Synthesis and characterization of poly(dichlorophenylene oxide)s based on the electro-oxidation of bis(2,4,6-trichlorophenoxo)bis(pyridine)copper(II) complex

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Electroinitiated polymerization of bis(2,4,6-trichlorophenoxo)bis(pyridine)copper(II) complex was achieved in dimethylformamide by constant potential electrolysis under air and N_2. The polymers obtained at several potentials were characterized by ^{1}H n.m.r., ^{13}C n.m.r., *FT*i.r. and d.s.c., and were found to be branched. The kinetics of the polymerization were followed by *in situ* cyclic voltammetry measurements at 13.5 and 20°C during electrolysis. As found for the thermal polymerization of this complex, electroinitiation begins after 50 min at 13.5°C, whereas the induction period is negligible for electrolysis at 20°C.

(Keywords: poly(dichlorophenylene oxide); bis(2,4,6-trichlorophenoxo)copper(II) complex; electro-oxidation; ^{1}H n.m.r.; ^{13}C n.m.r.)

INTRODUCTION

The synthesis of poly(dichlorophenylene oxide) is achieved by the decomposition of complexed copper trichlorophenolates either thermally in solution[1–7] and in the solid state[8], or electrochemically[9,10]. Investigations have shown that the molecular weights of the polymers produced are very sensitive to the method of synthesis. The ease with which the thermal decomposition of such complexes occurs is profoundly affected by the nature of the neutral ligands on the copper. A chelate ligand (ethylene diamine, *N*,*N*,*N'*,*N'*-tetramethylethylenediamine, dimethylsulfoxide or dimethylformamide) is expected to stabilize copper(II) relative to copper(I) while the reverse is expected for a monodentate ligand (pyridine)[1–3,5–8]. In the electroinitiation of these complexes, however, no induction period is reported[9,10]. Much effort has been directed towards the study of the thermal decomposition of the complexes[1–8]. However, very little is known about the electroinitiated polymerization behaviour of this complex with a non-chelating ligand, pyridine. The aim of this paper is to present results concerning the determination of the structure by ^{1}H n.m.r., ^{13}C n.m.r. and *FT*i.r. measurements and molecular weight determination as well as the kinetics of the polymerization by *in situ* cyclic voltammetry measurements during electrolysis at different temperatures.

EXPERIMENTAL

Materials

2,4,6-Trichlorophenol was analytical grade (Aldrich Chemical Co. Ltd) and was used without purification.

Pyridine was used as a non-chelating ligand (Merck Co.).

N,*N'*-dimethylformamide (DMF) purchased from Merck was stirred with anhydrous copper sulfate for 48 h and distilled under 5 mmHg.

Copper sulfate ($CuSO_4.5H_2O$) was commercially available reagent grade.

Tetrabutylammoniumfluoroborate (TBAFB) was provided by Merck Co. This was used as an electrolyte for cyclic voltammetry measurements and electrolysis.

Deuterated chloroform was provided from Merck Co. for ^{1}H n.m.r. and ^{13}C n.m.r. spectrophotometric measurements.

Complexes of bis(2,4,6-trichlorophenoxo)bis(pyridine)-copper(II) ($Py_2Cu(TCP)_2$) in aqueous solution were prepared by the standard procedure given in the literature[11]. The complex was characterized by elemental analysis using a Hewlett-Packard Fund 185 CHN analyser with a flow rate of 100 cm^3 min^{-1}, an oxidation furnace temperature of 1050°C, a reduction furnace temperature of 500°C and a column oven temperature of 80°C. The complex was found to contain C 43.1%, H 2.7%, N 4.54%. The expected values based on calculations were C 43.1%, H 2.3%, N 4.6%. The experimental errors are ± 0.3.

Spectral analyses were done by *FT*i.r. (in KBr) using a Perkin-Elmer model 1710.

Cyclic voltammetry

The cyclic voltammetry (c.v.) system consisted of a function generator (Tacussel Pilote Servoit), a potentiostat (Tacussel, PRT 30. 0.1) and a recorder (Sefram X-Y). The cell contained three electrodes: working (Pt bead), counter (3 cm Pt wire) and reference[12]

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(a luggin capillary containing Ag^0/Ag^+ (0.01 M)). The supporting electrolyte was 0.1 M TBAFB. The measurements were carried out in DMF–TBAFB as solvent–electrolyte couple at 20°C. All the cyclic voltammograms were taken at a scan rate of $200\,mV\,s^{-1}$.

