

# Electrically Conductive Composite of Polypyrrole and Liquid Crystalline Copoly(Ester-Amide)s

JINGSHENG BAO, CHAOCHOU XU, WEI CAI, and XIAN-TONG BI\*

Institute of Chemistry, Academia Sinica, Beijing 100080, China

## SYNOPSIS

The modification of the mechanical properties of polypyrrole (PPY) by electrochemical preparation of conductive composite film from pyrrole (PY) and three kinds of liquid crystalline copoly(ester-amide)—PEA(H), PEA(C), PEA(O)—are presented. The electrical conductivity of the PEA(H)/PPY, PEA(C)/PPY, and PEA(O)/PPY composites are the same order of magnitude as PPY. The mechanical properties of the composite films are much better than that of pure PPY, and the composite films have good conductivity and thermostability. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

It is well known that the polypyrrole (PPY) films, which are synthesized by electrochemical polymerization, show high electrical conductivity with good stability in air,<sup>1-3</sup> but the pure PPY films are difficult to process to a desired material because of its insolubility and brittleness, and the mechanical properties of PPY are too low to use. Recently, some papers were published about modifying the properties of PPY. One of the routes of improving the flexibility of the conducting polymer is to make a composite material by electrochemical-polymerizing polypyrrole in a matrix of another polymer, this method having been reported by some other papers.<sup>4,5</sup> We have prepared the PPY/Nylon-6, PPY/polyurethane, PPY/poly(p-phenylene-terephthalamide) (PPTA) composites, those films having high tensile strength and conductivity.<sup>4-8</sup>

In this paper, the modification of the mechanical properties of poly-pyrrole (PPY) by electrochemical preparation of conductive composite films from pyrrole (PY) and three kinds of liquid crystalline copoly(ester-amide)—PEA(H), PEA(C) and PEA(O)—are presented.

The electrical conductivity of the PEA(H)/PPY, PEA(C)/PPY, and PEA(O)/PPY composites are

the same order of magnitude as PPY. The mechanical properties of the composite films are much better than that of pure PPY, and the composite films have good conductivity and thermostability.

## EXPERIMENTAL

### Materials

Pyrrole was purified by distillation over NaOH under N<sub>2</sub>, b.p. 128–129°C; *N*-methyl pyrrolidone (NMP) was vacuum distilled after being dried by 5 Å molecular sieves, b.p. 76–77°C/6 mm Hg; 2,5-dichloro-terephthaloyl chloride (DCC) was synthesized according to the literature;<sup>9</sup> *p*-aminobenzoic acid m.p. 185–188°C; diphenyl chlorophosphate (DPCP) b.p. 314–316°C/272 mm Hg; pyridine (PY) was refluxed over potassium hydroxide for 2 h and then distilled; hydroquinone (HQ), methylhydroquinone (MHQ), and chlorohydroquinone (CHQ) were recrystallized.

### Synthesis of Bis(6-hydroxyhexyl)terephthalate

Dimethyl terephthalate [19.4 g (0.1 M)] and 118.2 g (1 M) 1,6-hexandiol with a few drops of tetrabutyl titanate (Ti(oBu)<sub>4</sub>) were added to a 500 mL three-necked reaction bottle equipped with a condenser, drying tube, distilling head, and stirrer. The reaction mixture was heated at 180°C for 5 h, until all the methanol had distilled off. The residue was poured

\* To whom correspondence should be addressed.

into an excess of water, and the precipitate was separated by a suction filter, and then the ppt. was washed with water several times until all the unreacted 1,6-hexandiol had been removed. The products were dissolved in chloroform and dried with anhydrous magnesium sulfate, and the chloroform was removed by distillation. The pure bis(6-hydroxyhexyl)terephthalate (BHT) (m.p. 72°C) was obtained by recrystallizing the crude product from benzene.

#### Synthesis of *N,N'*-Di(4-benzencarboxylic acid)-2,5-dichloroterephthalamide

*N*-methyl pyrrolidone (NMP) (50 mL) and 8.23 g (0.06 *M*) of *p*-aminobenzoic acid were added to a 500 mL three-necked reaction bottle equipped with a condenser, dropping funnel, drying tube, stirrer, and a N<sub>2</sub> inlet tube. The mixture was cooled to about 4°C with an ice-water bath; after the *p*-aminobenzoic acid was dissolved, the solution of 8.16 g (0.03 *M*) 2,5-dichloroterephthaloyl chloride (DCC) in 50 mL NMP was added from the dropping funnel with rapid stirring, and the reaction temperature was kept under 10°C. The reaction was continued for 2 h at room temperature, then the reaction temperature was raised to and maintained at 60°C for 3 h; after that, the reaction was continued over night at room temperature. The reaction products were poured into an excess of water. The precipitate was filtered off and washed with 1*N* HCl and water several times; the product was recrystallized from dimethylformamide (DMF)/H<sub>2</sub>O (60/40) and dried in a dynamic vacuum oven at 60°C, and the pure *N,N'*-bis(4-benzen carboxylic acid)-2,5-dichloroterephthalamide (CCA) was obtained.

