# Synthesis of Polycarbonate-*co*-Poly(*p*-ethylphenol) and CdS Nanocomposites

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Received 11 March 1998; accepted 7 September 1998

ABSTRACT: The enzyme-catalyzed synthesis of poly(*p*-ethylphenol) (PEP) was modified by copolymerization with polycarbonates through triphosgene at low temperature to form polycarbonate-*co*-poly(*p*-ethylphenol) (PC-*co*-PEP). FTIR, NMR, GPC, and thermal analysis verified the formation of PC-*co*-PEP. The copolymers have an optical absorption in the UV range. CdS semiconductor nanocrystallites were synthesized in reversed micelles with subsequent *in situ* enzymatic copolymerization of *p*-ethylphenol and 4-hydroxythiophenol in the same medium. TEM and ATR-FTIR showed that the polymer precipitated in spherical morphologies, incorporating CdS nanocrystals into the polymer matrix, with surface hydroxyl groups. The polymer/CdS core was then dispersed into polycarbonate. The polymer/CdS nanocomposites showed higher optical aborbance in the UV-vis range when compared to the polymer matrix without CdS. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1851–1868, 1999

Key words: enzyme; nanocomposite; sodium sulfide; polyethylphenol; polycarbonate

# INTRODUCTION

Inorganic/polymer nanocomposite materials have evoked wide interest due to their novel optical and electronic properties.<sup>1</sup> Here, we present our ongoing research in this area involving polyphenol–CdS nanocomposite materials. Polyphenols have been widely used as matrix materials. The enzymatic synthesis of polyphenols was recently reported.<sup>2–4</sup> The biochemical reaction, catalyzed by horseradish peroxidase, can be carried out under ambient conditions. Neither formaldehyde nor a heavy metal catalyst is necessary to form polyphenol. Due to the conjugation along the polymer backbone, it possesses optical absorption in the UV range. The molecular weights  $(M_w)$  of poly(*p*-ethylphenol) (PEP) prepared by enzymatic methods are generally below 2000. This is due to the lack of branching at the *para* position of the monomer, since it is blocked by the ethyl group.<sup>2</sup> If PEP is incorporated with other polymers to form copolymers, the latter will possess improved molecular weights. Therefore, desirable film-formation properties will be obtained, while preserving the optical and electronic character of polyethylphenol.

Recently, the synthesis of nanosized semiconductor CdS crystallites in reversed micelles has evoked much interest, due to the self-assembled structures providing a method which restricts the growth of the crystallites.<sup>2</sup> Such quantum-sized particles have an increasing band gap with decreasing particle size, due to quantum confinement of the charge carriers. These properties have significant technological applications in photocatalysis<sup>5,6</sup> and as nonlinear optical materials.<sup>7,8</sup> The absorption characteristics of CdS nanoparticles are affected by the crystallite size, and

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Journal of Applied Polymer Science, Vol. 72, 1851–1868 (1999)

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Scheme 1 Transesterification reaction to form PC-co-PEP (1).

the luminescence is a strong function of the surface characteristics.

In this article, we report a chemoenzymatic approach toward the synthesis of polymer/CdS nanocomposites. The synthesis of polycarbonate*co*-poly(*p*-ethylphenol/hydroxythiophenol) (PC-*co*-PEHTP) is directed toward obtaining optically clear polymer thin films and improved opticalabsorption characteristics.

#### **EXPERIMENTAL**

#### Characterization

Gel permeation chromatography (GPC) was carried out on a Millipore chromatograph equipped with a refractive index detector and Waters polystyrene Ultrastyragel gel columns to obtain the molecular weight distribution. The eluent was THF, and the columns operated under a flow rate of 1 mL/min. A calibration plot, constructed with polystyrene standards in the range of 980–500,000, was used to determine the molecular weights. IR spectra were obtained on a Nicolet-60 SX FTIR, and UV-vis absorption spectra, on a Perkin–Elmer Lambda 6 spectrophotometer. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer instrument from 30 to 900°C at a heating rate of 20°C/min in a nitrogen environment. DSC thermograms were obtained on a DSC 2920 differential scanning calorimeter. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a Bruker DMX-500 spectrometer, using tetramethysilane (TMS) as an internal standard in CDCl<sub>3</sub> at room temperature. The X-ray diffraction (XRD) pattern was obtained on a Nirelco/Philips XRD.

