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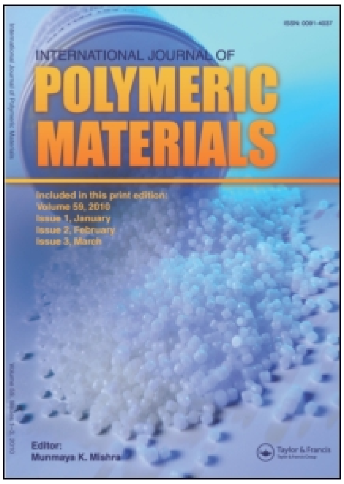

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Chemical and Electrochemical Polymerization of Thiophene Derivatives

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Chemical and Electrochemical Polymerization of Thiophene Derivatives

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The synthesis and some physical properties of polymers containing the thiophene ring are described. The polymerization of 3-phenylthiophene (1), 2-phenyl-thiophene (2), 2,5-diphenylthiophene (3), 2-(2-thienyl) pyridine (4) and 3,6-bis(2-thienyl)pyridazine (5) under electrochemical and chemical conditions are reported. The monomers were prepared by the nickel or palladium catalyzed cross-coupling reactions and were electrochemically polymerized using galvanostatic conditions (platinum electrodes) or chemically polymerized by oxidation with iron trichloride. The effect of monomer concentration, electrolyte and solvent were studied. From the examined polymers only poly(3-phenylthiophene) showed significant properties, considering morphology and conductivity. The other polymers gave mainly powder or porous films with low conductivity. The thermogravimetry analysis of poly (3-phenylthiophene) showed a wide temperature range of thermal stability, only over 450°C considerable weight loss was observed. Scanning electron microscopy (SEM) of samples obtained under different conditions demonstrated the dependence of the morphology upon monomer structures, nature of the dopant and synthetic route employed.

KEY WORDS Thiophenes, electrochemical polymerization, chemical polymerization, electrical conductivity, doping, thermal stability.

INTRODUCTION

The conducting polymers have generated widespread interest as potential choice materials for a variety of applications. Among them, we can mention their use as electronic switching materials,[1] electrooptic devices,[2] electrode materials in rechargeable and storage batteries,[3] solar batteries,[4] radiation detectors[5] and sensors.[6] Different synthetic routes have been employed to obtain the conducting materials. Electrochemical and chemical methods are, however, the most widely used procedures for the polymer synthesis and many reports and reviews have been published to this respect.[7]

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This paper reports the electrochemical polymerization and chemical polymerization by oxidation with iron trichloride of 2 and 3-thiophene derivatives. Electrochemical polymerizations were carried out using different electrolyte salts, solvents and monomer concentration.

