Atom Transfer Rearrangement Radical Polymerization of Diammine-bis(2,4,6-trihalophenolato)copper(II) Complexes in the Solid State

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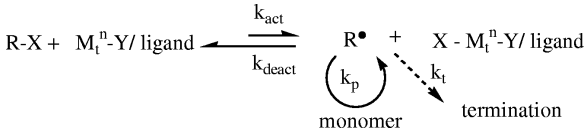
The synthesis of the poly(dichloro- or dibromophenylene oxide)s was achieved by the thermal decomposition of diammine-bis(2,4,6-trihalophenolato)copper(II) complexes in the solid state by atom transfer rearrangement radical polymerization. The thermal decomposition was performed either at different temperature ranges, 110 – 250 °C, for 3 h, or at the maximum conversion temperature for different time intervals, 3 – 48 h. Maximum yields of polymers were obtained at 190 °C and 3 h. The polymers were characterized by FTIR, ^{1}H and ^{13}C NMR spectroscopy, SEM, TGA and molecular weight determination by viscometrical methods. All the polymers were rigid, having high T_g values between 178 and 189 °C. Only small amounts of Cu were detected by AAS.

Key words: Atom Transfer Rearrangement Radical Polymerization (ATRRP), Diammine-bis(trihalophenolato) Copper(II), Poly(dihalophenylene Oxide), Solid State Polymerization

Introduction

Controlled 'living' polymerizations such as the copper catalyst mediated atom transfer radical polymerization (ATRP) have been utilized recently for the synthesis of well-defined, narrow polydispersity polymers [1 – 4]. The suggested general mechanism for ATRP is:



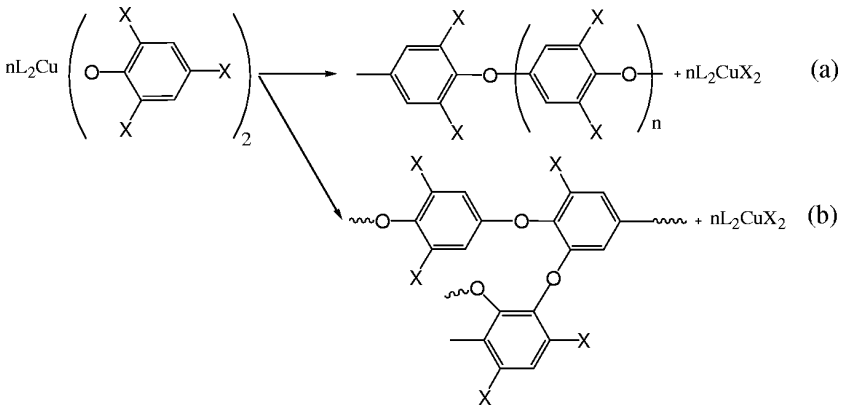
The radicals, or active species, are generated through a reversible redox process catalyzed by a transition metal complex which undergoes a one electron oxidation with concomitant abstraction of a halogen atom, X, from a dormant species, R-X [5].

Poly(phenylene oxide)s are polyethers having aromatic groups connected by oxygen atoms in the backbone structure. These polymers have been synthesized from a series of $ML_2(THP)_2$ complexes where L and THP represent a neutral ligand and a 2,4,6-trihalophenolate group, respectively, *via* solid state thermal decomposition, electroinitiation or thermal decomposition in solution [6 – 25].

Harrod and co-workers carried out the synthesis of poly(dihalophenylene oxide)s by decomposition of copper(II) complexes containing a series of amine ligands [10, 11, 31].

We depict the suggested general chemical reaction, where L is a neutral ligand and X a halogen atom. The decomposition reaction of the complexes took place through the formation of an oxygen radical in the trihalophenolate groups used as free radical initiators. It was claimed that the chain extension occurred by attack of the free radical initiators at the polymer chain in *para* or/and *ortho* positions. *Para*-positions led *via* 1,4 addition to poly(1,4-phenylene oxide)s (a) and *ortho*-positions *via* 1,2 addition to poly(1,2 phenylene oxide)s (b). It is also possible that 1,4 and 1,2 additions occur at the same monomeric unit [27, 28].

