Chemical Grafting of Aniline and *o*-Toluidine onto Poly(ethylene terephthalate) Fiber

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ABSTRACT: Graft copolymerization of poly(aniline) and poly(*o*-toluidine) onto poly(ethylene terephthalate) fiber was conducted by using peroxydisulfate as a lone initiator under nitrogen atmosphere at various experimental conditions in aqueous hydrochloric acid medium. The grafting of poly(aniline) and poly(*o*-toluidine) onto poly(ethylene terephthalate) fiber was verified by recording cyclic voltammetry of the grafted fiber, conductivity measurements, and thermal analysis. Graft parameters—such as % grafting, % efficiency, and the rate of grafting—were followed. Grafting was always accompanied by homopolymerization. The rate of homopolymerization was also followed in all experimental conditions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 121–128, 1999

Key words: graft copolymerization; aniline; *o*-toluidine; poly(ethylene terephthalate) fiber

INTRODUCTION

Free radical graft copolymerization of vinyl monomers onto natural^{1,2} and synthetic^{3,4} fibers has been reported by several workers. It is believed that the graft copolymerization occurs through the abstraction of hydrogen atom from the carbon-containing hydroxyl group,¹ the polymer backbone-containing amino group,⁵ and backbones containing active carbon atom.⁶ Various free radical initiators are used for this purpose.^{7–9} Among those, peroxy disulfate ion was proven to be an excellent choice, with minimum side products.^{10,11}

Aniline and various ring-substituted anilines are polymerized by chemical^{12,13} and electrochemical^{14,15} methods. Graft copolymerization of electrically conducting polymers onto natural and synthetic polymers have been performed by electrochemical methods.¹⁶ Recently, Toppare and colleagues¹⁷ prepared a conducting polymer composite, and they reported that the composites prepared electrochemically gave the best results in terms of conductivity and air stability. Li and colleagues¹⁸ grafted poly(aniline) (PANI) onto the backbone of amino-functionalized polystyrene by using ammonium persulfate as a lone initiator. Li and coworkers¹⁹ conducted the graft copolymerization of PANI onto polyaminostyrene backbone and provided spectroscopic evidence for the grafting of PANI. PANI was also grafted onto different polymer backbones (silk and wool fibers) through the electrochemical method.²⁰

In the previously described studies, the probability of simultaneous homopolymerization and isolation of grafted polymer from the homopolymer has not been well accounted. The present study directs its attention to examine the extent of homopolymer formation during grafting of PANI and poly(o-toluidine) (POT) onto poly(ethylene terephthalate) (PET) fiber and to the isolation of the grafted backbone from the homopolymer. A comparison of the grafting parameters of PANI and POT onto the same backbone under identical conditions will also been investigated.

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EXPERIMENTAL

Aniline (AN) (Fischer AR) and *o*-toluidine (OT) (SRL AR) were used after distillation under vacuum. Potassium peroxy disulfate (PDS) (CDH AR) was used as such. To remove any adhering impurities and expose the reactive sites of PET (a gift sample from Madura Coats, Madurai, India), the fiber was swollen in 2% phenol solution for 48 h, washed with water, and dried. Hydrochloric acid (HCl) (Fischer AR), *N*-methyl pyrrolidone (NMP) (SRL), acetone (Ranbaxy AR), and the other chemicals were used without further purification.

Procedure

A typical graft copolymerization study was conducted as described.

PET (W_1, g) was immersed in definite concentration of HCl (to adjust acidity) in a polymer tube and thermostated for 30 min. The required amount of monomer (ANI or OT) was added and deaerated for another 15 min. Graft copolymerization was initiated by the addition of calculated volumes of PDS (using standard solutions). The time of adding PDS was taken as the starting time for the reaction. (Polymerization conditions were selected in such a way that no polymerization occurred in the absence of added oxidant). This was ascertained by a separate experiment. At the end of the reaction time, the reaction was arrested by blowing air into the polymer tube to stop further reactions.

The reaction mixture was filtered using a G4sintered crucible and washed with 1.00M HCl several times, dried (at 80°C for 4 h), and weighed until constant weight. This gives the total weight of the grafted polymer along with the homopolymer (W_2, g) . The grafted PET was soxhlet with NMP for several hours to remove the homopolymer (no color changes were seen in the grafted fiber). The extraction was repeated until separation of the homopolymer from the grafted sample was completed. This was ascertained by drying the fiber in vacuum until constant weight (W_3, g) . The difference in $(W_3 - W_1)$ gives the weight of the grafted polymer. The difference in $(W_2 - W_3)$ gives the weight of the homopolymer PANI or POT.