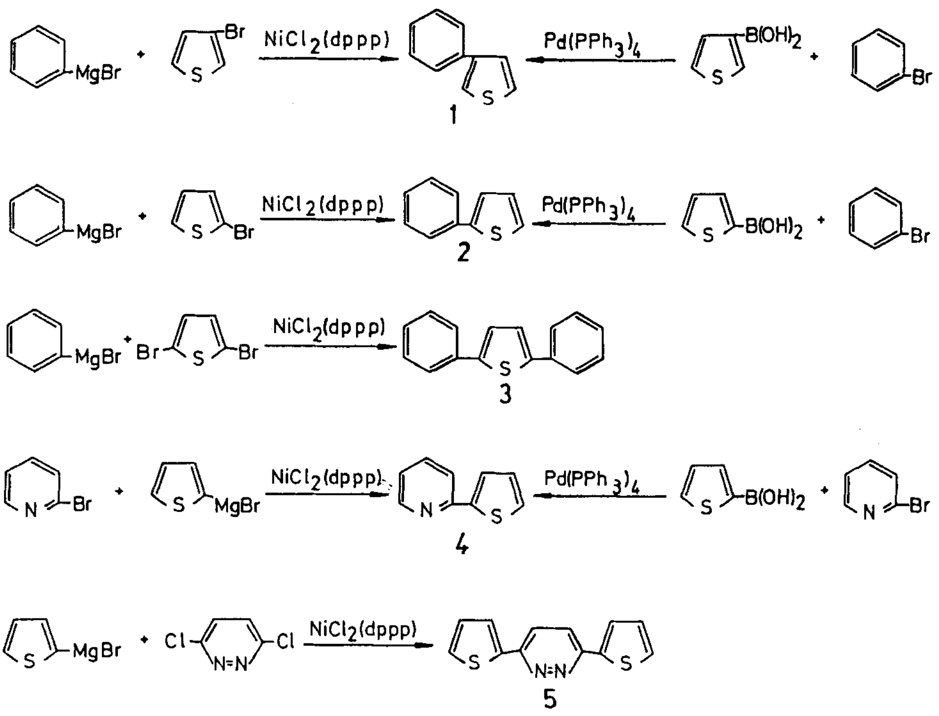
EXPERIMENTAL

Materials

Monomers. The synthesis of the monomers was performed following different methodologies and was conducted according to the cross coupling reactions of Kumada's method[8] with nickel(diphenylphosphine propane) chloride, Ni(dppp), catalyst or boronic acids with palladium tetrakis-triphenylphosphine, Pd(Ph$_3$)$_4$ catalyst.[9,10]

The Scheme I illustrates the synthetic routes for the preparation of the different monomers and their respective methods.

2-phenyl- and 3-phenylthiophene were prepared following the procedure of Kumada[11] and Gronowitz,[12] 2-(2-thienyl)pyridine and 2,5 diphenylthiophene were prepared according to Kumada[11] and Kauffmann[13] respectively. 3,6-bis(2-thienyl)pyridazine was synthesized according to Monthéard.[14]



SCHEME I Synthetic routes of thiophene derivatives.

The monomers 1–5 were characterized by their corresponding spectra, such as ^{1}H-NMR, ^{13}C-NMR, IR, UV and compared with those reported in literature. In all cases good agreement was found.

CHEMICAL POLYMERIZATION VIA OXIDATION WITH IRON TRICHLORIDE

The solvent used in all polymerizations were p.a. quality reagent (E. Merck) and were dried according to the known procedures reported in literature. Polymerization of the thiophene derivatives were performed using iron trichloride in acetonitrile or nitromethane solution as indicated in Table I. To the air degassed solution of the monomer at 25°C, a 0.1–0.3 M of iron trichloride solution was added and a precipitate appeared. The mixed solution was kept at 25°C under argon bubbling and continuous stirring during 2 h. The precipitate was then washed with acetonitrile, methanol and dried under vacuum at 60°C. The obtained precipitates, ranged from red to black powder depending on the monomer used.

ELECTROCHEMICAL POLYMERIZATION

The polymerization reactions were carried out using two types of electrochemical cell with different geometries. One of them was a two compartment cell with a glass-fritt as separator where the electrodes were arranged in a vertical position,

TABLE I

Results of chemical polymerization of thiophene derivatives

Monomer	monomer	FeCl$_3$	Solvent	Type of product
2-phenyl-thiophene	0,025M	0,10M	AN	powder black
2-phenyl-thiophene	0,025M	0,10M	NM	powder brown
2-phenyl-thiophene	0,070M	0,28M	NM	powder black
3-phenyl-thiophene	0,070M	0,28M	NM	powder redish
2-(2-thienyl)pyridine	0,025M	0,10M	AN	powder brown
3,6-bis(2-thienyl)pyridazine	0,045M	0,18M	NM	powder brown
2,5-diphenylthiophene	0,070M	0,28M	CH$_2$Cl$_2$/NM	powder brown
2,5-diphenylthiophene	0,075M	0,30M	CH$_2$Cl$_2$/NM	powder brown

NM = nitromethane AN = acetonitrile

separated two centimeter to each other (platinum working electrodes, 2 cm^2). The other cell was a one-compartment cell with an horizontal arrangement of the electrodes, being the working electrode a 3 cm^2 platinum disk, supported in a teflon structure. Acetonitrile, nitrobenzene, dichloromethane and propylene carbonate were used as solvents and tetrabutylammonium tetrafluorobate (TBABF$_4$), tetrabutylammonium hexafluorophosphate (TBAPF$_6$) or lithium perchlorate (LiClO$_4$) as supporting electrolyte. Current densities of 3 mA/cm^2 were used and the polymerization were carried out at room temperatures and purged with argon or nitrogen gas for about 10 minutes before applying the current.

