

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Effects of Reaction Conditions on the Structure of Plasma-Polymerized Ethylene

J. M. Tibbitt^a; A. T. Bell^a; M. Shen^a

^a Department of Chemical Engineering, University of California Berkeley, California

To cite this Article Tibbitt, J. M. , Bell, A. T. and Shen, M.(1977) 'Effects of Reaction Conditions on the Structure of Plasma-Polymerized Ethylene', *Journal of Macromolecular Science, Part A*, 11: 1, 139 – 148

To link to this Article: DOI: 10.1080/00222337708061258

URL: <http://dx.doi.org/10.1080/00222337708061258>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Effects of Reaction Conditions on the Structure of Plasma-Polymerized Ethylene

J. M. TIBBITT, A. T. BELL, and M. SHEN

Department of Chemical Engineering
University of California
Berkeley, California 94720

ABSTRACT

Liquid and solid polymeric products were derived from a low-pressure glow discharge of ethylene. Polymerization pressure, discharge power, and monomer flow rate were systematically varied. Products were analyzed by infrared spectroscopy to determine the concentrations of characteristic functional groups in each. Polymer form, apparent crosslink density, and deposition rate were also reported. Structural variations and the form of the polymerization products can be explained in terms of the prevailing discharge conditions and the deposition rate, both of which are functions of the reactor operating parameters. It was found that the degree of crosslinking in rigid films of plasma polymerized ethylene is in the range of 6 to 16 chain carbons between crosslinks.

INTRODUCTION

Liquid and solid products are derived from reactions that occur in a glow discharge of an organic or organometallic vapor. This process,

referred to as plasma polymerization, yields materials that are totally amorphous, highly crosslinked, and exhibit a completely irregular structure containing random points of unsaturation and pendant aromatic rings. In a recent publication [1] we have used a quantitative analysis of IR and NMR spectra to define the concentrations of functional groups present in plasma polymerized hydrocarbons. This method also allows calculation of an apparent crosslink density of these materials. In the present work, we have applied this technique to the evaluation of the structural changes in plasma-polymerized ethylene when the reaction parameters pressure, power level, and monomer flow rate are systematically varied. Structural characteristics of the products at all studied reaction conditions have been represented on two characteristic maps and are qualitatively shown to depend on the ratio of the rate of radical production to the rate of chain growth.

EXPERIMENTAL

A detailed description of the plasma reactors has been given [2]. The central component of this apparatus is an evacuable bell jar containing two circular parallel electrodes. A glow discharge of monomer vapor is sustained by an International Plasma Corporation Model 3001 rf generator which operates at 13.56 MHz and delivers up to 150 W. The temperature of the grounded, lower electrode is held constant by circulating water of the appropriate temperature. This electrode was covered by aluminum foil which served as the polymerization substrate. The polymer deposition rate was determined by weighing the foil before and after reaction and dividing the weight gain by the deposition time. Polymer was also collected on NaCl crystals, positioned 2 in. from the center of the electrode. The sample deposited on these crystals was characterized by infrared spectroscopy by using a Perkin-Elmer Model 137 spectrophotometer.

CP grade ethylene was obtained from the Matheson Gas Co. and used without further purification. The pressure, monomer flow rate, and discharge power used during each polymerization were recorded.

RESULTS

Tables 1-3 present the data obtained when ethylene was polymerized at different pressures, monomer flow rates, and discharge powers. The first four columns on the left-hand side of these tables

TABLE 1. Effect of Reactor Pressure on Plasma Polymerization of Ethylene

Polymerization conditions				Deposition rate ($\mu\text{m/hr}$)	Polymer form	Functional group concentrations (mmole/g polymer)				Apparent crosslink density χ_c (backbone carbons/ crosslink)
Monomer flow rate (STP cc/min)	Power (W)	Pressure (Torr)	Deposition rate			[CH ₃]	[CH ₂]	[CH]	[C=C]	
50	38	1.0	2.9	Film	8.2	11.3	15.1	1.7	0.42	11.7
50	38	2.0	3.5	Film	6.2	13.2	15.2	1.3	0.32	8.3
50	38	3.2	2.2	Film	4.2	13.4	17.0	1.5	0.38	6.1
50	38	5.0	1.8	Film	4.1	9.2	20.6	1.6	0.40	4.6
50	80	1.0	6.4	Film > powder	5.6	8.1	20.9	1.3	0.34	5.0
50	80	2.0	10.8	Film	6.2	10.3	18.0	1.5	0.39	6.6
50	80	3.2	15.4	Tacky film	8.7	14.6	11.3	2.9	0.72	43.1
50	80	5.0	17.6	Oil	8.3	16.8	9.5	4.8	1.20	∞
85	80	1.0	5.1	Film	5.7	9.5	19.4	1.4	0.36	5.6
85	80	2.0	3.5	Film	5.4	10.6	18.6	1.3	0.32	5.9
85	80	3.2	5.8	Tacky film	7.2	15.3	12.0	1.8	0.44	17.6
85	80	5.0	6.9	Oil	8.2	16.9	9.5	4.8	1.20	∞

