Polymer Bulletin 23, 543–547 (1990)

Polymer Bulletin

Model filled polymers

IV. Preparation of conducting composite polymers beads

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SUMMARY

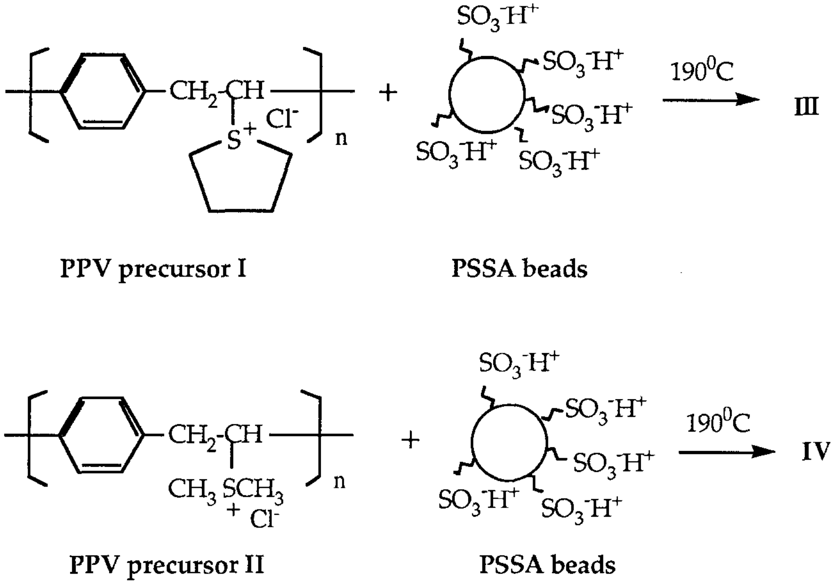
Polyphenylene vinylene (PPV) coated polystyrene (PS) beads which have moderate conductivity when doped were prepared by mixing monodisperse crosslinked PS beads, the surfaces of which had been sulfonated to render them anionic, with cationic PPV precursor polymers. Two different PPV precursor polymers, poly (p-xylylidene tetrathiophenium chloride) and poly (p-xylylene-α-dimethylsulphonium chloride), were employed. Monodisperse crosslinked PS beads were sulfonated in the gas phase using fuming sulfuric acid to yield the surface activated monodisperse polystyrene sulfonic acid (PSSA) beads. Chemical doping with AsF_5, of pellets prepared by pressing the coated beads resulted in conductivities as high as 10^{-1}S/cm. The integrity of the polymer beads was determined by Scanning Electron Microscopy (SEM) and arsenic was found throughout the samples by examing fracture surfaces of the pressed coated pellets using EDXS.

INTRODUCTION

Since conducting polymers are often virtually insoluble and non-processible, their general applications have been limited. Thus, there is a great deal of interest in synthesizing processible forms of conducting polymers. One method which addresses this problem was developed by Karasz[1-3] et al. using a two-step preparation of PPV. Their synthesis involved the polymerization of a bis-sulphonium salt monomer to a water-soluble sulphonium salt polyelectrolyte precursor polymer which could subsequently be converted to PPV by thermal elimination.

This paper describes a new method for preparing conducting polymer coated polymeric beads in the micron size range. Our procedure utilizes monodisperse crosslinked PS beads which have been treated with SO_3 above fuming sulfuric acid to sulfonate the bead surfaces. Gas phase sulfonation prevents the swelling of the beads that occurs in solution.[4] These anionically charged beads are subsequently mixed with a dilute aqueous solution of cationically charged precursor polymer resulting in individually coated beads (Figure 1); they become conductive upon subsequent heating and doping.

Figure 1



EXPERIMENTAL

Monodisperse crosslinked polystyrene beads (453nm) were synthesized via emulsifier-free emulsion polymerization[5] as described previously. The PS beads were then sulfonated in the gas phase using an enclosed glass chamber. Within the chamber, a small glass container held the PS beads above fuming sulfuric acid (containing 16-24% SO_3) in the bottom of the larger glass chamber. Slow continuous-rotation for three days at room temperature exposed all the beads. The white PS beads became yellowish after this treatment. The sulfonated beads were placed in a vacuum oven at room temperature for one day to remove excess SO_3 and impurities. X-ray Photoelectron Spectroscopy (VG Scientific ESCALAB MKII instrument) and Auger (Perkin Elmer) analysis were used to analyze surfaces of the sulfonated beads. Elemental analysis (Controlled Equipment Corporation 240XA at 970^{0}C) was done by Oneida Research Services.

Two different PPV precursor polymers, poly(xylylidene tetrathiophenium chloride), I, and poly(p-xylylene-α-dimethylsulphonium chloride), II, were used to coat the sulfonated PS beads. PPV precursors I and II were prepared as described in the literature.[6,7] The elemental analysis of the bis-sulphonium monomers and the infrared spectra of the PPV films obtained from I and II were found to agree with published data.

Sulfonated PS beads were mixed with aqueous 0.2M PPV precursor I by stirring for 30 minutes at room temperature. Small aggregates were broken either with mechanical agitation or sonication. The mixture was then filtered and dried in a vacuum oven at room temperature for 4 days. The resulting yellowish beads were heated to 190°C for 3 days under vacuum and turned light green which we took as an indication of the formation of composite polymer beads, III (Figure 1). These composite beads were then pressed between PTFE sheets in a hydraulic press at 170°C and 2500 lb for 20 minutes to form a pellet. Two pressed pellets were doped with AsF_5 at approximately 100 torr and conductivities were measured after various periods of time. These measurements were done in air immediately after removal of the samples from the doping chamber and utilized a Keithley Model 197 Auto-ranging Microvolt DMM connected to an Alessi C4S & C4R 4-Point Probe.

