

Polymerization in an Electrodeless Glow Discharge.

III. Organic Compounds Without Olefinic Doublebond

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Synopsis

The rates of polymer deposition from various organic compounds which do not contain an olefinic doublebond in an electrodeless glow discharge were studied. The polymerization rates of these unconventional monomers are by and large similar to those of olefinic monomers reported in the previous study (part II). The rate of polymer deposition R_0 from pure monomer flow can be characterized, according to the analysis used in part II, by $R_0 = \alpha p_M^2$ and $R_0 = kF_w$, where p_M is the vapor pressure of the monomer, F_w is the weight basis flow rate of the monomer. Type A monomers which predominantly polymerize and type B monomers which decompose in a glow discharge were also found with these unconventional monomers. The effects of structural factors on the values of α and k and on the classification of types A and B were examined. These structures and groups—aromatic, heteroaromatic, nitrogen-containing (e.g., $>NH$, $-NH_2$, $-CN$), Si-containing, and olefinic doublebond—favor the polymerization. These structures

and groups—oxygen-containing (e.g., $\overset{\text{O}}{\parallel}\text{C}$, $\overset{\text{O}}{\parallel}\text{C}-\text{O}$, $-\text{O}-$, $-\text{OH}$), chlorine, aliphatic hydrocarbon chains, and cyclic hydrocarbon chains—favor the decomposition of the monomer in a glow discharge. It is postulated that the polymerization of organic compounds proceed by the recombination of excited species (probably free radicals) created by glow discharge and reexcitation followed by further recombinations in the vapor phase and at the interface.

INTRODUCTION

In part II of this series of studies,¹ the polymerization of olefinic compounds in an electrodeless glow discharge was investigated. The results indicated that the rate R_0 ($\text{g}/\text{cm}^2 \cdot \text{min}$) of polymer deposition in a glow region of monomer flow is proportional to the flow rate of monomer based on weight F_w (g/min), i.e., $R_0 = kF_w$. Since F_w is related to the volume flow rate F_v ($\text{cc}(\text{S.T.P.})/\text{min}$) and the molecular weight of a monomer M by

$$F_w = \frac{M}{2.24 \times 10^4} F_v$$

and F_v is related to the pressure of monomer p_M in the flow system by $F_v = \alpha_v p_M^2$, R_0 can be generally expressed by $R_0 = \alpha p_M^2$.

The constant a provides a deposition rate constant of a glow discharge. The constant k , which can be calculated from a and the flow rate constant α_v , can be considered to be the specific polymerization rate constant of a monomer in a glow discharge.

The values of a were found to be roughly proportional to $M^{2.5}$ and the values of k to be proportional to $M^{1.5}$. The values of k for various olefinic monomers were found to be within an order of magnitude, indicating that polymerization in a glow discharge is not related to the reactivities of olefinic double bonds.

It was postulated that growing species (in a glow region of discharge) deposit onto the wall of the discharge vessel owing to the decrease of vapor pressure as the molecular weights of excited species increase. The addition polymerization of olefinic double bond was found to play a small role in the vapor-phase polymerization in a glow discharge.

On the other hand, it has been known that varieties of organic compounds which do not contain olefinic double bond (accordingly not considered "monomers" in a general sense) polymerize in various kinds of electric discharge.²⁻¹¹

The comparison of polymerization schemes for unconventional monomers and for olefinic monomers would provide more insight into the nature of glow discharge polymerization.

The results obtained in the previous study (part II), in comparison with data obtained by other workers,¹²⁻²⁰ indicated that the deposition of polymer is highly dependent on (1) the frequency of discharge and (2) the location of the surface on which polymer deposits, i.e., onto the electrode surface or, in the case of electrodeless discharge, whether the surface is in a glow region or in a quenched region and also whether the surface is parallel or perpendicular to the flow direction.