Rate Measurements

The rate of grafting (R_g) , rate of homopolymerization (R_h) , % grafting, and % efficiency were calculated as follows:

% grafting =
$$\frac{W_3 - W_1}{W_1} \times 100$$

% efficiency = $\frac{W_3 - W_1}{W_4} \times 100$

Rate of grafting
$$(R_g) = rac{W_3 - W_1}{V.t.M} imes 1000$$

where $W_3 - W_1$ is weight of the grafted polymer, V is total volume of the reaction mixture, t is reaction time, and M is molecular weight of ANI or OT.

Simultaneous Homopolymerization

Rate of homopolymerization was determined as follows:

Rate of homopolymerization (R_h)

 $=rac{W_2-W_3}{V.t.M} imes 1000$

where $W_2 - W_3$ is weight of the homopolymer, PANI, or POT.

Cyclic Voltammetric Study

The PANI- or POT-grafted PET fiber was allowed to stand overnight in aqueous ammonia solution (the fiber turned blue), and the fiber was then washed well with acetone (2–3 times) to remove any adhering materials. The dried fiber was immersed in formic acid and made into a paste. The paste was dip-coated on to a Pt microworking electrode (surface area of 9.50×10^{-2} cm²). Cyclic voltammograms (CVs) were recorded (using BAS 100 A Electrochemical Analyzer) for the grafted PANI or POT-coated Pt electrode with HCl as a background electrolyte by cycling the potential in the range of 0.00 to 0.80 V and Ag/AgCl as reference electrode.

Thermal Gravimetric Analysis (TGA)

TGA was conducted for both grafted and ungrafted fibers by using the Dupont 2000 instrument.

	Weight of Grafted Fiber (g)									
Grafted Fiber Under Process	PANI				РОТ					
Before treatment with ammonia	0.1000	0.1500	0.2500	0.3000	0.3500	0.1000	0.1500	0.2000	0.2500	0.3000
After treatment with ammonia	0.0976	0.1445	0.2400	0.2855	0.3309	0.0970	0.1440	0.1863	0.2300	0.2546
After treatment with NMP	0.0976	0.1445	0.2400	0.2855	0.3309	0.0970	0.1440	0.1863	0.2300	0.2546

Table I Weight Changes in the Grafted Fiber

 $[ANI]/[OT] = 0.30 \text{ mol } L^{-1}; [PDS] = 0.01 \text{ mol } L^{-1}; [HCl] = 1.00 \text{ mol } L^{-1}; \text{ temperature} = 45^{\circ}C.$

Conductivity Measurements

Conductivity of both PANI- and POT-grafted fibers were measured by using the Keithley 617 programmable Electrometer instrument.

RESULTS AND DISCUSSION

Graft copolymerization of ANI and OT onto PET fiber was performed separately under nitrogen atmosphere at various experimental conditions, such as different [ANI] or [OT], [PDS], and the fiber amount. In each of the cases, while varying the concentration of one of the components, the other experimental conditions were kept constant.

It was found that the medium becomes green immediately on the addition of the initiator in all the experimental conditions, and green particles of PANI or POT were also found to precipitate during the course of the reactions. A systematic procedure was therefore adopted for following the course of grafting, as well as the simultaneous homopolymerization of ANI or OT as described in the Experimental section. The possibility of grafting PANI or POT onto PET fiber was checked by the following method.

The homopolymer (PANI or POT) was separated from the grafted fiber and care was taken to remove the possible adherent particles of PANI or POT on the PET fiber by physical adsorption. This was done in a systematic experimental analysis of the grafted fiber. Such a method is adopted for the first time herein to separate possible adherent homopolymers.

