

The Preparation and Polymerization of Ethylene-d₄

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Synopsis

A direct method for preparing deuterated ethylene by reducing acetylene-d₂ with chromous ions in a dimethylformamide/deuterium oxide mixture is described. This method gives a good yield of precursor gas of relatively high purity. The gas was polymerized with a Ziegler-type catalyst to produce deuterated polyethylene with sufficient purity and melt flow properties for use in laser fusion studies. A reaction variables study showed that polymerization of deuterated ethylene yields polymers with higher molecular weights than those obtained using normal ethylene. The study also indicated that the deuterium content of the polymer decreases with increasing reaction temperature, thus dictating that the process operates near room temperature. Several mechanical and chemical properties of the deuterated polymer were determined and are reported.

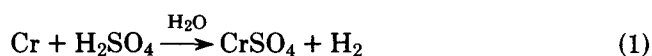
INTRODUCTION

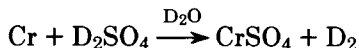
Studies were undertaken to develop a laboratory process for producing deuterated ethylene and polymerizing this precursor to form a polymer which would have suitable molecular weight and melt flow properties for fabrication into the laser targets used in controlled fusion experiments. Work by Patterson and du Vigneaud¹ indicated that a heterogeneous chemical reduction of deuterioacetylene by reaction with aqueous chromous chloride to ethylene-d₂ was possible, and further investigation by Castro and Stephens² showed that the use of dimethylformamide (DMF) in admixture with a reducing solution enhanced the rate of reduction of substituted acetylenes, particularly that of terminally substituted acetylenes. Chemical reduction seemed to be a convenient approach to the synthesis of small quantities of perdeuterated ethylene and offered both safety and economic advantages. Of the existing methods used to produce polyethylene, the polymerization of ethylene gas using a Ziegler-type catalyst seemed most suitable for meeting the objectives of this work.³

Although many process variables affect the nature of the polymer produced and/or the reaction profile, the following work was confined to evaluating the effects of temperature, pressure, and catalyst ratio on polymer yield and to determining the molecular weight and deuterium content of the polymer. These data are given in this report.

DEUTERATED ETHYLENE PREPARATION

Initial studies of the reduction of acetylene by chromous ions in a DMF/water mixture were conducted using protonated compounds. A procedure for preparing Cr²⁺ ions by direct oxidation of chromium metal with sulfuric acid is described as follows⁴:



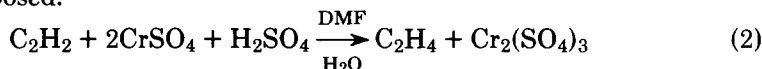


If the reaction is carried out in the absence of oxygen and if an excess of chromium metal is present, the reaction stops when chromium reaches the 2+ valence state. Cr^{2+} can be easily oxidized to Cr^{3+} by oxygen and can be slowly oxidized by water in the absence of excess chromium metal.

Reaction (1) is highly desirable because only chromous sulfate remains in solution and, in addition, because concentrations of 1.4*N* can be approached. The reaction is rapid and goes to completion in about 3 hr. The final reducing solution was prepared by adding an equal volume of DMF to the aqueous chromous sulfate solution. A nitrogen atmosphere was maintained over the diluted mixture to avoid reoxidation of chromous ions.

Acetylene gas prepared in an acetylene generator was bubbled through the DMF, water, and chromous sulfate mixture in a gas-washing bottle. Samples of the effluent gas stream were collected by water displacement and analyzed by gas chromatography. The first samples taken indicated that the effluent gas contained approximately 60% ethylene. To specifically identify ethylene, samples were collected in a gas-sampling cell and analyzed by infrared. Figure 1 shows the spectrum of the sample collected and indicates that the gas is a mixture of ethylene and acetylene.