Polymer synthesis

Electroinitiated polymerizations using a constant potential electrolysis system were carried out for 3 h at room temperature under different atmospheres in the H-type polymerization cell described elsewhere[10,13,14]. The polymerization cell had three electrodes; working electrode (5 mm diameter graphite rod as anode), counter electrode ($6\,cm^2$ stainless steel foil as cathode) and the reference (Ag^0/Ag^+ (0.01 M)). The electrolysis was achieved at +0.3, +0.65 and +1.0 V at 20°C with complex concentration of 10^{-2} M under air and under N_2. When cathodic peak potentials of −0.7, −0.9, −1.6 and −2.04 V were applied, however, polymers were obtained only in the anode compartment.

The kinetics of the polymerization were followed by the previously reported c.v. technique[10,13,14] at anodic peaks of +0.701 and +0.757 V for two different temperatures, namely 20 and 13.5°C.

Polymer characterization

^1H n.m.r. and ^{13}C n.m.r. spectra of the polymers were recorded on a Bruker AC 200 NMR spectrophotometer using deuterated chloroform as solvent.

The number-average molecular weight ($\bar{M}_n$) of the polymer was determined in camphor (m.p. 175°C, $K_f = -39.7$) by a cryoscopic method[14].

The glass transition temperature, T_g, was determined by d.s.c. (DSC-TA-3000 system) with a scanning rate of $10\,K\,min^{-1}$ and a sample weight of around 3–4 mg.

RESULTS AND DISCUSSION

Prior to electrolysis, the exact peak potentials of $Py_2Cu(TCP)_2$ complex were determined in DMF by c.v. (*Figure 1*). The c.v. of the complex gives three oxidations $E_{p,a}$ at +0.3, +0.65 and +1.1 V and three reductions $E_{p,c}$ at −0.7, −1.6 and −2.04 V peak potentials *versus* Ag^0/Ag^+ (*Table 1*). The chosen solvent–electrolyte couple, DMF–TBAFB, was inert between −2.5 and +1.5 V at room temperature.

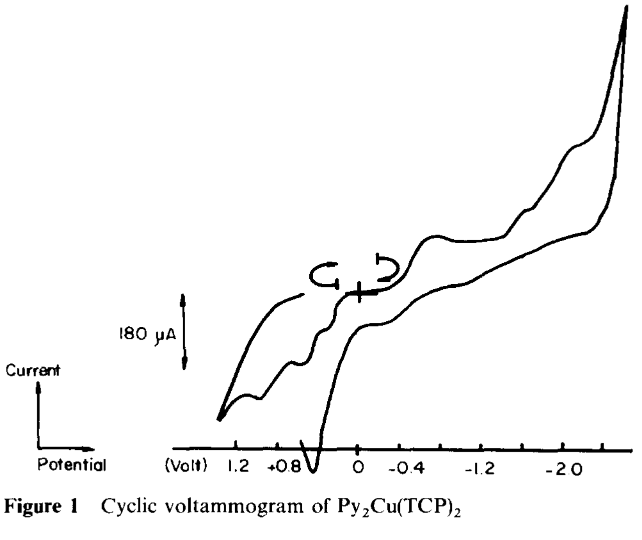

Figure 1 Cyclic voltammogram of $Py_2Cu(TCP)_2$

Table 1 Electroinitiated polymerization of bis(2,4,6-trichlorophenoxo)-bis(pyridine)copper(II) complex

E_{pol}[a] (V)	Yield[b] (%)	
	Under nitrogen	Under air
+0.3	26	24
+0.65	40	39
+1.1[c]	49	38
−0.7[c,d]	–	7
−0.9[c,d]	29	28
−1.6[c,d]	29	30
−2.04[c,d]	33	31

[a] E_{pol} = polymerization potential obtained from c.v. measurement of $Py_2Cu(TCP)_2$ complex
[b] Polymer recovered from anolyte at the end of 3 h of electrolysis
[c] Peak potential used as polymerization potential
[d] Polymer obtained only at anode compartment