In a typical reaction, to a solution of 70 ml. acetonitrile, 2.69 g (16.8 mmol) of 3-phenylthiophene and 0.65 g (1.68 mmol) of TBAPF$_6$ were added, the solution was bubbled 10 minutes with argon and then a current of 3 mA/cm^2 was applied to the electrodes for a period of 21 h. The electrode containing the polymer film was then washed with methanol and petroleum ether. The film was carefully separated from the electrode by means of an scalpel and then dried under vacuum at 60°C during 8 h.

Conductivity measurements were carried out by using the four probe method, as reported by van der Pauw.[15]

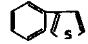
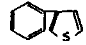
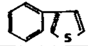
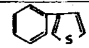
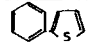
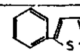
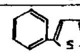
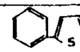
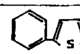
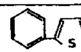
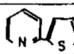
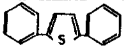
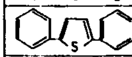
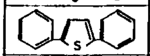
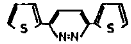
RESULTS AND DISCUSSION

The results of the polymerization of the different monomers are shown in Table I and II, which resume the experimental conditions of chemical and electrochemical polymerization respectively, Table II illustrates the values of conductivity obtained for the poly(3-phenylthiophene). The DSC-TGA thermogram of poly(3-phenylthiophene) is presented in Figure 1. The scanning electron micrographs (SEM) of chemical and electrochemical obtained poly(3-phenylthiophene) are shown in Figures 2 and 3.

The chemical oxidation polymerization with iron trichloride of the thiophene derivatives (Table I) gave black to dark brown powder which were insoluble in common organic solvents. Ueda[16] reported as product of the chemical polymerization of 3-phenylthiophene a red solid, soluble in organic solvent such as chloroform, toluene, tetrahydrofuran, dimethylsulfoxide and dimethylformamide. A transparent film was cast from this polymer solution (the polymer is in undoped state). This author used 2,5 dibromo-3-phenyl thiophene as starting material and polymerized was carried out using (dppp)NiCl$_2$ as catalyst. In our case a red polymer was also obtained, however, it is not soluble in organic solvents, probably due to the different structure of the oxidation obtained polymer as compared with a chemical polymerization where polymer chains are all connected in the same way. All the thiophene derivatives treated with iron trichloride were insoluble and no changes were observed in the product of polymerization when the experimental conditions were modified. No great differences were observed in chemical polymerization when acetonitrile or nitromethane or a mixture methylenechloride-nitromethane were used as solvents. Measurements of conductivity of these polymers gave values less than 10^{-6} S/cm.

TABLE II

Results of electrochemical polymerization of thiophene derivatives

Structure	Monomer mol l^{-1}	Electrolyte	Electrolyte mol l^{-1}	Solvent	Cathode	Reaction time (h)	Weight(mg)	Type of product
	0.24	$LiClO_4$	0.024	AN	Itoglass	2.70	10	film and powder
	0.24	$LiClO_4$	0.048	AN	Al	3.20	80	film
	0.24	$TBAPF_6$	0.048	NB	Al	9.70	(a)	blue solution
	0.24	$TBAPF_6$	0.048	AN	Ni	23.00	130	film
	0.24	$TBAPF_6$	0.024	AN	Ni	21.70	100	film
	0.24	$LiClO_4$	0.024	AN	Ni	20.70	80	film
	0.24	$LiClO_4$	0.048	AN	Al	3.75	20	powder
	0.24	$TBAPF_6$	0.048	AN	Al	10.75	(a)	green solution
	0.24	$TBAPF_6$	0.048	AN	Ni	7.00	(b)	powder
	0.24	$TBAPF_6$	0.048	AN	Ni	26.00	20	powder
	0.24	$LiClO_4$	0.048	AN	Ni	25.00	140	powder
	0.24	$TBAPF_6$	0.048	AN	Ni	31.00	140	powder
	0.047	$LiClO_4$	0.0018	AN	Al	5.00	(a)	brown solution
	0.17	$TBAPF_6$	0.034	NB	Al	7.50	(a)	blue solution
	0.17	$TBAPF_6$	0.034	PC	Ni	9.00	(a)	green solution
	0.17	$TBAPF_6$	0.001	AN/CH_2Cl_2	Ni	29.75	(b)	powder
	0.05	$TBAPF_6$	0.0018	AN/CH_2Cl_2	Al	25.92	(b)	film

