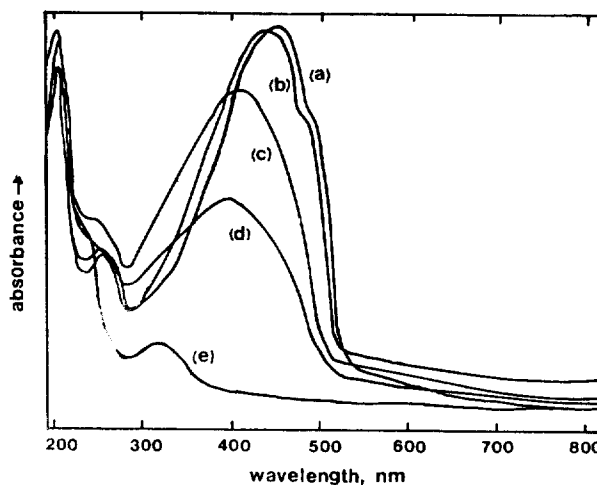This suggests that the four methyl groups in durene unit

reduce effective π-conjugation between phenylene and vinylene units, which is in contrast with the fact that methyl group usually causes red or bathochromic shift.[25] This anomaly can be attributed to the destruction of coplanarity of phenylene vinylene units by the presence of four methyl groups in TMPV units that exert steric crowding. A molecular model clearly demonstrates that methyl protons are in too close proximity to vinylene protons if phenylene and vinylene units are assumed to be coplanar. In order to avoid such steric crowding, the phenylene rings have to twist around to a certain degree relative to each other and the π-system looses coplanar overlapping. The loss of coplanarity would diminish the effective π-delocalization resulting in blue shift in UV-VIS spectra. This phenomenon is expected to be more pronounced as the content of TMPV units increases in copoly-

Table 2. The Degree of Doping and Electrical Conductivities of Poly(PV-co-TMPV)s
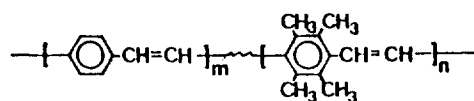
Copolymer	Molar ratio of *m:n*	Draw ratio *L/Lo*	Degree of doping		Maximum Conductivity, Scm⁻¹
			Wt.%	FeCl₄⁻/RU*	
PPV	100:0	5	~0	~ 0	6.0×10^{-7}
		1	~0	~ 0	5.0×10^{-7}
3-poly(PV-co-TMPV)	97.4:2.6	5	12	0.06	2.5×10^{1}
		1	13	0.07	6.8×10^{-1}
7-poly(PV-co-TMPV)	92.6:7.4	5	61	0.33	1.6×10^{2}
		1	95	0.51	7.5
18-poly(PV-co-TMPV)	82.5:17.5	5	26	0.15	1.1×10^{1}
		1	44	0.25	1.2
30-poly(PV-co-TMPV)	70.0:30.0	5	24	0.14	1.0×10^{-1}
		1	12	0.07	5.0×10^{-2}
42-poly(PV-co-TMPV)	58.3:41.7	5	11	0.07	4.5×10^{-3}
		1	13	0.08	2.5×10^{-3}

*RU stands for average repeating unit.
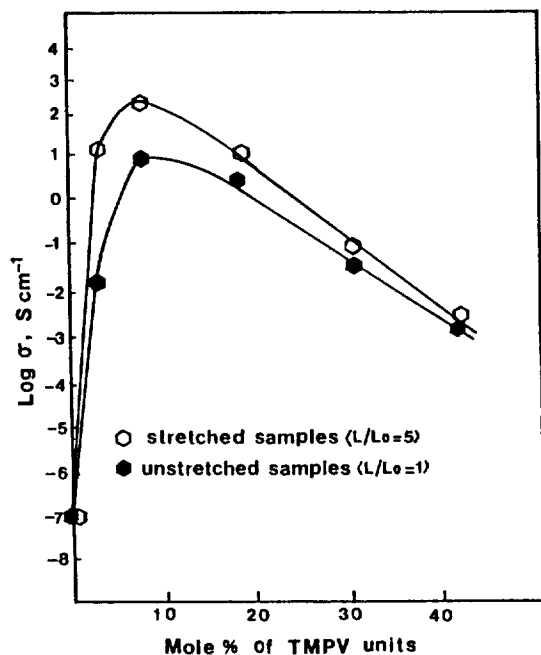
Figure 5. Maximum conductivities of poly(PV-co-TMPV)s doped with $FeCl_3$.

the electron–donating property of methyl groups that facilitate easier doping or oxidation of the polymer chain by the dopant, $FeCl_3$. The presence of methyl substituents on TMPV units, of course, is expected to cause a morphological changes probably leading to increase in the interchain distance. This also will make it easier for the doping species to approach polymer chains. Such positive effects by methyl substituents, however, are reduced when the content of TMPV units becomes high because of destruction of coplanarity of phenylene vinylene units as discussed above in the UV–VIS absorption characteristics of these copolymers. This effect should diminish the degree of π–electrons delocalization, which in turn is anticipated to lower the conductivity. In other words, the negative steric effect by the methyl substituent overtakes its positive electronic effect at high contents of TMPV units; competition between the two opposing effects by the methyl substituents results in such a dependence of electrical conductivity on the composition as we observed for the present copolymers. Our results emphasize how important it is to consider both electronic and steric effects when the dependence of electrical conductivity on the nature of substituents is to be studied.

mers, which is in accord with what we actually observe in this investigation.

