

Polymerization of Organic Compounds in An Electrodeless Glow Discharge.

V. Amines and Nitriles

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Synopsis

Polymerizations of amines and nitriles in a glow discharge generated by inductive coupling of 13.5-MHz radio frequency are investigated by employing the measurement of closed-system pressure change. It is found that nitrogen in those compounds are incorporated into polymer in a nearly stoichiometric manner and that the polymerization of those compounds are very much similar to that of hydrocarbons. Hydrogen detachments, opening of double bond and/or cyclic structure, opening of triple bond including $C\equiv N$, and opening of aromatic and hetero-aromatic structures contribute to polymerization of amines and nitriles.

INTRODUCTION

In part IV of this series of studies,¹ polymerization of hydrocarbons was investigated using pressure measurement of a closed-system glow discharge. It was found that the change in pressure of a closed system that contains only hydrocarbon and is subjected to a glow discharge is mainly caused by the polymerization of the organic compound and the production of hydrogen gas. It was concluded that at least three basic reactions contribute to the polymerization of hydrocarbons: (1) hydrogen detachment, (2) opening of double bond and cyclic structure, and (3) opening of triple bond. In this study, the same experimental technique is applied to amines, nitriles, and pyridine derivatives in order to compare the polymerization of nitrogen-containing organic compounds with that of hydrocarbons.

EXPERIMENTAL

The experimental procedure described in part IV of this series¹ is used in this study. The parameters used are

Monomer-type parameter

$$\gamma = \frac{p_{\infty}}{p_0}$$

Fraction of residual vapor

$$X = \frac{p_{\infty} - p_{H_2}}{p_0}$$

Yield of hydrogen

$$Y = p_{H_2}/p_0$$

Yield of polymer

$$Z = (1 - X)$$

where p_0 is the original vapor pressure of organic compounds in a closed system, p_{∞} is the pressure at the end of the reaction, and p_{H_2} is the pressure reading of p_{∞} with liquid nitrogen trap. The half-time of reaction, $t_{1/2}$, is read from the pressure-time recording.

RESULTS AND DISCUSSION

The value of hydrogen yield obtained by this technique is dependent on the existence of noncondensable (at liquid nitrogen temperature) gases in the residual gas. In the case of hydrocarbons in the previous study, mass spectroscopy was used to ensure the absence of CH_4 formed by the glow discharge. With nitrogen-containing organic compounds, the smallest nitrogen-containing molecules, such as methylamine and ammonia, are all condensable at liquid nitrogen temperature. Therefore, the main concern is the production of N_2 gas. Due to a generally high background peak of N_2 in the mass spectroscopy, the residual gas analysis by mass spectroscopy was not used in this study to insure the accuracy of hydrogen yield determination. Elemental analysis of polymers formed from selected monomers in a glow discharge was used to confirm that N_2 gas is not evolved during the polymerization. Results are shown in Table I. The ratios N/C in polymers are nearly identical to those for monomers, indicating that N_2 gas is not evolved in a glow discharge, and the pressure measurement with liquid nitrogen trap can be used as a means of estimating the hydrogen yield.

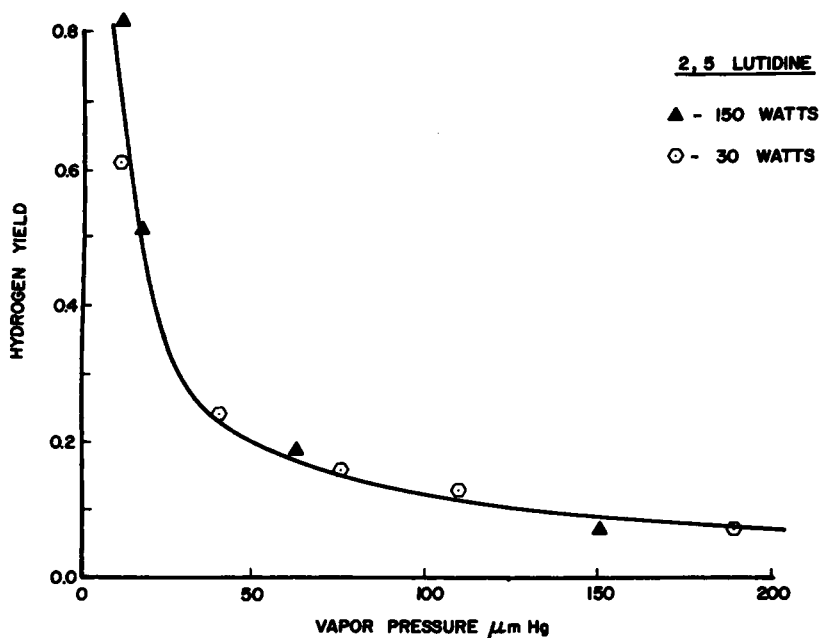


Fig. 1. Dependence of hydrogen yield of 2,5-lutidine on vapor pressure and discharge wattage.