Under conditions used in the previous study, i.e., relatively high-frequency (13.56 MHz) rf electrodeless glow discharge, the deposition surface parallel to the flow direction, and in the glow region, the vapor phase polymerization seems to predominate. With olefinic monomers, however, the possibility of plasma-initiated polymerization of sorbed monomer on the surface always exists. This possibility will be virtually eliminated by the use of unconventional monomer, since these compounds do not polymerize by other means.

Based on this consideration, a study is extended to the polymerization of various organic compounds using the identical condition used for the study of glow discharge polymerization of olefinic monomers previously reported (part II).

EXPERIMENTAL

The apparatus and method used in this study are identical to those described in the previous paper (part II). The rate of polymer deposition was measured by weighing the glass slide placed in a glow region of a

reaction tube. The surface on which deposition occurs is parallel to the direction of the monomer flow.

The glow discharge was initiated by 13.56 MHz rf with pure monomer flow system (without carrier gas). The relationship between polymer deposition rate R_0 and the pressure of monomer in a flow system p_M (before a glow discharge is initiated) found for olefinic monomers previously described (in part II) was also found with general organic compounds investigated in this study, i.e., R_0 is given by

$$R_0 = ap_M^2.$$

For each monomer, the amount of deposition onto a slide for a given time and wattage was determined for at least three different values of monomer pressure p_M , consequently, at different steady-state flow rates. From the slope of a plot of polymer deposition rates versus p_M^2 , which yields a straight line, the value of a for a monomer was calculated. The flow rate of monomer was measured by monitoring the initial rate of pressure increase when the downstream side of a steady-state flow was closed. The flow rate F_v , in cc(S.T.P.)/min is related to the steady-state flow pressure p_M by

$$F_v = \alpha_v p_M^2.$$

The specific rate constant of polymer k is calculated from values of a , α_v , and the molecular weight of a vapor, M , by

$$k = \frac{a \cdot 2.24 \times 10^4}{\alpha_v M}.$$

The value of $\alpha_v \cdot M / 2.24 \times 10^4$ is listed as α_w in the results.

The pressure of monomer flow p_g in a glow discharge is different from the steady-state flow pressure p_M before a glow discharge is initiated. The rate $p_g/p_M = \delta$ seems to indicate the extent of decomposition of a monomer. The monomers which predominantly polymerize have $\delta < 1$, and the monomers which decompose in a glow discharge have $\delta > 1$.

The value of δ for a monomer is different at varying values of p_M ; however, the sign of $(\delta - 1)$ does not change with the value of p_M so that the value of δ can be used as an indication of behavior of the monomer in a glow discharge. The values of δ listed in the results are selected from the nearest value of p_M obtainable with a monomer to a common value of 40μ Hg.

The wattage to run a glow discharge was settled on as the lowest wattage from arbitrarily chosen levels of 30, 60, 100, and 150 watts which would maintain a glow in the entire length of the reaction tube. At higher p_M , it is necessary to apply a higher wattage to maintain a glow. Therefore, the wattage selected to use for a monomer was that which correlated with the highest p_M value suitable for a monomer.

RESULTS AND DISCUSSION

Organic compounds investigated in this study can be also classified into two groups, depending on the pressure change in glow discharge,

i.e., type A compounds which show a decrease of flow pressure in glow discharge ($\delta < 1$) and type B compounds which show an increase of the flow pressure ($\delta > 1$). Results are tabulated in Table I for type A compounds and in Table II for type B compounds.

Results are compared in the following tables according to the chemical structure of compounds. In Table III, values of a , k , and δ for vinyl monomers and corresponding saturated vinyl monomers (with the exception of allylamine versus *n*-butylamine) are compared. All vinyl monomers cited in this table are Type A monomers ($\delta < 1$). As seen in the results, the vinyl group does contribute to the polymerization of compounds since vinyl monomers have larger a and k values and smaller δ values than those for corresponding ethyl-substituted compounds. As it has been pointed out in the previous study (part I), it is quite evident that the major polymerization mechanism in glow discharge is not by the addition polymerization of a vinyl double bond, since the difference between the polymerization rate of vinyl compounds and the corresponding ethyl-substituted compounds is less than 50% of vinyl compounds.

