

## Synthesis of conducting polysiloxane – polypyrrole graft copolymers

Ozge Gunaydin<sup>1</sup>, Levent Toppare<sup>1</sup> (✉), Yusuf Yagci<sup>2</sup> (✉), Valeria Harabagiu<sup>3</sup>, Mariana Pintela<sup>3</sup>, Bogdan C. Simionescu<sup>3,4</sup>

<sup>1</sup>Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

<sup>2</sup>Department of Chemistry, Istanbul Technical University, 80626 Istanbul, Turkey

<sup>3</sup>P. Poni' Institute of Macromolecular Chemistry, 6600 Jassy, Romania

<sup>4</sup>Department of Macromolecules 'Gh Asachi' Technical University, 6600 Jassy, Romania

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### Summary

Polysiloxane-polypyrrole graft copolymers have been synthesized by a series of chemical reactions and subsequent electropolymerization. First, the hydrosilation of 4-vinyl aniline by dimethyl-methylhydrosiloxane copolymer gave the corresponding aminophenyl functional polydimethylsiloxane (PDMS-NH<sub>2</sub>). The side chain pyrrole functionalized polysiloxanes were then prepared by the reaction of PDMS-NH<sub>2</sub> with glycidylpyrrole. Finally, the synthesis of graft copolymers of polysiloxane and pyrrole has been achieved electrochemically by using two different electrolytes, *p*-toluene sulfonic acid (PTSA) and tetrabutylammonium tetrafluoroborate (TBAFB). Characterization of these graft copolymers were performed by a combination of techniques consisting of scanning electron microscopy (SEM), thermal gravimetry (TGA), differential scanning calorimetry (DSC) analyses and FT-IR studies. The conductivities were measured by four-probe technique.

### Introduction

Conducting polymers, synthesized by electrochemical methods have some advantages like simplicity, reproducibility and thickness control. Polypyrrole, one of the most studied polymers [1,2,3], was first synthesized by electrochemical polymerization in 1968 [4]. As a result of its electroactivity, high electrical conductivity and stability it is frequently used in commercial applications such as sensors, batteries, molecular devices and membranes. However, some difficulties appear in processing conducting polymers since they have poor mechanical and physical properties. In order to make them as processible as conventional polymers, several approaches have been developed, one of which is to prepare graft and block copolymers with desired end groups like pyrrole or thiophene [5,6,7,8].

Polysiloxanes are materials that find many applications in a variety of industrial areas. The high flexibility and hydrophobicity, high thermal and chemical resistance, good resistance against radiation and solubility in nonpolar and/or low polarity solvents are some of their main properties. The most widely used member of

this class is polydimethylsiloxanes. To prepare polymeric materials that have good properties, polysiloxanes having reactive group substituted at the silicon atom (organofunctional substituents) were used as starting compounds. The flexible siloxane moiety may also improve the physical properties of conducting polymers.

There are several ways to prepare organofunctional polysiloxanes [9]. Mostly, the preparation methods start from the synthesis of silicofunctional polydimethylsiloxanes containing Si-H bonds followed by the hydrosilation of unsaturated compounds. Another method is to provide cationic or anionic equilibration of cyclic siloxanes together with disiloxanes as an end-blocking agent. In addition to that, reactions of functional siloxanes with some reagents provide desired functionality. All these methods are used to prepare organofunctional polysiloxanes containing hydroxyalkyl, hydroxyaryl, carboxyl, aminoalkyl, epoxy, methacryloxyalkyl and mercaptoalkyl groups [10]. Synthesis of some chain- or end-functionalized polysiloxanes [7,11,12,13] and their use in preparing copolymers [14,15] were also presented previously. Conducting H-type block copolymers of N-pyrrolyl terminated polysiloxane and polypyrrole with electrochemical methods were described as well [7].

In this work graft copolymers of pyrrole functionalized polysiloxane and polypyrrole were synthesized by electrochemical methods. This is to achieve the growth of polypyrrole chains through pyrrole moieties present on the polysiloxane.