The morphology of the polymer/CdS nanocomposites was characterized by transmission (TEM) and scanning electron microscopy (SEM). For TEM analysis, micrographs were obtained at an acceleration voltage of 200 kV on a JEOL 2010 TEM. For SEM analysis, a drop of the sample dispersed in isooctane was placed on a glass slide,



Scheme 2 Synthesis of PC-co-PEP (2) via triphosgene.

dried, and coated with a 10-nm-thick gold film. The micrograph was taken at an acceleration voltage of 30 kV on a Philips ElectroScan 2020 environmental SEM.

#### Materials

Reversed micellar solutions were prepared using the anionic surfactant, bis(2-ethylhexyl) sodium sulfosuccinate (AOT) from Aldrich. Pyridine and triethylamine (Acros) were purified by distillation over barium oxide.

Horseradish peroxidase (HRP) type II enzyme, HEPES buffer, and hydrogen peroxide were purchased from Sigma Chemical Co. The monomers p-ethylphenol (EP) and 4-hydroxythiophenol (HTP), isooctane, CdCl<sub>2</sub>, and Na<sub>2</sub>S were obtained from Acros. Bisphenol A and triphosgene were also from Acros. All were used as received. Deionized water was used throughout.

# Methods

#### Synthesis of PEP

PEP was synthesized according to the procedure of Akkara et al.<sup>2</sup>

# *Synthesis of Polycarbonate [PC (1)]* and PC-*co*-PEP Through Transesterificaton [PC-*co*-PEP (1)]

Equimolar amounts of bisphenol A and diphenol carbonate (0.002 mol) with PEP and sodium methoxide were mixed under  $N_2$ , then heated to 150°C under a vacuum with stirring. The reaction was continued for about 1 h with the temperature increasing up to 170–180°C. The product yield was 85%. The transesterification reaction to form the copolymer is presented in Scheme 1. White crystalline phenol was released during the process and the reaction mixture turned viscous, indicating polymer formation.

# *Synthesis of PC-co*-PEP Through Triphosgene [PC-*co*-PEP (2)]

A 1 : 3 mol ratio of triphosgene and bisphenol A (1.7 : 5.1 mmol) with PEP (10 wt %) were dissolved in 15 mL pyridine at 20°C while stirring. Triethylamine, 5.1 mmol (Et<sub>3</sub>N : triphosgene = 3 : 1 mol), was added dropwise to the solution. After 8 h, the reaction mixture was added into deionzed water and the precipitated polymer was washed with water several times. The polymer was purified by redissolving in pyridine and reprecipitat-



Figure 1 IR spectra of (a) PEP, (b) PC, (c) PC-co-PEP (1), and (d) PC-co-PEP (2).

ing in dioxane several times. Then, it was dried in a vacuum oven for 48 h The yield was 80%.

#### Synthesis of the PEHTP/CdS Composites

Stock aqueous CdCl<sub>2</sub> and Na<sub>2</sub>S solutions, 0.9M, were prepared, and 0.45 mL of each solution was added separately into 0.5M AOT ( $w_0 = [H_2O]/$ [AOT] = 10). Then, these two separate reversed micellar solutions containing CdCl<sub>2</sub> and Na<sub>2</sub>S were filtered and mixed together. Subsequently, PEP was polymerized in the same system according to a modified procedure of Akkara et al.<sup>2</sup> The modifications are as follows: An aqueous enzyme solution was added to the above CdS solution, followed by the addition of monomers of EP and HTP to make up the final reaction mixture. The final reaction condition was  $w_0 = 15$ , AOT 0.5M, monomers 0.15M with a molar ratio of EP/HTP = 8/2, and 0.5 mg/mL HRP. The polymerization was initiated by the dropwise addition of hydrogen peroxide. The polymerization seemed not to be affected by the presence of CdS and the color of the reaction mixture turned dark green. The above synthesis was maintained for less than 1 h under an argon environment throughout. The

PEHTP/CdS composite particles were centrifuged and washed extensively with isooctane and ovendried at room temperature overnight.

#### Dispersion of PEHTP/CdS Composites into PC

The dispersion of PEHTP/CdS into PC was similar to the synthesis of PC-*co*-PEP. The PC was produced through triphosgene at ambient conditions with dispersed PEHTP/CdS.