Results are summarized in Table II using parameters described in the experimental section. Data shown in Table II were taken at a fixed initial pressure of 150 $\mu\text{m Hg}$ and with a fixed wattage of 30 W. The dependence of hydrogen yield on the vapor pressure and discharge wattage was examined for 2,5-lutidine.

TABLE I
Elemental Analysis*

		C, %	H, %	N, %	O, %
Acrylonitrile	polymer	59.16	5.61	24.68	10.55
	monomer	67.9	5.7	26.4	0
	polymer	1	1.13	0.36	0.13
Propionitrile	polymer	55.19	7.30	18.56	18.95
	monomer	65.4	9.2	25.4	0
	polymer	1	1.58	0.29	0.26
Propylamine	polymer	63.32	8.89	18.02	9.86
	monomer	60.9	15.4	23.7	0
	polymer	1	1.68	0.25	0.12
	monomer	1	3.01	0.33	0

* Monomer data are theoretical.

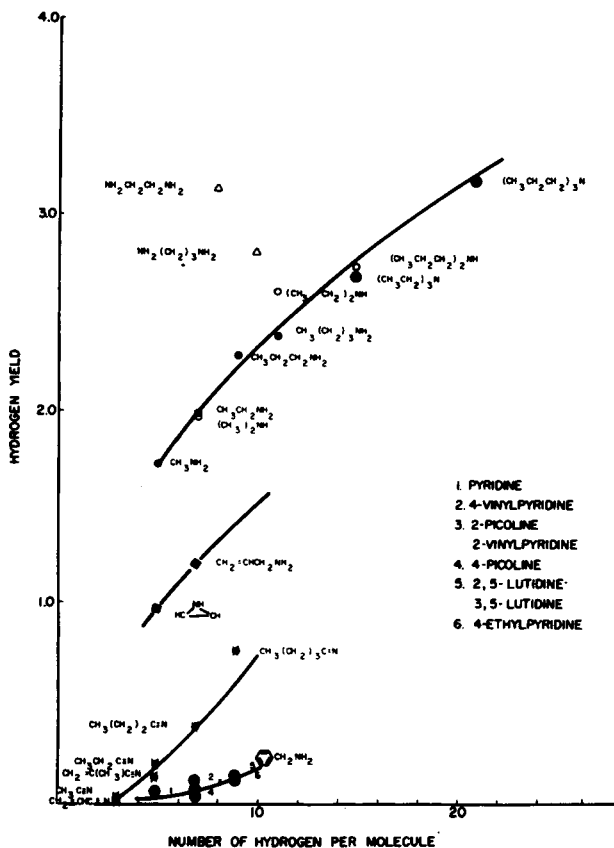
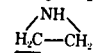
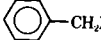










Fig. 2. Hydrogen yields as function of numbers of hydrogen in the monomers (amines, nitriles, and pyridine derivatives).

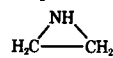
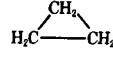


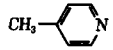
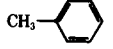
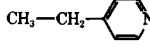
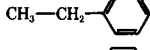
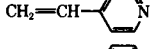
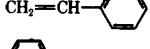
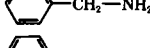
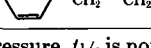
TABLE II
 Polymerization Parameters of Amine, Nitrile, and Pyridine Derivatives

Compound	Structure	$t_{1/2}$, sec	Monomer-type parameter γ	Fraction of residual vapor X	Hydrogen yield Y	Polymer yield Z
Methylamine	CH_3NH_2	1.5	1.82	0.0767	1.74	0.923
Ethylamine	$\text{CH}_3\text{CH}_2\text{NH}_2$	2.5	2.12	0.127	1.99	0.873
<i>n</i> -Propylamine	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	3	2.40	0.114	2.29	0.886
<i>n</i> -Butylamine	$\text{CH}_3(\text{CH}_2)_3\text{NH}_2$	3	2.52	0.131	2.39	0.869
Dimethylamine	$(\text{CH}_3)_2\text{NH}$	1.75	2.09	0.111	1.98	0.890
Diethylamine	$(\text{CH}_3\text{CH}_2)_2\text{NH}$	3.5	2.71	0.103	2.61	0.898
Dipropylamine	$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}$	3.5	2.94	0.198	2.74	0.802
Triethylamine	$(\text{CH}_3\text{CH}_2)_3\text{N}$	4.5	2.85	0.161	2.69	0.839
Tripropylamine	$(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{N}$	8.75	3.33	0.150	3.18	0.851
Ethylenimine		0.75 min	1.050	0.033	1.02	0.967
Benzylamine		17.5	0.279	0.037	0.242	0.963
Allylamine	$\text{CH}_2=\text{CHCH}_2\text{NH}_2$	2	1.309	0.068	1.24	0.932
Ethylenediamine	$\text{NH}_2(\text{CH}_2)_2\text{NH}_2$	5	3.26	0.116	3.144	0.885
Diaminopropane	$\text{NH}_2(\text{CH}_2)_3\text{NH}_2$	4	2.95	0.135	2.815	0.865
Acetonitrile	$\text{CH}_3\text{C}\equiv\text{N}$	7.25	0.0689	0.0118	0.0571	0.988
Propionitrile	$\text{CH}_3\text{CH}_2\text{C}\equiv\text{N}$	15	0.241	0.0278	0.213	0.973
<i>n</i> -Butyronitrile	$\text{CH}_3(\text{CH}_2)_3\text{C}\equiv\text{N}$	33	0.444	0.0319	0.416	0.968
Valeronitrile	$\text{CH}_3(\text{CH}_2)_4\text{C}\equiv\text{N}$	27.5	0.860	0.0563	0.804	0.944
Acrylonitrile	$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	2.25	0.0425	0.00642	0.0361	0.994
Methacrylonitrile	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}\equiv\text{N}$	3.5	0.159	0.0144	0.145	0.986
Pyridine		3	0.0669	0.00067	0.063	0.999
2-Picoline		5	0.103	0.00784	0.0948	0.992
4-Picoline		3	0.0690	0.0062	0.063	0.994
2,5-Lutidine		6	0.170	0.0267	0.143	0.973
3,5-Lutidine		8	0.167	0.0224	0.144	0.978
4-Ethylpyridine		10	0.159	0.0265	0.133	0.973
4-Vinylpyridine		5	0.157	0.0294	0.128	0.971
2-Vinylpyridine		6	0.125	0.0329	0.0921	0.967