The large magnitude of the conversion obtained was totally unexpected because the residence time of the gas in the reducing mixture was short (about 1 sec), and the literature² suggested that complete reduction would require at least 5 min under the most favorable conditions. The following stoichiometric reaction is proposed:



As mentioned previously, the high conversion of acetylene to ethylene was unexpected, particularly in view of the fact that the reaction system is heterogeneous. Acetylene, however, is quite soluble in DMF, and it is probable that the reduction of acetylene takes place in solution rather than the gaseous phase by a mechanism involving the reaction of the 1:1 acetylene/ Cr^{2+} complex with Cr^{2+} as suggested by Castro.² Ethylene, on the other hand, is not as soluble in DMF, so that once formed, ethylene would have a tendency to effervesce. So, from the standpoint of the solubilities of the gases, these reaction conditions are favorable for the formation of ethylene.

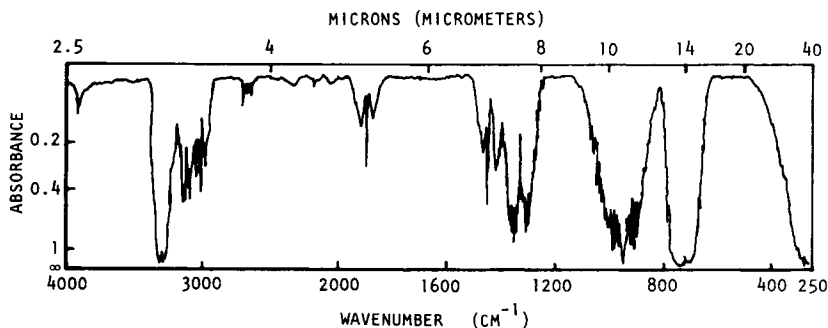
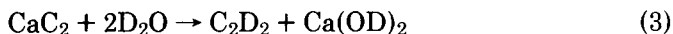


Fig. 1. Infrared spectrum of a mixture of ethylene and acetylene gases emerging from reducing solution.

Improvements in the reaction rate could be realized by providing a longer reaction column or reaction path to increase the time of gas-to-liquid contact. This provision would essentially increase the residence time. In order to increase the residence time of the reaction, a more elaborate gas train (Fig. 2) was used, and in this case deuterated reagents were used to synthesize the precursor gas. The pertinent reactions involved in preparing deuterated ethylene are the following:



Although the DMF used was protonated, the protons are not particularly labile and do not undergo significant isotopic exchange during the reaction time required for the gas generation step.

As shown in Figure 2, calcium carbide contained in dropping funnel 1 is fed through a manually operated Teflon stopcock and into heavy water contained in vessel 2, where deuterated acetylene gas is formed. Parts 1 and 2, therefore, constituted the acetylene generator. Acetylene-d₂ is piped to the bottom of reaction column 4 and is converted to deuterated ethylene during passage through the reducing medium. The effluent gas from column 4 is piped to item 5 and enters the reducing medium through a gas diffuser. After passing through Item 5, the gas is piped to item 6 and passes into and through the reducing me-