The difference between vinyl and ethyl-substituted compounds, particularly the extent of decomposition and polymerization reflected in the value of δ , is dependent on the structure of compounds onto which these substituents are attached. It is interesting to note that nearly all type B compounds are saturated (straight or cyclic) compounds. The structural effect of saturated versus unsaturated cyclic compounds is compared in Table IV. All saturated cyclic compounds (listed in the table) are type B, whereas all corresponding aromatic and heterocyclic aromatic compounds belong to type A. The effects of straight chain and cyclic structures together with corresponding aromatic compounds are compared in Table V. The cyclic structure (saturated) compounds seem to be a little more stable in glow discharge than are the corresponding straight-chain compounds; however, the extent of stabilization is marginal. The aromatic and heterocyclic compounds polymerize more efficiently than nonaromatic compounds.

The structural variations of aliphatic compounds are compared in Table VI using normal, secondary, and tertiary butylamines. The sizes of substituents of aromatic and heterocyclic aromatic compounds are compared in Table VII. Due to the increase of molecular weight, the larger substituents lead to higher a values; however, the characteristic polymerization rates given by k are not affected very much.

The trends found with vinyl monomers are also found with these unconventional monomers: (1) Type A and type B monomers are also found with unconventional monomers. (2) Type A monomers have higher values of a and k than do those for type B. (3) The higher the molecular weight of a type A compound, the higher the value of a . (4) Type B monomers need higher wattage to maintain a glow than do those for type A monomers. (5) Groups or substituents which cause the decomposition of vinyl monomers behave in a similar manner in the unconventional monomers.







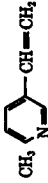

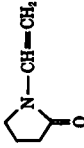
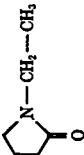





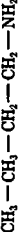
TABLE I
 Polymerization of Unconventional Monomers—Type A

Monomer	Molecular weight	α_w , g/min·torr ²	$a \times 10^4$, g/cm ² ·min ⁻¹ · torr ²	$k \times 10^4$, cm ⁻²	Wattage	$p_0/p_M = \delta$
4-Methylbenzylamine	121.2	1.31	14.4	10.99	60	10/33 = 0.30
5-Ethyl-2-methyl- pyridine	121.2	1.75	12.9	7.38	30	10/43 = 0.23
Benzylamine	107.2	1.44	11.5	7.94	30	6/35 = 0.17
<i>tert</i> -Butylbenzene	134.2	2.49	10.9	4.41	30	14/40 = 0.35
2-Phenylpropane	120.2	2.57	10.4	4.05	60	8/50 = 0.16
4-Ethylpyridine	107.2	2.12	10.0	4.72	30	6/40 = 0.15
Ethylbenzene	106.2	2.08	9.4	4.52	60	7/52 = 0.13
4-Picoline	93.1	1.51	8.8	5.83	60	4/50 = 0.08
3,5-Lutidine	107.2	1.50	8.8	5.82	30	7/56 = 0.13
1-Methyl-2-pyrrolidone	99.1	1.59	8.3	5.24	30	48/48 = 1.00
Toluene	92.1	1.63	8.2	5.03	60	4/50 = 0.08
<i>tert</i> -Butylpyridine	135.2	2.13	8.1	3.81	30	9/40 = 0.23
2-Methylfuran	82.1	1.58	7.8	4.96	30	8/35 = 0.23
Pyridine	79.1	1.29	7.5	5.81	30	3/30 = 0.10
2,5-Lutidine	107.2	1.69	7.3	4.28	30	7/40 = 0.18
Furan	68.1	1.18	6.6	5.59	30	7/42 = 0.17
Pyrrrole	67.1	1.20	6.0	5.03	30	6/55 = 0.11
Benzene	78.1	1.38	6.0	4.35	30	3/55 = 0.05
Propionitrile	55.1	1.09	4.9	4.49	30	23/65 = 0.35
N-Methylpyrrole	85.1	1.43	5.7	4.01	30	7/50 = 0.14