The results are shown in Figure 1. As it was found with hydrocarbons, the hydrogen yield does not depend on the discharge wattage but increases at lower vapor pressure (below 40 $\mu\text{m Hg}$).

In Figure 2, hydrogen yields are plotted against numbers of hydrogen in the monomer. The general trends observed with hydrocarbons¹ are also evident with nitrogen-containing compounds. The figure indicated four distinct groups: (1) normal amines, (2) cyclic and double bond-containing amines, (3) nitrile, and (4) aromatic amines and heterocyclic amines. The hydrogen yields of nitriles are

TABLE III
 Comparison of Hydrocarbons and Nitrogen-Containing Compounds

Monomer	Structure	Hydrogen yield	$t_{1/2}$, sec
<i>n</i> -Propylamine	$\text{CH}_3\text{—CH}_2\text{—NH}_2$	2.29	3
Propane	$\text{CH}_3\text{—CH}_2\text{—CH}_3$	1.70	3
Acetonitrile	$\text{CH}_3\text{—C}\equiv\text{N}$	0.057	7.25
Methylacetylene	$\text{CH}_3\text{—C}\equiv\text{CH}$	0.171	2.25
Propionitrile	$\text{CH}_3\text{—CH}_2\text{—C}\equiv\text{N}$	0.213	15
Ethylacetylene	$\text{CH}_3\text{—CH}_2\text{—C}\equiv\text{CH}$	0.447	5.5
Acrylonitrile	$\text{CH}_2\text{=CH—C}\equiv\text{N}$	0.036	2.25
Butadiene	$\text{CH}_2\text{=CH—CH}\equiv\text{CH}_2$	0.452	3.75
Ethylenimine		1.02	— ^a
Cyclopropane		0.873	0.5
Pyridine		0.063	3
Benzene		0.107	2
4-Picoline		0.063	3
Toluene		0.172	3
4-Ethylpyridine		0.133	10
Ethylbenzene		0.278	6
4-Vinylpyridine		0.128	5
Styrene		0.088	4
Benzylamine		0.242	17.5
Ethylbenzene		0.278	6

^a Due to a small change in pressure, $t_{1/2}$ is not measurable.

considerably smaller than those for cyclic and double bond-containing compounds and close to those for aromatic and heteroaromatic compounds, which seems to indicate that nitriles polymerize via the opening of the $\text{C}\equiv\text{N}$ triple bond.

Since data are similar to those for hydrocarbons, some data for hydrocarbons and nitrogen compounds are compared in Table III. The hydrogen yields of amines with straight hydrocarbon chains are higher than those for corresponding hydrocarbons. The hydrogen yields of heteroaromatic amines and nitriles are smaller than those for hydrocarbons. The rates of polymerization (based on the value of $t_{1/2}$) of nitrogen compounds are lower than those for corresponding hydrocarbons.

It may be concluded that nitrogen-containing compounds polymerize in a glow discharge by a similar mechanism described for the polymerization of hydrocarbons.¹ The very smooth increase of hydrogen yield as a function of a number of hydrogen atoms in the monomer suggests that the following three major routes of polymerization occur simultaneously in plasma polymerization, i.e., free-radical formation by (1) hydrogen detachment, (2) opening of double bond and cyclic

structure, and (3) opening of triple bond (including $C\equiv N$) and aromatic and heteroaromatic structures.

This study is supported in part by the Office of Saline Water, U.S. Department of the Interior, Contract No. 14-30-3157, and by the National Heart and Lung Institute, NIH, U.S. Department of Health, Education, and Welfare, Contract No. NIH-N01-HB-3-2913.

Reference

1. H. Yasuda, M. O. Bumgarner, and J. J. Hillman, *J. Appl. Polym. Sci.*, **19**, 531 (1975).

Received November 13, 1974