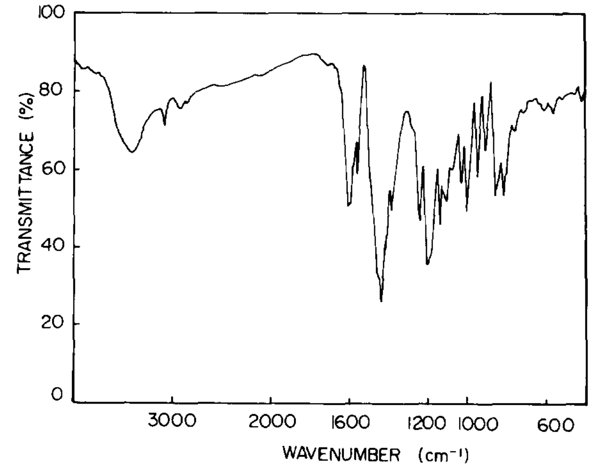

Figure 2 *FT*i.r. spectrum of poly(dichlorophenylene oxide)

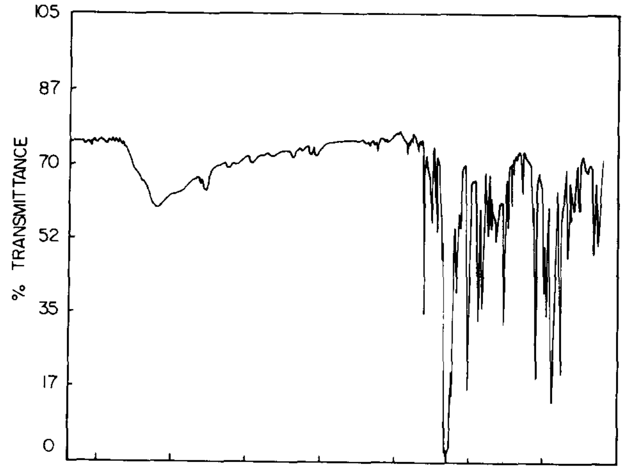

Figure 3 I.r. spectrum of $Py_2Cu(TCP)_2$ complex

The poly(dichlorophenylene oxide)s were only obtained from the anolyte when the complex was electrolysed at these potentials by constant potential electrolysis. The calculated yields for the polymerizations are based on the initial weight of the complexes. Since the ligand and the copper do not incorporate into the polymer, the results appear to be low. The percentage yields after 3 h increase with increasing oxidation potential of the electrolysis under air, but a higher yield is observed under N_2. In the case of applied reduction potential almost the same percentage yield is obtained under either atmosphere. Percentage yields are presented in *Table 1* under different conditions. All the polymers were found to be structurally the same and have rather high T_g values (173°C) with a molecular weight of 2250.

