

Chemistry of Electrical ²⁸²Discharge Polymerizations

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INTRODUCTION

The conversion of volatile organic compounds into liquid and solid products by the action of a high-voltage gas discharge has been investigated by many people over the past 100 years and more (1). Recently some companies have been reported to be working on the application of this principle to the coating of containers (2), steel strip (3) or fabric (4). These references all have indicated that work was to be under low-pressure conditions where the only gases would be the volatile monomer. In this paper I will describe some results obtained under atmospheric-pressure conditions, with the electrical discharge taking place in a mixture of nitrogen and volatile organic compounds.

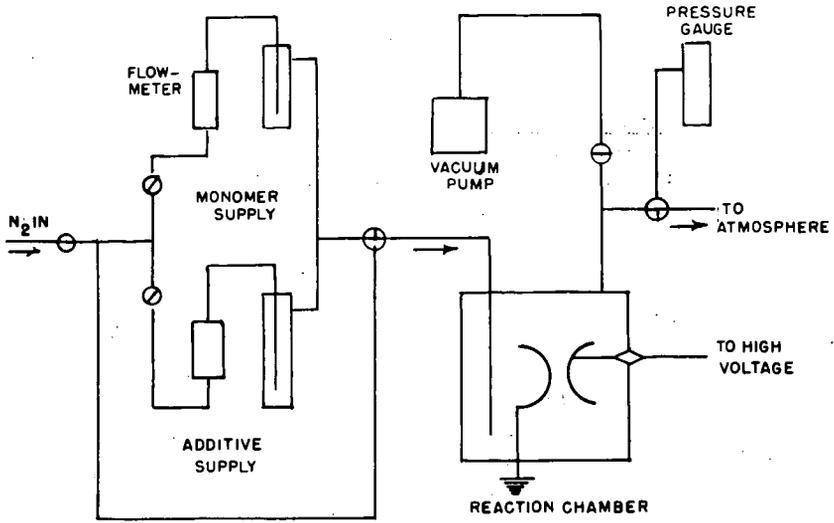
EXPERIMENTAL METHODS

All polymerizations were carried out at room temperature in a mixture of organic vapors and nitrogen at a total pressure of one atmosphere. The gases were delivered to the reaction zone through the system shown schematically in Figure 1. Nitrogen passed through liquid monomer in one bubble tube and through additive in another tube. The nitrogen and entrained vapors entered the enclosed reaction chamber at one corner and exited to the atmosphere at the opposite corner. The ratio of monomer to additive was determined by weighing the tubes before and after the experiment.

Details of the reaction chamber are shown in Figure 2. Polymerization was initiated by corona discharge between two cylindrical, parallel, insulated electrodes (A) made by lining the inner surfaces of Pyrex glass tubing with aluminum foil. The glass tubing had a wall thickness of 2.5 mm. and an outside diameter of 63 mm. The two glass surfaces were separated by a gap of 4 mm. The alternating current high voltage was supplied by a Tesla generator, manufactured by Lepel High Frequency Laboratories, Inc. (Model HFSG-2). The peak voltage, as estimated by spark length in air, was about 20,000 volts.

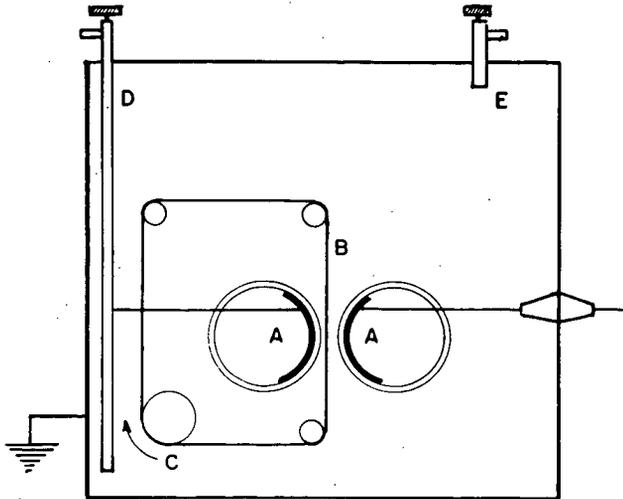
A moving strip of flexible substrate, (B) was positioned in the electrode gap. As shown in Figure 2, this substrate, which in most cases was 2-mil (50 microns) poly(ethylene terephthalate) film, was formed into a closed loop 47 cm. long and 5 cm. wide and was moved by the rotating roller, C. Vapors entered through D and exited through E.