Since the 1980'ies, Kısakürek and *et al.* have been working on the polymerization of $CuL_X(THP)_2$ complexes where L was a neutral ligand such as N,N,N',N'-tetramethylethylenediamine (TMEDA), ethylenediamine (en), dimethylsulfoxide (DMSO) or N,N-dimethylformamide (DMF), and x was 2, 3 or 4 [12, 27, 28]. Various decomposition techniques were used, such as electroinitiation and thermal decomposition in solution or in the solid state, or microwave initiation in the solid state [30]. Beside the



decomposition methods, the types of the ligands and halogen substituents were effective regarding the structure, molecular weight, intrinsic viscosity and conversion of the polymers. Electrochemical decomposition methods generally lead to the lowest molecular weight polymers, whereas the highest ones were observed in the thermal decomposition of $Ce(TCP)_3(Py)_2$ complexes in the solid state [24].

In the present study, the aim was to investigate the effect of a small neutral ligand, NH_3, and of the type of the phenol (TCPH or TBPH) on the solid state thermal decomposition of helically structured diammine-bis(2,4,6-trihalophenolato)Cu(II) complexes.

Experimental Section

Materials

Analytical grade 2,4,6-trichlorophenol (TCPH) (Merck) and 2,4,6-tribromophenol (TBPH) (Merck) were used without further purification. Reagent grade NaOH (Merck) was used for the preparation of sodium 2,4,6- trichloro- and tribromophenolate. Toluene (Merck) was the solvent for the polymer. Commercially available technical grade ethyl alcohol was fractionally distilled and used as a non-solvent for the polymers.

Synthesis of polymers

The decomposition of 3 g batches of complex was performed in a glass holder (4 cm in diameter with 3.5 cm height) in a Stuart scientific-type oven at constant temperature. The decomposed complex was dissolved in toluene and the insoluble byproduct, L_2CuX_2 (X = Halogen), was removed by filtration. The polymer was precipitated with ethanol containing a few drops of concentrated HCl. The precipitated polymer was recovered by filtration and dried under vacuum to constant weight at r. t. % conversion and weight loss were calculated for each set as follows:

$$\%\ \text{Conversion} = \frac{\text{Weight of the polymeric product}}{\text{Initial weight of the complex}} \times 100$$

$$\%\ \text{Weight loss} = \frac{\text{Weight loss}}{\text{Initial weight of the complex}} \times 100$$

Characterization techniques

A Nicolet 510 FTIR spectrometer was used between 4000 and 400 cm^{-1} to obtain IR spectra of poly(dihalophenylene oxide)s dispersed in KBr pellets.

^1H NMR and ^1H-decoupled ^{13}C NMR spectra were recorded on a Bruker DPX-400, 400 MHz, high-performance digital FT NMR instrument, using $CDCl_3$ as a solvent and TMS as an internal reference.

Weight losses of the polymers with temperature were determined by a DuPont thermal analyst General V4.1C DuPont 2000 thermogravimetric analyzer. Synthesized polymers were heated from 30 to 850 °C with a heating rate of 10 °C/min under a nitrogen atmosphere.

Intrinsic viscosities of poly(dichlorophenylene oxide)s and poly(dibromo-phenylene oxide)s were measured using a Schott Geräte AVS 400-model automatic viscometer equipped with a Schott Geräte CT 1150 Model thermostat at 30 °C with an efflux time of 124 s in toluene.

Analysis of the surface morphologies of films was performed by using a JEOL JSM-6400 scanning electron microscope having a photo edit attachment Noran instrument EDS energy dispersion analyzer.

A Philips 9200X FAAS instrument was used for copper analyses at the 324.8 nm resonance line of copper with a band-pass of 0.7 nm. A fuel-rich air-acetylene flame with a 50 mm burner slot was used for the atomization.

Results and Discussion

The $Cu(NH_3)_2(TCP)_2$ **(C1)** and $Cu(NH_3)_2(TBP)_2$ **(C2)** complexes have been structurally characterized

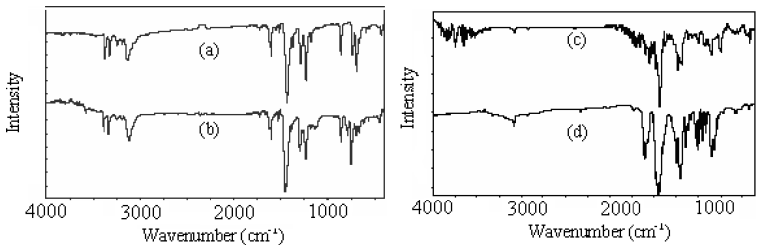


Fig. 1. FTIR spectra of **C1** (a), **C2** (b), **P1** (c) and **P2** (d).