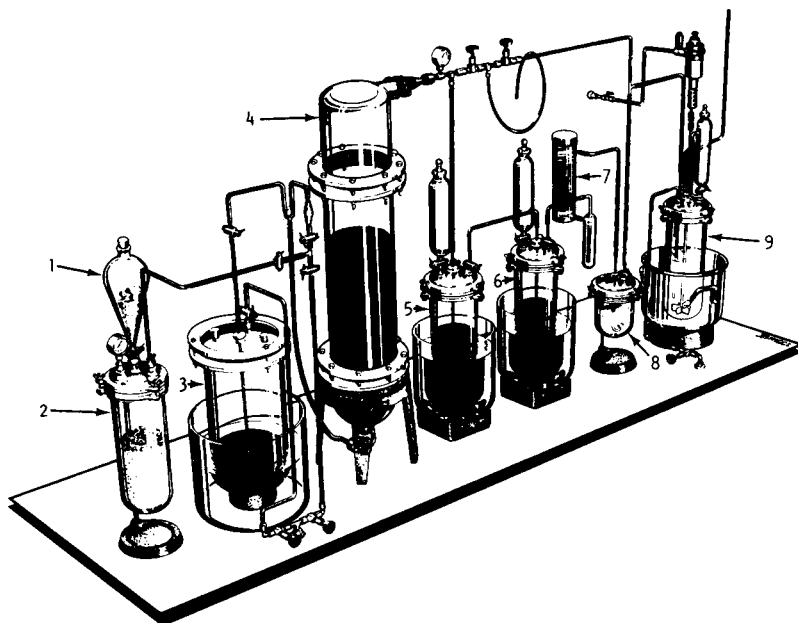


Fig. 2. Representation of gas train used for studying the reaction of acetylene gas: (1) dropping funnel containing calcium carbide; (2) acetylene generator containing deuterium oxide; (3) chromous sulfate preparation vessel; (4) reaction column containing chromous sulfate, deuterium oxide, and dimethylformamide; (5) scrubber containing chromous sulfate, deuterium oxide, and dimethylformamide; (6) scrubber containing chromous sulfate, deuterium oxide, and dimethylformamide; (7) dryer; (8) active hydrogen scrubber containing triisobutylaluminum-cyclohexane; (9) polymerization reactor.

dium as in item 5. Deuterated ethylene gas exiting vessel 6 passes through a dryer containing CaCl_2 (7) which removes the bulk of the deuterium oxide vapor contained in the gas. The gas is then piped through scrubber 8, which contains a solution of triisobutylaluminum in cyclohexane to remove any remaining active hydrogen (deuterium) compounds entrained in the gas.

Samples of the gas were taken at this point and analyzed by mass spectroscopy for composition and isotopic purity. The results indicated the presence of traces of cyclohexane, which was expected, and an isotopic purity (per cent deuterated ethylene) approaching 100. Three runs in which deuterated ethylene was produced yielded similar results in terms of production rate and isotopic purity. In all cases the product gas was polymerized to yield deuterated polyethylene (reactor 9) in a continuous process.

Although a method for preparing a high-purity deuterated ethylene gas was developed, the compression and bottling of the gas was not undertaken because of the availability of compressed gas from another source. Therefore, the second phase of this study, the preparation of deuterated polyethylene, was conducted using commercially available compressed gas.

EXPERIMENTAL

Polymerization reactions were carried out in batches in a 2-l. stirred glass reactor equipped with cooling coils for temperature control. The reaction medium was cyclohexane, which was distilled over sodium and sparged with nitrogen before use. The catalyst system was triisobutylaluminum and titanium tetrachloride.

The deuterated ethylene gas used in this phase of the work was composed of 94.95% C_2D_4 and 4.83% C_2D_6 . The remaining components of the gas consisted of a series of minor components having the general formulae $\text{C}_2\text{D}_2\text{H}_2$, $\text{C}_2\text{D}_3\text{H}$, C_2D_2 , and $\text{C}_3\text{D}_x\text{H}_x$. The overall atomic percent deuterium content of the gas was 99.44%.

In the polymerization procedure, the reactor was charged with the appropriate quantity of cyclohexane, usually 1500 ml, and then purged with nitrogen for about 20 min before the reactor was closed. Stirring was initiated, and triisobutylaluminum was injected, as a 10% solution in cyclohexane, through a septum into the reactor. Titanium tetrachloride, as a 20% cyclohexane solution, was added in a similar manner to the reaction medium, and the finely divided Ziegler catalyst was formed.

As the reactor is pressurized with ethylene- d_4 , solid polymer begins to form almost immediately. Pressure and temperature are held constant during the course of the reaction. Most reactions were run for 1 hr before termination, which was accomplished by flushing the reaction mixture into a receiver containing isopropyl alcohol. The yield of polymer varied depending upon reaction conditions. Products were purified by refluxing the reaction mixture in isopropyl alcohol under a nitrogen blanket, followed by filtration and washing with methanol before drying.