Electrical Conductivity. Electrical conductivities of polymer films (15–20 μm thick) were measured at room temperature using a standard four–line probe technique. All of the undoped polymer films had conductivities less than 10^{-6} Scm^{-1}, but their conductivities increased rapidly on doping with $FeCl_3$. The maximum conductivity values for stretched and unstretched polymer films, draw ratios and degree of doping are listed in Table 2. We stopped doping the polymers in $FeCl_3$ solution in nitromethane after 5–20 minutes depending on the thickness and composition of the films. Prolonged doping damaged the integrity of the films and some of them even broke apart when left too long in the dopant solution.

The data shown in Table 2 reveal a few interesting points. The copolymer films were readily doped with $FeCl_3$ in contrary to the fact that PPV films are hardly doped with the same dopant. The degree of doping and the maximum conductivity value increased rapidly initially with the content of TMPV unit in the copolymer reaching the maximum at the composition containing about 7 mole% of TMPV unit followed by a gradual decrease (Figure 5). As given in Table 1 the copolymer film containing 7.4 mole % of TMPV units, when doped with $FeCl_3$, showed a maximum conductivity of 1.6 × 10² Scm^{-1} for the stretched sample and 7.5 × 10⁰ Scm^{-1} for the unstretched sample, respectively. The conductivity of stretched fims, in general, is an order of magnitude greater along the stretching direction than the conductivity of the unstretched, original films. Similar observations were repeatedly reported for many other polymers.[6,15,20]

Now a question arises why electrical conductivity reaches the maximum value followed by a steady decrease as the content of TMPV units in copolymers increases. Initial increase in electrical conductivity with TMPV unit can be ascribed to

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Carbonylation of Benzal Chlorides to Alkyl Phenylacetates using Fe(CO)₅

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Various substituted benzal chlorides are converted into alkyl phenylacetates ($ArCH_2COOR$) under CO atmosphere on reaction with a catalytic amount of $Fe(CO)_5$, a base, and an alcohol. The optimum conditions are found as atmospheric pressure of CO, 40 °C, potassium hydroxide as base, and medium of alcohol.

Introduction

The technology of transition metal complexes catalyzed carbonylation reaction is being currently used for large volume chemicals.[1] Many applications are reported on the carbonylation of benzyl halides with CO using cobalt,[2] Iron,[3] ruthenium,[4] rhodium,[5] and palladium[6] complexes. However, there are a few reports on the carbonylation of benzal halides as the geminal dihalide compound to give alkyl phenylacetates[7] and phenylacetic acids.[8] As the similar report, cobalt catalyzed carbonylation of methylene dihalides leads to the corresponding carboxylates in the presence of Zn powder.[9]

We herein wish to report a simple method for $Fe(CO)_5$ catalyzed carbonylation of benzal chlorides which leads to alkyl phenylacetates in moderate yields in the presence of base under CO atmosphere.

Results and Discussion

Benzal chlorides react with a variety of alcohols in a catalytic amount of $Fe(CO)_5$ at 40 °C under an atmospheric pressure of CO for 20 hours to give alkyl phenylacetates in moderate yields.

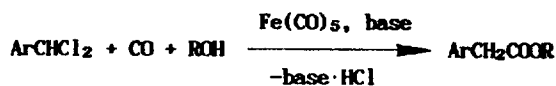particularly, in these reactions, the effects of reaction pa-

$$ArCHCl_2 + CO + ROH \xrightarrow[-base \cdot HCl]{Fe(CO)_5, \ base} ArCH_2COOR$$

Equation 1

rameters on the alkoxycarbonylation of benzal chlorides in the presence of alcohols are discussed in details below. In Table 1, a series of bases are screened for carbonylation of benzal chloride with ethanol at atmospheric pressure of CO. Base in this reaction is used for the purpose of both acid scavenger and catalyst activator. Of the several different bases examined (KOH, K_2CO_3, $NaOEt$, $Ca(OH)_2$), KOH is by far the best for selective carbonylation (No. 1), although side products such as toluene and benzaldehyde are generated in some extents. When $NaOEt$ is used, the reaction proceeds in small quantities and remained part is recovered as reactant (Nos. 10–11). When $Ca(OH)_2$ is used, the reaction does not proceed (Nos. 12–13).

In the use of KOH, the reaction temperature gives a small contribution in the reaction course. At room temperature, product obtained in lower yield (28%, No. 3) than temperature range of 40 °C to 70 °C (40%, Nos. 1, 4). And CO pressure inversely effects on the formation of carbonylated product (No. 14). But in the case of K_2CO_3, CO pressure does not change very significantly the amounts of carbonylated product (Nos. 9, 15–16).

Table 2 summarizes the carbonylation of various benzal chlorides in the presence of KOH. In the case of benzal chloride, the highest yield of carbonylated product is obtained using ethanol. Other alcohols, such as methanol, n–, iso–propanol, or n–butanol give low yields compared with ethanol.

The carbonylation of substituted benzal chlorides is studied using ethanol. Chlorobenzal- and methylbenzal chlorides give similar yields for carbonylation compared with