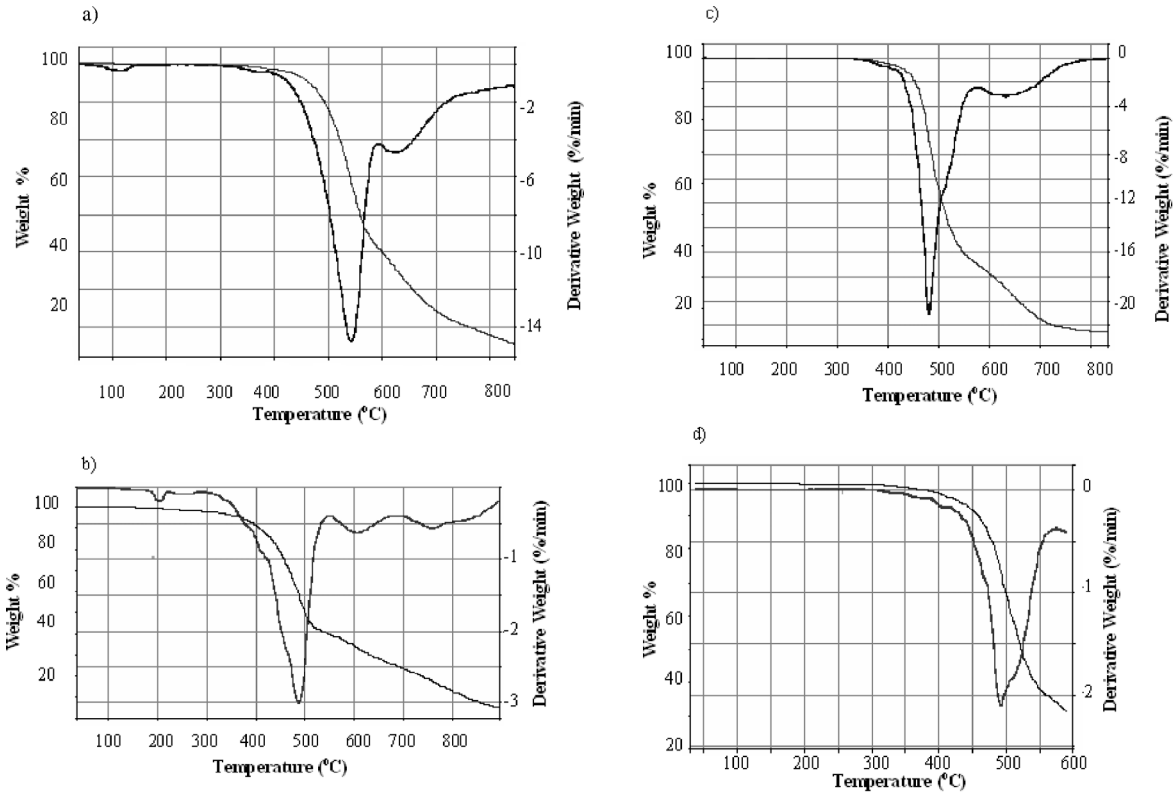


Fig. 2. TGA of **C1** (a), **C2** (b), **P1** (c) and **P2** (d).

as tetragonally elongated octahedral species by single crystal X-ray diffraction [32, 33]. FTIR spectra of **C1** and **C2** exhibit the characteristic absoptions as given in the literature [27, 33]. Both complexes were characterized by aromatic C-H and N-H stretching at 3420 – 3000 cm^{-1}, C=C ring stretching at 1260 – 1605 cm^{-1}, C-O stretching at 1237 cm^{-1}, and C-Cl and C-Br stretching at 832 – 630 and 760 – 630 cm^{-1}, respectively (Fig. 1a,b). In the FTIR spectra of the poly(dihalophenylene oxide)s, (**P1**, **P2**) the N-H stretching absorption at $> 3000\ cm^{-1}$ have disappeared and the appearance of new peaks was observed due to formation of the polymers (Fig. 1c and d). The polymers are characterized by the following absorption peaks: $\sim 1605\ cm^{-1}$ (aromatic rings); $\sim$ 1500 – 1200 cm^{-1} (C=C ring stretching); $\sim$ 1200 – 900 cm^{-1} (aromatic ether group); below $\sim 900\ cm^{-1}$ (C-Br and C-Cl) as in the literature [19 – 23, 25 – 28].