TABLE 2. Effect of Reaction Power on Plasma Polymerization of Ethylene

Polymerization conditions				Functional group concentration (mmole/g polymer)				Apparent crosslink density X c (backbone carbons/ crosslink)
Monomer flow rate (STP cc/min)	Power (W)	Pressure (Torr)	Deposition rate ($\mu\text{m/hr}$)	Polymer form	[CH ₃]	[CH ₂]	[CH] [C=C] [C ₆ H ₅]	
50	25	1.0	0.81	Film	8.9	12.2	13.5 3.1 0.70	19.7
50	50	1.0	5.1	Film \gg powder	7.6	10.4	16.6 1.5 0.37	8.7
50	80	1.0	6.4	Film $>$ powder	5.6	8.1	20.9 1.3 0.34	5.0
50	35	3.2	2.2	Film \gg tacky film	4.2	13.4	17.0 1.5 0.38	6.1
50	80	3.2	15.4	Tacky film	8.7	14.6	11.3 2.9 0.72	43.1
50	100	3.2	20.2	Tacky film	8.2	14.9	11.5 2.4 0.61	30.3
50	40	5.0	1.8	Film \gg tacky film	4.1	9.2	20.6 1.6 0.40	4.6
50	85	5.0	17.6	Oil	8.3	16.8	9.5 4.8 1.20	∞

TABLE 3. Effect of Monomer Flow Rate on Plasma Polymerization of Ethylene

Polymerization conditions				Deposition rate ($\mu\text{m/hr}$)	Polymer form	Functional group concentration (mmole/g polymer)				Apparent crosslink density $\times c$ (backbone carbons/ crosslink)
Monomer flow rate (STP cc/min)	Power (W)	Pressure (Torr)	[CH ₃]			[CH ₂]	[CH]	[C=C]	[C ₆ H ₅]	
20	80	1.0	10.1	Powder \approx film	3.9	6.3	24.4	0.67	0.17	3.6
50	80	1.0	6.4	Film $>$ powder	5.6	8.1	20.9	1.3	0.34	5.0
85	80	1.0	5.1	Film	5.7	9.5	19.4	1.4	0.36	5.6
50	80	2.0	10.8	Film	6.2	10.3	18.0	1.5	0.39	6.6
85	80	2.0	Unstable	Film	5.4	10.6	18.6	1.3	0.32	5.9
20	80	3.2	discharge							
50	80	3.2	15.4	Tacky film	8.7	14.6	11.3	2.9	0.72	43.1
85	80	3.2	5.8	Tacky film $>$ film	7.2	15.3	12.0	1.8	0.44	17.6
20	80	5.0	Unstable							
50	80	5.0	discharge							
85	80	5.0	17.6	Oil	8.3	16.8	9.5	4.8	1.20	∞
85	80	5.0	6.9	Oil	7.9	17.1	9.6	4.0	1.00	∞

identify the reaction conditions and the observed deposition rates. The form of the product (*viz.* oil, film, powder) is given in the fifth column, together with a qualitative measure of the distribution if more than one form was present. The molar concentrations of methyl, methylene, tertiary carbon, olefinic, and phynyl groups were obtained by a quantitative interpretation of the infrared spectra of each polymer sample, following the procedures described in reference [1]. The last column in Tables 1-3 lists the apparent crosslink density, χ_c , which represents the number of chain carbons between crosslinks.