The grafted fiber (green color) was allowed to stand in aqueous ammonia solution for the conversion of the doped PANI or POT to neutral form (blue color).²¹ This process would convert both doped PANI or POT in grafted, as well as the physically adsorbed, homopolymers PANI or POT to neutral forms. The grafted fiber was then dried and soaked in NMP to remove the possible adhered neutral PANI or POT on the PET fiber. In the first conversion of doped to neutral polymer (on treatment with aqueous ammonia solution), 5% to 20% weight loss²² was noted (Table I) in the fiber weight in both PANI or POT grafting cases. This is in accordance with the removal of dopant ions during the conversion of doped polymer to neutral polymer. However, there was no significant difference in the weight of the grafted polymer after treatment with NMP. The color of the fiber remains blue even after the treatment with NMP. The above two combined facts (no weight loss after the treatment with NMP and the blue color of the fiber) provide evidence for the possible incorporation of PANI or POT units on the backbone of the PET fiber during grafting.

This was further evident while recording the CV of the grafted fiber. The CVs of the grafted



Figure 1 CVs recorded for PANI film (A) and PANIgrafted PET film (B) at the sweep rate of 100 mV s^{-1} in 1.00*M* HCl.



Figure 2 CVs recorded for POT film (A) and POTgrafted PET film (B) at the sweep rate of 100 mV s⁻¹ in 1.00*M* HCl.

polymer-coated Pt electrode in 1M HCl are presented in Figures 1 and 2. For the sake of comparison, the homopolymers formed PANI or POT were also made into a film on the Pt surface, and CVs of the PANI or POT homopolymer-coated electrodes were presented in Figures 1 and 2. The CVs of PANI, the homopolymer, and PANIgrafted copolymer-coated electrodes showed resemblance to each other (Fig. 1). The first anodic peak in the CV remains unchanged in these two film-coated electrodes; however, the second anodic peak in the grafted fiber-coated electrode was shifted to a more positive value in comparison with PANI homopolymer-coated electrodes. This could be attributed to the resistive PET background in the grafted case. Similar observation was seen in the CV of POT-grafted PET fiber (Fig. 2). This observation auguments the chemical grafting of PANI or POT onto PET fiber.

Effect of Monomer Concentration on Graft Parameters

Table II presents the variations in % grafting, % efficiency, rate of grafting, and rate of homopoly-

merization of ANI or OT with the monomer concentrations of 0.20 mol L^{-1} to 0.60 mol L^{-1} . It is interesting to note that the R_h and R_g increases with an increase in [ANI] and [OT]. R_h was found to be low with OT as a monomer in comparison with ANI. R_g was found to be high for OT than ANI in all of the previously described experimental conditions. This gives an indication that POT could be better grafted onto PET than PANI. The % grafting and % efficiency values also show the same trend.

Effect of Initiator Concentration on Graft Parameters

Table III presents the effect of varying the [PDS] on graft parameters. The [PDS] was varied from $0.005 \text{ mol } \text{L}^{-1}$ to $0.025 \text{ mol } \text{L}^{-1}$ while keeping other experimental conditions as constant. Here again R_h was found to be higher with ANI as monomer in the concentration range of PDS, 0.005 mol L⁻¹ to 0.025 mol L⁻¹. After that, R_h showed a decreasing trend with an increase in [PDS] in the case of ANI, in contrast to the OT that shows a steady increase in R_h . These observations are also in accordance with the higher R_g , % grafting, and % efficiency for OT in comparison with ANI for low [PDS]. However, at higher [PDS], > 0.02 mol L⁻¹, a perusal at Table III shows that % grafting efficiency was found to be lower for OT than ANI.

Effect of Amount of Fiber on Graft Parameters

The effect of amount of fiber on graft parameters was studied under conditions described in Table IV, and the graft parameters are presented for comparison. The values of R_h showed different trends in these two monomers. R_h was found to increase with the amount of fiber in OT case.

	$R_h imes 10^7 \ ({ m mol}\ { m L}^{-1}\ { m s}^{-1})$		$R_g imes 10^7 \ ({ m mol} \ { m L}^{-1} \ { m s}^{-1})$		% Grafting		% Efficiency	
$(\text{mol } L^{-1})$	а	b	а	b	а	b	а	b
0.20	37.18	13.16	8.98	10.36	3.70	5.00	0.81	0.94
0.30	42.23	29.75	9.32	12.64	3.85	6.10	0.56	0.77
0.40	45.92	32.66	10.84	13.79	4.45	6.65	0.48	0.63
0.50	52.41	34.73	9.99	14.93	4.10	7.20	0.36	0.54
0.60	43.01	34.11	9.45	15.03	3.90	7.25	0.28	0.46

Table II Effect of [ANI]/[OT] on Graft Parameters

^a = [ANI]; ^b = [OT]; [PDS] = 0.01 mol L^{-1} ; [HCl] = 1.00 mol L^{-1} ; temperature = 45°C; weight of PET = 0.20 g.