(a) product remains in solution (b) very small amount

PC = propilenecarbonate AN = acetonitrile NB = nitrobenzene

The electrochemical polymerization of thiophene derivatives under galvanostatic conditions (Table II) gave mostly dark blue film in the case of 3-phenylthiophene. With others monomers only soluble oligomers or sponge-like product were obtained. A good result for a polymer was obtained when acetonitrile and $TBAPF_6$ was employed as electrolyte and the monomer to electrolyte ratio was 5:1. Our results showed that the nature of the used cathode, ITO glass, alumina foil or nickel did not have any meaningful influence on the film quality. In the electrochemical work, from the two different cell geometries utilized, the one with horizontal disposition of the electrodes gave the better results, since the film adherence to the electrode is facilitated by the gravity.

The 2-(2-thienyl)pyridine and 2-phenylthiophene provided only a light powder

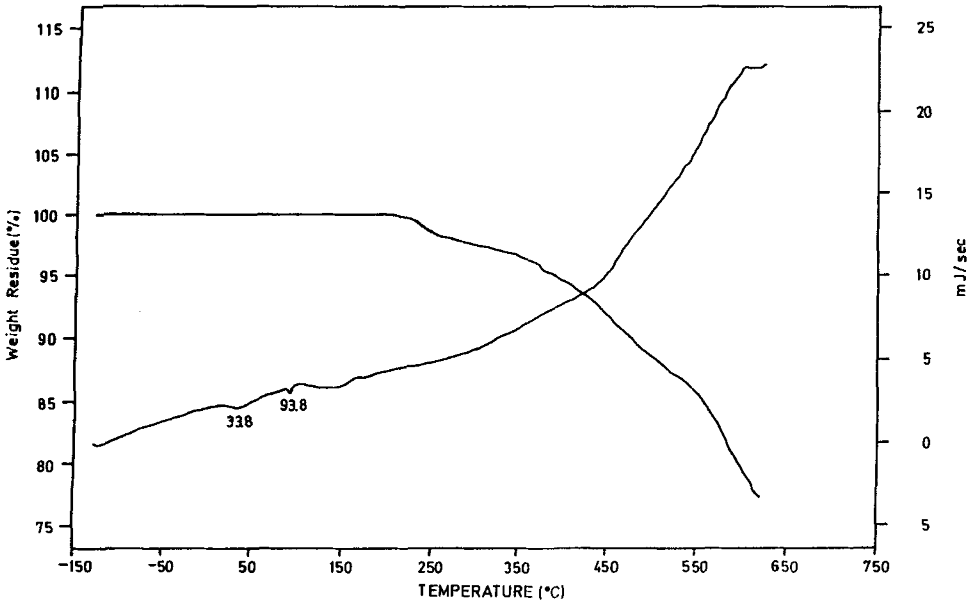


FIGURE 1 DSC-TGA thermogram of 3-phenythiophene.

or soluble oligomers (bluish or green solution) independently of the experimental conditions examined. That means, that 2-substituted thiophenes do not yield high polymer under these circumstances, because the conjugation goes trough the double bonds (α,α' position of thiophene ring) and when one of this position is blocked, then a disruption of conjugation occurs, avoiding the growing of polymer chain. A special case were the 3,6-bis(2-thienyl)piridazine and 2,5-diphenylthiophene, in the first case one of the α position is occupied by the piridazine ring and in spite of this fact, a thin polymer film was obtained. The explanation for this result is to consider certain coplanarity between the thiophene rings and piridazine, which allows the polymerization in some extension and the thiophene rings in both extreme behave as if they had both α and α' position free. This behavior could be explained by solvatation effects on nitrogen free electron pairs, from pyridazine, which would avoid by steric hindrance the free rotation. In the case of 2,5-diphenylthiophene, considering the obtained results (not a film at all), the situation should be a little different, so that a free rotation of phenyl group through the single bonds connected to the tiophene ring is imaginable and in this way a growing chain is not feasible.