## Experimental

### *Materials*

Pyrrole (Py) and epichlorohydrin (EPI) were distilled under nitrogen before use. Tetrahydrofuran (THF) was purified by refluxing over KOH for 24 h and over sodium wire. Toluene was first purified by azeotropic distillation and then simply distilled over sodium wire. Pyrrolyl potassium was prepared by reacting distilled pyrrole and potassium hydride (KH). Disperse KH (35 wt. %, 26.3 g, 0.23 mol) was washed with dry hexane twice in order to remove mineral oil. Toluene (185 ml) and pyrrole 18.9 ml (0.27 mol) were then added successively to the purified KH under dry nitrogen. The mixture was then refluxed for 24 h. After evaporating the solvent, nitrogen was kept bubbling through the flask. The pale yellow product was dried in vacuum under nitrogen for 2 days in order to remove any pyrrole remnants. N-Methyl pyrrolidone (Aldrich) and *p*-toluene sulfonic acid (Sigma) were used as received. Acetonitrile (Merck), dichloromethane (Merck) and chloroform (Merck) were used without purification. TBAFB (Merck) was dried before use.

### *Preparation of side chain 4-aminophenyl functionalized polydimethylsiloxane*

4-Aminophenyl functionalized polydimethylsiloxane (PDMS-Ph-NH<sub>2</sub>) was obtained by the hydrosilation of 4-vinylaniline (VA) with dimethyl-methylhydrosiloxane copolymer of a molecular weight Mn= 8000 with a SiMe<sub>2</sub>/Si(H)Me molar ratio 6.5/1 as described elsewhere [11]. The hydrosilation was performed in toluene at 100-110 °C, under nitrogen, in the presence of H<sub>2</sub>PtCl<sub>6</sub> catalyst (2 % solution in isopropanol). The hydro-polydimethyl siloxane was dissolved in toluene (50 % w/w concentration) in a predried round bottomed vessel fitted with magnetic stirrer, reflux condenser and dropping funnel. The solution was warmed at the reaction temperature, then the

catalyst solution was added. A 50 % w/w toluene solution of VA (VA/Si-H = 1to1 molar ratio) was then added and the reaction mixture was stirred at the reaction temperature for 6 hours, until the IR spectrum of the mixture showed the disappearance of the 2120-2160  $\text{cm}^{-1}$  Si-H characteristic band. The functionalized polysiloxane was recovered by toluene. Excess VA was removed by distillation. The final product was obtained by removing poly(4-aminostyrene) formed during thermal treatment in diethyl ether, and evaporating the solvent.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\sigma$  ( ppm) ; 0.05–0.15 ( $\text{CH}_3\text{-Si}$ ); 0.88-0.92 (m,  $\text{CH}_2\text{-Si}$ ); 1.32-1.34 (d,  $-\text{CH}(\text{CH}_3)\text{-Si}$ ); 1.99-2.05 (q,  $\text{CH}(\text{CH}_3)\text{-Si}$ ); 2.57-2.61 (t,  $\text{Si-CH}_2\text{-CH}_2\text{-}\phi$ ), 6.60-6.63 (d,  $\phi\text{-NH}_2$ (ortho)); 6.98-6.99(d,  $\phi\text{-NH}_2$ (meta))

$\text{Si}(\text{CH}_3)_2/\text{Si}(\text{Ph-NH}_2)\text{CH}_3 = 6.9/1$ . From the ratio of integrals of Si- $\text{CH}_2$  and SiCH protons, a  $\beta$  isomer to  $\alpha$  isomer ratio of about 9/1 was determined.

#### *Preparation of N-Glycidylpyrrole*

N-Glycidylpyrrole (GPy) was synthesized by reacting 1.05 g (10mmol) PyK with 0.94 ml (12 mmol) EPI in 8 ml THF in the presence of 18-crown-6 (0.26 g/mmol) at 40 °C, under inert atmosphere for 10 h. The mixture was filtered to remove the organic salt. The solvent and excess EPI were then distilled off. The remaining product was dissolved in  $\text{CH}_2\text{Cl}_2$  and washed several times with saturated brine. After solvent distillation, 1.15 g GPy (94 yield) was obtained.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\sigma$  ( ppm): 2.65-3.55 (epoxy); 3.8-4.0 ( $\text{NCH}_2$ ); 6.1 ( $\text{CHCH-N}$ ); 6.6 ( $\text{CH=CH-N}$ ).