#### **Film Formation**

Polymers were dissolved separately in THF to form a  $\sim 1\%$  solution and spin-cast on a quartz substrate, first at a spinning rate of 300-500 rpm, then subsequently at 5000-7000 rpm, to obtain thin, optically clear films.

# **RESULTS AND DISCUSSION**

# PEP and PC-co-PEP Synthesis and Characterization

# Copolymerization

The modification of PEP can be achieved by copolymerization with PC to form PC-co-PEP through triphosgene at low temperature as shown in Scheme 2. Triphosgene is a stable crystalline solid (mp = 80°C, bp = 206°C), which is easy to transport and store. It can be used as a phosgene substitute in common phosgene reactions.<sup>9</sup> Triphosgene, 1/3 mol, reacts under the influence of a nucleophile,  $Et_3N$ , in a manner similar to 1 mol of phosgene, which can also arise as an intermediate. Scheme 2 illustrates the function of triphosgene as a phosgene substitute in the copolymerization of PC with PEP.

To compare the PC (2) and PC-co-PEP (2) obtained through triphosgene with those prepared by the traditional transesterification method, the synthesis of PC (1) and PC-co-PEP (PC-co-PEP) (1) through transesterification was also conducted as outlined in Scheme 1.

#### FTIR and NMR Characterization

Figure 1 presents the IR spectra of PEP, PC, and their copolymers by different routes, that is, by transesterification (route 1) and triphosgene (route 2). The spectra of the two samples of PCco-PEP were similar, which indicated that the two polymers had similar compositions. The absorptions at ~1770, 1223, and 1286 cm<sup>-1</sup> are assigned to the C=O and C-O-C (symmetric

and asymmetric) stretching vibration. In both PEP and PC, broad peaks were observed at  $\sim$ 3400 cm<sup>-1</sup>, assigned to the phenolic hydroxyl group absorption. These two broad peaks were essentially absent or very weak in both PC-co-PEP (1) and (2). This indicated that the OH groups of the PEP and bisphenol A or PC had reacted to form chemical bonds as illustrated in Schemes 1 and 2, leading to the formation of PC-co-PEP (1) and PC-co-PEP (2), respectively. Thus, essentially, PEP was chemically incorporated into PC chains via reaction of its OH groups with PC. Furthermore, from the IR spectra, it was observed that the methylene CH<sub>2</sub> scissoring bands (1462 and 1464 cm<sup>-1</sup>) appearing in PEP and PC-co-PEP were absent in pure PC. On the other hand, the CH<sub>2</sub> scissoring peak was weaker in both copolymers than in pure PEP, which probably indicated that the amount of PEP was a minor component in the copolymers. Table I lists the details of the infrared frequencies and assignments for homopolymers, that is, PEP and PC, and copolymers PC-co-PEP (1) and (2), respectively.

Figure 2 exhibits the <sup>1</sup>H-NMR spectra of the copolymers. In Figure 2(a), for PC-*co*-PEP (1), the peak at  $\delta 6.7 - \delta 7.2$  is due to the aromatic protons. Multiple peaks appearing at  $\sim \delta 1.6$  were ascribed

 Table I
 Infrared-Active Mode Frequencies, Relative Strengths, and Assignments for Homo- and Copolymers

Assignment	$PEP (cm^{-1})$	$PC (cm^{-1})$	PC-co-PEP $(1)$ (cm <sup>-1</sup> )	$PC-co-PEP(2) (cm^{-1})$
OH stretch	$\sim \! 3400  (s)$	$\sim \! 3400  (s)$	$\sim 3400 \; (vw)$	$\sim 3400 \ (vw)$
Aromatic CH stretch	3039 (w)	3060 (w)		
		3039 (w)		
Aliphatic CH stretch	2962 (s)	2968 (s)	2966 (m)	2968 (m)
$(CH_3 \text{ and } CH_2)$	2929 (m)	2935 (w)	2931 (w)	2933 (w)
0 2			2894 (vw)	
	2871 (m)	2873 (w)	2871 (w)	2873 (w)
C=O stretch	$1662 \ (m-w)^{a}$	1772 (s)	1770 (s)	1770 (s)
Aromatic C=C	1589 (m)	1612 (m)	1595 (m)	1595 (m)
ring stretch	1504 (s)	1508 (s)	1504 (s)	1504 (m)
	1458 (s)			
$CH_2$ scissor	1458 (s)		1462 (m)	1464 (m)
C—OH stretch	1213 (vs)	1194 (vs)	1159 (vs)	1159 (vs)
C—O—C stretch ( $\gamma_{as}$		1234 (vs)	1223 (vs)	1223 (vs)
and $\gamma_s$ )		1163 (vs)	1186 (vs)	1186 (vs)
Aromatic CH in-plane	1061 (w)	1082 (m)	1080 (m)	1080 (m)
bend	1014 (w)	1014 (s)	1012 (m)	1014 (m)
Aromatic CH out-of-	877 (m)	889 (w-m)	885 (w-m)	885 (m)
plane bend	823 (m)	831 (m)	827 (m)	827 (s)