#### Synthesis of Copoly(ester-amides)

The polymers were prepared by solution polycondensation. For example, 70 mL pyridine (py), 4.259

g (0.009 *M*) CCA and 5.2 mL (0.025 *M*) diphenyl chlorophosphate (DPCP) were added to a 250 mL three-necked reaction bottle equipped with a condenser, drying tube, stirrer, and a N<sub>2</sub> inlet tube. The reaction proceeded at 120°C for 10 min, then 20 mL pyridine solution of 2.199 g (0.06 *M*) BHT and 0.33 g (0.003 *M*) hydroquinone (HQ) were rapidly added. The reaction products were poured into an excess of water, the precipitate was filtered off, and washed with methanol several times, the product was dried in a dynamic vacuum oven at 65°C, and the copoly(ester-amide) PEA(H) was obtained. Copoly(ester-amides) PEA(C) and PEA(O) were synthesized by a similar method.

#### Electrochemical Polymerization of Pyrrole into Copoly(ester-amide) Films

Pyrrole (0.5 mol), in a one-compartment cell, was electrochemically polymerized on a copoly(ester-amide) film coated Ni working electrode in a mixed solvent of EG/H<sub>2</sub>O (1/1) with electrolyte 0.4 mol TSONa and a Ni counter electrode by direct electrical current.

#### Characterization

The electrical conductivity was measured by a four point probe method. IR spectra were measured on a Perkin-Elmer 180 spectrophotometer. The thermal properties were measured under N<sub>2</sub> atmosphere using a Du Pont 1090 Thermal Analyzer coupled to the TGA module and a heating rate of 20°C/min. Mettler FP 51, FP 52, and an Olympus B071 polarized microscope with a hot stage were used to study the liquid crystalline properties of terephthalate and copolymers. X-ray diffraction pattern was obtained using a diffractometer and CuK radiation.

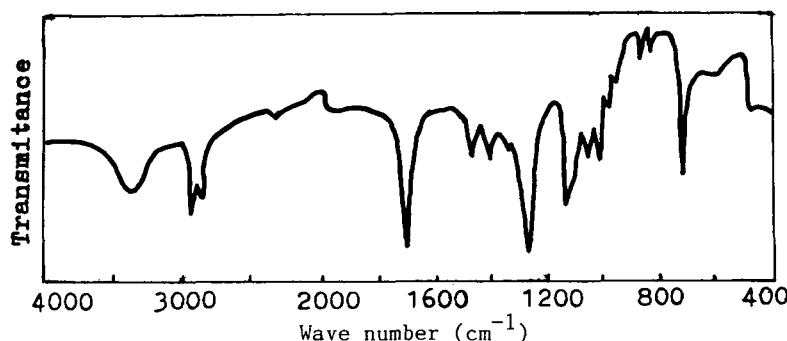


Figure 1 IR spectrum of BHT.

**Table I** Elementary Analysis of CCA

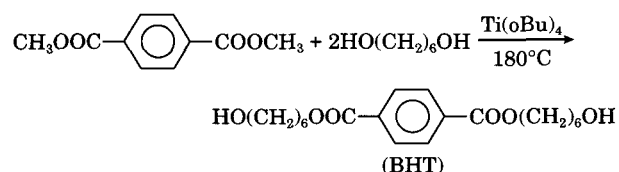
Element	Calc.	Found
C%	55.83	55.78
H%	2.98	3.01
Cl%	14.98	14.86
N%	5.92	5.87

## RESULTS AND DISCUSSION

### Terephthalate (BHT)

#### Synthesis

It was synthesized from dimethylterephthalate and 1,6-hexandiol catalyzing with a few drops of  $Ti(oBu)_4$ , the reaction is shown as following:

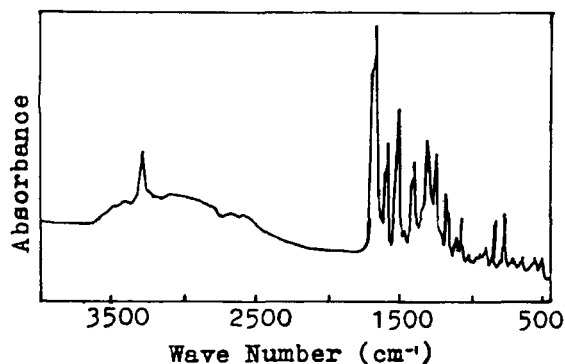
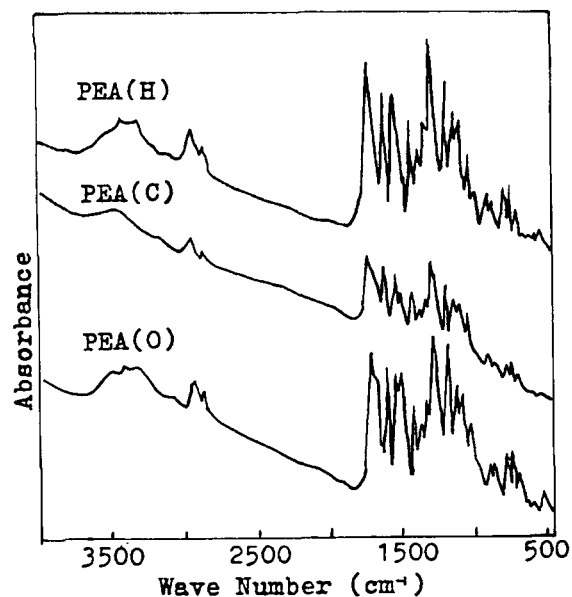


The elemental analysis of the terephthalate (BHT) is: C% (Calc. 65.54 Found 65.45), H% (Calc. 8.20 Found 8.20). There is good agreement with the calculated results.

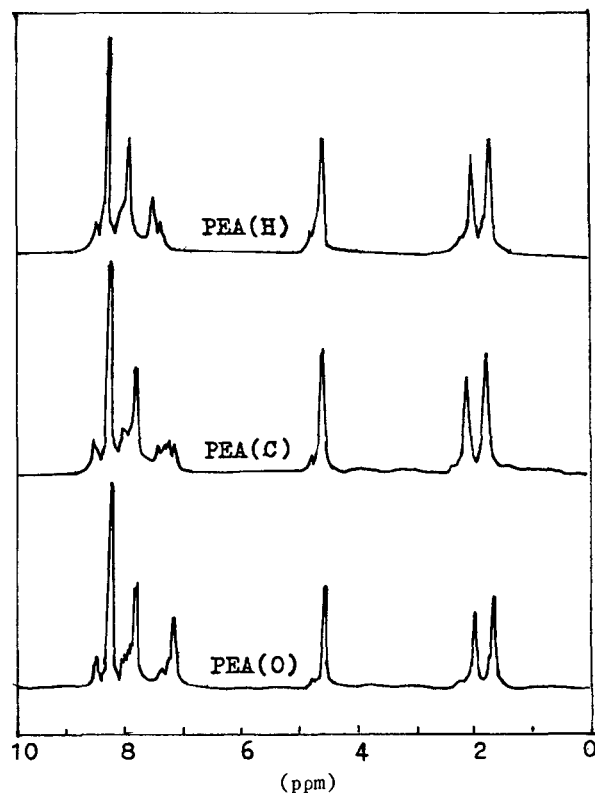
#### IR Spectrum

The IR spectrum of bis(6-hydroxyhexyl) terephthalate (BHT) is shown in Figure 1.

The absorption peak at  $3400\text{ cm}^{-1}$  is from the —OH end groups; that at  $1720\text{ cm}^{-1}$  is  $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$

**Figure 2** FT-IR spectrum of CCA.**Figure 3** FT-IR spectra of PEA.

stretch; the peaks at  $1275$ ,  $1130$ , and  $1060\text{ cm}^{-1}$  indicate the presence of ester groups and the strong absorption peaks at  $2920$ ,  $2850$ ,  $1475$ , and  $730\text{ cm}^{-1}$  correspond to  $\text{—CH}_2\text{—}$  groups.