#### *Preparation of side chain pyrrole functionalized polydimethylsiloxane*

The reaction between PDMS- $\text{NH}_2$  and Gpy ( $\text{NH}_2/\text{Gpy}$  in 1/1 molar ratio) was performed by stirring the reagents in the presence of isopropanol ( $\text{NH}_2/\text{OH}$  in 1/1 molar ratio) at 80 °C for 24 h. The side chain pyrrole functionalized polysiloxane was recovered by vacuum distillation of isopropanol. The polysiloxane was washed with petroleum ether, water and dried over  $\text{Na}_2\text{SO}_4$ . Liquid phase was then removed by distillation.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\sigma$  ( ppm) : 0.05–0.15 ( $\text{CH}_3\text{Si}$ ); 0.88-0.92 (m,  $\text{CH}_2\text{-Si}$ ); 1.32-1.34 (d,  $-\text{CH}(\text{CH}_3)\text{Si}$ ); 1.9-2.0 (q,  $-\text{CH}(\text{CH}_3)\text{-Si}$ ); 2.70-2.80 (t,  $-\text{CH}_2\text{-NH-}\phi$ ); 3.8-3.9 (m,  $\text{CH-OH}$ ); 3.90-4.00 (m,  $\text{CH}_2\text{-Py}$ ); 6.18 ( $-\text{CH=CH-N}$ ); 6.62-6.80 ( $\phi$  and  $-\text{CH=CH-N}$ ).  
 $\text{Si}(\text{CH}_3)_2 / \text{Si}(\text{Ph-Py})\text{CH}_3 = 7/1$ .

#### *Synthesis of conducting polysiloxane-polyrrole (PPy) copolymer*

Graft copolymer films of pyrrole-functionalized polysiloxane (PSi) were synthesized electrochemically in two different systems. Wenking POS 73 potentiostat was used to supply a constant potential in electrochemical syntheses. Electrolyses were carried out in a three-compartment cell (60 ml.).

A 1% solution of insulating polysiloxane was prepared in N-methylpyrrolidone (NMP) and both sides of the Pt were coated with polysiloxane. Since NMP has high boiling point (202°C) the electrodes were dried under vacuum for 6 hours. Two

different systems were used: In the first one electrolysis was performed in aqueous system by using *P*-toluene sulfonic acid (PTSA) as the supporting electrolyte (0.05 M) and 100 $\mu$ l (1.44mmol) of pyrrole at 1.1 V versus  $\text{Ag}^0/\text{Ag}^+$  at room temperature using coated electrodes under inert atmosphere. Films were washed with water to remove PTSA after the electrolyses. In the second one acetonitrile was used as the solvent and tetrabutylammonium tetrafluoroborate (TBAFB) was used as the supporting electrolyte (0.01M). After introducing 100 $\mu$ l (1.44mmol) pyrrole to reaction medium, electrolysis was performed at 1.2 V under inert atmosphere at room temperature. The polymers were washed in acetonitrile to remove TBAFB. Same electrolysis was performed in dichloromethane/TBAFB at 1.5V, and films were washed in dichloromethane to remove TBAFB. Then, all films were washed in NMP to remove unbound insulating polymer (polysiloxane). Since chloroform is miscible with NMP it is used to remove NMP and then dried under vacuum.

Graft copolymers of polysiloxane and polypyrrole were characterized by scanning electron microscopy (SEM), thermal gravimetry (TGA), differential scanning calorimetry (DSC) analyses and FT-IR studies. The conductivities were measured by four-probe technique.