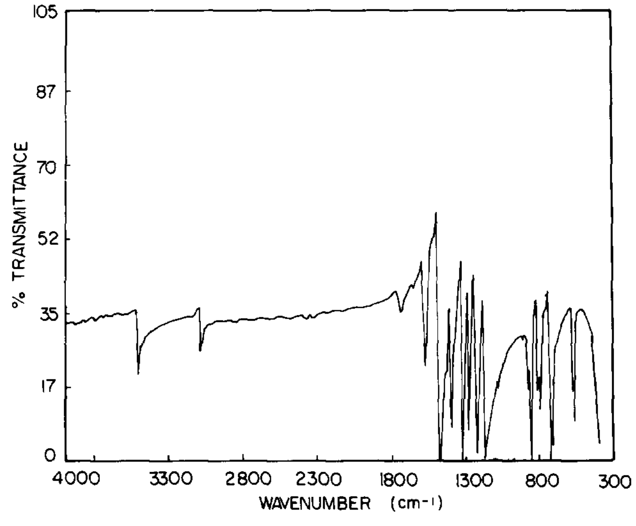

Figure 4 I.r. spectrum of TCP

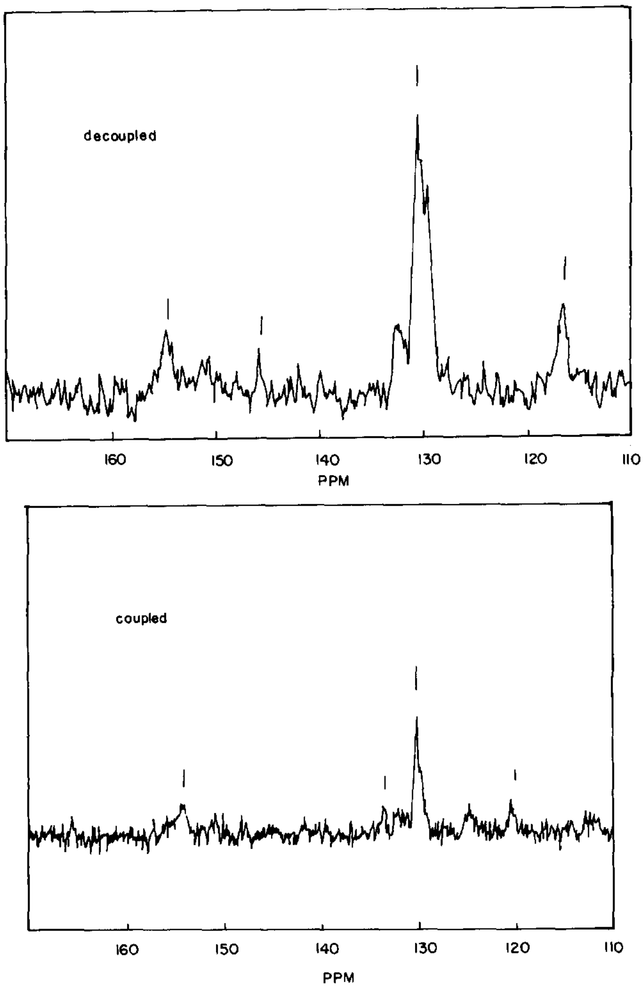

Figure 5 ^{13}C n.m.r. coupled and decoupled spectra

The *FT*i.r. spectrum of poly(dichlorophenylene oxide) is characterized by 1380, 1400, 1560 and 1600 cm^{-1} (C=C stretchings); 960, 1000 and 1030 cm^{-1} (C–O stretchings); 810 and 850 cm^{-1} (out-of-plane C–H bendings) (*Figure 2*). In addition to the peaks present in the i.r. spectrum of the polymer, the bands due to N–H (3335 cm^{-1}) and N–C (1065 cm^{-1}) absorptions were noted (*Figure 3*) and the phenolic O–H peak of trichlorophenol (TCP) at 3500 cm^{-1} disappeared in the complex (*Figure 4*).

The polymers synthesized at various potentials were characterized by using ^{13}C n.m.r. and ^{1}H n.m.r.

Theoretical ^{13}C n.m.r. chemical shift data for the three probable modes of ternary catenation products of TCP were calculated by using the appropriate correlation tables[15]. ^{13}C n.m.r. coupled and decoupled spectra are given in *Figure 5*. The observed and the calculated values could predict that a polymer chain of TCP having a high degree of stereoregularity (structure c in *Figure 6*) should exhibit a fairly simple ^{13}C n.m.r. spectrum. On the other hand, structures a and b should display fairly complex spectra. The observed and calculated ^{13}C n.m.r. spectra correlated equally well to the three possible modes of ternary catenation products. The ^{1}H n.m.r. spectrum is more informative in this respect.

The ^{1}H n.m.r. spectrum of the polymer indicates that 1,2- and 1,4-additions are taking place at equal rates (*Figure 7*). The peak at $\delta = 6.8$ ppm is assigned to protons of 2,6-dichloro-1,4-phenylene oxide units and the peak