RESULTS

Effect of Catalyst Ratio on Molecular Weight

In initial experimental runs, attempts were made to produce a 2.0-melt index (melt index is a function of the molecular weight) deuterated polymer by using a catalyst system where the Al/Ti ratio was 1.0. But in every case the polymer produced was either highly crosslinked or had an extremely high molecular weight, characterized by a lack of solubility in hot xylene. Similar runs made with protonated ethylene resulted in products with the expected melt indices and solubilities. Standard series runs where the Al/Ti ratio was varied show that the dependence of melt index on Al/Ti is quite different for ethylene and ethylene-d₄ (Fig. 3). In addition, the magnitude of the slope of the curve indicated that melt index is quite sensitive to changes in Al/Ti ratio for a given set of reaction conditions.

The differences shown in Figure 3 suggest that the termination step in the kinetic sequence may be influenced by an isotopic effect, since ethylene-d₄ appears to undergo a greater degree of polymerization per unit time than does

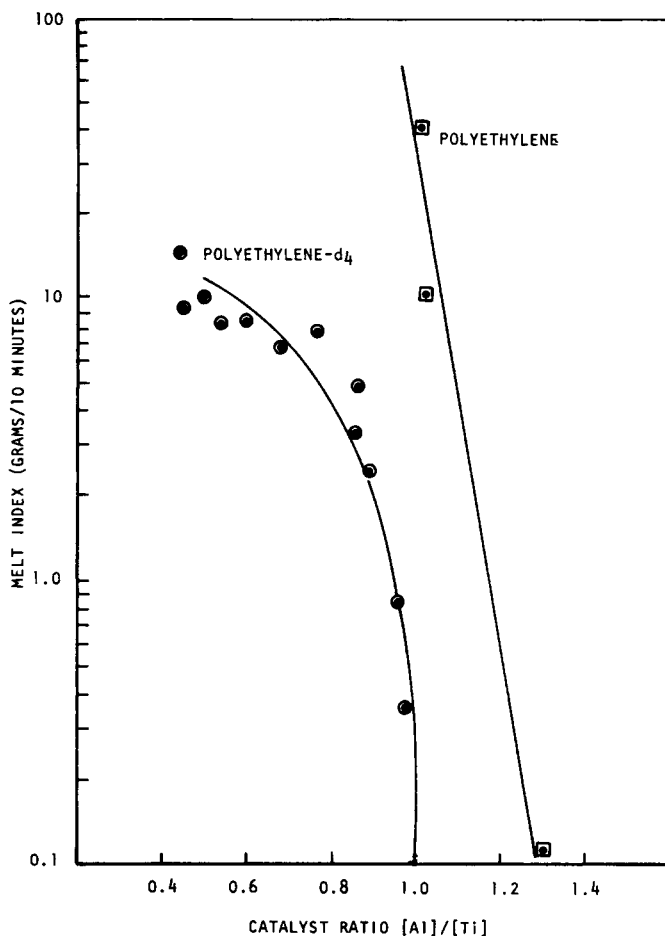


Fig. 3. Variation in Al/Ti ratio to show dependence of melt index.

normal ethylene under similar reaction conditions. Since laser target fabrication is favored by good flow properties or higher melt index, catalyst ratios around 0.4 were found to produce material having good processing characteristics.⁵

General Properties of Deuterated Polyethylene

Deuterated polyethylene and normal polyethylene are similar in many respects, such as visual appearance and melting points (near 130°C). The density of the deuterated polymer, however, lies in the range of 1.092–1.095 compared to 0.95 for normal linear polyethylene. The difference in density appears to be merely due to the difference in monomer molecular weight rather than to any gross differences in solid-state structure. It is an interesting fact that the deuterium concentration in linear deuterated polyethylene is higher than that in frozen elemental deuterium. For example, at 18.7°K solid deuterium contains 0.1976 g D/cm³, while linear deuterated polyethylene at room temperature contains 0.2737 g D/cm³. It is this property that makes deuterated polyethylene an attractive candidate as the fuel or target material in laser fusion studies.