## Results and Discussion

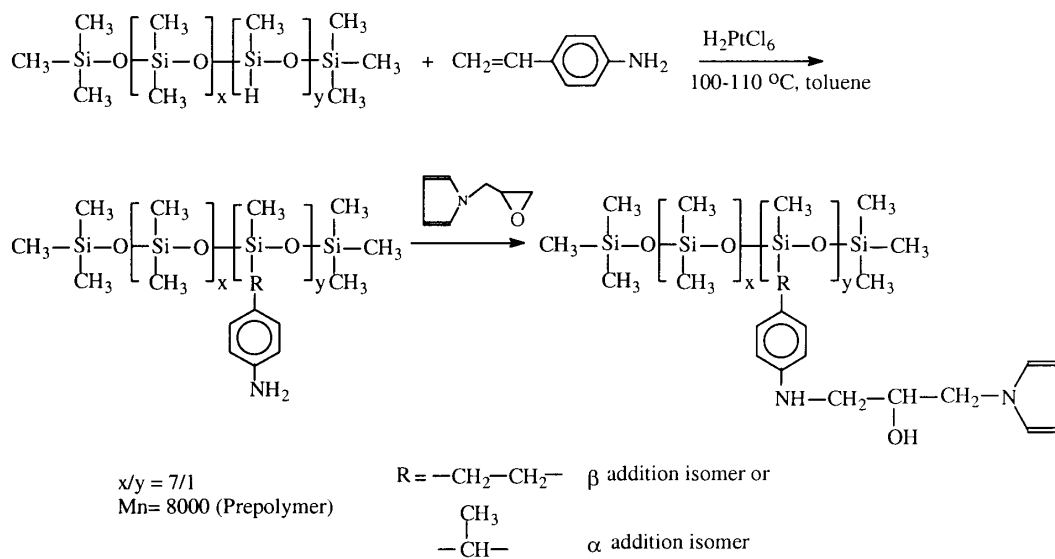
### *Synthesis of side chain pyrrole functionalized polysiloxane*

Side chain pyrrolyl-functionalized polydimethylsiloxane (PDMS-PY) was prepared by a multistep procedure according to scheme 1. The alkylation of pyrrole can be performed through the reaction between pyrrole salts and halogenated organic compounds [16,17]. The position of the electrophilic attack on the pyrrolyl anion is largely dependent on the nature of pyrrolyl salt cation of the halogenated compound and the solvent. The increase in cation radius and the polarity of the solvent provides a higher N/C substitution ratio. Under the condition mentioned in the experimental section the reaction of pyrrole potassium salt gives rise only to N-substituted pyrrole. No evidence of the carbon-linked glycidyl group was found since the H-NMR spectrum lacks peaks 5.8-6.0 ppm [18]. The reaction between amino compounds and epoxy terminated polysiloxanes was previously described in detail [19]. In the present case, the amino groups were attached to the siloxane chain as the side aminophenyl units, by a two step procedure, i.e., the hydrosilation of 4-vinylaniline with dimethyl-hydromethyl siloxane copolymers followed by the reaction of amino-functionalized polysiloxane with glycidyl pyrrole. The substitution degree of amino- and pyrrole-functionalized polysiloxane was determined from  $^1\text{H-NMR}$  spectra (see experimental section). Pyrrole functionalized polysiloxane was electrochemically grafted with polypyrrole according to scheme 2.

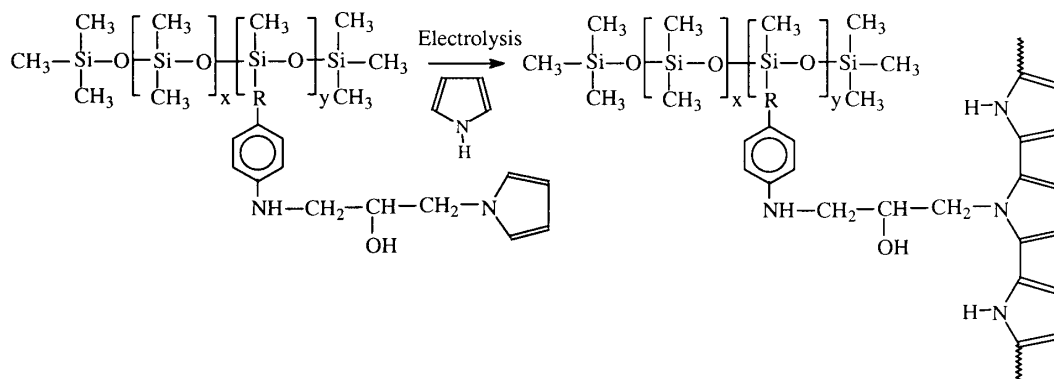
PTSA doped films were synthesized in one hour. TBAFB doped films in acetonitrile medium were obtained in 2.5 hours but in dichloromethane films were obtained at 8 hours. In all cases black freestanding films could be peeled off easily, however PTSA system films were of better quality in that matter.