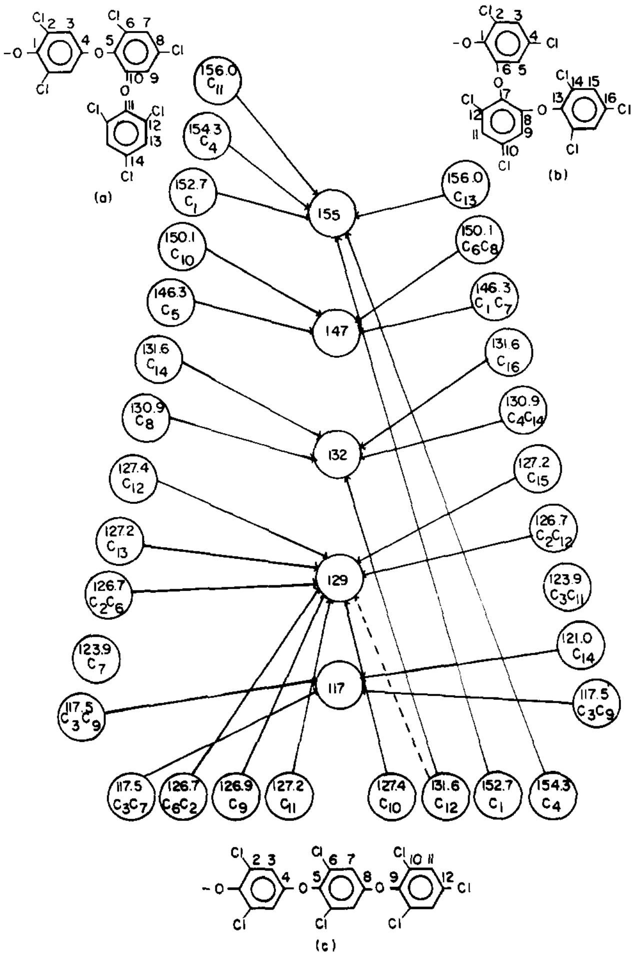

Figure 6 Schematic representation of ^{13}C n.m.r. data for various forms of polymer obtained from $Py_2Cu(TCP)_2$

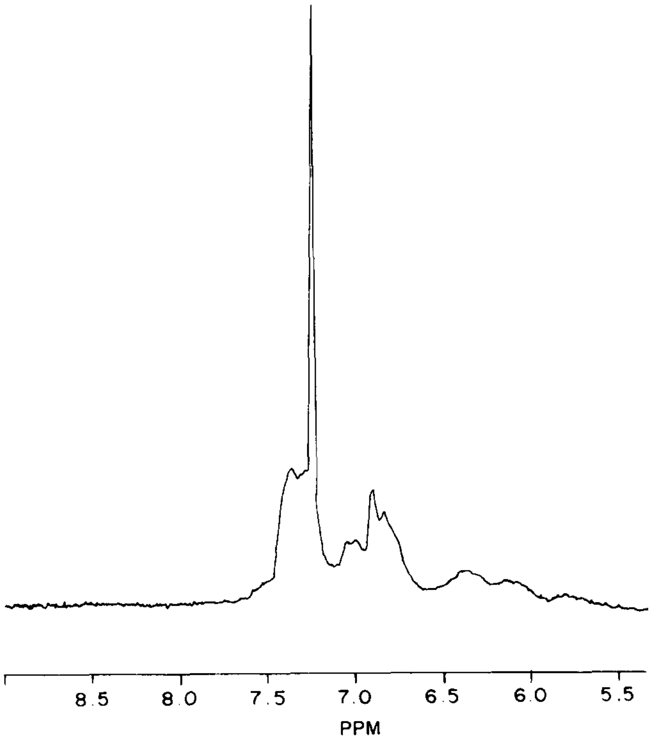

Figure 7 ^{1}H n.m.r. spectra of polymer obtained from Py$_2$Cu(TCP)$_2$

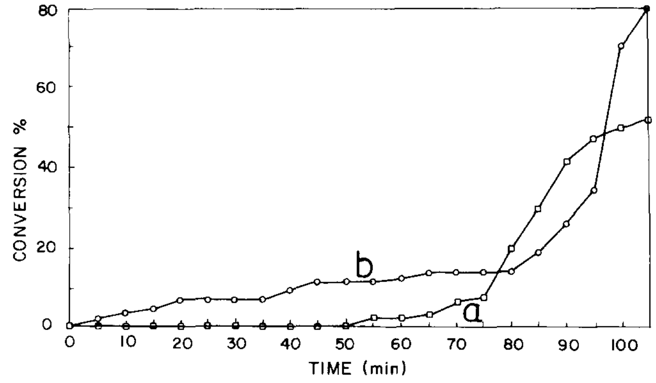

Figure 8 Conversion–time relation in the polymerization of Py$_2$Cu(TCP)$_2$ at (a) +0.757 V, 13.5°C and (b) at +0.701 V, room temperature

at $\delta = 7.4$ to proton 5 of 4,6-dichloro-1,2-phenylene oxide units. A second doublet due to proton 3 is presumably obscured. The higher field broad lines can be assigned to branch units of 1,2-, 1,4- and 1,6-additions taking place on the same phenol molecule. A sharp peak at $\delta = 7.2$ ppm is due to deuterated chloroform.

