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RESEARCH ARTICLE

Electropolymerization of Quinoline using Biphasic System

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Abstract

The electrochemical polymerization of quinoline has been studied using mixed two phases of formaldehyde containing electrolyte and toluene/ benzene containing monomer intimately mixed. Tetra alkyl ammonium halides and lithium perchlorate and iodates have been used as supporting electrolyte to catalyze the process .The presence of the two phases helps in dissolution of the polymer formed thereby preventing contamination on the electrodes. The inclusion of air or hydroquinone had an inhibition effect on the all the systems under study which is suggestive of a radical mechanism operating.

Experiment

Materials required

Quinoline (Fluka A.G.),Toluene/Benzene,H_2SO_4 (10%), $LiClO_4$ (fluka),$LiBF_4$(Fluka) and LiI (Fluka) Tetra methyl ammonium halides (BDH) were used after purification .

Cell Assembly

The electrochemical polymerization was carried out in a single compartment cell without separating the cathode and the anode. The arrangement for bubbling pure and dried N_2 gas was provided in the assembly. Aluminium sheets of working area 2.0cm^2 were used as cathode as well as anode. Also mercury pool is used as cathode and Carbon rod as anode. The Polarization study was carried out with respect to SCE at 30^{0}C.

ELECTROLYSIS AND WORK UP

The electrolysis was carried out by varying (1) the supporting electrolyte and solvent of non polar phase (II) the concentration of monomer and (III) the current strength. The electrolysis was carried out in a cell whose temperature was maintained and the contents were intimately mixed by a magnetic stirrer. The contents of the cell and the electrolyte were subject to purging of nitrogen gas about thirty minutes to remove dissolved oxygen. In order to determine the yield of polymers at one time e.g., after an hour, the electrolysis was terminated at that time and the whole of non polar phase precipitated by excess of acidified methanol and the resulting brown polymer was dried in an air oven 100^{0}C and the yield determined.

Result and Discussion

The poly quinoline obtained by this novel technique was confirmed to be syndiotactic by its ^{1}H NMR and IR spectral data..Elementary analysis gives results which are approximately the same as the theoretical findings for quinoline.

Experimental %

C, 82.75 N , 10.55 H , 5.19

C_9H_7N (theoretical) C, 83.72, N, 10.85 H,5.01

It can therefore be taken that the reaction leads to the formation of quinoline polymers.

Spectra are exactly the same for polyquinoline specimens prepared at different polymerization times. There is a band in the 1600cm^{-1} regions, which can be ascribed to the valence vibrations of the

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conjugated bonds in the chain. The spectra of polyquinoline contain bands in the 740- 830cm^{-1} ranges which can only be ascribed to the C-H stretching vibrations outside the plane in the phenyl ring. It is also interesting to note that besides the 750cm^{-1} band typical of ortho substituted benzene all the spectra also contain the 820cm^{-1} band which is typical of para substituted rings.

EFFECT OF THE SUPPORTING ELECTROLYTE AND THE SOLVENTS

The results of electro polymerization of quinoline are summarized in table I . It infers that $LiClO_4$ is most suitable in producing polymer of both higher molecular weight and giving high yields. Therefore, it can be assumed that polymerization depends upon both the nature of cations and anions used as supporting electrolyte .

The effect of electrolyte concentration on the rate of polymerization at different current strength shows that the rate of polymerization increases with increasing electrolyte concentration and attains a maxima before reaching a constant value at higher electrolyte concentration.

Table 1

Electrolyte	Yield in gms of Polymer in		% yield in Toluene	% conv--ersion	Toluene Rp %/hr	Polymer--ization efficiency
	Benzene	Tolu.				
1.$LiClO_4$	29.06	29.72	30.68	0.4602	0.1532	102.8
2.$LiBF_4$	27.99	28.15	29.05	0.4357	0.1452	97.3
3.LiI	27.82	28.01	28.91	0.4336	0.1445	96.8
4.$(Me)_4NCl$	24.01	24.71	25.50	0.3825	0.1275	85.4
5.$(Me)_4NBr$	22.72	23.39	24.14	0.3621	0.1207	80.9
6.$(Me)_4NI$	22.53	23.16	23.08	0.3462	0.1154	77.3

EFFECT OF MONOMER CONCENTRATION

With changing monomer concentration the yield is greatly affected. The yield increases the percentage attains a constant value at higher monomer concentration (beyond 1.7 mol/lit) . From data it can be indicated that the yield is proportional to monomer concentration but at too high concentration the yield remains unaffected. The highest Rp 0.1534 per hour at 1.7 mol/lit.

EFFECT OF CURRENT

The percentage of conversion was observed with respect to charge passed and the result shows that with increasing current the percentage of conversion also increasing but only to certain limit e.g. until it attains a maxima and consequently a constant value for quinoline Rp max 0.1534 per hour at 40 mA.

The observation do reveal that the biphasic system is more suitable than monophasic one.

SIGNIFICANCE

Polymeric quinones have excited interest by virtue of their application as resins or as simple oxidoreductive models. Fundamental information on the resins substrate interaction and on the effect of polymeric environment and of visceral group and linkage on the quinine.

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