A comparison of the infrared spectra for polyethylene-d₄ and polyethylene shows the magnitude of the shift in characteristic absorption frequencies due to the substitution of deuterium for hydrogen in the polyethylene structure (Fig. 4).

The molecular weights (\bar{M}_w and \bar{M}_n) of selected samples of deuterated polyethylene were characterized by melt flow index, gel permeation chromatography (GPC), and membrane osmometry (MO). A summary of the values obtained is listed in Table I, and a correlation of melt index with weight average molecular weight (\bar{M}_w) is shown in Figure 5.

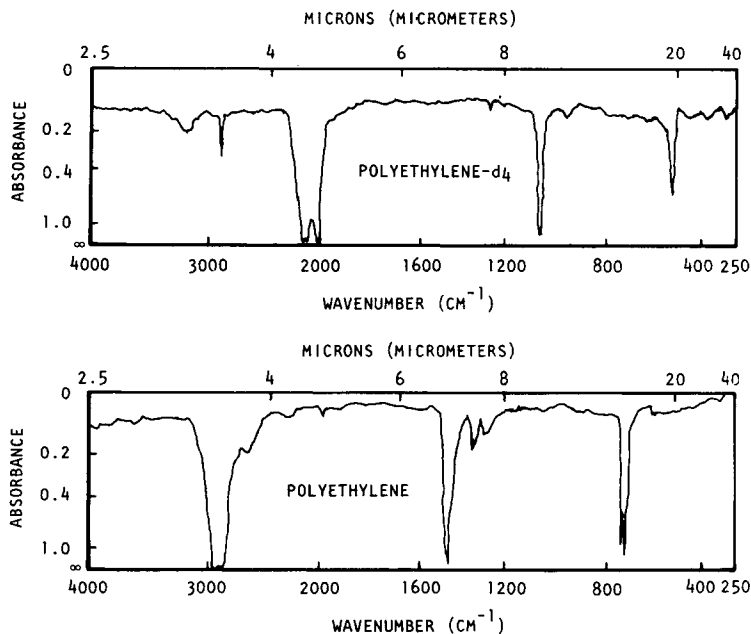


Fig. 4. Infrared spectra of polyethylene-d₄ and polyethylene.

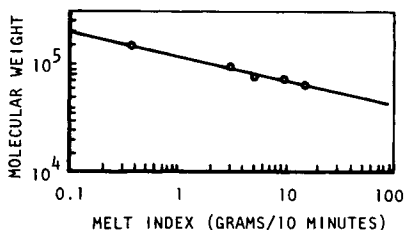


Fig. 5. Melt-index correlation with molecular weight.

Effect of Pressure on Polymer Yield

The effect of pressure on the polymer yield of the process was studied in a series of experimental runs. The pressure was varied over three levels (3.5, 5.0, and 7.0 psi, or 24, 34, and 48 kPa), and several runs were made at each level to establish an average yield for each run. All runs were made at 35°C. The results, plotted in Figure 6, show that the yield appears to be a linear function of the pressure. The curve does not pass through the origin because of several factors, one being the expression of ethylene pressure in psig rather than absolute pressure. The curve was developed from average yields and the relationship between the subject variables may not be as explicit as indicated, but from a practical view the curve allows some prediction of yields obtainable with the experimental setup described in this work.

Effect of Reaction Temperature on Yield and Deuterium Content

The effect of polymerization reaction temperature on the polymer yield and deuterium content was studied in a series of experimental runs where the temperature was varied from 30° to about 50°C. In all runs the ethylene-d₄ pressure was maintained at 7 psig (48 kPa), and the catalyst ratio and concentration remained constant. All reactions were run for a period of 1 hr.