The TGA thermograms revealed that weight losses start at about 350 and 360 °C for **C1**, **C2** and **P1**, **P2**, respectively, indicating a high thermal stability, Fig. 2a – d. The thermograms also show that as the temperature reached about 800 °C, approximately 95% of **C1** and 87% **C2** were lost. For **P1** and **P2**, the remaining residues were less than 30% beyond 600 °C. This change could be due to loss of pendant groups.

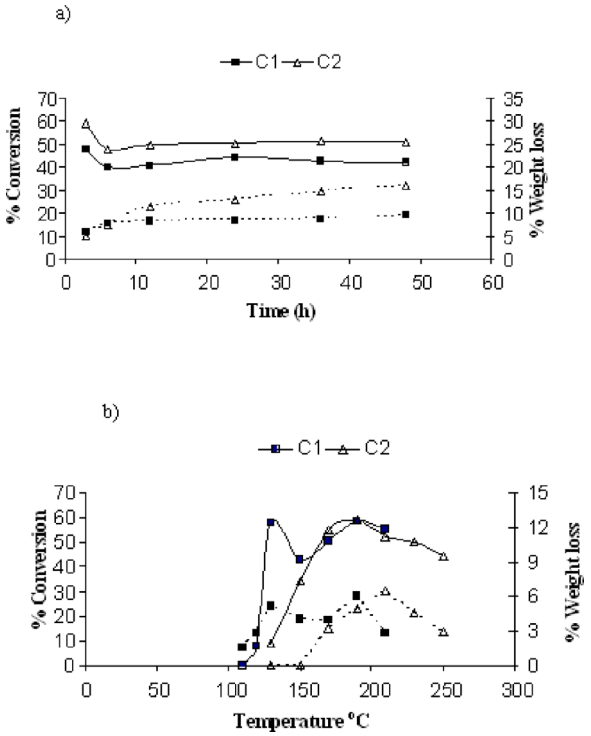


Fig. 3. Change in % conversion and % weight loss for **C1** and **C2** complexes (a) at 190 °C for different time intervals, and (b) at different temperatures but at constant time of 3 h. Solid line: % conversion, dashed line: % weight loss.

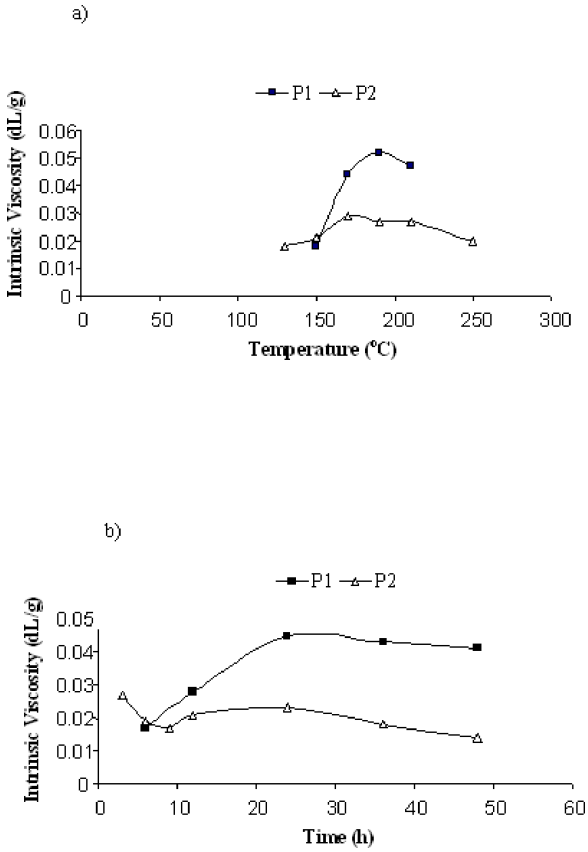


Fig. 4. Intrinsic viscosity *versus* (a) temperature at constant time (3 h) and (b) time at constant temperature, 190 °C, of **P1** and **P2**.

The thermal decomposition of **C1** and **C2** was carried out in the solid state. The polymerization was achieved for **C1** at different temperatures, 110–210 °C, but for a constant time, 3 h. Two maximum conversions, 58.0 and 58.5%, and weight losses, 5.1 and 6.0%, were observed at 130 °C and 190 °C, respectively. MS studies revealed that the weight loss mainly originated from phenol and to some extent from the ligand NH_3. The conversion slightly increased with temperature to 120 °C, followed by a sharp increment at 130 °C (58.0%). The conversion then slightly changed with temperature between 190 °C (42.7%) and 210 °C (58.5%). However, there was a slight increase in weight loss as the temperature was raised. When the complex was exposed for a longer time at 190 °C, the rise in the weight loss and the decline in the conversion were slightly affected (Fig. 3a).