<sup>a</sup> Pummerer's ketone arise from o-p coupling in the polymerization of p-ethylphenol, and subsequent arrangement may lead to ketonic structures incorporated into the chain.<sup>4</sup>



to varying stereochemical configurations of methyl groups in the PC. The protons attached to the methyl carbons experienced varying extents of deshielding from the aromatic rings and, hence, had different chemical shifts leading to multiple peaks. The minor peaks at  $\delta 1.2$  and  $\delta 2.6$  were



Figure 3 TGA thermograms of homo- and copolymers.

assigned to the methyl group  $(CH_3)$  and the methylene group  $(CH_2)$ , respectively, in PEP, which indicated that PEP was chemically incorporated into PC. This was corroborated by the IR spectra discussed above. Similar assignments were made for the minor peaks at  $\delta 1.2$  and  $\delta 2.8$  in Figure 2(b) for PC-co-PEP (2). These spectra illustrated that both the copolymers formed at high temperature through transesterification and low temperature through triphosgene have similar compositions but different composition ratios; for example, PEP/PC in PC-co-PEP (1) [Fig. 2(a)] had a ratio of 0.109/3: 0.541/6 = 0.4/1, and in PC-co-PEP (2), a ratio of 0.076/3 : 1.009/6 = 0.15 : 1, which were consistent with their respective starting materials' ratios. The latter method provides us with a facile method for synthesizing polymers under

ambient conditions. PEP was chemically linked to the PC, that is, PC-*co*-PEP was formed.

#### **GPC** Measurements

Based on the GPC results, the pristine PCs showed a slight difference in molecular weights between high- and low-temperature products (Table II). The copolymers of PC-*co*-PEP had increased molecular weights compared with pristine PC due to the linkage between PC and PEP, which led to a near doubling of molecular weights. The linkage results from the chemical reaction between PC and PEP are shown in Schemes 1 and 2.

#### Thermal Analysis

Phenolic polymers prepared in AOT/isooctane reversed micelles catalyzed by an enzyme in the

	Polymer				
Molecular Weight	PEP	PC (1) <sup>a</sup>	PC (2) <sup>b</sup>	PC- $co$ -PEP $(1)^{a}$	$PC-co-PEP (2)^{b}$
$M_n$	1700	3700	3600	4100	4500
$M_w^{+}$	2600	6900	5800	10,000	10,100

 Table II
 Molecular Weights of Homo- and Copolymers

<sup>a</sup> Synthesized by transesterification.

<sup>b</sup> Synthesized through triphosgene.

Polymers	30–100°C (%)	100–200°C (%)	300–600°C (%)	600–900°C (%)	Residuals (%)
PEP	0.5	5	60	65	35
PC	1	12	88	90	10
PC-co-PEP(1)	0.5	7	74	75	25
PC-co-PEP(2)	5	15	84	87	13

Table III Phenolic Copolymer Integrated Weight Loss at Various Temperatures

presence of hydrogen peroxide were reported to be thermally stable up to 300°C.<sup>3</sup> Figure 3 illustrates the thermogravimetric analysis (TGA) results of PEP, PC, and PEP-co-PCs. PEP exhibited a 0.5% weight loss at 100°C, which was attributed to the evaporation of moisture, then a 5% integrated loss at 200°C and a 7-8% integrated loss at  $300^{\circ}$ C. The residue weight at  $900^{\circ}$ C was  $\sim 38\%$ , consistent with the results of Akkara et al.<sup>2</sup> Pristine PC showed less heat resistance compared with PEP. It started to degrade at 100°C, and after 400°C, the thermal decomposition integrated loss was 38%. PC-co-PEP (1) indicated good heat resistance below 200°C, but it degraded above 300°C. In the case of PC-co-PEP (2), it showed that the copolymer decomposed in the range of 100-200°C, then stabilized between 200 to 350°C; subsequently, the weight dropped very

quickly after 400°C. Table III summarizes the TGA results. In general, residue remained after the polymers were heated to 900°C in nitrogen.