**Figure 4**  $^1\text{H-NMR}$  spectra of PEA in  $\text{CF}_3\text{COOD}$ .

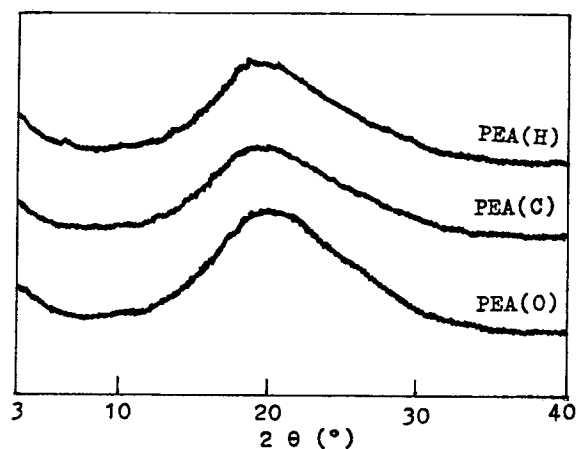


Figure 5 X-ray diffraction pattern of PEA.

### Liquid Crystalline Behavior

The phase transition temperatures were observed using a polarizing microscope equipped with a hot stage and a heating rate of 1°C/min. The optical texture of terephthalate BHT was observed, and it was established that only nematic mesophase is formed.

### *N,N'*-Bis(4-benzene carboxylic acid) 2,5-dichloroterephthalamide (CCA)

#### Synthesis

*N,N'*-Bis(4-benzene carboxylic acid) 2,5-dichloroterephthalamide was synthesized from *p*-amino-

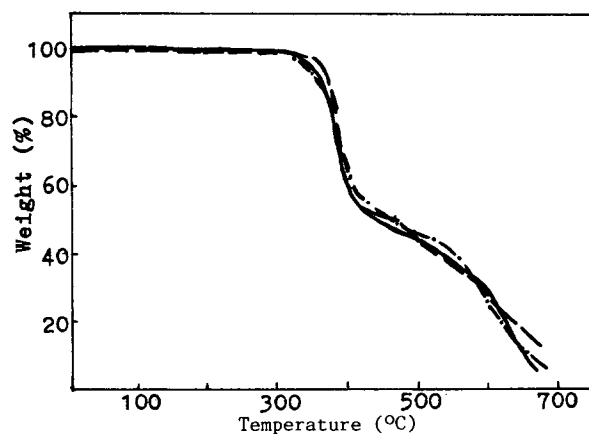
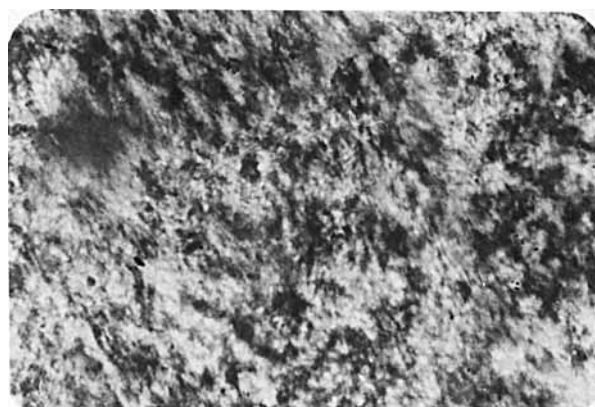


Figure 6 TGA curves of PEA: —: PEA(H) — —: PEA(C) — · —: PEA(O).

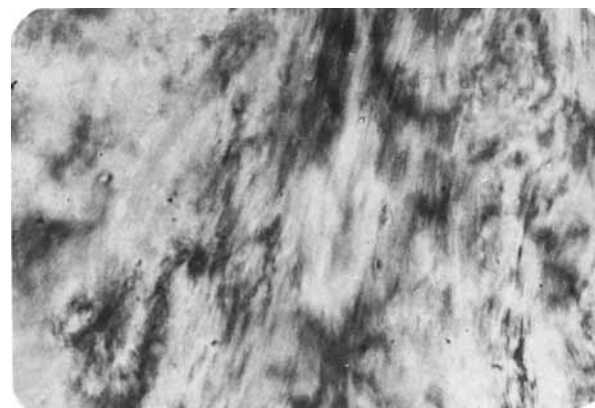
benzoic acid and 2,5-dichloroterephthaloyl chloride in NMP solvent; the condensation reaction is shown as following:



(a)



(b)



(c)

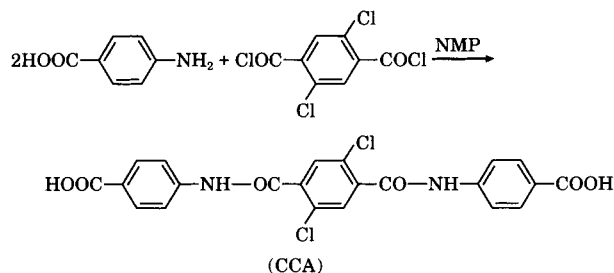
Figure 7 Optical micrographs of copoly(ester-amide)s. (a) PEA(H) at 250°C; (b) PEA(C) at 250°C; (c) PEA(O) at 220°C.