TABLE II
 Polymerization of Unconventional Monomers—Type B







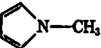
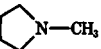
Monomer	Molecular weight	α_w , g/min·torr ²	$\alpha \times 10^4$, g/cm ² ·min·- torr ²	$k \times 10^4$, cm ⁻²	Wattage	$p_o/p_M = \delta$
Triethylsilane	116.2	2.08	13.1	6.33	100	98/50 = 1.96
N-Methylpyrrolidine	85.2	1.43	5.7	4.01	60	78/60 = 1.30
Pyrrolidine	71.1	1.22	5.1	4.18	60	84/60 = 1.40
1-Ethyl-2-pyrrolidone	113.2	1.23	4.6	3.76	60	75/47 = 1.60
1,1-Dichloroethane	99.0	1.50	4.5	2.98	60	64/55 = 1.16
sec-Butylamine	73.1	1.37	3.7	2.68	60	95/60 = 1.58
n-Butylamine	73.1	1.45	3.7	2.52	60	126/65 = 1.94
1,3-Diaminopropane	74.1	1.26	3.5	2.80	60	134/65 = 2.06
Morpholine	87.1	1.37	3.4	2.50	100	160/65 = 2.46
tert-Butylamine	73.1	1.41	3.0	2.14	60	88/53 = 1.66
n-Hexane	86.2	1.57	2.7	1.74	60	126/60 = 2.10
Cyclohexane	84.1	1.59	2.7	1.71	30	95/60 = 1.58
Cyclopentanone	84.1	1.37	2.0	1.44	60	89/48 = 1.85
γ -Butyrolactone	86.1	1.25	1.6	1.24	60	101/38 = 2.66
Dimethylformamide	73.1	1.19	1.4	1.15	100	220/80 = 2.75
Cyclohexanol	100.2	1.64	1.3	0.81	60	117/50 = 2.34
1-Hexanol	102.2	1.69	1.3	0.79	60	110/40 = 2.75
Methyl propionate	88.1	1.40	0.8	0.57	100	178/50 = 3.56
Ethylene oxide	44.1	0.68	0.6	0.86	60	85/38 = 2.23
Dimethyl sulfoxide	78.1	1.40	0.6	0.40	100	130/56 = 2.32
Tetrahydrofuran	72.1	1.35	0.4	0.32	100	138/70 = 1.97

TABLE III
 Polymerization Parameters: Vinyl vs. Saturated Vinyl Compounds^a

	Vinyl monomer			Saturated vinyl monomer			
	<i>a</i>	<i>k</i>	δ	<i>a</i>	<i>k</i>	δ	
	16.4	7.59	0.10		10.0	4.72	0.10
	13.8	5.33	0.26		10.4	4.05	0.16
	12.1	5.65	0.10		9.4	4.52	0.14
	11.9	7.65	0.16		12.9	7.38	0.24
	9.7	7.75	0.61		4.6	3.76	1.60
	7.2	5.71	0.16		4.9	4.49	0.35
	5.8	5.47	0.70		4.5	2.98	1.16
	3.2	2.86	0.66		3.7	2.52	1.94

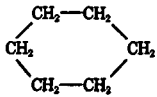
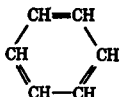
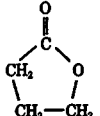
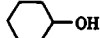
^a *a* in units of $\text{g}/\text{cm}^2 \cdot \text{min} \cdot \text{torr}^2 \times 10^4$; *k* in units of $\text{cm}^{-2} \times 10^4$.

TABLE IV
Polymerization Parameters: Saturated vs. Unsaturated Rings^a

Compound	$a \times 10^4$	$k \times 10^4$	δ
	6.0	4.35	0.06
	2.7	1.71	1.58
	6.6	5.59	0.17
	0.43	0.32	1.97
	6.0	5.03	0.11
	5.1	4.18	1.40
	5.7	4.01	0.14
	5.7	4.01	1.30

^a a in units of $\text{g}/\text{cm}^2 \cdot \text{min} \cdot \text{torr}^2$; k in units of cm^{-2} .