The DSC thermograms (Fig. 4) show that the homo- and copolymers underwent reactions in the nitrogen environment. The DSC data of PEP [Fig. 4(a)] exhibited two peaks. The first one, an endothermic peak at  $115^{\circ}$ C (45 J/g), could be attributed to the volatilization of solvent; the second one (58 J/g) at  $176^{\circ}$ C was due to an exothermic crosslinking reaction, as in PEP chains linking each other.<sup>3</sup> This exothermic reaction was not reversible after heat treatment, as verified by the DSC measurement. Figure 4(b) showed two endothermic peaks: The first one (28 J/g) at  $48^{\circ}$ C was the loss of low molecular oligomers trapped inside the polymer; the second one (54.6 J/g) at  $158^{\circ}$ C was attributed to an endothermic reaction, such



**Figure 4** DSC thermograms of homo- and copolymers: (a) PEP; (b) PC; (c) PC-*co*-PEP (1); (d) PC-*co*-PEP (2).

as the motion of the polymer chains or the melting of a minor crystalline region. The  $T_g$  is also superimposed in this region. DSC analysis of PC-co-PEP(1) [Fig. 4(c)] exhibited three peaks: The first one (28.7 J/g) at 52°C was also assigned to the loss of small molecules, the second peak (11.4 J/g) at 123°C was due to the exothermic crosslinking reaction of PEP segments, and the last one (47.3 J/g) at 194°C was the endothermic reaction within the copolymer. Similarly, PC-co-PEP (2) [Fig. 4(d)] also indicated three heat flows with assignments the same as above. The difference in the two thermograms consistent with the NMR results lies in the magnitude and position of the peaks due to the different composition ratios between PC-co-PEP (1) and (2). Table IV lists various transitions in the DSC thermograms.

# **UV Optical Absorption**

Figure 5presents the UV absorption of the polymers. Both UV spectra exhibited similar characteristics: PEP showed a stronger and wider absorption than that of PC in the UV range of 250-300 nm. PC-co-PEP exhibited a comparable absorption to PEP, which indicated that the incorporation of PC with PEP did not interrupt the electronic properties of the conjugated backbone. The difference spectrum between PC-co-PEP and PC screened the contribution of PC and exhibited two peaks: The difference spectrum peak at 240 nm was due to the wider UV absorbance of PEP and the second one was at 280 nm. These two bands were attributed to the  $\pi$ - $\pi$ <sup>\*</sup> transitions of the aromatic fragments. For pristine PEP film, two distinct absorptions, one at 200-260 nm and one at 280–310 nm, were assigned to  $\pi$ - $\pi$ \* transitions in polyphenol, which is consistent with results reported previously.<sup>4</sup> A very weak band was also observed at 390 nm attributed to the  $n-\pi^*$  transition in the carbonyl group of Pummerer's ketone.<sup>4</sup> This band was very weak due to the forbidden nature of the  $n-\pi^*$  transition. In the PEP UV absorption, this third band was essentially absent due to both the forbidden transition and the minor amounts of carbonyl groups in PEP. The width of the difference spectra reflects the amounts of PEP in the copolymer. For example, the difference spectrum of PC-co-PEP (1) had a wider absorption than that of PC-co-PEP (2). Both PC-co-PEP products showed wider and stronger UV absorptions compared with their respective pristine PC, because of the incorporation of PEP into the PC chains.

# CdS and PEHTP-co-PC/CdS Nanocomposites

# GPC and TGA Measurements of PEHTP

Table V lists the molecular weight data for the *p*-ethylphenol/4-hydroxylthiophenol (PEHTP) copolymers, and it is shown that the molecular weights increase with the 4-hydroxythiophenol (HTP) monomer content, which is consistent with previous results.<sup>2</sup> Figure 6 presents the TGA results of the PEHTP copolymers. They exhibited a similar trend in their decomposition as to that of PEP. They start to degrade at 300°C, with a residue of 50% at 500°C and of 38–40% at 900°C.

