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Chemical synthesis of polymers containing *N*-ethyl-3.7-phenothiazinediyl groups

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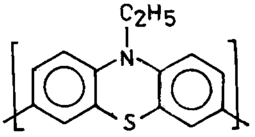
SUMMARY

Poly(N-ethyl 3.7-phenothiazinediyl) (1) and poly(N-ethyl 3.7-phenothiazinediyl-co-acetylene) (2) were synthesized by homo- and copolycondensation of 3.7-dibromo N-ethylphenothiazine and 1.2-dibromoethene using a Grignard reaction and $NiCl_2$ or $NiCl_2.2PPh_3$ as catalyst. Polymers are soluble in common organic solvents and after doping with iodine have an electrical conductivity of 10^{-7} -10^{-6} $\Omega^{-1}.cm^{-1}$.

INTRODUCTION

Unlike polyacetylene,the first organic polymer which has changed to a conducting state by doping,heterocyclic polymers are of increasing interest owing to their enhanced thermal and oxidative stabilities in both doped and neutral states.Thus,very many studies are dealing with chemical and electrochemical synthesis of polythiophene and polypyrrole,the best known conducting polymers containing heterocycles (1). The introduction of the substituents into the heterocyclic nucleus confers to these polymers solubility,melt processability and other interesting properties ,i.e.,optical activity,self dopability,crystal liquid behaviour,etc (2,3). Other modifications of this polymer class is by exchange of the heterocyclic nature. Until now polycarbazoles (4-6),polyisothianaphthene (7),polyindole (7) and polyfuran (8) were synthesized.

This paper reports on the chemical synthesis of polymers containing another heterocyclic nucleus,i.e.,N-ethyl 3.7-phenothiazinediyl ,and on some of their properties.



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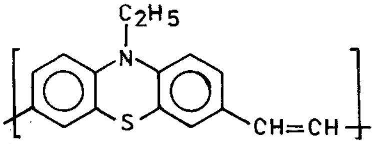

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EXPERIMENTAL PART

Reagents: Phenothiazine (technical grade) was purified by recrystallization from benzene and methanol. 1.2-dibromoethene (Fluka) was distilled before use. Magnesium Grignard was used as received. $NiCl_2$ was a commercial product and $NiBr_2.2PPh_3$ was synthesized according to the known method (9).Tetrahydrofuran (THF) and dimethylsulfoxide (DMSO) were purified and dried by usual methods.

Polymer synthesis was performed by homo- and copolycondensation of 3.7-dibromo N-ethylphenothiazine and 1.2-dibromoethene in presence of magnesium Grignard using $NiCl_2$ or $NiBr_2.2PPh_3$ as catalyst,according to the general reaction:

$$X - Ar - X \ + Mg \longrightarrow X - Mg - ArX \ / \ X - Ar - X \ / \ XMg - Ar - MgX \xrightarrow{\text{catalyst}} X -(-Ar-)_n-X \ +nMgX_2$$

N-ethylphenothiazine and 3.7-dibromo N-ethylphenothiazine were obtained by known methods (10,11).

Poly(N-ethyl 3.7-phenothiazinediyl) (1): In the first step Grignard reagent was synthesized from 19.25 g (50 mmol) of 3.7-dibromo N-ethylphenothiazine and 1.22 g (50 mmol) Mg powder in 50 ml dried THF at reflux temperature and 8 hr. Then 50 mg $NiBr_2.2PPh_3$ was added and the reaction mixture was refluxed during 4 hr.The mixture was poured in methanol and the yellow precipitate was filtered,dried and reprecipitated from THF or DMSO with methanol. Yield = 68 %.

Poly(N-ethyl 3.7-phenothiazinediyl-co-acetylene) (2) : The copolymer was synthesized similarly to (1) starting from 3.85 g (0.01 mole) 3.7-dibromo N-ethylphenothiazine ,0.448 g (0.02 mole) Mg ,1.86 g (0.01 mole) 1.2-dibromoethene and 20 mg $NiCl_2$ or $NiBr_2.2PPh_3$ in 50 ml dried THF . A light brown polymer was obtained with 43 % yield.

Polymer characterization was carried out by elemental analysis and IR (Perkin Elmer 577 apparatus) and ^1H-NMR (JEOL-C-60 HL,60MHz spectrometer) spectroscopy. Molecular weights were calculated from bromine analysis (considering that polymer chains contain bromine atoms at both ends) and determined by vapour pressure osmmometry.

RESULTS AND DISCUSSION

All synthesized polymers are products of yellow or light brown colour,amorphous,soluble in THF,DMSO and halogenated solvents and have a low molecular weight (Table 1).

^1H-NMR spectra (Figure 1) show the presence of ethyl group from phenothiazine nucleus ($-CH_3$;1.22 - 1.65 ppm and $-CH_2$ -N- 3.55-4.10 ppm) and aromatic protons (6.6 - 7.4 ppm) . The ratio between integrals attributed to aliphatic and aromatic protons corresponds very well to the proposed structure. Ethylenic protons appear in the same region as the aromatic protons.

IR spectra (KBr pellets) of the polymers are presented in Figure 2 and they contain the characteristic peaks of the out

Table 1: Elemental analysis and molecular weights of the polymers

Polymer	Yield	Elemental analysis			Molecular weight	
	%	C,%	H,%	Br,%	(a)	(b)
1	68.0	65.7	5.1	15.07	1060	1870
2	43.0	70.3	5.3	10.8	1470	1750

(a) calculated from elemental analysis of bromine
(b) determined by vapour pressure osmometry in THF at 45^{0}C.

