

NOTES

Electrochemical Polymerization of Acenaphthylene in Nitrobenzene and Nitromethane

We have reported the electrochemical polymerization of acenaphthylene in acetic anhydride and acetonitrile solutions containing perchlorate in detail in a previous paper.¹ Subsequently, it was found that the polymerization proceeded in nitrobenzene, nitromethane, and dichloromethane solutions containing perchlorate at the anode. This paper deals with the electrochemical polymerization of acenaphthylene in the nitrobenzene and nitromethane solutions containing tetrabutylammonium perchlorate at the anode.

As seen in Table I, no polymer was obtained when bromide or iodide salts in nitrobenzene and nitromethane solutions were used in place of perchlorate. These same solutions yielded no polymer in the absence of an electrical current.

The yields and intrinsic viscosities of the polymers in purification by reprecipitation once formed in nitrobenzene and nitromethane solutions containing tetrabutylammonium perchlorate are listed in Table II. The yields and intrinsic viscosities of the polymers in purification by reprecipitation several times formed in nitrobenzene lacked reproducibility (will be described later). The reaction systems in nitrobenzene or nitromethane were in the liquid, semisolid, and solid states or in the liquid states at 30°, 0°, and -10°C, respectively; and also, current did not pass through the solutions of nitrobenzene at temperatures below -10°C. When the reaction system was kept for 60 min at room temperature after electrolysis in each solvent and then was poured into methanol, the yields of polymers increased in comparison with those reaction systems poured into methanol immediately after electrolysis. That is to say, the presence of a very active species in the electrolyzed solutions was proved by a remarkable aftereffect in nitrobenzene and nitromethane solutions. The electrochemical polymerization of various monomers has been investigated in considerable detail by both Breitenbach et al.² and Funt et al.³

The infrared spectroscopic studies showed that the structures of the polymers so formed in each solvent were similar to those of the polymers produced by the usual cationic polymerization, and that a small number of nitrobenzene groups existed in the polymers formed in the nitrobenzene solution even in purification by reprecipitation two times; the mole ratios of acenaphthylene/nitrobenzene in the polymers were estimated to be about 6 to 8 by the analyses of nitrogen content of the polymers. No group existed in the polymers formed in nitromethane solution.

The production of perchloric acid by electrolysis was confirmed on the basis of the pH change before and after the electrolysis of the solution and the formation of colored complex produced by the reaction of perchloric acid and nitrobenzene. In addition, the amount of perchloric acid produced in electrolyzed solution except acenaphthylene were measured by the method of JIS K2501 (Japan), as shown in Table III.

The presence of very active species (perchloric acid) produced in the electrolyzed solution and the infrared spectroscopic studies suggested that the hydrogen cation of perchloric acid which was produced by electrolysis of nitrobenzene and nitromethane solutions containing tetrabutylammonium perchlorate initiated the polymerization, and, in addition, nitrobenzene may have terminated the polymerization because of the negative character of the nitro group in nitrobenzene. However, the mechanism of polymerization by perchloric acid is interpreted by Pepper et al.⁴ as a transfer-dominated living polymerization with a fast initiation and no termination and by Masuda et al.⁵ in terms of counterion exchange and a tertiary function of the added tetrabutylammonium salt. Therefore, the purification of polymer is repeated several times, considering that the purification of polymer is a matter of immediate importance. Consequently, the nitrobenzene group in polymer disappeared when purification was repeated several times. It

was known that the separation of polyacenaphthylene of low molecular weight and nitrobenzene was a difficult process.

The addition of *N,N'*-diphenyl-*N*-picrylhydrazyl did not suppress polymerization, and the electrochemical copolymerization of acenaphthylene and isobutyl vinyl ether or acrylonitrile proceeds probably by a cationic mechanism in each solvent.

TABLE I
Effect of Supporting Electrolyte on Polymer Formation
in Nitrobenzene and Nitromethane at 30°C and 0°C^a

Supporting electrolyte	Result
LiClO ₄	polymerization
(C ₄ H ₉) ₄ NClO ₄	polymerization
(C ₄ H ₉) ₄ NBr	no polymerization
(C ₄ H ₉) ₄ NI	no polymerization
LiAlH ₄ , NaCl, CH ₃ COONa	electrolyte does not dissolve in solution

^a Acenaphthylene, 1.00 g; solvent, 60 ml; supporting electrolyte, 0.4 g or saturated; magnitude of current, 20 mA or current in maximum voltage (500 volts); reaction time, 30 min.

TABLE II
Yield and Intrinsic Viscosity of Polymer Formed in Nitrobenzene and Nitromethane
Solutions Containing Tetrabutylammonium Perchlorate^a

Reaction temp., °C	Solvent	Yield of polymer formed at the anode, g	Intrinsic viscosity, ml/g
30	nitrobenzene	0.334	4.5
30 ^b	nitrobenzene	0.434	4.7
0	nitrobenzene	0.349	4.9
0 ^b	nitrobenzene	0.436	5.1
-10	nitrobenzene	0.238	5.2
-10 ^b	nitrobenzene	0.440	5.0
30	nitromethane	0.166	3.5
30 ^b	nitromethane	0.214	4.5
0	nitromethane	0.097	4.5
0 ^b	nitromethane	0.139	3.0
-30	nitromethane	0.094	5.0
-30 ^b	nitromethane	0.216	3.9

^a Acenaphthylene, 1.00 g; electrolyte, 0.40 g; solvent, 60 ml; magnitude of current, 20 mA; reaction time, 30 min.

^b Kept for 60 min at room temp. after electrolysis and poured into methanol.

TABLE III
Amount of Perchloric Acid Produced
in Electrolyzed Solution Except Acenaphthylene^a

Solvent	Reaction temp., °C	Amount of perchloric acid, mg/ml
Nitrobenzene	30	1.17
Nitrobenzene	0	1.07
Nitromethane	30	0.80
Nitromethane	0	0.80

^a Tetrabutylammonium perchlorate, 0.400 g; magnitude of current, 20 mA; solvent, 60 ml; reaction time, 30 min.

The intrinsic viscosities of the polymers were in the range of 3.0 to 5.0 ml/g in nitromethane solution, the same as those (ca. 3.5 to 4.7 ml/g) of polyacenaphthylene¹ formed in acetic anhydride and acetonitrile solutions.

About 3.8 to 5.4 moles (calculated from the mole ratios of acenaphthylene to nitrobenzene in Table II) or 1.6 to 2.8 moles of monomer in nitrobenzene or nitromethane solution were polymerized per electrochemical equivalent passed through the solution.

A typical experimental procedure (Table II) is as follows: The water contents of nitrobenzene, nitromethane, acenaphthylene, and tetrabutylammonium perchlorate were 0.008%, 0.13%, 0.030%, and 0.059%, respectively, by the Karl Fisher method. Anhydrous tetrabutylammonium perchlorate (0.40 g) was dissolved in a solution of 60 ml dry solvent and 1.00 g dry acenaphthylene. This solution in anhydrous system was placed in a two-compartment electrolysis apparatus, a medium-porosity fritted dish being used to separate the anode and cathode. Electrodes were 3.14-cm² disks of platinum foil. A direct current of 20 mA was passed through the solution for 30 min. At the end of this time, the material in the anode compartment showed a light black color.

The detailed mechanism of the electrochemical polymerization is currently under investigation.

References

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Received July 23, 1975

Revised September 2, 1975