# Synthesis of PEHTP/CdS Nanocomposites

CdS was prepared in a  $w_0 = 10$  reversed micellar solution by a modification of the literature procedure.<sup>2</sup> The particles were obtained instantly, as indicated by the yellow color of the solution. This modified synthesis of CdS is illustrated in Scheme 3(a). Henglein reported previously that there is a correlation between the CdS particle sizes and the wavelength of absorption onset. As the particles became smaller, the onset of absorption shifted to shorter wavelengths.<sup>10</sup> In our case, the

	Peak 1		Peak 2		Peak 3	
Polymers	T (°C)	Enthalpy (J/g)	T (°C)	Enthalpy (J/g)	T (°C)	Enthalpy (J/g)
PEP	115	$45^{\mathrm{a}}$	176	$-58^{\mathrm{b}}$	_	_
PC	48	28		_	158	55
PC-co-PEP(1)	52	29	123	-11.4	194	47.3
$\text{PC-}co\text{-}\text{PEP}\ (2)$	61	21	142	-6.6	176	24.2

Table IV Phenolic Homo- and Copolymer Transitions

<sup>a</sup> Endothermic peak.

<sup>b</sup> Negative sign stands for exothermic peak.



#### Wavelength (nm)

**Figure 5(a)** UV-Visible absorbtion spectra of PEP, PC(1), PC-co-PEP(1) and their difference spectrum.

CdS absorption edge was about 420 nm, and the particle size of CdS calculated from the absorption edge was 5 nm. There is also an approximation correlation between  $w_0$  and the radius (r) of the microemulsion, that is, r (nm)  $\approx 0.18 \ w_0$ .<sup>11</sup>

Thus, for  $w_0 = 10$ , the CdS diameter is theoretically 4–5 nm, which is consistent with the UVabsorption results. Aging effects over a period of hours exist for the lower  $w_0$  values such as for the 2.5 and 5 systems. Previous reports indicated that



#### Wavelength (nm)

**Figure 5(b)** UV-Visible absorption spectra of PEP, PC(2), PC-co-PEP(2) and their difference spectrum.

there is a red shift in the absorbance onset with time due to Ostwald effects in lower  $w_0$  value systems, and this growth process reaches equilibrium after 24 h. In our experiment, we also observed the aging effects. Only in high  $w_0$  value

(e.g., 10) systems, the absorption spectrum does not change significantly with time. However, higher  $w_0$  values (>15) give rise to flocculation– sedimentation of the particles over a period of hours, such that these systems are not stable.

	М	м	Violda (%)
	IVI n	M <sub>w</sub>	Tielus (%)
100/0	1700	2600	85
80/20	2100	3100	87
70/30	2400	3200	70

 Table V
 PEHTP Copolymer Molecular Weights

 and Yields
 Performance

This has been reported previously<sup>12</sup> and also observed in our experiments. For  $w_0$  values  $\geq 10$ , photodegradation is observed when the solutions are left in a glass vial without deoxygenation as observed by Henglein and coworkers.<sup>13,14</sup> This has been attributed to photoanodic dissociation according to the following equation:

$$\mathrm{CdS} + 2 \mathrm{O}_2 \xrightarrow{h \gamma} \mathrm{Cd}^{2+} + \mathrm{SO}_4^{2-}$$

Therefore, we chose  $w_0 = 10$  in reversed micelles and used argon to protect the reaction throughout the process.

After the CdS nanoclusters were obtained, an aqueous enzyme solution with a buffer was injected into the CdS solution, followed by the addition of the monomers EP and HTP and  $H_2O_2$  to initiate the polymerization. Based on TEM, XRD, and IR data discussed below, the enzyme diffuses



**FIGURE 6** TGA thermograms of PEHTP copolymers: (a) EP/HTP: 100/0; (b) EP/HTP: 80/20; (c) EP/HTP: 70/30.



**Scheme 3(a)** The schematic formation of CdS nanoclusters in reversed micelles.



Scheme 3(b) Schematic formation of PETHP/CdS composites.



**Scheme 4(a)** The schematic procedure of forming polymer/CdS nanocomposites.

into the micelle cores containing trapped CdS nanoclusters inside and with the monomers on the periphery of the micelle. Upon the addition of  $H_2O_2$ , the polymerization was initiated and the PEHTP (EP : HTP = 80/20) polymers were obtained promptly and surrounded the CdS nanoclusters. Thus, PEHTP/CdS nanocomposites were obtained. The reaction was maintained under argon for less than 1 h, and dark green composites were obtained. Thus, via this procedure, CdS/ PEHTP nanocomposites were synthesized in the same reversed micellar medium right after CdS nanoparticles were formed. The entire process was protected by inert gas to avoid oxidation and other side reactions. These procedures are outlined in Scheme 3(b,c).