Polymer which formed in the corona zone deposited both on the glass electrode coverings and on the moving substrates. The substrate strip was dried and weighed before and after the polymerization. The coated strips were also baked in a circulating air oven and reweighed. The final weight gain was taken as the yield. In some cases polymer was



VAPOR POLYMERIZATION - SCHEMATIC LAYOUT

Figure 1



VAPOR POLYMERIZATION ON MOVING SUBSTRATE

Figure 2

removed from the glass surfaces by solvent and recovered for infrared or chemical analysis.

RESULTS

Survey of Polymerizable Compounds

A number of volatile organic compounds were subjected to corona discharge with a wide variety of results. In almost all cases a deposit of oily or solid brown material formed on the substrate strip. The weight gain resulting from 15 minutes of corona polymerization ranged from tenths of a milligram to over 30 milligrams. When the coated strips were heated at 150°C for 10 minutes, part of the added weight was lost. Some of this is thought to be unreacted monomer which was absorbed by the substrate and coating. Another part of it could be very-low-molecular-weight products of the corona reaction. A third possibility is thermal decomposition of the coating.

The compounds which gave the heaviest coatings after heating, (taking into account the amount of monomer volatilized) included triallylamine, acrylonitrile, toluene and styrene. As the list in Table 1 shows it is not necessary for the monomer to be a vinyl compound in the strict sense of the word in order for a non-volatile polymer product to form in corona discharge. Toluene, benzene, benzotrifluoride and even acetone gave measurable yields. There seems to be no pattern of relationship between the structure of a monomer and its yield in corona polymerization.

TABLE 1

Corona-Polymerizable Compounds (Arranged in Order of Yield)

Triallylamine	Benzotrifluoride
Acrylonitrile	4-Vinyl cyclohexene
Toluene	Ethyl acrylate
Styrene	1-Octene
Acrylic Acid	Allyl amine
Benzene	Vinyl acetate
	Acetone

Effect of Additives

It was found that many halogenated organic compounds, when added to the monomer being volatilized, had the effect of giving a higher yield. Chloroform, bromoform and iodoform were more effective with styrene than some other additives. The yields after oven heating are given in Table 2, expressed as milligrams of weight gain per gram of styrene vaporized. It is interesting to note that the yield is usually increased more by a moderate amount of additive and not so much by a larger amount. Bromine itself reacted immediately with the styrene in the bubble tube but produced the largest yield of all additives tested. Chlorine and iodine seemed to have the reverse or no effect.

TABLE 2

Effect of Halogenated Additives on Corona Polymerization of Styrene
Yield in Milligrams per Gram of Styrene

<u>Additive</u>	<u>Percent Added</u>	<u>Yield</u>	<u>Additive</u>	<u>Percent Added</u>	<u>Yield</u>
Chloroform	0.5	22.4	Chlorine	7	5.6
Bromoform	0.5	11.6	Bromine	1	19.0
Bromoform	1.0	14.2	Bromine	5	32.0
Bromoform	2.5	19.7	Bromine	10	16.7
Bromoform	5.0	19.2	Iodine	5	9.7
Bromoform	10.0	12.0	None	0	10.7
Iodoform	5.0	21.2	-	-	-

Other additives that enhanced the yields of styrene polymer were carbon tetrachloride, 1,2-dibromo-1,1,2,2-tetrafluoroethane, 1-bromobutane and 2-bromobutane. Yields from monomers other than styrene were not all increased by halogenated additives; some even were decreased. It was impossible to develop any rational relationship between monomer structure and susceptibility of the monomer to yield enhancement by halogenated additive.