The thermal stability of the polymers was examined by DSC and TGA analysis. A typical trace of poly(3-phenyl)thiophene is shown in Figure 1. The temperature ranged from − 150 to 500°C. Two small endothermic peaks were observed at 33.8°C and 93.8°C in DSC curve. These peaks can be assigned to some degree of hydrogen fluoride and water evolution from the sample, product of partial hydrolysis, since this sample was doped with $TBAPF_6$. A peak observed at higher temperatures (160°C) might be due to some rearranging of the polymer chain or more probably, to the loss of some small molecular weight fractions. By observing the TGA curve,

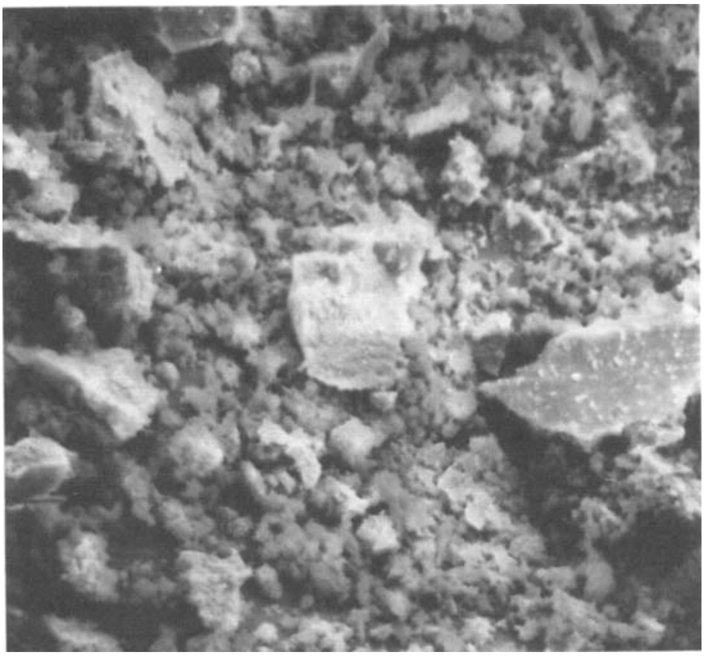


FIGURE 2 SEM microphotograph of 3-phenylthiophene obtained by chemical oxidation with iron trichloride (×3000).

the sample was quite stable between 30 and 300°C (no dramatic changes were observed). Between 166 and 195°C small weight loss begins to be apparent (11% weight loss) and over the 450°C a complete decomposition occurs. Ueda[16] reported a glass transition of 177°C for the chemically prepared poly(3-phenyl)thiophene (nickel catalyzed), this transition was not observed in our sample. The TGA curve has a similar profile as that reported by Ueda.[16]

By the examination of the SEM microphotographs, is evident from Figures 2 and 3 that a different morphology is obtained upon the polymerization method. Figure 2 shows the poly(3-phenyl)thiophene obtained by chemical oxidation with iron trichloride, while Figure 3 corresponds to the poly(3-phenyl)thiophene obtained electrochemically by using tetrabutylammonium hexafluorphosphate ($TBAPF_6$) as electrolyte and acetonitrile as solvent. It can be seen that different size particles showing different morphology are observed. In the case of electrochemical polymerization (Figure 3), regular size particles with a globular morphology are observed which are formed on the electrode surface. This surface is well polished for each polymerization and the nucleation of polymer monolayer is very regular through the reaction, consequently a good quality film is obtained by electrochemically polymerization. The poly(3-phenyl)thiophene obtained by chemical oxidation with iron trichloride (Figure 2) shows an amorphous structure with different size particles. The polymer is precipitated from the solution once the iron trichloride is added and the particles form insoluble conglomerate with irregular sizes.

