

Polymer-supported copolymerization of poly(phenylene vinylene)

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SUMMARY

A series of phenyl ring di-substituted α,α' -dichloro-p-xylene monomers were copolymerized in situ onto a cross-linked chloromethylated polystyrene resin. A phase-transfer catalyst was employed to facilitate this multiphase heterogeneous polymerization. The electrical as well as the thermogravimetric properties of the conducting grafted resins are reported.

INTRODUCTION

Typical intrinsic conducting polymers have inflexible conjugated backbone structures which prohibit them from processing by conventional methods (1-3). Various techniques have been adopted to improve their processability. They included: electrochemical synthesis in which a 'doped' conducting polymer is deposited directly on a finishing substrate (such as a gel-supported electrode), preparation of a soluble precursor for the conducting polymer, making block or graft copolymer of the conducting species with a soluble component, using a special doping carrier such as AsF_3 , etc. (1-3). The direct deposition method has the advantage of developing a 2 dimensional pattern on a substrate using less steps and the mechanical or dielectric strength for the circuitry is provided by the substrate.

Recent studies (4,5) have indicated that phenyl ring di-substituted α,α' -dichloro-p-xylene monomers can be polymerized to di-substituted poly(p-phenylene vinylene) (p-PPV) oligomers of intermediate molecular weight using phase-transfer catalyzed (PTC) polymerization procedures. The solubility of the conjugated polymer was found to increase with the bulkiness of the di-substituted pendant group. Instead of solvent casting, however, in this report the conducting polymer was grafted onto a chloromethylated polystyrene resin having the same reactive functional group as the monomer. Some applications for the conducting polymer grafted resin are such as filler for a conductive composite, color pigment, reactive polymer support, etc..

Recent findings (6,7) also demonstrated that the p-PPV conducting polymers can be used to fabricate light emitting diode or other nonlinear optical devices. Our preliminary investigation has indicated that the p-PPV grafted resin has a much stronger photo-luminescent effect than a solvent casted thin film based on the same di-butoxy phenyl ring substituted monomer after illumination with an Excimer laser at a 308 nm wavelength. The enhanced effects are the results of larger surface area for fluorescence as well as quenching effects of the resin matrix.

EXPERIMENTAL

All chemicals and solvents were reagent grade and used 'as received' unless specified otherwise. The supporting polymer resin used was a chloromethylated polystyrene (CMPS) cross-linked with 2% divinyl benzene (DVB) beads from Merck. The resin has an apparent specific volume of 2.5 mL/g (approx. 60-80 mesh size) and a chlorine content of 4-5% (i.e., 0.47 mmole Cl/g). The monomers used and their abbreviations were: 1,4-bis(chloromethyl)-2,5-dibutoxybenzene (p-BuODCX); 1,4-bis(chloromethyl)-2,5-dimethoxybenzene (p-MeODCX); 1,4-bis(chloromethyl)-2,5-dimethylbenzene (p-MeDCX); and α,α' -dichloro-p-xylene (p-DCX). All monomers, except p-DCX, were prepared in our laboratory using methods described earlier (4).

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A typical polymerization procedure is as follows. 0.3 gm of the CMPS was swelled in a 10 mL 50/50 (v/v) mixture of dimethyl sulfoxide (DMSO) and toluene. 10 mL of 55 wt. % sodium hydroxide solution was added to the resin together with 1 gm of sodium chloride. The solution was stirred in a 40-60°C water bath until complete dissolution of alkali and salts. Different molar ratios (0.5, 1, 5, 10, 20, 30) of the p-BuODCX monomer to resin chlorine content were used. The monomer and 0.5 mmole of the phase-transfer catalyst, tetrabutylammonium bromide (TBAB), were dissolved in 20 mL of a 50/50 (v/v) DMSO/toluene mixture. The monomer solution was added to the resin dropwise (at about 20 ml/hr) under vigorous stirring. The reaction mixture was allowed to react for 5 hours and precipitated using a large quantity of water. Air or nitrogen atmosphere was used for the synthesis. The colored product was collected by filtration and washed several times with warm water until the filtrate was pH neutral. The product was then dried in vacuum. For the separation of homopolymers from those grafted on the resin, the product labelled as 'unextracted' was washed by toluene under reflux conditions for 5 hours to produce 'extracted' resin. Effects of hydroxide concentration at 67, 75, and 83 wt. % were also studied using a 20 : 1 molar ratio of p-BuODCX monomer to resin chlorine content.

Sample pellets of 0.5 inch in diameter and 0.5 to 1 mm thick were prepared for physical properties characterization from die-cast the conducting grafted resins using a KBr die and a 12-ton lab. press. The pellets were solution doped using 98 wt. % sulfuric acid for different time periods. The doped pellet was blotted to dryness using filter paper before use. Conductivity measurements were carried out using a DC multimeter (Cole Palmer 1559-70) and a two-point knife-edge fixture under ambient conditions. Thermogravimetric analysis (TGA) on the resins was conducted on a Shimadzu TGA-40 thermal gravimetric analyzer from room temperature to 600°C at a heating rate of 5°C/min under nitrogen purge. Infrared spectrum on KBr diluted sample pellets was obtained on a Hitachi Model 270-30 IR spectrophotometer. A Jeol Model T330 scanning electron microscope (SEM) was also employed for microscopy studies.

