

Molecular Intermediates in Glow Discharge Polymerization

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Synopsis

Mass spectral analysis of gaseous effluents from glow discharge polymerization of propylene confirms the formation of molecular propyne as an intermediate in the polymerization reaction. Observation of oligomeric species of mass number 138 or higher at the lowest monomer feed rate of the study indicates that a certain fraction of polymerization occurs in the gas phase.

INTRODUCTION

Glow discharge (plasma) polymerization has gained considerable importance in last two decades.¹⁻³ It is because of the following four major advantages of the glow discharge polymerization technique over the conventional methods of film preparation:

1. Ultrathin films (100 Å) can be deposited at near ambient temperature.
2. Choice of monomers is unlimited, e.g., any organic compound capable of being transformed into vapor form can be polymerized.
3. The process parameters can be altered, and different polymers can be formed from the same monomer.
4. The adhesion of polymer to substrates is excellent.⁴

As a result of the above characteristics of the technique, the glow discharge polymers (also called plasma polymers) have found useful applications in electronics, bioengineering, membranes and corrosion protection.

One of the most disputed aspects of glow discharge polymerization is the mechanism of polymer formation. Two views are commonly expressed: One involves the formation of a well-defined molecular intermediate as the major active species in polymer formation⁵ and the other considers the building of polymer from a completely fragmented monomer.⁶ In the following text, evidences are presented which confirm the formation of a molecular intermediate in glow discharge polymerization of propylene. Mass spectrometry is used to identify the intermediate products.

EXPERIMENTAL

Polymerization was conducted in a tubular glass reactor (1 m long and 75 mm in diameter) operated at a radio frequency of 27.12 MHz by inductive

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coupling with a Tomac Diathermic Unit (Model 1565) at an approximate but constant energy output of 50–100 W. Details of polymerization and the equipment used are described elsewhere.⁷ Propylene was used as the monomer and its feed rate in the reactor was computed from a knowledge of the rate of pressure decrease observed in the monomer inlet system during the experiment. The rate of polymer deposition was calculated from the observed increase in mass of an aluminum foil placed vertically in the reactor.

A nuclide 12-90-G single-focusing mass spectrometer having a resolution capacity of 10,000 was used to identify the components of the gaseous effluent leaving the plasma reactor during polymerization. Samples were collected at the farthest end of the reactor in gas sample holders. The sample collection was started 15 min after the discharge was turned on and continued for 10 min. The gas sample holder was cooled from outside with liquid N₂ during this time. The mass spectral analysis was performed at ionization voltages of 12 and 70 eV, respectively.

In another set of experiments the gaseous effluents from the glow discharge polymerization of propylene were collected in a liquid N₂ cold trap and redistilled into the monomer inlet systems by differential cooling. The rate of glow discharge polymerization of the gaseous effluents was compared with that of other hydrocarbon monomers under similar conditions.

RESULTS AND DISCUSSION

The results of the mass-spectrometric analysis of the effluents from glow discharge polymerization of propylene at three different monomer feed rates are presented in Table I. The collection process, however, excluded the non-condensable species such as H₂ and CH₄, which may constitute a significant fraction of the gaseous effluent.

The most intense peak at 12 eV ionization voltage at all three monomer feed rates corresponds to the monomer, propylene (C₃H₆) ion. Since the collection of the effluents in each case was conducted near the outlet of the reactor, it indicates that a 100% conversion of monomer to polymer does not take place in the existing reactor even at the lowest monomer feed rate studied. It should be remembered that the energy input per unit monomer is maximum at the lowest monomer feed rate. The above conclusion is supplemented by the fact that the polymerization efficiency (mol % of monomer converted into polymer) of propylene glow discharge polymerization is only 65% at 30 μmol/min monomer feed rate and 2% at 300 μmol/min in monomer feed rate. These results are reported separately.⁸ The next most intense peak at the lowest (52 μmol/min) monomer feed rate in Table I corresponds to propyne (C₃H₄) ion followed by acetylene (C₂H₂) ion and allyl (C₃H₅) ion peaks. At medium (158 μmol/min) and highest (340 μmol/min) monomer feed rates, the allyl (C₃H₅) ion peak is second most intense peak followed by the propyne (C₃H₄) ion peak.