The results given above were all derived from experiments in which the additive and the monomer were mixed and volatilized from a single bubble tube. Thus, the exact composition of the vapor was not known. A new set of experiments was carried out using separate bubble tubes for monomer and additive. The weight changes of the tubes during a run were used to calculate mole ratios of additive to styrene. The results of experiments with four additives are shown in Figure 3. The conversion to polymer of styrene without additives was 0.75 to 0.9 percent. As increasing amounts of bromoform, 1-bromobutane or 2-bromobutane were added, the conversion increased and then fell off again. The pattern of points in the case of 1-bromobutane was widely scattered but most of the points lay well above the level for styrene itself. With 2-bromo-2-methylpropane as an additive there was no significant increase in conversion. The weight gain from the additives alone, with no styrene, were all low compared to styrene.

In considering chemical explanations for corona polymerization, both free radical and ionic intermediates are possibilities. Experiments were run with various additives to styrene that might be expected to inhibit each kind of reaction through combination with the active intermediate but no clear-cut reduction in yield was observed. Benzoquinone at 1 and 2 mole percent gave normal yields. Water and butyl amine were extensively studied but, as Figure 4 demonstrates, the tendency for these supposed cation scavengers to depress the conversion is slight and not clear-cut. Butyl amine alone gave a surprisingly high yield. Ammonia, triethylamine, acetone and carbon dioxide as additives had no substantial effect on yield.

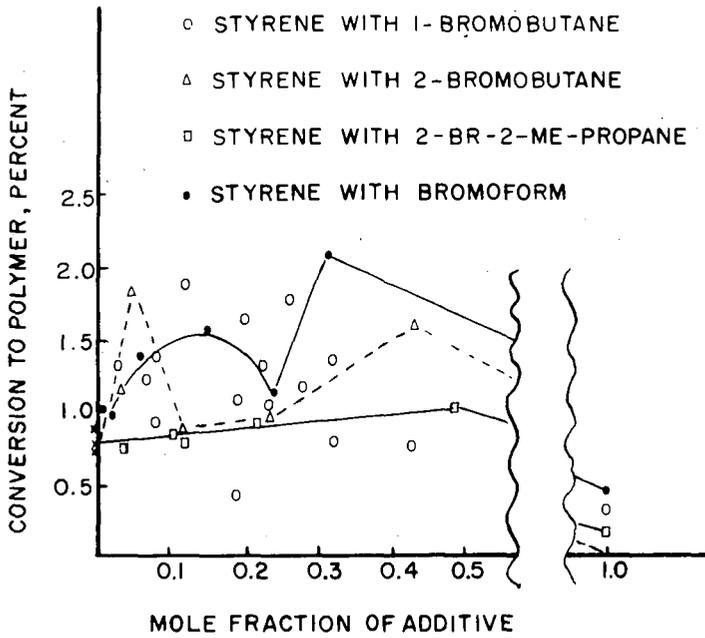


Figure 3

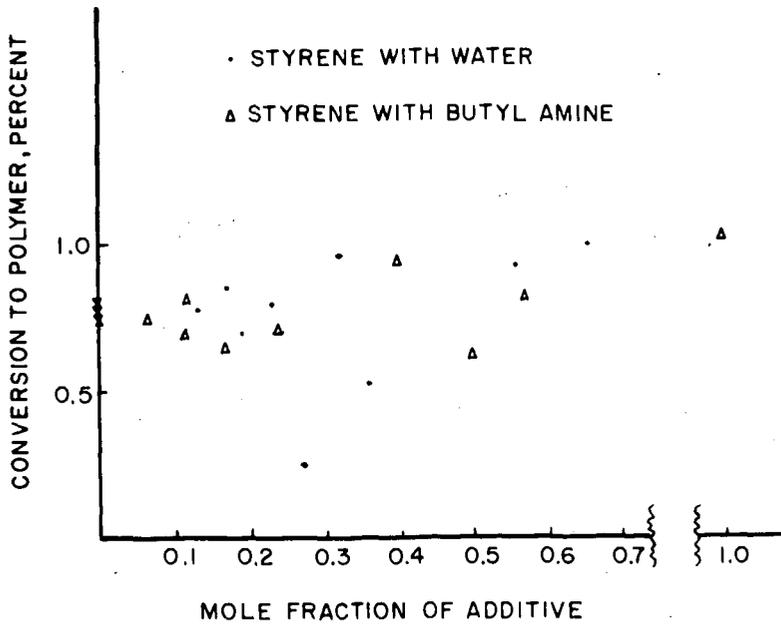


Figure 4

Some evidence was collected on the chemical nature of some of the products. The products deposited on the moving film and on the glass electrode covers were always easily dissolved in common solvents like acetone, chloroform and benzene, indicating low molecular weight and that there was little cross-linking.