The results of this study, given in Figure 7, show that the polymer yield is inversely proportional to the polymerization temperature. This result may at first seem somewhat surprising since the reaction rate or yield is expected to increase with increasing temperature. In this case, however, the inverse dependence of yield on temperature at constant pressure most likely results from a decrease in the solubility of ethylene gas in the reaction medium at elevated temperatures, thereby decreasing the level of monomer available for polymerization. The value of the specific rate constant, of course, may increase with temperature, but the

TABLE I
Molecular Weight Averages of Selected Deuterated Polyethylene Samples

Sample no.	Melt index, g/10 min	GPC			MO \bar{M}_n , g/mole
		\bar{M}_w , g/mole	\bar{M}_n , g/mole	\bar{M}_w/\bar{M}_n	
17D	5.0	75,700	19,920	3.80	22,350
20D	3.0	93,860	29,330	3.20	—
25D	0.36	143,000	38,940	3.67	40,700
29D	14.4	63,840	20,400	3.13	23,380
32D	9.4	73,450	13,723	5.36	23,380

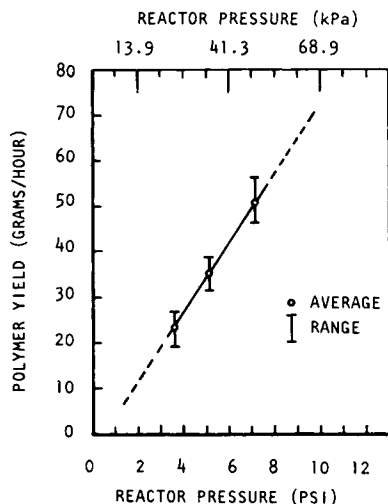


Fig. 6. Effect of pressure on polymer yield.

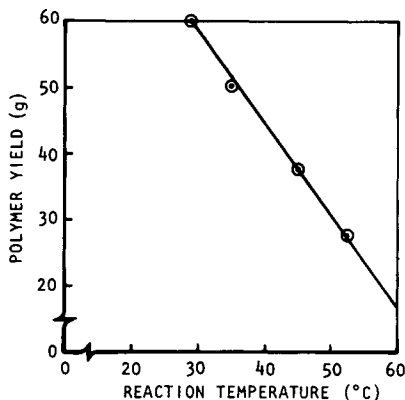


Fig. 7. Effect of temperature on polymer yield.

decrease in monomer concentration effected by the temperature increase appears to be a more sensitive factor affecting yield.

The deuterium content of the polymer appears to be inversely dependent upon the polymerization temperature as indicated by the data tabulated in Table II. No reason for this trend is apparent unless, perhaps, chain transfer with the solvent or some other reaction mechanism involving isotopic exchange becomes significant at higher temperatures. It is indeed fortunate, however, that the polymer yield and the deuterium contents are dependent upon temperature in

TABLE II
Effect of Polymerization Temperature on Polymer Deuterium Content

Run no.	26-D	27-D	28-D	29-D
Temperature, °C	30	34	44	48.5
Atomic per cent deuterium	96.4	95.7	95.7	93.2

the same manner. The choice for an optimum operating temperature is therefore obvious.

CONCLUSIONS

A direct method for preparing deuterated ethylene by reducing deuterated acetylene with chromous sulfate in a DMF/water mixture is described. This procedure gives a good yield of precursor gas of relatively high purity. The process appears to be adaptable to the production of sufficient quantities of deuterated ethylene gas for laboratory synthesis.

In addition, several reaction conditions involved in the polymerization of deuterated ethylene were investigated to characterize the effects polymerization parameters have on the polymer produced. This work resulted in the establishment of a laboratory process for synthesizing deuterated polymers having good melt flow properties.

It was found that the polymerization of perdeuterated ethylene at low pressure using a Ziegler catalyst produces a linear polymer similar to that one would expect using normal ethylene. The deuterated monomer, however, undergoes a greater degree of polymerization than does normal ethylene under the same conditions, so that lower catalyst ratios are required to produce deuterated polymer with good flow properties. The indication that the deuterium content of the polymer decreases with increasing temperature essentially dictates that the process operating temperature must be held around room temperature. A lower operating temperature also enhances polymer production since an inverse dependence of yield on temperature was shown.

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