The identification of propyne (C₃H₄) ion peak of reasonable intensity in all the spectra recorded at 12 eV ionization voltage indicates an active involvement of propyne molecule in the glow discharge polymerization of propylene. In order to confirm that the propyne is not a mass fragmentation

product formed during the mass spectral analysis of propylene in the effluents, the mass spectrum of propylene was separately recorded at 12 eV ionization voltage. The results indicated that the propyne contribution, from propylene mass spectrometry, is negligible compared to the observed propyne concentration in the spectra of effluents.

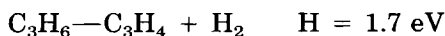
The involvement of intermediate molecular propyne in propylene glow discharge polymerization is also indicated by the fact that the propyne ion concentration in the mass spectra of effluents increases as the monomer feed rate decreases. As we stated earlier the polymerization efficiency of the propylene also follows the same pattern.

When the ionization voltage in the mass spectrometer is increased to 70 eV, the allyl (C_3H_5) ion peak is observed as the most intense peak at all feed rates followed by (C_3H_3) or (C_3H_6) ion peaks. The formation of (C_3H_5) ion results from the unreacted monomer, propylene (C_3H_6) ion, of the effluent during mass spectrometry, perhaps by a simple H-abstraction process. Similarly (C_3H_3) ion may result from the propyne (C_3H_4) ion of the affluent and thus confirm to the theory of molecular intermediate formation. The concentration of (C_3H_3) ions at low medium and high monomer feed rates follows the same pattern as that recorded at 12 eV ionization voltage.

The presence of propyne in the effluents of propylene glow discharge polymerization is also indicated by the qualitative analysis of the gaseous condensate of the liquid N_2 trap placed between the reactor and the vacuum pump. An immediate formation of an explosive silver acetylide was noticed on interaction of the condensate with 1% alcoholic silver nitrate solution. This reaction is characteristic of all terminal acetylenes.⁹ Other evidence in favor of propyne intermediate was obtained by the infrared and NMR analysis of liquid N_2 condensate and is discussed elsewhere.⁷

An indirect evidence of the formation of propyne type intermediate in the glow discharge polymerization of propylene is offered by the polymerization (recycling) of gaseous effluents collected during prior polymerization. Comparison of the rates of polymer deposition as demonstrated in Table II clearly indicates that the effluents contain a significant amount of a species more reactive than propylene itself. Since alkynes have the highest rate of polymer deposition among hydrocarbons (Table III), it is reasoned that the gaseous effluents (especially the effluent^{II} obtained at low monomer feed rate) contained a large amount of propyne in the mixture.

Based on the above observations and the fact that radicals are predominantly involved in the glow discharge polymerization of hydrocarbons,⁷ it is postulated that the following dehydrogenation reactions predominate in propylene glow discharge polymerization and perhaps constitute the rate determining steps:



The heat of reaction in each case has been calculated from the heats of

TABLE I
 Mass Analysis of Gaseous Effluents from Polymerization

Int. %	High feed rate (340 $\mu\text{mol min}^{-1}$)		Medium feed rate (158 $\mu\text{mol min}^{-1}$)		Low feed rate (52 $\mu\text{mol min}^{-1}$)		Int. %
	12 eV	70 eV	12 eV	70 eV	12 eV	70 eV	
100	C_3H_6^+	C_3H_5^+	C_3H_6^+	C_3H_5^+	C_3H_6^+	C_3H_5^+ C_3H_3^+	100
80		C_3H_6^+		C_3H_6^+		C_2H_4^+ C_3H_6^+ C_2H_2^+	80
60		C_3H_3^+		C_3H_3^+		C_3H_4^+	60
40	C_3H_5^+		C_3H_5^+		C_3H_4^+		50 40
20	C_4H_6^+	C_3H_6^+		C_3H_6^+		C_2H_3^+	
	C_3H_4^+	C_2H_8^+	C_4H_8^+		C_3H_5^+ C_4H_8^+ C_4H_2^+	C_4H_2^+	
		C_3H_2^+	C_3H_6^+		C_3H_6^+ C_6H_6^+ C_4H_6^+ C_2H_6^+ C_5H_6^+	C_3H_2^+ C_3H_6^+	
10	C_3H_6^+	C_2H_4^+	C_2H_2^+	C_3H^+	C_3H^+ C_4H_8^+ C_4H_7^+	C_2H_4^+ C_4H_4^+ $\text{C}_4\text{H}_{10}^+$ C_6H_7^+ C_5H_4^+ $\text{C}_6\text{H}_{13}^+$	10
		C_2H_2^+	C_2H_4^+	C_6H_6^+ C_6H_7^+	C_2H_4^+	C_4H_3^+	
			C_2H_4^+		$\text{C}_7\text{H}_{11}^+$	C_4H_3^+	

TABLE II
Polymerization of Effluent Gases from Propylene Glow Discharge

Reactant	Reactant feed rate ($\mu\text{mol min}^{-1}$)	Rate of polymer deposition at 137 mm substrate position ($10^{-5} \text{ kg m}^{-2} \text{ min}^{-1}$)
Effluent I ^a	100	0.66
Effluent II ^b	130	0.95
Propylene	100	0.53
Propylene	130	0.50

^a From propylene glow discharge polymerization at $276 \mu\text{mol min}^{-1}$ feed rate and 420 min reaction time. Effluent polymerization time: 2 h.

^b From propylene glow discharge polymerization at $49 \mu\text{mol min}^{-1}$ feed rate, and 240 min reaction time. Effluent polymerization time: 30 min.

formation of the species involved. Such heats are readily available in glow discharges.¹⁰ The propynylic intermediate once formed reacts in a variety of ways, depending on the conditions of the glow discharge polymerization, to build up the complex polymer structure. The formation of aromatics observed in the mass, IR, NMR spectra⁷ of effluents may result by simple or cross union of the three alkyne molecules.

Additional evidence in favor of reactive intermediates comes from the photolysis studies of propylene¹¹ and by a comparison of the rate of polymer deposition of propane, propylene, and propyne gases under identical conditions, as reported in Table III. The extra amount of energy required for the conversion of propane into a reactive intermediate (propyne) explains the lowest rate of propane polymerization in the series.

Another interesting feature of the propylene glow discharge polymerization which is evident from the mass spectral analysis of gaseous effluent in Table I is the observation of a considerable amount of oligomeric species of mass number 138 or higher at $52 \mu\text{mol/min}$ monomer feed rate. Considering the fact that collection of gaseous effluents was done at the farthest

TABLE III

Monomer ^a	C/H	Deposition rate ($10^{-5} \text{ kg m}^{-2} \text{ min}^{-1}$)	
		"O" position	135 mm position
Methane	0.25	0.53	0.21
Ethane	0.34	0.79	0.29
Propane	0.37	0.55	0.20
Propylene	0.50	1.58	0.51
Ethylene	0.50	—	0.56
Propyne	0.75	4.28	1.27
Allene	0.75	4.20	1.30
Allyl bromide	0.60	14.8	5.37

^a Monomer feed rate: $160 \pm 10 \mu\text{mol min}^{-1}$; polymerization time: 1 h.

end of the reactor, and that ionization voltage in mass spectral analysis would bring further fragmentation of heavier unstable molecular species, the above observation clearly indicates that a certain degree of polymerization proceeds in the gas phase. No species of mass number greater than 43 is observed to a significant degree in the mass spectrum of pure propylene.

Thus the results of mass spectroscopy confirm the view of a molecular intermediate formation in glow discharge polymerization of an alkene. Limited evidence also suggests a gas phase propagation during polymerization.

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