Infrared spectra were obtained of polymers made from styrene, benzene and toluene by dissolving the deposit from the glass electrode cover with chloroform and evaporating the solution on a salt plate. The spectra were all similar and closely resembled conventional polystyrene. As Figure 5 shows, there were additional absorptions at 1050, 1220, 1720 and 3400 wave numbers indicating oxygenated products of various kinds including hydroxyl or amino, ester and probably ether. These spectra are very similar to those published by Jesch, Bloor and Kronick (5).

The infrared evidence of oxygen-containing groups was obtained on a styrene product which was prepared and transferred in a nitrogen atmosphere. The only contact with air was during the time the spectrum had been run. The sample was exposed to the atmosphere for 24 hours and it changed only slightly. As Figure 6 shows there was little further increase of bands attributed to oxygenated groups. The only noticeable change in the spectrum was in the relative peak heights at 700 and 760 wave numbers. The spectrum of a product made with 1-bromobutane mixed with the styrene was almost identical to the unmodified styrene product with a stronger absorption ascribed to ketone carbonyl at 1720 wave numbers.

The final evidence of chemical composition was elemental analysis. The styrene product had considerably less carbon than styrene itself, as seen in Table 3. It also contained a significant amount of nitrogen and, as determined by difference, a large amount of oxygen. Heating the polymer in air did not change the composition significantly. Styrene polymer made in the presence of 25 to 30 weight-percent 1-bromobutane had almost the same analysis plus a significant bromine content.

TABLE 3
Elemental Analysis of Corona Polymers

<u>Monomer</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>Br</u>	<u>O (by difference)</u>
Styrene, unheated product	72.23	6.86	3.2	-	17.71
Styrene, oven-heated	73.46	6.68	3.39	-	16.47
Styrene plus bromobutane					
unheated product	73.74	6.95	3.59	6.08	9.64
oven-heated product	73.29	6.69	3.56	6.97	9.49
Styrene, calculated	92.26	7.74	-	-	-
Bromobutane, calculated	35.06	6.62	-	58.32	-