RESULTS AND DISCUSSION

A color change was observed as soon as the monomer/PTC solution was added into the strong base solution containing CMPS. The colored products were phenyl ring di-substituted poly(p-phenylene vinylene) confirmed by IR spectral analysis (5). The conducting grafted resins have colors ranging from yellow for p-DCX, deep yellow for p-MeDCX and reddish-orange for p-MeODCX and p-BuODCX. The difference in color is due to the extent of conjugation as well as the electron donating effects of the di-substituted moieties (4). The detailed phase-transfer catalyzed reaction mechanism has been described in a separate communication (8). The chemical structure of the di-substituted polymers is presented in Figure 1.

Both the nitrogen and air atmospheric conditions for synthesis produced similar polymer yield. The nitrogen blanketed reactions, however, gave products with darker overall color as well as slight improvement in electrical conductivity after doping. The darker color indicated a higher degree of conjugation and is consistent with an increase in conductivity. Similar results were also obtained when higher hydroxide concentrations were used. By comparing the electrical properties of the doped products and their yields, the optimum hydroxide concentration was found to be between 55 to 67 wt. %. The volume resistivity of the doped conducting grafted resins attained a maximum value when a 20 : 1 monomer to resin chlorine content mole ratio was used. After extraction by toluene, the solution turned slightly to the color of the conducting polymer indicated that a portion of the polymer thus formed was of soluble low molecular weight homopolymers. The resistivity of the 'extracted' and 'unextracted' resins remained approximately the same (see Table 1) suggesting saturated coverage of the CPMS resins by the conducting polymer when the optimum monomer to resin ratio was used.

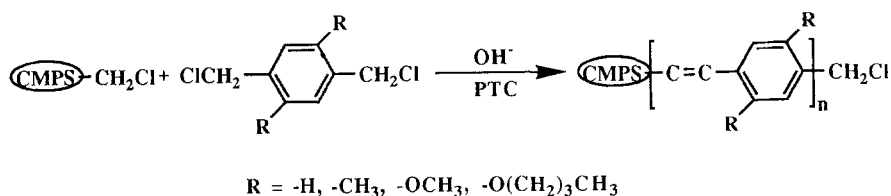


Figure 1. Chemical structure of the various conducting grafted resins.