TABLE V
Polymerization Parameters: Straight vs. Cyclic Structures^a

Compound	$a \times 10^4$	$k \times 10^4$	δ
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	2.7	1.74	2.10
	2.7	1.71	1.58
	6.0	4.35	0.05
$\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_3$	0.8	0.57	3.56
	1.6	1.24	2.66
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$	1.3	0.79	2.75
	1.3	0.81	2.34


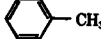
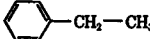
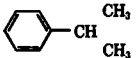
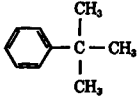

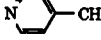
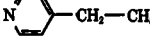
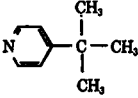

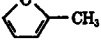

^a a in units of $\text{g}/\text{cm}^2 \cdot \text{min} \cdot \text{torr}^2$; k in units of cm^{-2} .

TABLE VI
Polymerization Parameters: Effects of Aliphatic Chain Structure^a

Compound	$a \times 10^4$	$k \times 10^4$	δ
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$	3.7	2.52	1.94
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—CH}_2\text{—CH—NH}_2 \end{array}$	3.7	2.68	1.58
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—C—NH}_2 \\ \\ \text{CH}_3 \end{array}$	3.0	2.16	1.66

^a a in units of $\text{g/cm}^2 \cdot \text{min} \cdot \text{torr}^2$; k in units of cm^{-2} .

TABLE VII
Polymerization Parameters: Effects of Size of Substituent^a

Compounds	$a \times 10^4$	$k \times 10^4$	δ
	6.0	4.35	0.06
	8.2	5.03	0.08
	9.4	4.52	0.14
	10.4	4.05	0.16
	10.9	4.41	0.35
	7.5	5.81	0.10
	8.8	5.83	0.08
	10.0	4.72	0.10
	8.1	3.81	0.23
	6.6	5.59	0.17
	7.8	4.96	0.23
	10.0	7.04	0.11

^a a in units of $\text{g/cm}^2 \cdot \text{min} \cdot \text{torr}^2$; k in units of cm^{-2} .

From these observations, it may be postulated that the polymerization of organic compounds in the glow region of an electrodeless glow discharge proceeds in the vapor phase, and that the growing species deposit on the surface exposed to the glow discharge. The reexcitation of growing species in vapor phase and at the interface yield highly crosslinked polymer deposition. Some structures in organic compounds cause decomposition of the compounds in glow discharge; hence, they do not remain as in the resultant polymer deposition. The general trend of polymer deposition can be qualitatively explained by the contributions of two types of structures or substituent groups. These are

1. *Structures which favor polymer deposition and remain in the polymer (not necessarily as the original form):* aromatic, heterocyclic aromatic, nitrogen-containing groups (e.g., $>NH$, $-NH_2$, $-CN$), Si-containing groups, olefinic double bond.

2. *Structures which favor decomposition of compound in the glow discharges and do not remain or only a part remain in the polymers:* oxygen-containing

groups, (e.g., $\begin{array}{c} O \\ || \\ -C- \end{array}$, $\begin{array}{c} O \\ || \\ -C-O- \end{array}$, $-O-$, $-OH$), $-Cl$, aliphatic hydrocarbon chain, cyclic hydrocarbon.

The overall behavior of an organic compound seems to reflect the contributions of all type A and type B structures in the molecule. Using symbols A and B to represent the structures mentioned above, general organic compounds can be represented by the following combinations: (1) A-A'; (2) A-B; (3) B-B'. A-A' compounds will be in type A, and B-B' compounds will be in type B. A-B type compounds may be in type A or in type B, depending on the nature of A and B.