Table II Solubility of PEA in Various Solvents

Polymer	H <sub>2</sub> SO <sub>4</sub>	CF <sub>3</sub> COOH	NMP	DMAc	DMF	Py	DMSO	TCEP*	CHCl <sub>3</sub>	THF
PEA(H)	+	+	+	+	+	+	+	+	±	-
PEA(C)	+	+	+	+	+	+	+	+	±	-
PEA(O)	+	+	+	+	+	+	+	+	±	-

\* TCEP: tetrachloroethane/phenol (60/40).

+: Dissolve ±: swell -: undissolve.



The elemental analysis results of the terephthalamide (CCA) are shown in Table I.

The experimental results are in agreement with the calculated results.

### IR Spectrum

The IR spectrum of *N,N'*-bis(4-benzene carboxylic acid) 2,5-dichloroterephthalamide (CCA) is shown in Figure 2.

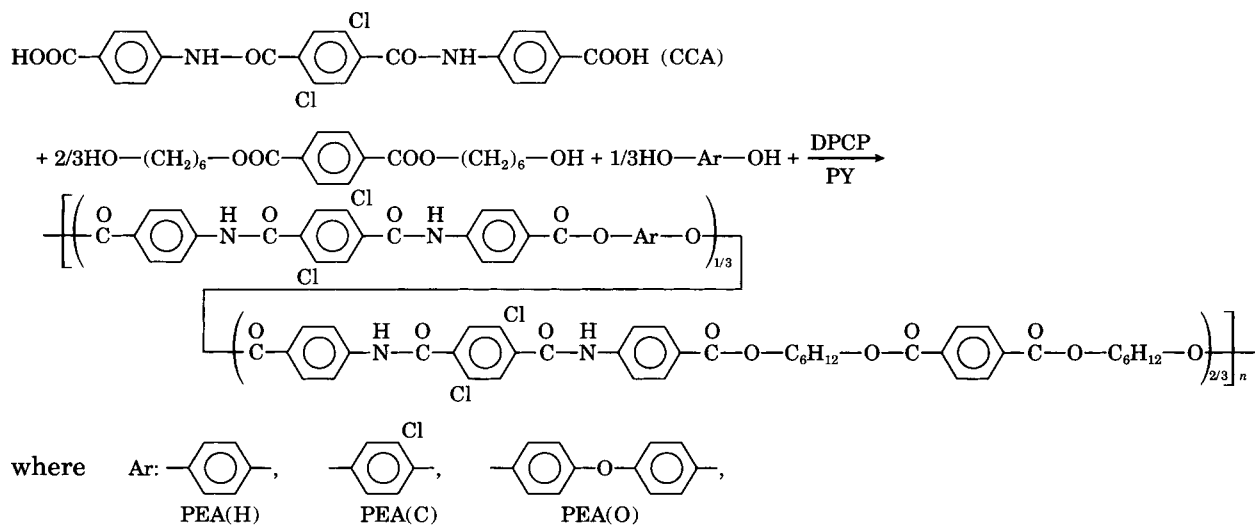
The infrared spectrum (Fig. 3) express that a broad peak between 2500–3500 cm<sup>-1</sup> is the carbox-

ylic O—H stretch vibrational absorption peak, the peak at 1403 cm<sup>-1</sup> is the bend vibrational absorption peak, and the peak at 1403 cm<sup>-1</sup> is the bend vibrational absorption peak of O—H. The 1315 cm<sup>-1</sup> peak is from C—O stretch absorption. The peaks appeared at 3202, 1070, 1505, and 1200 cm<sup>-1</sup> are correlated to the bands I, II, and III of amide N—H stretch vibration. The peak at 1090 cm<sup>-1</sup> belongs to Ar—Cl. And the absorption peaks at 1605, 1513, and 1460 cm<sup>-1</sup> are C=C stretch vibration of benzene ring.