Several trends in the data can be observed from inspection of Tables 1-3. Table 1 shows that the concentrations of methyl, methylene, vinyl, and aromatic groups increase with pressure at constant monomer flowrate and at power levels above 50 W (ca. 0.14 W/cm² electrode surface), while there is a consistent decrease in tertiary carbon concentration. These circumstances generally lead to decreased crosslink densities with increasing pressure. On the other hand, at low power levels, these trends are exactly reversed, suggesting that some mechanistic changes may occur as power is increased above a certain level.

Table 2, which outlines structural changes effected by varying the power level at fixed monomer flowrate and pressure, again shows two types of behavior. At low pressure (1.0 Torr), only the tertiary carbon concentration increases with power, leading to increased crosslink density at high power levels. But at pressures above 3.2 Torr, trends in functional group concentrations reverse and decreases in crosslink density with increasing power are observed.

The data in Table 3 illustrate the effects of varying the monomer flow rate while holding the discharge power and pressure constant. These data show that the plasma polymer structure is much less sensitive to the volumetric feed rate of monomer than to either pressure or power level variations. This is reflected in the relative constancy of the functional group concentrations and crosslink densities as well as the distribution of product forms.

DISCUSSION

The effect of polymerization conditions on the polymer form obtained, its crosslink density, and rate of deposition are shown in Figs. 1 and 2. These characteristic maps are based upon the information presented in Tables 1-3, plus additional results obtained with other polymerization conditions. In each of the figures, regions have been identified in which the predominant polymer form is an oil, film, or powder.

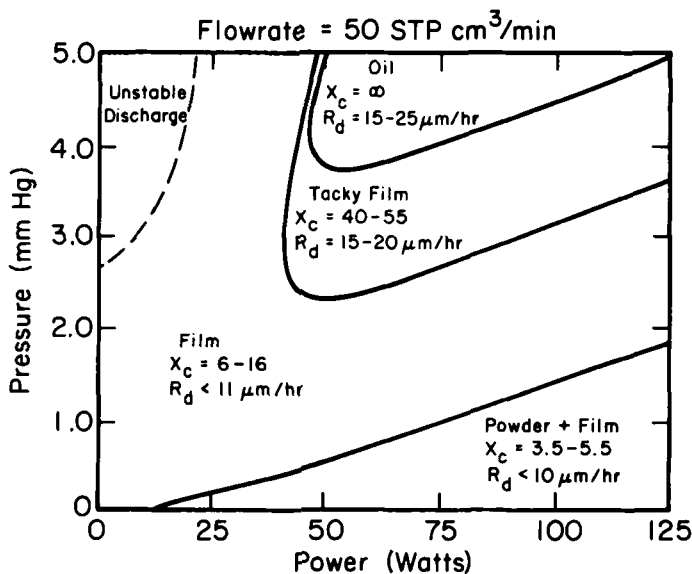


FIG. 1. Dependence of ethylene polymer form, deposition rate, and crosslink density on pressure and discharge power at 50 STP cc/min flow rate.

It should be recognized that the boundaries between regions are not sharply defined and that the indicated boundaries are only approximate.

A full interpretation of the relationship between the form of polymer obtained and the polymerization conditions used depends upon an understanding of the mechanism and kinetics of polymer formation. Unfortunately, the current state of knowledge concerning plasma polymerization is insufficient to allow for such detailed explanations, hence, only a qualitative interpretation can be postulated.

It has been proposed by Kobayashi et al. [2-4] that plasma polymerization is initiated through the collision of free electrons present in the plasma with monomer molecules, resulting in the formation of free radicals. The primary radicals then diffuse to the surface on which polymer is being deposited and are adsorbed. Monomer diffusing out of the gas phase reacts with the adsorbed primary radicals to produce radicals of higher molecular weight. Polymerization by further addition of monomer causes the growth

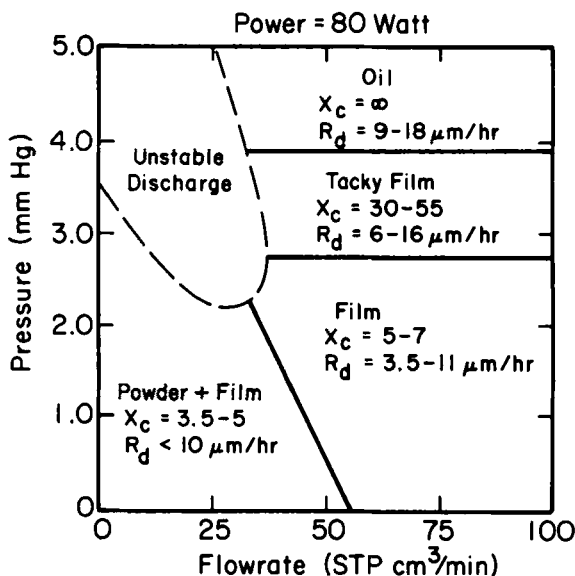


FIG. 2. Dependence of ethylene polymer form, deposition rate, and crosslink density on discharge pressure and monomer flow rate at 80 W power level.