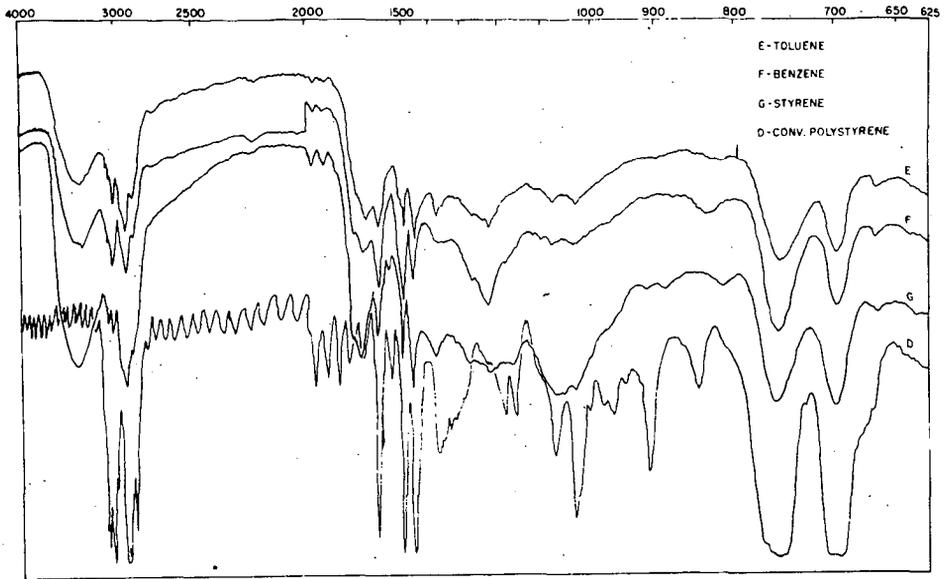


Figure 5

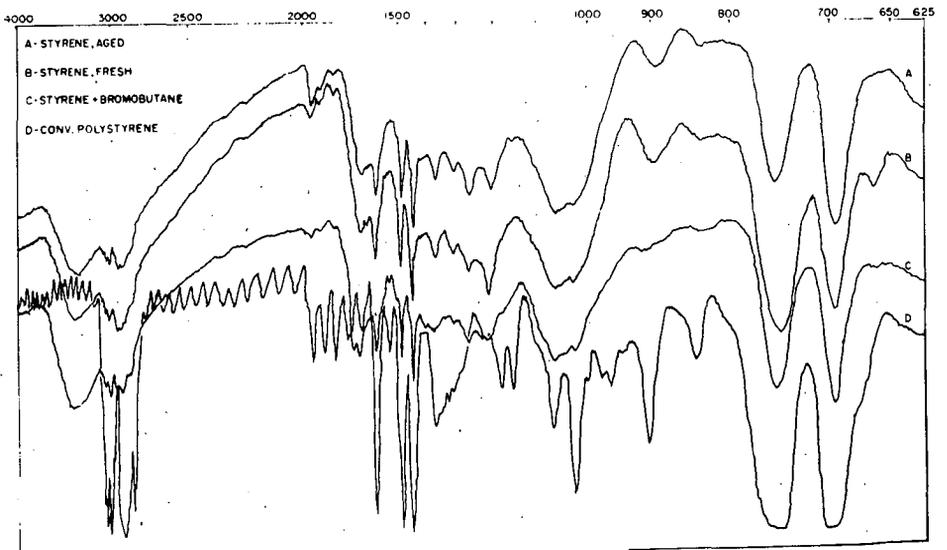
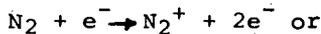


Figure 6

DISCUSSION

The salient features of the information presented above might be summarized as follows. In a mixture of organic vapor and nitrogen subjected to high-frequency, high-voltage, electrodeless discharge, the nitrogen, the organic compound and trace amounts of oxygen and water are activated and combine chemically to yield products of higher molecular weight than the starting materials. These products condense on any solid surface available and may even undergo further chemical reaction within themselves and with more monomeric material which is not electrically activated.

The chemical mechanism of this series of reactions must be complex, possibly produced by simple ionization through collision with a rapidly-moving electron followed by expulsion of two secondary electrons:



These are the products ordinarily found in mass spectrometry and on exposure to gamma or beta radiation. These activated cationic products may activate vinyl polymerization or undergo secondary reactions, yielding neutral free radicals or even anions, either of similar structure or in the form of fragments and combination or rearrangement products. In the present case there exists the further possibility that reaction products become reactivated, since they are formed in the presence of the high-voltage field, and undergo further reaction.

The simplest mechanism to consider would be polymerization of the vinyl monomers to long-chain products after initiation by some active species. The fact that non-vinyl compounds gave good yields may be explained through a mechanism involving some fragmentation of every monomer molecule and combination of the fragments to products of higher molecular weight. The vinyl monomers could be reacting through this non-vinyl mechanism also.

The action of halogenated additives suggests that the yield of reactive intermediates is increased by some of them and that these intermediates increase the initiation of vinyl polymerization. There is not enough data to establish this firmly. It may also be considered that, by changing the dielectric constant of the gas mixture, the additive can increase the efficiency of energy transfer from the electric field to the monomer.

The other additives had little or no effect, indicating that the situation is not very similar to bulk or solution polymerizations by free radical or ionic catalysis such as are now being actively studied by several laboratories (6,7). Certainly we do not have a simple vinyl polymerization. Otherwise some of the potential inhibitors would have shown an effect.

One of the unexpected results was ²⁹⁰the fixation of nitrogen. This can be seen in retrospect to be related to work with discharge-activated nitrogen which has been reported from time-to-time (8,9,10).

No complete mechanistic explanation will be presented. More experiments are in process but it is not expected that a system which is as potentially complex as this can soon be completely explained.

ACKNOWLEDGEMENTS

The able assistance of Messrs. Roger Kolsky and Walter Miner and the helpful analytical interpretations of Mr. Elliot Baum are gratefully acknowledged.

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