### Copoly(ester-amide)s (PEA)

#### Synthesis

Three kinds of liquid crystalline copoly(ester-amide)—PEA (H), PEA (C), and PEA (O)—were synthesized by the direct polycondensation with diphenyl chlorophosphate (DPCP); the reaction is shown as following:



**Table III** The Phase Transition Temperature of Polymers

Polymer	$T_m$ (°C)	$T_d$ (°C)	Stiropalescence
PEA(H)	243.7	363	Strong
PEA(C)	240.5	359	Strong
PEA(O)	198.8	362	Strong

### Characterizations

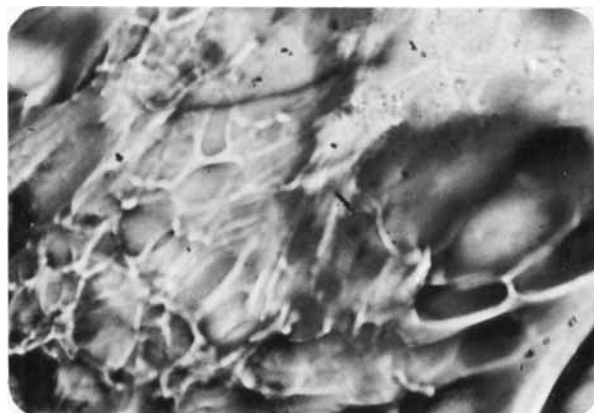
The copoly(ester-amide)s were characterized by FT-IR, <sup>1</sup>H-NMR, X-ray diffraction, thermostability, solubility, and polarized microscope.

*IR Spectra of PEA.* The spectra of PEA(H), PEA(C), and PEA(O) are shown in Figure 3.

The absorption peak at 3400 cm<sup>-1</sup> is from the —OH end group; the 1720 cm<sup>-1</sup> peak is a —C— stretch; the peaks at 1272, 1170, and 1070 cm<sup>-1</sup> indicate the presence of an ester group, and the absorption peaks at 2925, 2850, and 730 cm<sup>-1</sup> correspond to —CH<sub>2</sub>— groups.

*H-NMR Spectra of PEA.* All poly(ester-amide)s were identified by their NMR spectra. The measurements of NMR spectra were carried out in trifluoroacetic acid-d at room temperature and tetramethylsilane as an internal reference standard. The H-NMR spectra of PEA(H), PEA(C), and PEA(O) are shown in Figure 4.

The NMR spectra showed that a complex multiplet in the chemical shift range from 7.2–8.4 ppm due to the protons of phenyl bonded to the amide carbonyl and ester carbonyl were observed. And the peaks for the protons of methylene group at 4.7, 2.1, and 1.8 ppm, and the methylene bonded to ester carbonyl appeared at 4.7 ppm.

**Figure 8** Optical micrograph of PEA(C).

*X-Ray Diffraction of PEA.* The X-ray diffraction pattern of PEA(H), PEA(C), and PEA(O) are shown in Figure 5. The curves presented a broad band around 2θ at 20°.

*Thermostability of PEA.* TGA curves of PEA(H), PEA(C), and PEA(O) are shown in Figure 6.

The results showed that copolymers have much better thermostability, with the beginning weight loss greater than 300°C.

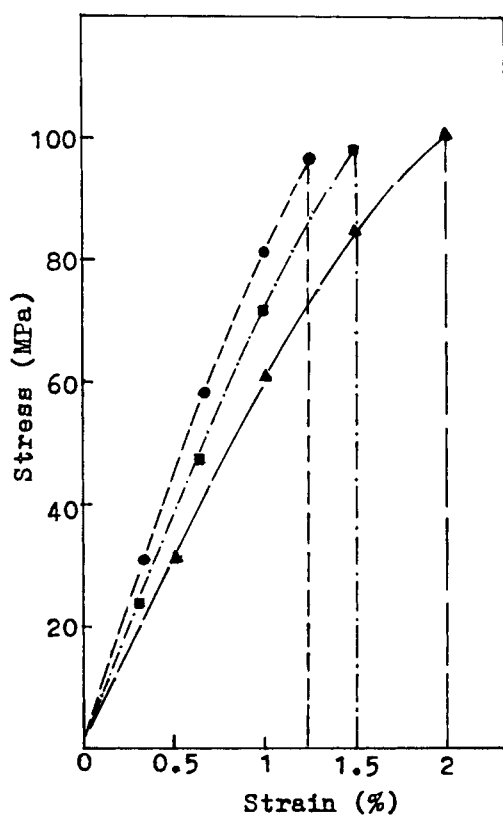
*Solubility of PEA.* The solubility of PEA(H), PEA(C), and PEA(O) are shown in Table II.

The experimental results showed that the copolymers have very good solubility, they are not only dissolved in strong acid (H<sub>2</sub>SO<sub>4</sub>, CF<sub>3</sub>COOH) but are also dissolved in organic solvents (NMP, DMAC, Py, DMSO, TCEP) and swell in chloroform but undissolve in THF.

*Liquid Crystalline Behavior of PEA.* Observed is the phase transition temperature of copolymers by a polarizing microscope equipped with a hot stage at a heating rate of 1°C/min; the results are shown in Table III.