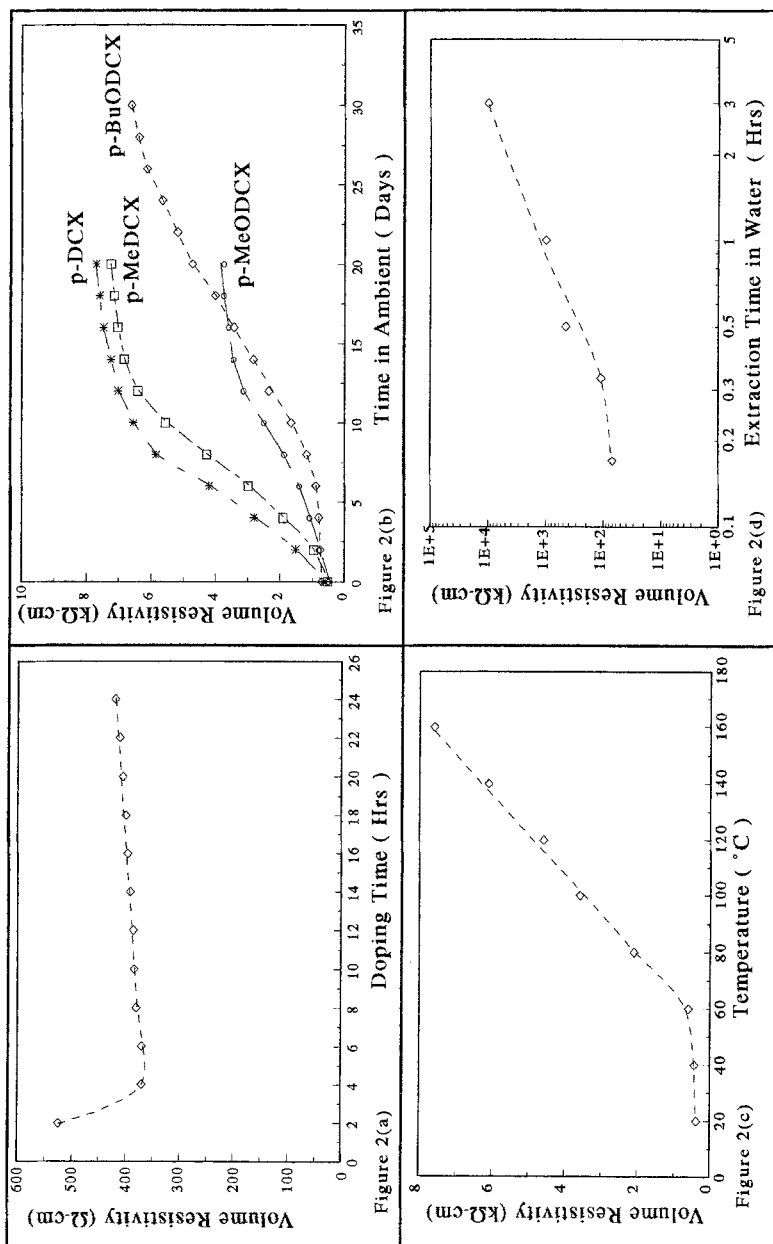


Figure 2. (a) Effects of doping time in conc. sulfuric acid on the volume resistivity of a 20 : 1 p-BuODCX grafted resin. (b) Stability of the various doped samples after exposing to air at room temperature for long time. The resins used were 1 : 2 p-BuODCX, 20 : 1 p-MeODCX, 20 : 1 p-MeDCX, and 20 : 1 p-DCX grafted resin. (c) Stability of a doped 20 : 1 p-BuODCX grafted resin after exposing to high temperature in air. (d) Change in electrical properties of a doped 20 : 1 p-MeODCX grafted resin after extracted by water at room temperature for different time periods.

After compressed into pellet, the conducting grafted resins were solution doped by conc. sulfuric acid. The pellet turned immediately black indicating successful oxidation of the conjugated products by the acid. For long doping period, the acid turned blackish which was due to solubility of the remaining unextracted homopolymers. A 5 hours doping time for a 20:1 p-BuODCX grafted resin gave optimum electrical property (see Figure 2a). The amount of dopant absorbed and the volume resistivity for the resin copolymerized with different monomers are listed in Table 1. The large amount of acid absorbed was probably due to sulfonation of the polystyrene matrix. The

Table 1. Physical Properties of the Conducting Grafted Resins

Monomer	Monomer to resin Cl ratio ^(a)	gm H ₂ SO ₄ per gm grafted resin ^(b)		Volume Resistivity (ohm-cm)		Onset Degradation Temperature (°C) ^(c)
		unext.	ext.	unext.	ext.	
p-BuODCX	20 : 1	0.60	0.68	431	387	193, 393
p-MeODCX	20 : 1	1.06	0.89	508	491	210, 325
p-MeDCX	20 : 1	0.71	0.58	562	518	243, 334
p-DCX	20 : 1	0.47	0.45	686	654	275, 335
CMPS				4.3 x 10 ^{12(d)}		378

(a) Under nitrogen and 55% hydroxide concentration; (b) 'ext.' and 'unext.' stand for resins extracted and unextracted by toluene before doping; (c) determined by TGA under nitrogen at a scan rate of 5°C/min.; (d) the pure CMPS resin was acid treated and bound by epoxy resin before electrical measurement.

volume resistivity was calculated based on the dimension of the pellet not corrected for interstitial voids and the volume of the insulating polystyrene matrix. Before the grafting reaction, the CMPS resins have the shape of hollow spheres with smooth surface texture according to the SEM studies. The conducting grafted pellet, however, was found to be composed of crushed smaller pieces (probably due to the high pressure applied during pellet formation) of the spherical resins on which only the outer surface has the conducting polymer grafted. As a result, the volume resistivity of the doped pellet is 1 to 2 order of magnitude higher than a similar thin homopolymer film (9).

The two alkoxy substituted monomer grafted resins provided the lowest resistivities. This may be due to the strong electron donating alkoxy groups have affecting a highly mobile π -electron system. The alkoxy di-substituted polymers were also found to have higher affinity to the free radical anion dopant as manifested by the stability of their electrical conductivities. Figure 2(b) shows that both the alkoxy monomer grafted resins retained their low electrical resistivities for a longer time period after exposure to ambient conditions (18-20°C, 50-60% RH). The loss in conductivity after exposure to air is mainly due to the evaporation or neutralization of the HSO₃⁻ anion by moisture in air. Eventually, their resistivities returned to the level of the undoped (but acid treated) state. The electrical properties of the pellet were further investigated by exposing doped p-BuODCX grafted pellets to higher temperatures and different extraction times in water at room temperature. The sample resistivity increased rapidly above 60°C (Figure 2(c)) and increased even more rapidly in water (Figure 2(d)). The onset degradation temperatures for the various conducting grafted resins determined by TGA are also tabulated in Table 1. The degradation above 300°C is due to the polystyrene matrix whereas degradation at a lower temperature was due to the di-substituted poly(p-phenylene vinylene) (4).

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