[PDS]	$R_h imes 10^7 \ ({ m mol} \ { m L}^{-1} \ { m s}^{-1})$		$R_g imes 10^7 \ ({ m mol} \ { m L}^{-1} \ { m s}^{-1})$		% Grafting		% Efficiency	
$(\text{mol}\ \text{L}^{-1})$	а	b	а	b	а	b	а	b
0.005	20.21	15.55	3.81	14.93	1.60	7.20	0.41	0.63
0.010	39.01	24.15	6.82	23.12	2.85	11.65	0.55	0.97
0.015	68.01	60.55	9.22	26.12	3.85	12.60	0.74	1.58
0.020	89.12	108.66	12.36	28.61	5.15	13.80	1.10	1.73
0.025	76.71	136.14	18.33	32.76	7.65	15.80	1.36	1.98

Table III Effect of [PDS] on Graft Parameters

 $[ANI]^{a}/[OT]^{b} = 0.30 \text{ mol } L^{-1}; [HCl] = 1.00 \text{ mol } L^{-1}; \text{ temperature} = 45^{\circ}C; \text{ weight of PET} = 0.20 \text{ g}.$

However, R_h showed an increasing trend only up to a particular weight of fiber followed by a decreasing trend in the ANI case. The graft parameters, % grafting, and % efficiency were found to be higher for OT, and support OT monomer has better graft parameters.

Tzou and Gregory²³ studied the effect of added fiber on chemical polymerization of ANI in the presence and absence of PET fiber. No correlation was tried to relate the changes in the rate of homopolymerization in that study. In the electrochemical polymerization of ANI, Wei and colleagues²⁴ proposed an autoacceleration effect by the electrode surface in an attempt to explain the changes in the induction time during the polymerization. A kinetic equation was proposed consisting of two components:

$$R_p = k[M] + k'[M][P]$$

where k is the rate constant formation of PANI on a bare Pt electrode surface and k' is rate constant on the PANI-coated Pt surface. Shim and Park²⁵ proposed an electrochemical mechanism to supplement this result.

In the case of chemical polymerization of ANI or OT, a similar consideration, based on the above kinetic model, may be considered, including the additional effect due to the added oxidizing agent, as well as the heterogeneous phase. In the present case, the added fiber for grafting and the formed homopolymer may cause the autoacceleration effect due to the surface effect.

Using the previously described facts, the rate of PANI or POT formation was monitored for different [PDS] and [ANI] or [OT].

To arrive at the kinetic equation as applicable to the present case, it is worthwhile to analyze the dependence of R_p (ANI) on [ANI], [PDS], and the amount of PET fiber. It can be seen that R_p -(PANI) versus [ANI] (Fig. 4, plot A) is found to be linear, with a definite intercept and R_p versus [PDS] (Fig. 3, plot A) is a straight line and with negligible intercept. Using the above facts,

 $R_p(\text{ANI}) = k_1[\text{ANI}][\text{PDS}] + k_2[\text{ANI}][\text{TAS}] + k_3$

Weight	$R_h imes 10^7 \ ({ m mol} \ { m L}^{-1} \ { m s}^{-1})$		$R_g imes 10^7 \ ({ m mol} \ { m L}^{-1} \ { m s}^{-1})$		% Grafting		% Efficiency	
(g)	а	b	а	b	а	b	а	b
0.10	33.16	20.03	6.32	8.79	5.30	8.30	0.38	0.52
0.15	35.91	25.27	9.42	11.55	5.26	7.33	0.57	0.69
0.25	42.71	35.83	14.07	17.28	4.72	6.60	0.84	1.04
0.30	34.59	38.92	19.44	29.36	4.10	9.33	1.17	1.76
0.35	28.27	43.15	23.02	41.89	3.90	11.43	1.38	2.51

 Table IV
 Effect of Weight of Fiber on Graft Parameters

 $[ANI]^{a}/[OT]^{b} = 0.30 \text{ mol } L^{-1}; [HCl] = 1.00 \text{ mol } L^{-1}; [PDS] = 0.01 \text{ mol } L^{-1}; \text{ temperature} = 45^{\circ}C.$



Figure 3 Effect of [PDS] on R_h . [ANI]^A/[OT]^B = 0.30 mol L⁻¹, [HCl] = 1.00 mol L⁻¹, temperature = 45°C, weight of PET = 0.20 g.

where k_1 , k_2 , and k_3 are rate constants for the formation of PANI on bare, due to surface effect by homopolymers, backbone fiber and due to the grafted surface, respectively. [TAS] = total available surface (includes homopolymer and backbone on weight basis).