**Table IV** Electrical Conductivity and Mechanical Properties of PEA/PPY Composites

Matrix Film	Composite	Electrical Conductivity S/cm	Tensile Strength (Mpa)	Elongation at Break (%)
PEA(H)	PEA(H)/PPY	78	101	2
PEA(C)	PEA(C)/PPY	75	98	1.5
PEA(O)	PEA(O)/PPY	77	96	1.2



**Figure 9** Stress-strain curves for PEA/PPY composites:  $\blacktriangle$  PEA(H)/PPY,  $\blacksquare$  PEA(C)/PPY,  $\bullet$  PEA(O)/PPY.

Figure 7 (a-c) shows the optical micrographs for PEA(H), PEA(C), and PEA(O), respectively.

The results of Table III and Figure 7 show that the copolymers have very good thermotropic liquid crystalline properties and the mesophase is in a broad temperature range.

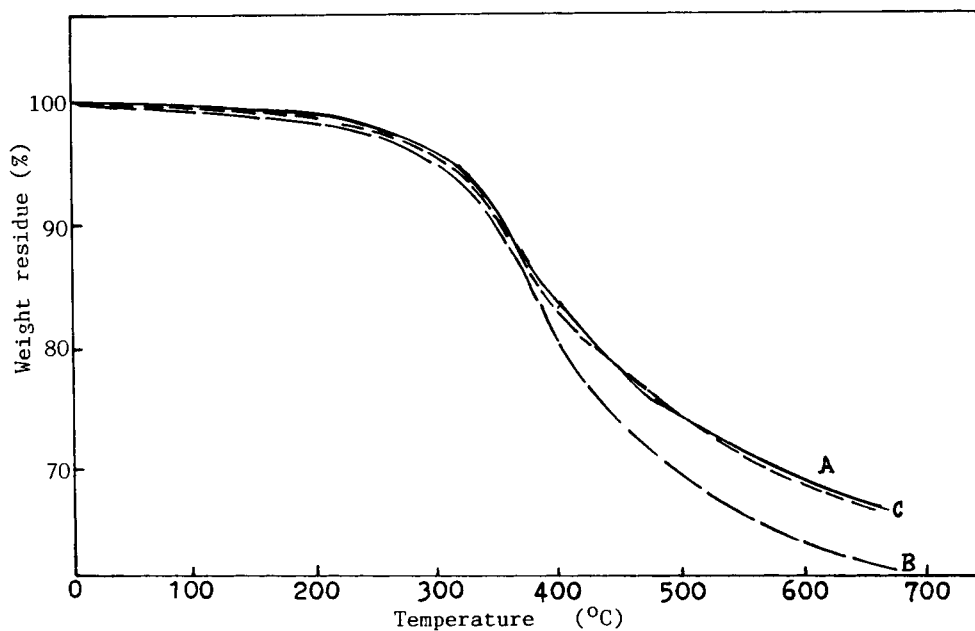
Figure 8 is the optical micrograph for a solution of PEA(C) in NMP-CaCl<sub>2</sub> (5%). The lyotropic liquid crystalline behavior was observed when the concentration was above their critical concentration (C\*). All of the results show that the copoly (ester-amide)s have both thermotropic and lyotropic liquid crystalline behavior.

#### Polyester-amide/Polypyrrole (PEA/PPY) Molecular Composites

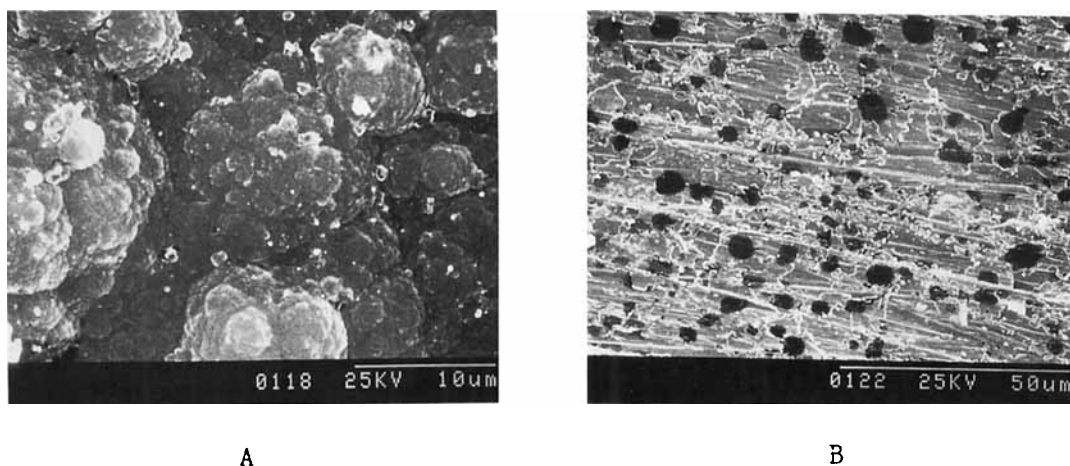
The PEA(H)/PPY, PEA(C)/PPY, and PEA(O)/PPY were prepared by electrochemical polymerization on a copoly (ester-amide) film coated Ni working electrode in a mixed solvent with TsONa electrolyte and a Ni counter electrode by direct electrical current.