In the PEHTP/CdS composites, the existence of sulfhydryl groups would passivate the CdS to

form covalent bonds between CdS and the polymers,<sup>2</sup> which prevented Ostwald ripening effects from occurring as compared with uncapped CdS. The PEHTP/CdS nanocomposites were dispersed into a PC matrix by the reaction of PC with PEHTP. As illustrated above, PEP could be incorporated into PC to form the PC-co-PEP polymer. Since PEHTP is the copolymer of EP and HTP (molar ratio: 8/2), therefore, PEHTP was chemically bonded with PC to form a polymer matrix (PEHTP-co-PC) with  $M_n = 8100$  and  $M_w = 121,00$ . In this fashion, CdS clusters were also dispersed into this polymer matrix. The procedure of synthesizing CdS and the PEHTP/CdS nanocomposites and dispersing them into the PC matrix is shown in Scheme 4(a). There exist some possible physical entanglements between PEHTP and PC besides chemical bonding. CdS is attached to the SH group<sup>2</sup> and is therefore dispersed into the polymer matrix (Scheme 5).



**Scheme 4(b)** Synthesis of PEHTP by enzyme polymerization [2]



**Scheme 5** Proposed chemical structure of PC/PEHTP/CdS nanocomposites after PEHTP/CdS dispersion in PC.

#### X-ray and Morphology Studies

XRD, TEM, and SEM were used to determine the crystalline structure. Figure 7 shows the XRD pattern of the PEHTP/CdS composites. The latter displayed three broad but distinct peaks at  $2\theta$  values of 26.58°, 44.05°, and 52.28°, matching the (111), (220), and (311) crystalline planes of cubic CdS, indicating its formation. The broad nature of the XRD peaks could be attributed to the presence of nanosized particles, which is consistent with the conclusion from the CdS UV-vis absorbance spectrum. The observed rising background centered around  $2\theta = 25^{\circ}$  is due to the presence of the amorphous polymer.

To elucidate the size and crystal structure, TEM was used to characterize the crystallites and to develop a statistical description of the size distribution. Figure 8(a) presents the TEM micrograph and diffraction pattern of CdS clusters encapsulated into polymer cores caused by the reversed micelle. The CdS clusters inside the core, indicated by the dark spots, were distributed uniformly inside the PEHTP matrix, with an average size of 4-6 nm, consistent with the UV absorbance spectrum and the calculated micelle size (4-5 nm in diameter). On observing the TEM carefully, it was noticed that the clusters were not



Figure 7 XRD pattern of PEHTP/CdS nanocomposites.



(a)



(b)

**Figure 8** (a) TEM of PEHTP/CdS nanocomposites; (b) diffraction pattern of CdS clusters encapsulated into the PEHTP core.

aggregated, probably because the polymer trapped the CdS clusters and separated them. The diffraction pattern [Fig. 8(b)] indicated that the nanocrystallites were cubic CdS with the planes of (111), (220), and (311), respectively. This was consistent with the TEM results. Compared with the results of Akkara et al.,<sup>2</sup> we found

that the CdS clusters entrapped into the PEHTP core exhibit more homogeneous morphology and the particle sizes range from 4 to 8 nm, whereas their TEM shows a crystallite size from 3 to 20 nm and they suggested that the cluster may be representative of a region of polymer chain aggregation. The differences in the TEM result from the variations in the synthesis methods.

SEM (Fig. 9) shows the surface morphology of the PEHTP/CdS composites. Previous studies showed that PEP exhibited separate spheres in the range of 1–1.5  $\mu$ m when the synthesis was carried out in an environment of spherical micelles.<sup>2</sup> It was very interesting to notice that the PEHTP/CdS composites showed less irregular spherical morphology compared with PEP. Nevertheless, the particles were essentially spheres with a much smaller size in the range of 0.07– 0.10  $\mu$ m.

### ATR-FTIR Analysis

The TEM exhibits that CdS particles were encapsulated in the PEHTP core. The encapsulation of CdS inside the PEHTP core leads to an abundance of hydroxyl groups toward the outside of



Figure 9 SEM of PEHTP/CdS nanocomposites.