C2 was also polymerized within a temperature range of 130–250 °C for 3 h. Maximum conversion of 59.3% was achieved at 190 °C which could be due to a significant increase in the rate of polymerization. The DSC thermogram has a broad exothermic peak. The weight loss developed to 6.5% at 140 °C and then dropped to 2.9% at 150 °C. When the complex was exposed for a longer time at 190 °C, the growth in the weight loss was affected more than the reduction in the conversion (Fig. 3a).

For **P1**, the intrinsic viscosity, $[\eta]$, increased with temperature, reaching the maximum value of 0.058 dl/g at maximum conversion (190 °C, Fig. 4a). Among the polymers synthesized in the solid state until now, the second highest intrinsic viscosity value of 0.058 dl/g ($M_w = 7.1 \times 10^4$) was achieved from the decomposition of $Ce(TCP)_3(Py)_2$ complexes [24]. The time effect on intrinsic viscosity followed the same trend as the conversion data (Fig. 4b).

For **P2**, the intrinsic viscosity increased with temperature and reached the maximum value of 0.027 dl/g at 170 °C. The $[\eta]$ values were generally lower for **P2** compared to **P1**. An interesting observation for **P1** and **P2** polymers concerns the color of the polymers,

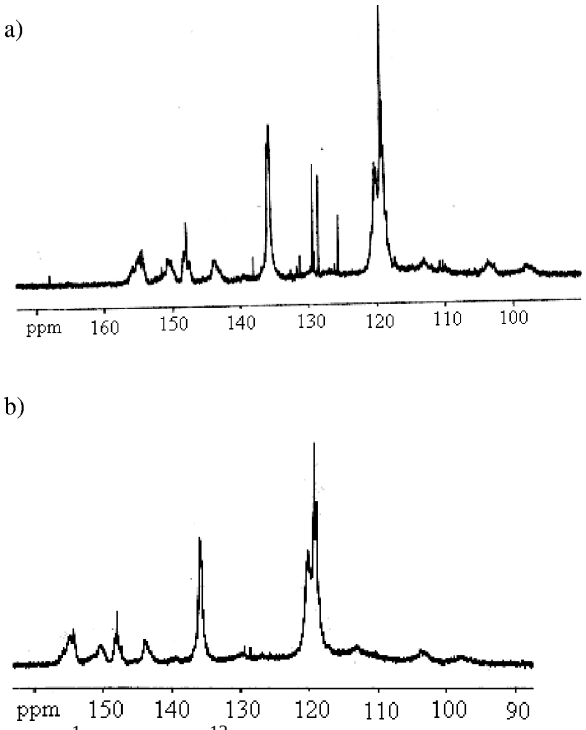


Fig. 5. ^{1}H decoupled ^{13}C NMR spectra of **P1** (a) and **P2** (b).

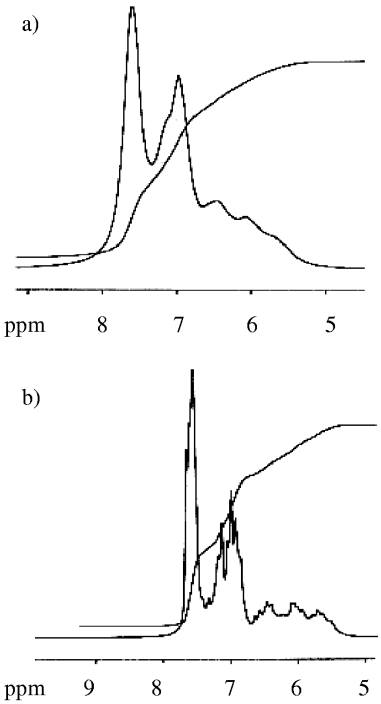


Fig. 6. ^{1}H NMR Spectrum of **P1** (a) and **P2** (b).

which was reddish brown instead of the usual white. It is believed that the color change might be due to the presence of copper in the polymers. The copper contents were determined by Atomic Absorption Spectrophotometry for the first time as follows:

Polymer	Copper, wt %
P1 190 °C (48 h)	0.09
P2 190 °C (48 h)	0.04

The $\{^{1}H\}^{13}C$ NMR spectra of **P1** and **P2** are shown in Fig. 5a,b. The theoretical ^{13}C NMR chemical shift data for the three main possible addition products (1,2, 1,4 or both) were calculated by appropriate correlation tables [29]. Data for **P1** and **P2** correlate well with the structures of 1,2 and 1,4 addition products. The ^{1}H NMR spectra of **P1** and **P2** are quite similar except for the relative intensities of the two main peaks at 7.6 and 7.75 ppm which are due to 1,2 addition and those at 7.0 and 7.1 ppm due to 1,4 addition, respectively (Fig. 6a,b). The broader peaks at higher field indicate the presence of both the 1,2 and 1,4 addition products at the same monomeric unit. As a result, 1,2 addition appears to be slightly predominant for **P1** and mainly so for **P2** over 1,4 addition.

The glass transition temperatures of the polymers **P1** and **P2** were also determined and found to be quite high, 218 and 173 °C, respectively.

Scanning electron micrographs for different temperature preparations of **P1** and **P2** are given in Fig. 7. The polymers have a relatively featureless surface which lack any dominant morphology. For both polymers, energy dispersion analysis EDS showed no evidence for the presence of copper, which might be due to the lower detection limit of AAS compared to EDS.

Conclusions

Syntheses of poly(dihalophenylene oxide)s were achieved using helically structured diammine-bis (2,4,6-trihalophenolato)Cu(II) complexes in the solid state by atom transfer rearrangement radical polymerization. The intrinsic viscosity values for the products **P1** and **P2** were found to be 0.058 and 0.027 dl/g, respectively, which could be due to the enhanced diffusion of chlorine- compared to bromine- substituted phenols leading to longer chains. ^{1}H NMR and ^{13}C NMR results suggest that for **P1** and **P2** 1,2 and 1,4 addition occur at almost equal rate leading to branched polymers, with the 1,2 addition slightly more predom-

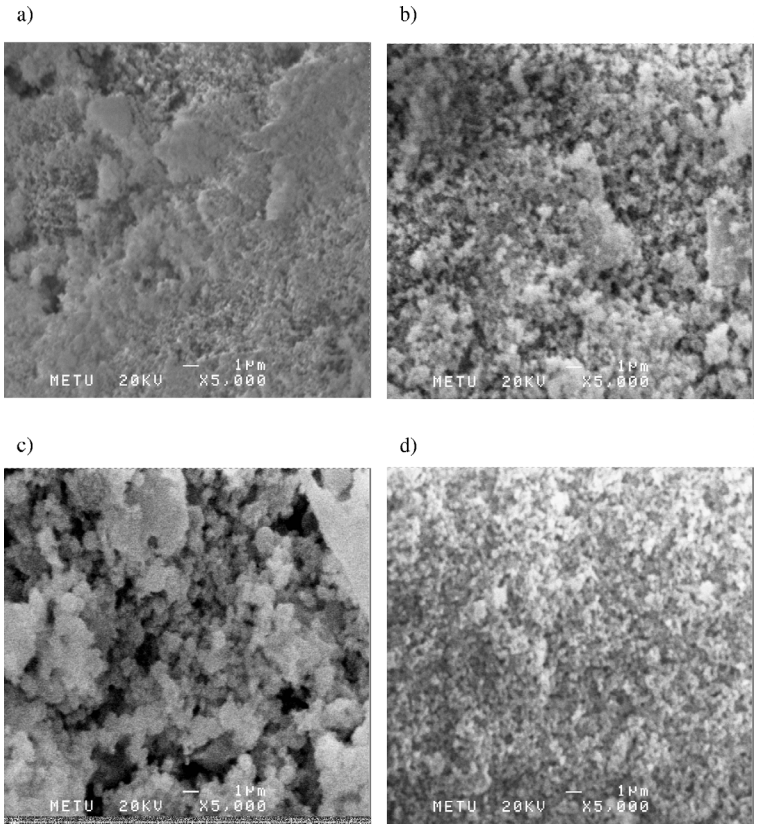


Fig. 7. SEM of powder **P2** (a) brown at 190 °C; (b) light brown at 150 °C, and of **P1**; (c) brown at 190 °C, (d) light brown at 170 °C.

inant for **P1** and mainly so for **P2** than the 1,4 addition. The optimum conditions to obtain the highest yields of **P1** and **P2** were 190 °C for 3 h to obtain the maximum intrinsic viscosity. A reddish-brown color was observed for all polymers for the first time, which might be due to quite small amounts of copper as was confirmed by AAS. All polymeric products had high T_g values indicating that they are rigid polymers.

Acknowledgement

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