of polymer chains. Chain growth is terminated when surface-bound radicals recombine or are trapped within the growing film. However, unlike conventional polymerization, radical-radical recombination does not necessarily lead to a termination of polymer growth for the following reason. The growing polymer surface is constantly bombarded by photons emitted by the plasma [5, 6] and by energetic ions and electrons which diffuse from the plasma. Upon interaction with the polymer, these fluxes of energy can cause new radical sites to be produced in existing polymer chains. The newly created sites can, in turn, act as centers for further polymerization. Since these sites are part of an existing chain, the new chain which grows out from it is a branch. If the radicals at the end of two branching chains recombine, a crosslink is formed.

Based upon the sequence of events outlined above, it would be anticipated that the extent of branching and crosslinking will depend upon the ratio of the rate of new radical site production to the rate of chain growth. When the ratio of rates is large, a more highly cross-linked product should be obtained; conversely when the ratio is low a

weakly crosslinked product is expected. The extent to which such a simple interpretation of the factors controlling the degree of crosslinking is correct can not be established on the basis of the available data, principally because there exists no measure of the rate of new site formation at the polymer surface. One does observe, however, that conditions under which the polymer deposition rate is low are conducive to producing a more highly crosslinked polymer and vice versa. This observation is not inconsistent with the postulated interpretation when it is recognized that slow polymer deposition results in a longer exposure of the polymer surface to the effects of the plasma and hence a greater opportunity to form new reactive sites.

The explanation of the relation between crosslink density and deposition rate offered above combined with the data of Tables 1-3 suggests certain consideration in tailor-making plasma-polymerized films. For instance, increased crosslinking can be obtained by increasing the power density at constant pressure and monomer flow-rate, decreasing monomer flow at constant power and pressure, or decreasing pressure at constant power and monomer feed rate. All these actions are expected to raise the site activation/chain growth ratio and thus the crosslink density according to our discussions. The data in Tables 1-3 support these explanations. This type of simple "rule-of-thumb" thinking should prove quite useful in the qualitative prediction of structural changes when reaction conditions are varied in plasma polymerization systems.

CONCLUSION

In this work, we have demonstrated that systematic variation of reaction parameters results in well defined changes in the concentrations of functional groups, the crosslink density and the product form of plasma-polymerized ethylene. A qualitative explanation of these structural changes which considers the effects of deposition rate and discharge conditions at the prevailing polymerization conditions has been offered. Simultaneously, the usefulness of spectrophotometric analysis in structural characterization of plasma polymers has been demonstrated. It is hoped that these discussions prove to be a useful aid in tailor-making plasma polymers for specific applications.

ACKNOWLEDGEMENT

This work was supported by the National Science Foundation through Grant GH-43410.

REFERENCES

- [1] J. M. Tibbitt, M. Shen, and A. T. Bell, J. Macromol. Sci.-Chem., A10, 1617 (1976).
- [2] H. Kobayashi, A. T. Bell, and M. Shen, J. Appl. Polym. Sci., 17, 885 (1973).
- [3] H. Kobayashi, M. Shen, and A. T. Bell, J. Macromol. Sci.-Chem., A8, 373 (1974).
- [4] H. Kobayashi, A. T. Bell, and M. Shen, Macromolecules, 7, 277 (1974).
- [5] M. Hudis, in Techniques and Applications of Plasma Chemistry, J. R. Hollahan and A. T. Bell, Eds., Wiley, New York, 1974.
- [6] N. Morosoff, B. Crist, M. Bumgarner, J. Hsu, and H. Yasuda, J. Macromol. Sci.-Chem., A10, 451 (1976).

Accepted by editor March 20, 1976

Received for publication May 5, 1976