If homopolymerization of ANI alone is the only possibility (without grafting onto PET), the rate constant k_1 would have been the simple rate constant of the formation of PANI. The rate constants as applicable to the ANI case are evaluated from the slope and intercept of the plots R_p (PANI) versus [PDS] (Fig. 3, plot A) and R_p (PANI) versus [ANI] (Fig. 4, plot A). It was found that the k_1 value for the present case is different from the one obtained by Tzou and Gregory^{23} for the simple PANI formation (rate constant = 0.0008 min^{-1}). For the present case, PANI \boldsymbol{k}_1 was found to be 0.96 min^{-1} , which is far higher than the simple homopolymerization rate constant and augumenting the autoacceleration effect on homopolymerization by TAS and grafting.

From the fact that R_p versus [PDS] (Fig. 3, plot A) passes through the origin, it can be inferred

that the surface factor rate constant $k_2\{k_2(TAS)\}$ and k_3 are low and obviously suggesting lower rate of grafting in comparison with homopolymerization. This is in accordance with the dependence of amount of fiber taken on $R_{\rm g}$ (Table IV) and suggests that grafting contributes through the third factor in eq. (1). Also R_p (PANI) versus [ANI] has a definite intercept that gives the value of k_3 as $1.62 \times 10^{-4} \text{ mol } \overline{\text{L}^{-1}} \text{ s}^{-1}$. This k_3 can now be taken as a contribution to the surface changes due to chemical grafting. A similar procedure gives k_1 and k_3 values for the POT case as 0.15 $\mathrm{min^{-1}}$ and 1.37×10^{-4} mol $\mathrm{L^{-1}}~\mathrm{s^{-1}}$, respectively. Two linear regions for $R_p(POT)$ versus [PDS] (Figure 3, plot B) were found. Although the lower region gives k_1 value lesser than PANI case, in the upper region the slope of the plot gives a higher k_1 value. This fact is in accordance with the trend of R_g toward changes in [PDS]. It may be inferred that, at lower [PDS], the POT grafting efficiency is more than PANI. However, in the higher [PDS], the reverse grafting efficiency was noticed.



Figure 4 Effect of $[ANI]^A/[OT]^B$ on R_h . [PDS] = 0.01 mol L^{-1} , [HCl] = 1.00 mol L^{-1} , temperature = 45°C, weight of PET = 0.20 g.

Such a surface effect was noticed for fabric, PANI, alumina by Tzou and Gregory,²³ but the changes in the surface factor could be correlated meaningfully. In the present case, surface effect was considered in two ways: (1) the surface auto-acceleration effect that causes an increase in homopolymerization; and (2) the added surface (fiber) gets chemically grafted simultaneously.

To provide further evidence for grafting, thermal analysis was recorded for the ungrafted and grafted PET fibers [Table V; (Fig. 5(A)]. It can be seen that 0.59% weight loss of PET backbone was found at 186°C, and this can be ascribed due to the evaporation of impurities. The major weight loss of 82% at 428°C corresponds to the degradation of the polymer backbone units.

For the grafted fiber (PET-g-PANI) [Table V; Fig. 5(B)], 9.21% weight loss at 160°C was noted. This can be due to the evaporation of the trapped HCl from grafted doped PANI units. 74.07% weight loss was noted at 440°C. The reduction in weight loss from 82% of the PET backbone and increase in polymer decomposition (424°C to 440°C) reveals the increased thermal stability of the grafted fiber than backbone. Another 18.07% weight loss at 600°C also adds evidence for the extrathermal stability due to PANI grafting.

In the case of (PET-g-POT) [Table V; Fig. 5(C)] fiber, 4.33% weight loss at 111°C was noted. This can be ascribed due to the evaporation of trapped HCl. 77.48% weight loss was noted at 429°C. This is due to PET backbone degradation. No extrathermal stability due to POT grafting was observed.