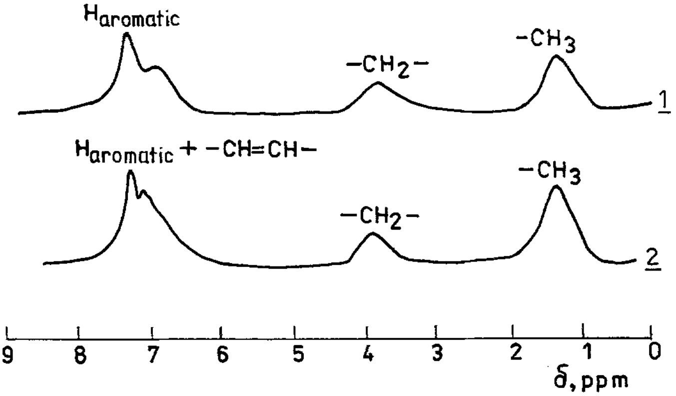

Figure 1: ^{1}H-NMR spectra (CDCl$_3$,55^{0}C) of phenothiazine polymers

of plane C-H bending vibrations of 1.2.4-trisubstituted aromatic ring (800 and 870 cm^{-3}). These bands are also present in the spectrum of 3.7-dibromo N-ethylphenothiazine monomer. Therefore, in the chemical polymerization of 3.7-dibromo N-ethyl phenothiazine the C-C bonds are formed at the carbons from 3 and 7 positions of the phenothiazine ring leading to polymers with 3.7-phenothiazinediyl groups in the main polymer chain.

As synthesized, both 1 and 2 are insulating polymers, their electrical conductivities are lower than 10^{-13}Ω^{-1}cm^{-1}. These polymers containing phenothiazine nuclei have a strong electron donor character and they may form charge transfer complexes with acceptors. The doping of these polymers was performed both in solution and solid state using iodine as acceptor. In the solid state the doping was carried out by exposing the polymer powders to dopant vapours (760 mm Hg and room temperature) and subsequently pumping for 30 minutes to remove excess dopant. The doping level was determined by weight uptake. Polymer 2 showsa higher doping rate than polymer 1 (Figure 3) and this behaviour arise from the favourable steric effect of the ethylene group inserted between two phenothiazine nuclei.

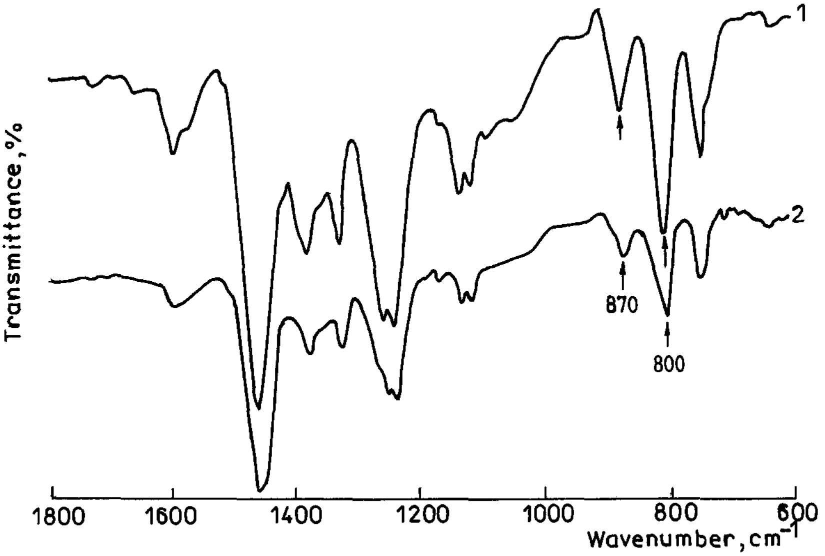

Figure 2: IR spectra (KBr pellet) of phenothiazine polymers

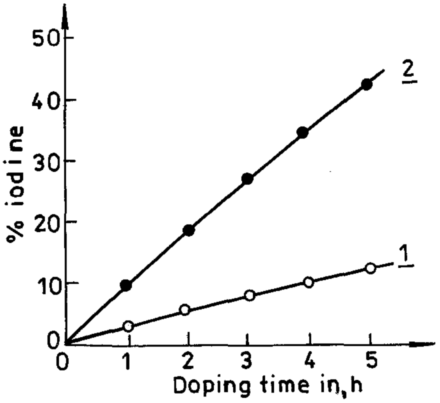

Figure 3: Typical doping curves

The conductivity of the powders doped with iodine is situated in the range 10^{-7} - $10^{-6}\,\Omega^{-1}$ .cm^{-1},measured by the standard four point probe : 2.2.$10^{-6}\,\Omega^{-1}$.cm^{-1} for polymer 1 (11 % mol iodine) and 4.5.10 Ω^{-1}.cm^{-1} for polymer 2 (18 % mol iodine). The lower electrical conductivity of the iodine doped polymers 1 and 2 as compared to other polymers containing smaller heterocycles in the main polymer chain (i.e.,polythiophene) can be attributed to the bulky phenothiazine group which may prevent an extensive delocalization of carriers along the conjugated system.Therefore,increasing of the heterocyclic nucleus bulkness permits to obtain soluble polymers but has an unfavourable effect on polymer electric properties.

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