In conclusion, our study of chemical and electrochemical polymerization of thio-

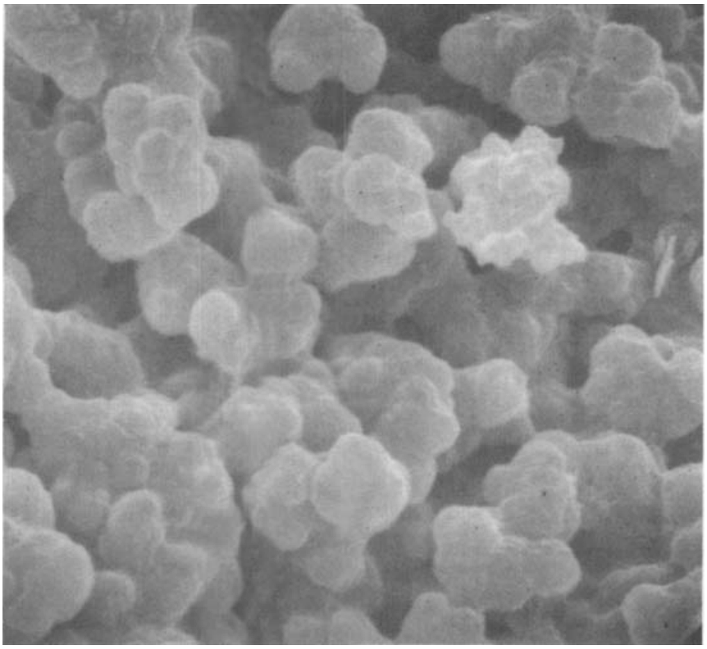


FIGURE 3 SEM microphotograph of 3-phenylthiophene obtained by electrochemical polymerization (×3000).

TABLE III

Conductivity of 3-phenylthiophene

Polymer	σ (S/cm)
poly(3-phenylthiophene)/TBAPF$_6$	0,9
poly(3-phenylthiophene)/LiClO$_4$	0,5

phene derivatives indicates that 3-substituted thiophenes are readily polymerizable and those 2-substituted are less active to polymerization because of rupture of conjugation, however there are some cases where the conjugation can be preserved although the α,α′ position are occupied, as in the case of 3,6-bis(2-thienyl)pyridazine, in this situation the coplanarity of the rings would explain the polymer formation. The morphology of the samples depend in great extension upon the chemical or electrochemical method chosen.

Acknowledgments

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References

1. T. Yoshino, S. Ura, S. Sasa, Y. Kaneto and Y. Inuishi, *Jpn. J. Appl. Phys.*, **21**, L507 (1982).
2. T. Yoshino, Y. Kaneto and Y. Inuishi, *Jpn. J. Appl. Phys.*, **22**, L157 (1983).
3. P. J. Nigrey, D. MacInnes, D. P. Nairns, A. G. MacDiarmid and A. J. Heeger. *J. Electrochem. Soc.*, **128**, 1651 (1981).
4. S. C. Chen, A. J. Heeger, Z. Kiss and A. G. MacDiarmid, *Appl. Phys. Lett.*, **36**, 1 (1980).
5. K. Yoshino, S. Hayashi, Y. Kaneto, J. Okube and T. Moriyama, *Jpn. Appl. Phys.*, **23**, L189 (1984).
6. R. J. Waltman and J. Bargon, *Can. J. Chem.*, **64**, 70 (1986).
7. A. O. Patil, A. Heeger and F. Wudl, *Chem. Rev.*, **88**, 183 (1988).
8. 1) M. Kumada and U. Tamao, *Org. Synth.*, **58**, 127 (1978); ii) U. Tamao, S. Kodama, J. Nakajima, M. Kumada, A. Minato and Suzuki, *Tetrahedron*, **38**, 3347 (1982).
9. N. Miyaura, T. Yanagi and A. Suzuki, *Synth. Commun.*, **11**, 513 (1981).
10. R. Miller and S. Dugar, *Organometallics*, **3**, 1261 (1984).
11. U. Tamao, S. Kodama, I. Nakajima and M. Kumada, *Tetrahedron*, **38**, 3347–3354 (1982).
12. S. Gronowitz and W. Lawitz, *Chemica Scripta*, **24**, 5–6 (1984).
13. T. Kauffmann, E. Wienhöfer and A. Woltermann, *Anew. Chem. Internat. Edit.*, **10**, (1971).
14. J. P. Monthéard and J. C. Dubois, *J. Heterocyclic Chem.*, **22**, 719–720 (1985); J. Monthéard and J. Belzart, *Synth. Commun.*, **14**, 289–292 (1984).
15. L. J. van der Pauw, *Philips Res. Repts.*, **16**, 187 (1961).
16. M. Ueda, Y. Miyagaji, T. Ito, Y. Oba and T. Stone, *Macromolecules*, **24**, 2694–2697 (1991).