#### Electrical Conductivity and Mechanical Properties of PEA/PPY Composites

The electrical conductivity of three kinds of polyesteramide composited with polypyrrole PEA(H)/



**Figure 10** TGA curves of PEA/PPY conducting composites: (A) PEA(H)/PPY, (B) PEA(C)/PPY, (C) PEA(O)/PPY.



**Figure 11** SEM photographs of PEA(H)/PPY composite film: (A) face to solution; (B) face to electrode.

PPY, PEA(C)/PPY, and PEA(O)/PPY are in the same order of magnitude for pure PPY (Table IV). And the mechanical properties of the three kinds of composites are all better than that of pure PPY (Table IV).

The stress-strain curves for PEA/PPY composites are shown in Figure 9.

#### **Thermostability of PEA/PPY Composites**

The TGA curves (Fig. 10) show that all of the starting points of weight loss of the PEA/PPY composites are 310°C and the 10% weight loss is at 360°C, which is a little bit better than that of pure PPY.<sup>10</sup>



**Figure 12** SEM photograph of PEA(H)/PPY composite (cross-section).

#### **Morphology of PEA/PPY Composite**

The scanning electron micrographs show that the surface morphology of PEA(H)/PPY composite that face solution is a typical polypyrrole surface and looks like cauliflower, and the composite surface face to electrode is a condensed flat area (Fig. 11).

The cross-section SEM picture shows the PEA(H)/PPY's inner structure is PPY condensed small balls homogeneously distributed in the PEA(H) matrix (Fig. 12).

#### **CONCLUSION**

Three kinds of liquid crystalline copoly(ester-amide)—PEA(H), PEA(C) and PEA(O)—were prepared by direct polycondensation with diphenyl chlorophosphate (DPCP) in pyridine, and that copoly(ester-amide)s have both thermotropic and lyotropic liquid crystalline behavior.

Three kinds of copoly(ester-amide) composited with polypyrrole PEA(H)/PPY, PEA(C)/PPY, and PEA(O)/PPY were prepared by electrochemical polymerization.

The electrical conductivity of PEA/PPY composites are in the same order of magnitude as pure PPY.

The mechanical properties of PEA/PPY composites are better than the pure PPY.



## REFERENCES

1. K. J. Wynne and G. B. Street, *Ind. Eng. Chem. Prod. Res. Dev.*, **21**, 23 (1982).
2. A. F. Diaz, J. I. Gastillo, J. A. Logan, and W.-Y. Lee, *J. Electroanal. Chem.*, **129**, 115 (1981); A. F. Diaz and K. K. Kanazawa, *J. Chem. Soc. Commun.*, **14**, 635 (1979).
3. K. K. Kanazawa, A. F. Diaz, W. D. Gill, P. M. Grant, G. B. Street, M. D. Gardini, and J. J. Kwak, *Synth. Met.*, **1**, 329 (1981).
4. O. Niwa and T. Tamamura, *J. Chem. Soc. Commun.*, **13**, 817 (1984).
5. M. D. Paoli, R. J. Waltman, A. F. Diaz, and J. J. Bargon, *J. Polym. Sci. Chem. Ed.*, **23**, 1687 (1985).
6. J. S. Bao, B. Z. Han, and X. T. Bi, *Acata Polymerica Sinica*, **5**, 376 (1987).
7. X. T. Bi, Q. B. Pei, B. Z. Han, and J. S. Bao, *Chinese J. Polym. Sci.*, **9**, 290 (1991).
8. J. S. Bao, C. C. Xu, W. Cai, and X. T. Bi, *Abstract of MRS'92 Fall Meeting*, Boston, U.S.A., 1992, p. 450.
9. Report of department of chemistry of Jiang-Xi Normal University, 1989.
10. X. T. Bi, *Acata Polymerica Sinica*, **4**, 452 (1991).

Received December 7, 1992

Accepted November 7, 1993