### *Conductivities of the films*

For both PTSA and TBAFB doped polysiloxane/PPy films, the conductivities of both



Scheme 1



Scheme 2

**Table 1.** Conductivities of the films

Polymer	Solution	Electrode
PPy/PSi (PTSA doped)	$3 \times 10^{-1}$ S/cm	$3 \times 10^{-1}$ S/cm
PPy/PSi ( $\text{BF}_4^-$ doped in ACN)	$3 \times 10^{-1}$ S/cm	2.3 S/cm
PPy/PSi ( $\text{BF}_4^-$ doped in DM)	$7 \times 10^{-1}$ S/cm	1 S/cm

the solution and the electrode sides were measured by the standard four-probe

technique. Conductivities of the graft copolymers lie between 0.3 –3.0 S/cm (Table 1).

#### *Cyclic Voltammetry*

Cyclic Voltammetry analysis of polysiloxane showed no detectable redox peaks in the beginning. After the fifth run it showed electroactivity until eleventh run due to the oxidation of dimers or oligomers, increasing with number of scans. Since the oxidation peak showed no increase in peak height, we can conclude that oligomers are dissolving in the solution i.e. leaving the electrode. Therefore, no coating was observed on the electrode surface.

Cyclic voltammetry experiments were performed for the bare platinum electrode and for the polysiloxane coated electrode with pyrrole in the presence of TBAFB. The results for the bare Pt first showed a 50 $\mu$ A current, then electroactivity increased with increasing number of scans and the anodic peak was observed at 0.48V. In the case of polysiloxane coated electrode no activity was observed in the beginning. However, after several runs a peak was observed at 0.68V, which was not the same as that of pure polypyrrole (0.48V), which supports the formation of a graft copolymer.

#### *FTIR analysis*

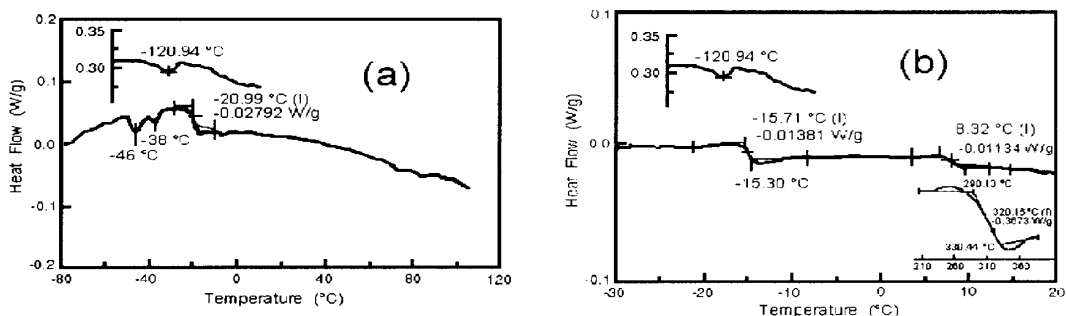
FTIR spectra of the films were recorded on a Matson 1000 ATIUNICAM FT-IR spectrometer. FTIR spectra of pyrrole functionalized polysiloxane showed peaks at 1267  $\text{cm}^{-1}$  and 804  $\text{cm}^{-1}$  which are due to  $\text{CH}_3$  –Si (symmetric deformation). Two typical peaks of polysiloxane at 1100-1028  $\text{cm}^{-1}$  were observed for Si-O-Si asymmetric stretching. Purified PSi/PPy copolymers present characteristic bands for both polymeric sequences, i.e. stretching vibrations of C=C at 1549  $\text{cm}^{-1}$  and C-N at 1464  $\text{cm}^{-1}$  for the polypyrrole chains and at 1100-1028  $\text{cm}^{-1}$  for the PSi sequences, that are additional proof for the formation of copolymer structure. The peaks at about 1100-1028  $\text{cm}^{-1}$  which can be seen in PSi/PPy copolymers (revealed with low intensity) also belong to the dopant ions (TBAFB, PTSA). FTIR analysis of polysiloxane doped either with PTSA or TBAFB showed C-Si peaks at about 1267  $\text{cm}^{-1}$  and 804  $\text{cm}^{-1}$ .