Figure 10 ATR and transmitted FTIR spectra of PEHTP/CdS nanocomposites.

the core's surface. This could be proved by the ATR–FTIR spectra.

The PEHTP/CdS composite was dissolved in THF and cast onto crystalline KBr to form a film. Both transmission and ATR-FTIR were performed on the same film. Figure 10 exhibits the normalized spectra using absorption peaks at  $\approx 2973$  cm<sup>-1</sup> as the standard. The broad peaks at  $\approx 3450 \text{ cm}^{-1}$  were attributed to the hydroxyl stretch absorption. The OH absorbance of the transmitted FTIR was the average measurement in the bulk film, while ATR-FTIR provided the surface information of the film. The integrated area ratio of 2.5/1 under the curves showed a significant difference: The amount of OH was much more abundant on the polymer surface than in the bulk polymer. This could be rationalized in that CdS clusters were passivated by sulfhydryl groups of PEHTP and formed the center of the composite cores with OH groups pointing outward. This is illustrated in Figure 11.

# UV Optical Absorption and TEM of PC/PEHTP/CdS PEP can be incorporated into PC by copolymerization through triphosgene at low temperature



Figure 11 Schematic structure of PEHTP/CdS composites.



#### Wavelength (nm)

**Figure 12** UV-vis absorption spectra of (a) PC, (b) PC-*co*-PEP, (c) difference spectrum of PC-*co*-PEP and PC, (d) PEP, and (e) PC/PEHTP/CdS composites.

as demonstrated above. PEHTP/CdS composites were dispersed into a PC matrix. Since PEHTP is the copolymer of PEP-*co*-poly(4-hydroxythiophenol), PEHTP can be also bonded covalently to PC.

The <sup>1</sup>H-NMR spectra of the PC/PEHTP/CdS was also obtained, but the structural information was very limited because of the broad and unresolved peaks in the aromatic region.

To investigate the doping effect of CdS on the PC's optical and electronic properties, the UV-vis absorption of pristine polymer and polymer/CdS composites was conducted. Figure 12 presents the UV absorption of the polymers and the polymer/ CdS composites. Our previous study exhibited that PEP showed a stronger and wider absorption than that of PC in the UV range of 250–300 nm. The difference spectrum between PC-co-PEP and PC screened the contribution of PC and exhibited two peaks, 240 and 280 nm, and these two bands were attributed to the  $\pi$ - $\pi$ <sup>\*</sup> transitions of the aromatic fragments. The PC/PEHTP/CdS film showed two distinct and stronger absorptions. compared with the pure PEP and PC-co-PEP film; one at 200-260 nm and the second at 280-310 nm were assigned to  $\pi - \pi^*$  transitions in polyphenol, which is consistent with results reported previously.<sup>4</sup> This increased UV-absorption effect was attributed to the doping of CdS nanoclusters. There is essentially no band at 390 nm ascribed to  $n-\pi^*$  due to the forbidden transition. The TEM of PC/PEHTP/CdS composites indicated that CdS particles still preserved the isolated morphology in the 6-nm range as observed for the TEM of PEHTP/CdS in Figure 8(a).

# **CONCLUSIONS**

Polyethylphenols prepared by enzyme catalysis were modified by copolymerization with polyphenol and PC via transesterification and triphosgene routes. This increased the molecular weights, thereby improving film formation and optical clarity. CdS semiconductor nanocrystallites synthesized in the microenvironment of water-in-oil reversed micelles were also successfully encapsulated into the polymer. This was obtained by first synthesizing the CdS in reversed micelles, followed by the copolymerization of *p*-ethylphenol and 4-hydroxythiophenol in the same reaction system. Sulfhydryl groups could passivate the CdS particles, and, therefore, they were covalently bonded inside the polymer cores. TEM micrographs and ATR-FTIR showed the spherical morphology of PEHTP/CdS composites with the hydroxyl group toward the outside. The PEHTP/CdS cores were dispersed into PC, and PEHTP could be incorporated into PC by chemical bonding. Thus, CdS clusters were dispersed into the polymer matrix. The polymer/CdS was stable in solution due to covalent bonding between the sulfhydryl group and CdS.

The authors thank Prof. M. J. Yacaman at ININ, Mexico, for the TEM. Discussions with Dr. J. Akkara of the U.S. Army Lab at Natick, MA, are gratefully acknowledged.

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