Notes to the Editor

Effect of reaction variables on oxidative polymerization of 1-naphthol using Cu^{I}-pyridine catalyst

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(Received 2 February 1977; revised 21 March 1977)

INTRODUCTION

Oxidative polymerization of 1-napthol using Cu^{I} chloride–pyridine initiator system has already been reported by us[1], following earlier investigations on similar polymerization with substituted phenol by Endres *et al.* and others[2–4]. We wish to report here the influence of some of the reaction variables on the oxidative polymerization of 1-naphthol and also the properties of polymer samples obtained under different reaction conditions. The relative rate of C=O and C–C coupling has been investigated using different ligand ratios (molar ratio of pyridine to copper) at constant catalyst concentration as well as varying monomer concentrations at a fixed ligand ratio with a view to obtaining some plausible mechanism of the polymerization reaction. The rate of oxygen absorption has not been reported since gas flow rate could not be made constant under different viscosity conditions during the entire polymerization reaction. Since earlier investigation[2] on such oxidative polymerization with substituted phenols did not indicate any appreciable influence of reaction temperature and solvent medium, these parameters were also not studied in the present investigation.

EXPERIMENTAL

Materials

Analytical grade nitrobenzene was used without further purification. 1-Naphthol was recrystallized and vacuum dried prior to polymerization. Cuprous chloride was freshly prepared using standard methods.

Pyridine (BDH) was purified by distilling and collecting the fraction 112°–115°C.

Polymerization procedure

A measured amount of cuprous chloride was added under a continuous stream of dried oxygen, to a mixture of nitrobenzene and pyridine kept at 40°C in a three-necked flask. 1-Naphthol was added in portions to this initiator system under vigorous stirring. A thick viscous mass was obtained in about 20 min. The reaction was allowed to continue for 2 h. The reaction mass was then cooled and directly filtered in order to obtain any quinone that was formed. The residue was washed with 50 ml of nitrobenzene; the washing along with the filtrate were poured into four volumes of acidified methanol. The crude precipitated polymer sample obtained was filtered and finally washed several times with acidified methanol. The polymer was dried *in vacuo* at 40°C. The quinone that was separated from the reaction mixture was dried under vacuum at 40°C for 3 h.

No dehydrating agent was used unlike earlier investigations even in the polymerization batches with low ligand ratios, due to the fact that these ionic agents might have a cocatalytic effect[5] on the C–O coupling reaction which might affect the overall rate of such reactions to a great extent. The water produced during the progress of the reaction had little effect (auto-retardation) for batches with higher ligand ratios. In the case of low ligand ratio batches also the effect was not reproducible. For cases where ligand ratios were more than 1000, pyridine was used as the only solvent.

Characterization of polymers

Infra-red spectral analysis of the polymer and the quinone samples was made using an INFRACOR-IR-120. Viscosity measurements of the polymers were made using a Ubbelohde viscometer at 25°C in chloroform solution.

Thermogravimetric analysis of three representative polymer samples were made using a Reglegu'e Automatic Thermogravimetric Analyser.

Acid and alkali resistance of the polymer samples were tested using thin film by standard methods.

RESULTS AND DISCUSSIONS

The fractional yield data of C–O coupled products at various ligand are given in *Table 1*. It is evident that the ligand ratio has got an important effect on the rate of C–O and C–C coupling reaction.

Table 1 Conditions: 1-napthol, 0.2 M; cuprous chloride, 0.005 M; temperature, 40°C

Pyridine (M)	Ligand ratio	Fractional yield C – O	Fractional yield C – C	Intrinsic viscosity C – O product (dl/g)
0.0035	0.7	0.183	0.752	–
0.0050	1.0	0.218	0.801	0.032
0.0100	2.0	0.547	0.190	0.094
0.0150	3.0	0.735	0.0800	0.105
0.050	10.0	0.893	0.0	0.104
0.500	100.0	0.965	0.0	0.112
9.00	1800.0	0.891	0.0	0.128
9.00	1800.0	0.905	0.0	0.120
As solvent	2000.0	0.942	0.0	0.098