#### *Thermal Properties*

##### *Thermal Gravimetry Analysis (TGA)*

The thermal gravimetry analyses of polysiloxane PPy/PSi (doped with PTSA) PPy/Psi (doped with  $\text{BF}_4^-$  in ACN) were performed by Du Pont 2000 Thermal Gravimetry Analyzer.

TGA thermograms of PSi-Py showed the main weight loss at 464 $^{\circ}$ C. Almost %25 of the polymers survived when heated to 850 $^{\circ}$ C. In the case of PTSA doped graft copolymer there were two weights loses at 91 $^{\circ}$ C and 343 $^{\circ}$ C, the former being due to the loss of water. The remaining weight is %60. The main reason for PTSA doped copolymer having lower decomposition temperature is due to the loss of dopant ion (just above 200 $^{\circ}$ C). Therefore, we can conclude that the copolymer doped with PTSA



**Figure 1.** DSC curves of pure polysiloxane (a) and PPy/PSi (PTSA doped) (b)

is thermally more stable than pure polysiloxane. It is also the case for  $\text{BF}_4^-$  doped copolymer, for which the remaining polymer is % 51. In addition, when compared with the H-type polysiloxane-polypyrrole block copolymer synthesized previously [6] and with pure polypyrrole (PTSA doped) which have the remaining percent about %49, it is clear that PPy/PSi (doped with PTSA) copolymer revealed higher decomposition temperatures with more remnants.

#### *Differential Scanning Calorimetry (DSC)*

DSC thermograms of the polysiloxane polymer were performed by heating from  $-130^\circ\text{C}$  to  $100^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ . As it was mentioned before statistical copolymer contains longer polydimethylsiloxane (PDMS) segments. Thermograms reveal two glass transition temperatures for polysiloxane around  $-120^\circ\text{C}$  and  $-20^\circ\text{C}$ , former being due to PDMS segment. In addition to that, the endotherm transitions at  $-46^\circ\text{C}$  and  $-38^\circ\text{C}$  are double melting peaks that could arise from the reorganization of small and imperfect domains of PDMS segments during heating [Fig. 1(a)] [20]. After obtaining graft copolymers doped with PTSA, the glass transition temperature for PDMS segment was found at  $-120^\circ\text{C}$  as expected. Furthermore, the temperatures at  $-15^\circ\text{C}$  and  $8^\circ\text{C}$  could be the transitions of PDMS rich phase and the  $T_g$  of pyrrolyl substituted siloxane, respectively. The increase of the melting and  $T_g$  temperatures could be explained by the restrictions arising after crosslinking with pyrrole sequences [Fig. 1(b)].  $330^\circ\text{C}$  was the decomposition temperature of the graft copolymer.

#### *Morphologies of the Films*

Scanning electron microscopy (SEM) studies were performed by JEOL JSM-6400. Graft copolymers doped with either PTSA or TBAFB were washed in NMP, the solvent of polysiloxane, subsequently they were washed in chloroform. The morphologies of the films were investigated by SEM. In PTSA system, solution sides of the washed and unwashed films have the same morphology with standard cauliflower structure. In the case where TBAFB was utilized as the supporting electrolyte, solution sides of washed and unwashed films have somewhat different morphologies. The incorporation of polysiloxane units are visible and leading to the destruction of common polypyrrole morphology. This may mean that the pyrrole units added to the pyrrole moiety of siloxane chain are shorter compare to that of the graft copolymer doped with PTSA anions.

## Conclusions

The synthesis of graft copolymers of pyrrole-functionalized polysiloxane with pyrrole was achieved in the presence of two different supporting electrolytes. It is seen that copolymers doped with PTSA resulted in outcomes that are better in quality. They also showed different morphologies in different solvents.

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