Table V Conductivity and TGA

Polymer	Conductivity $(Ohm^{-1} cm^{-1})$	Temperature (°C)	Weight Loss (%)
PET	0.88 G	186	0.59
		428	82.82
		484	6.60
PET-g-PANI	1.50M	160	9.21
		440	74.07
		600	15.07
PET-g-POT	3.30 G	111	4.33
		429	77.48

Graft copolymers were prepared under these conditions: [ANI] = 0.30 mol L^{-1} ; [HCl] = 1.00 mol L^{-1} ; PET = 0.20 g; [OT] = 0.30 mol L^{-1} ; [PDS] = 0.010 mol L^{-1} ; temperature = 45°C.



Figure 5 (A) Thermogram of PET fiber, (B) thermogram of PANI-grafted PET fiber, and (C) thermogram of POT-grafted PET fiber.

Table V shows the conductivity value of PANIor POT-grafted PET backbones. PANI-grafted PET backbone has a higher electrical conductivity value than the POT-grafted PET backbone.

REFERENCES

- Okeieimen, E. F.; Idehen, K. L.; Ahiedu, H. J Appl Polym Sci 1987, 34, 737.
- Padma Nayak, L.; Lenka, S.; Mishra, M. K. J Appl Polym Sci 1981, 36, 733.
- Gopalan, A.; Vasudevan, T.; Manisankar, P.; Paruthimal Kalaignan, G.; Ramasubramanian, A.; Hariharan, S. S. J Appl Polym Sci 1995, 56, 1299.
- Gopalan, A.; Vasudevan, T.; Manisankar, P.; Paruthimal Kalaignan, G.; Ramasubramanian, A.; Hariharan, S. S. J Appl Polym Sci 1995, 56, 1715.
- Nayak, N. C.; Das, H. K.; Singh, B. C. J Appl Polym Sci 1991, 42, 2391.
- Mukherjee, A. K.; Gupta, B. D. J Appl Polym Sci 1985, 30, 2253.
- Padma Nayak, L.; Lenka, S.; Mishra, M. K. J Appl Polym Sci 1980, 25, 63.
- Padma Nayak, L.; Lenka, S.; Mishra, M. K. J Appl Polym Sci 1981, 16, 2437.
- El-Rafie, M. H.; Khalil, M. I.; Hebbeish, A. J Appl Polym Sci 1975, 19, 1671.
- Bajbai, U. D. N.; Jain, A.; Rai, S. J Appl Polym Sci 1990, 39, 2187.
- Niezette, J.; Geurts, R.; Erilli, R. J Appl Polym Sci 1981, 26, 1073.
- MacDiarmid, A. G.; Chiang, J. C.; Halpern, M.; Huang, W. S.; Mu, S. L.; Somasiri, N. L. D.; Wu, W.; Yaniger, S. I. Mol Cryst Liq Cryst 1985, 121, 173.
- Genies, E. M.; Sintavis, C. T.; Syed, A. A. Mol Cryst Liq Cryst 1985, 121, 181.
- Wang, B.; Tans, J.; Wang, F. Synth Met 1986, 131, 329.

- 15. Bergeron, J. Y.; Chevalier, J. W.; Dao, L. H. J Chem Soc Chem Commun 1996, 1, 61.
- Bhadani, S. N.; Sen Gupta, S. K.; Sahu, G. C.; Kumari, M. J Polym Mater 1996, 13, 61.
- 17. Toppare, L.; Balci, N.; Bayrali, E. J Appl Polym Sci 1997, 64, 667.
- Li, S.; Dorg, H.; Cao, Y. Synth Met 1989, 29, E329.
- 19. Li, S.; Cao, Y.; Xue, Z. Synth Met 1987, 20, 141.
- 20. Bhadani, S. N.; Sen Gupta, S. K.; Gupta, M. K. Ind

J Text Res 1993, 18, 46.

- Wei, Y.; Focke, W. W.; Wnek, G. E. J Phys Chem 1989, 93, 495.
- Stilwell, D. E.; Park, S. M. J Electrochem Soc 1988, 135, 2491.
- Tzou, K. T.; Gregory, R. V. Synth Met 1992, 47, 267.
- 24. Wei, Y.; Sun, Y.; Tang, X. J Phys Chem 1989, 93, 4878.
- 25. Shim, Y. B.; Park, S. M. Synth Met 1989, 29, E169.