Westwood²⁰ found marked halogen deficiency in glow discharge polymers (onto an electrode) from halogenated vinyl monomers (A-B compounds), which agrees with the structural factors of monomers found in this study. The participation of aromatic structure (type A) in the polymer has been reported by Jesch et al.⁹ and by Kronick et al.¹⁰ Rather low yield (1.4%) of polymer was reported by Swift et al.⁶ in a radio frequency (electrodeless) glow discharge of carbon tetrachloride (i.e., B-B' compound), but considerably higher yields of polymers were observed by Stille and Rix⁸ in a similar discharge reaction of chlorobenzene (14%) and (*p*-, *m*-, and *o*-) dichlorobenzenes (70–77%), which are considered as A-B compounds.

Since the propagation process of vinyl monomer is absent in unconventional monomers, yet the rates of polymerization of the latter is very similar to those for vinyl monomers, the propagation in plasma polymerization necessitates the reexcitation of higher molecular weight compounds formed by coupling of radicals. In other words, plasma polymerization may correspond to a case of addition polymerization with (1) an extremely high rate of initiation, (2) an extremely short kinetic chain length, and (3) reinitiation of the terminated chain.

It has been generally recognized that the structure of glow discharge polymers are complex and/or polymers are partially degraded. These

aspects may be explained by the very short kinetic chain length and the reexcitation (reinitiation) of the terminated chains, which may occur either in the vapor phase or at the interface. The presence of free radicals in glow discharge polymers formed on an electrode has been confirmed by the use of a radical scavenger by Denaro et al.,¹⁴ and reaction mechanism based on free radicals are presented in a series of papers by Stille et al.^{6,7,8} for reactions of organic compounds (polymer being a by-product) in an electrodeless glow discharge. It seems, therefore, quite probable that the plasma polymerization proceeds by recombination of primary radicals.

The efficiency of polymerization is highly dependent on the stability of molecules when they are excited (or free radical is formed). Therefore, all aromatic and heteroaromatic compounds polymerize with high efficiency. By this mechanism, the rates of polymerization of vinyl and of saturated vinyl monomers should not be much different, as observed in experimental results.

CONCLUSION

The polymerization of organic compounds in an electrodeless radio frequency glow discharge in the low-pressure region (less than 200 μ Hg of pure vapor) can be summarized by the following aspects:

1. Polymerization seems to occur in the vapor phase.
2. Polymerization seems to proceed by recombination of primary radicals (formed by the hydrogen abstraction and/or by elimination of some atoms and substituent groups) and the reexcitation of the resultant molecules followed by the recombination.
3. As the molecular weight increases, the molecules (recombined radicals), the radicals, or some other excited species deposit from the vapor phase to form a highly crosslinked (and perhaps highly branched) polymer.
4. Many unconventional monomers (organic compounds without olefinic double bond), which do not polymerize by ordinary methods of polymerization, polymerize and form highly crosslinked polymers. The rates of polymerization of unconventional monomers are by and large similar to those of conventional monomers.
5. Organic compounds can be classified into two major types: one which polymerizes predominantly and the other which decomposes in plasma with only a part of the original molecules polymerizing.
6. Some structural factors were found to be responsible for the behavior of an organic compound in plasma. These structures and groups—aromatic, heteroaromatic, nitrogen-containing (e.g., $>NH$, $-NH_2$, $-CN$), Si-containing, and olefinic double bond—favor the polymerization. These

structures and groups—oxygen-containing (e.g., $\begin{array}{c} O \\ || \\ -C- \end{array}$, $\begin{array}{c} O \\ || \\ -C-O- \end{array}$, $-O-$, $-OH$), chlorine, aliphatic hydrocarbon chains, and cyclic hydrocarbon chains—favor the decomposition. These effects are dependent on the neighboring structure.

7. The rate constants of polymerization for organic compounds which predominantly polymerize are roughly proportional to the molecular weights of the compounds.

8. Some gases, particularly nitrogen, are consumed in plasma polymerization of organic compounds.

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