The same synthetic procedure was employed with precursor II to form composite polymer beads, IV, except that the doping period was longer (20 days). After measuring the conductivity in the usual way, this sample was exposed to the laboratory atmosphere for 24 hours and its conductivity was remeasured. Then this doped pellet was broken into small pieces and repressed in a hydraulic press at 150°C and 2500 lb for 15 minutes. It was subsequently redoped with AsF_5 for 4 days at 100 torr.

The fractured surfaces of pellets made from beads III and IV were observed by SEM (Cambridge Instruments) and the distribution of As in a sample doped for 8 days was determined via EDXS (Cambridge Instruments).

RESULTS AND DISCUSSION

The degree of sulfonation of the PSSA beads was obtained from elemental analysis, XPS and Auger analysis. Assuming sulfonation of each phenyl ring in a PS bead, the elemental composition (by mass) would be 52.2% C, 4.3% H, 26.1% O, and 17.4% S. Elemental analysis results were 84.72% C, 7.60% H, 4.59% O and 2.89% S which indicated that about one in every eight monomer units was sulfonated. Auger analysis confirmed the presence of sulfur and oxygen on the bead surfaces. XPS analysis, which ignores hydrogens, showed the elemental atomic composition to be 92.8% C, 6.0% O and 1.2% S. This technique also shows a trace of oxygen on the surface of "pure" PS beads which is probably due to a modest amount of surface oxidation. The unexpected 5 to 1 oxygen to sulfur ratio is probably due to this complication. Further studies on the sulfonation of PS beads are in progress.

The thermal elimination temperatures to form PPV from I and II are quite different. Precursor II was used in an attempt to make conducting composite beads but complete thermal elimination was impossible due to the high elimination temperature required to form PPV from II and the fact that PSSA beads decompose at the relatively modest temperature of 300°C. Elimination at temperatures lower than optimal prevents formation of the fully conjugated PPV polymer. Total elimination was possible for precursor III. From the data in Table 1, we observe that it was easier to dope III than IV;

furthermore, higher conductivities were observed with longer doping times. The spatial heterogeneity of the conductivity of the pellets made from IV was considerable (measured conductivities varied by about an order of magnitude).

When IV was exposed to laboratory air for one day, its conductivity decreased by less than an order of magnitude. Upon repressing at 150°C, the conductivity dropped to below 10^{-8}S/cm. Subsequent redoping appeared to be more facile than the original doping.

A comparison of the properties of neat PPV films and conducting composite beads is interesting. The conductivity of a PPV film made from precursor I was $1.8\text{x}10^{-2}$S/cm (Table 1) after doping for 8 days at 100 torr. The conductivity of the pellet prepared from the same precursor doped and measured under identical conditions was $2.4\text{x}10^{-4}$S/cm. The decreased conductivity for the beads was probably due to gaps between the beads. Also, as expected, the conductivities increased as the doping period increased from 6 to 8 days for III.

The fractured surface of a pellet made from III was examined with SEM (Figure 2). The diameters of the beads had increased from about 450 nm to close to 480 nms. The SEM clearly shows that the beads retain their integrity and the PPV appears to be reasonably uniformly coated on their surfaces. EDXS showed the presence of arsenic atoms throughout the fractured surface. Further work is in progress.

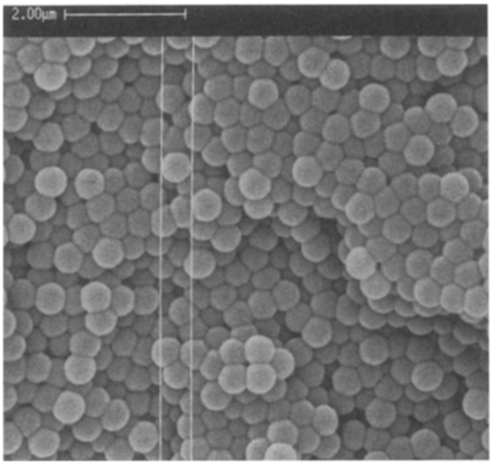
Table 1: Conductivity measurements of polymer composite beads

Composite beads	Time of doping (days)	Thickness of pellet (cm)	Conductivity (S/cm)
III	6	0.043	$5.1\text{x}10^{-5}$
	6	0.043	$1.2\text{x}10^{-5}$
	8	0.059	$2.4\text{x}10^{-4}$
IV	12	0.051	below 10^{-8}
	20	0.051	$1.4\text{x}10^{-1}$ -$5.7\text{x}10^{-2}$
	20[a]	0.051	$1.1\text{x}10^{-2}$
	20[b]	0.051	$2\text{x}10^{-4}$

PPV film	8 days doping	0.0002 cm	$1.8\text{x}10^{-2}$ S/cm

a exposed to air for one day
b repressed and redoped for 4 days

Figure 2: Fractured surface of a pellet made from III before doping



Acknowledgement: This work was supported by ONR through grant number (N00014-88k-0302). We appreciate the help of Mr. Jack Worrel for the EDXS measurements at U. S. C. and Drs. Alan Gotcher and James Tse for the XPS measurements done at the Avery International Research Center.

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Accepted February 14, 1990 K