Table 2 Conditions: 1-napthol, 0.2 M; temperature, 40° C

CuCl (M)	Ligand ratio	Fractional yield		Intrinsic viscosity (dl/g)
		C – O	C – C	
0.005	1	0.260	0.643	0.045
0.010	1	0.505	0.385	0.063
0.050	1	0.765	0.142	0.072

The catalyst complex formed at low ligand ratio is found to favour the formation of C–C coupled product. The higher yield of the C–C coupled product at ligand ratios above ten indicates that theoretical molar ratio of pyridine to copper is not the actual molar proportion so far as the active catalyst complex is concerned. At higher ligand ratios, when pyridine is the solvent there seems to be no significant change in the C–O coupling reaction rate. The viscosity data indicate that the degree of polymerization is also high at higher ligand ratios. This observation is also in conformity with the observation of Enders *et al.*[4] in case of oxidative polymerization of 2,6-dimethyl phenol.

Under identical conditions the increase in molar proportion of 1-napthol has little or no effect over the relative rate of C–O and C–C coupling reactions.

From *Table 2* it is observed that varying catalyst concentrations at constant ligand ratio has got also an important effect on the rate of C–O and C–C coupling reactions similar to those observed in case of varying ligand ratio. The formation of polymeric product (C–O coupling reaction) is favoured with increasing catalyst concentration keeping the ligand ratio constant.

Table 3 Conditions: 1-naphthol, 0.2 M; pyridine, 0.05 M; temperature, 40°C; polymerization, 2 h

CuCl (M)	Fractional yield		Intrinsic viscosity (dl/g)
	C – O	C – C	
0.005	0.965	0.0	0.065
0.010	0.872	0.125	0.068
0.020	0.833	0.138	0.074
0.030	0.754	0.172	0.078
0.040	0.737	0.195	0.075
0.050	0.765	0.142	0.072

Table 4 Conditions: cuprious chloride, 0.05 mol; ligand ratio, 1; temperature, 40°C; time, 2 h

1-napthol (M)	Fractional yield		Intrinsic viscosity (dl/g)
	C – O	C – C	
0.10	0.725	0.136	0.068
0.20	0.775	0.142	0.074
0.40	0.823	0.139	0.072
0.80	0.784	0.147	0.075

However the yield of C–O coupled product has been observed to decrease by increasing copper concentration while keeping the ligand ratio constant at 10 where maximum carbon oxygen coupling reaction occurs as evident in the earlier set of experiments.

According to these observations the catalytic complex that is formed at low ligand ratios favours the formation of C–C coupled product whereas the complex formed at high ligand ratio favours the formation of polyether. A plausible mechanism involving chain reaction with the catalyst complex at low ligand ratio may be suggested as follows. A C–C coupled quinine that is obtained at low ligand ratios, has been confirmed by i.r. analysis. The tetra coordinated complex formed predominantly at higher ratios of pyridine to copper appears to catalyse step reaction involving dehydration leading to the formation of a polyether.

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Effect of organic solvents on the stability of poly(L-glutamic acid) α-helix

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(Received 23 April 1977)

INTRODUCTION

The stability of the α-helical conformation of poly(L-glutamic acid) (PLGA) has been extensively studied especially in aqueous solutions. It is usually expressed as ΔF°, the free energy of the helix to coil transition between the uncharged conformers. This value can be obtained from the modified titration curve of the polyacid, according to the method of Zimm and Rice[1].

Some potentiometric studies have also been carried out in water–organic solvent mixtures and the main result is that the addition of organic solvent increases the stability of the helical conformation of PLGA[2–5]. Conio *et al.*[3] have studied the helical stability of PLGA in mixtures of water with aliphatic primary alcohols and found that, at constant molarity of the organic solvent, ΔF° increases with the length of the aliphatic alcohol chain. From their results, Dubin[5] has shown that the free energy ΔF° depends mainly on the dielectric constant of