A kinetic study was undertaken for the complex with concentration of 10^{-2} M by taking successive c.v. measurements at 0.7 V during electrolysis[10,16,17]. At low temperature, at the end of 50 min induction period, the percentage conversion increased slowly with time up to 7.1% and then a sharp increase up to 45% was observed (*Figure 8*). However, at 20°C, polymerization began immediately but the rate increased gradually up to 20% conversion and then a sharper increase up to 84.4% was followed by a plateau.

It has been reported that there is always an induction period in the thermal polymerization of bis(trichlorophenoxo)copper(II) complexes with various ligands (*Table 2*) but there is no induction period in the electroinitiated polymerization at room temperature[3,6,7,10]. There was a 50 min induction period in the electro-oxidation polymerization of this monomer as the temperature was decreased from 20 to 13.5°C.

Table 2 Induction periods for bis(trichlorophenoxo)copper(II) complexes with different ligands under various conditions

	Polymerization			
Ligand[a]	Solvent	*t* (°C)	Method	Induction period (min)
DMSO[b]	DMSO	50	Thermal	160
DMF[b]	DMF	50	Thermal	120
EN[c]	Toluene	70	Thermal	56
TMEN[c]	Toluene	70	Thermal	45
Pyridine[d]	Benzene	70	Thermal	30
Pyridine	DMF	20	Electroinitiated	–
Pyridine	DMF	13.5	Electroinitiated	50

[a] DMSO, dimethylsulfoxide; DMF, dimethylformamide; EN, ethylene diamine; TMEN, *N,N,N′,N′*-tetramethylethylenediamine
[b] From ref. 7
[c] From ref. 6
[d] From ref. 3

CONCLUSION

The experimental results indicate that the low molecular weight, rigid poly(dichlorophenylene oxide)s synthesized by electro-oxidation in DMF from bis(trichlorophenoxo)-bis(pyridine)copper(II) complex have a branched structure. The induction period for the polymerization changed from 0 to 50 min as the temperature decreased from 20 to 13.5°C.

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REFERENCES

1 Blanchard, H. S., Finkbeiner, H. and Russel, G. A. *J. Polym. Sci.* 1962, **58**, 469
2 Carr, B. G., Harrod, J. F. and van Gheluwe, P. *Macromolecules* 1973, **6**, 498
3 Carr, B. G. and Harrod, J. F. *J. Am. Chem. Soc.* 1973, **95**, 5707
4 Harrod, J. F., van Gheluwe, P., Kısakurek, D. and Shaver, A. *Macromolecules* 1981, **14**, 565
5 Kısakurek, D., Binboga, N. and Harrod, J. F. *Polymer* 1987, **28**, 1767
6 Unal, A. I., Sanlı, O. and Kısakurek, D. *Polymer* 1989, **30**, 344
7 Kısakurek, D. and Sanlı, O. *Makromol. Chem.* 1989, **190**, 1843
8 Basturkmen, M. and Kısakurek, D. *Polymer* 1993, **34**, 625
9 Sacak, M., Akbulut, U., Kısakurek, D., Turker, L. and Toppare, L. *J. Polym. Sci., Polym. Chem. Edn* 1989, **27**, 1599
10 Yigit, S., Kısakurek, D., Turker, L., Toppare, L. and Akbulut, U. *Polymer* 1989, **30**, 348
11 Harrod, J. F. *Can. J. Chem.* 1969, **47**, 637
12 Akbulut, U., Fernandez, J. F. and Birke, R. L. *J. Polym. Sci., Polym. Chem. Edn* 1975, **13**, 133
13 Akbulut, U., Eren, S. and Toppare, L. *J. Macromol. Sci. Chem.* 1974, **A21** (3), 335
14 Kısakurek, D., Sen, S., Aras, L., Turker, L. and Toppare, L. *Polymer* 1991, **32**, 1323
15 Boschke, F. L., Fresenius, W., Huber, J. F. K., Pungor, E., Rechnitzs, G. A., Simon, W. and West, Th. S. 'Tables of Spectral DATA for Structural Determination', Springer Verlag, Heidelburg, 1968
16 Toppare, L., Turker, L., Yigit, S., Kısakurek, D. and Akbulut, U. *Eur. Polym. J.* 1990, **26**, 255
17 Kısakurek, D. and Yigit, S. *Eur. Polym. J.* 1991, **27**, 955