Poly-1-Hexene, Synthesis and Solubililty in Dense Carbon Dioxide

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Synopsis

Several poly-1-hexene samples were prepared using different Ziegler-Natta catalysts, and their solubilities in dense carbon dioxide (CO_2) were studied. Despite the varied molecular weight distributions (MWD) in the polymers, a surprising correlation was found between intrinsic viscosity and dense CO_2 solubility. Due to the ability of dense CO_2 to extract low-molecular weight fractions preferentially, it is recommended that narrow MWD polymers be used, as far as possible, for dense CO_2 solubility determinations.

INTRODUCTION

Water-soluble polymers, such as hydrolyzed polyacrylamide and xanthan, are often applied as mobility-control agents in enhanced oil recovery (EOR) operations where water is used as the displacing fluid.[1,2] A small amount of such a polymeric additive increases the viscosity of water to match that of the oil being displaced. This addition decreases the mobility ratio (the ratio of the mobility* of displacing fluid to that of the displaced) and culminates in incremental recovery of trapped oil from porous reservoir rocks.

In another EOR technique (carbon dioxide flooding), however, where dense CO_2 (in either liquid or supercritical state) is used as the displacing fluid, parallel mobility-control agents are not applied due to the unavailability of materials, polymeric or otherwise, that would dissolve in and viscosify dense CO_2. For EOR applications, CO_2 is generally referred to as a dense fluid, irrespective of its subcritical or supercritical status, if the density exceeds 0.4 g/mL. The critical temperature of CO_2 is 31.04°C, and its critical pressure is 1076.1 psi. The viscosity of dense CO_2 is a function of its density. For example, at a density (ρ) of 0.8 g/mL, CO_2 viscosity is 0.075 centipoise (cp), while at $\rho = 0.6$ g/mL, the CO_2 viscosity is 0.05 cp. The prospective mobility-control agent should be capable of increasing the viscosity of dense CO_2 to 1 cp and above. Efforts are underway in this laboratory to find a suitable polymeric additive for mobility control in CO_2 EOR. In a previous paper,[3] we reported data on the solubilities in dense CO_2 of various commercially

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* Mobility, itself, is defined in petroleum engineering practice as the ratio of effective permeability of a fluid in a porous rock to the viscosity of that fluid. Thus, a mobility ratio greater than unity, involving the displacement of a viscous fluid by a less viscous one, is unfavorable since the frontal instability usually results in the growth of "viscous fingers" and early breakthrough of the displacing fluid.

available polymers. Since none of these polymers was soluble enough to viscosify dense CO_2 effectively, we have undertaken a program for the synthesis of new polymers based on the conclusions derived from previous work.[3,4] As a first step in this direction, poly-1-hexene samples were prepared using different Ziegler-Natta catalysts. The effect of variations in catalyst combination on the polymer yield, molecular weight and distribution, nature (crystallinity) of the polymer and polymer solubility in dense CO_2 was studied. The results obtained are presented here.

EXPERIMENTAL

Materials

$TiCl_4$, $AlEt_2Cl$, $VOCl_3$, $AlEt_3$, and 1-hexene, obtained from Aldrich Chemical Company, were used without further purification. Solvents were dried over $CaCl_2$ and were distilled and stored over sodium ribbon. Ultrapure (99.997%) nitrogen was passed through a commercial oxygen scavenger and P_2O_5 column before use. CO_2 used for solubility studies was $99 + \%$ pure. Methanol was of Baker analyzed grade.

POLYMERIZATION

Two polymerization procedures were used.

1. Polymerizations 1 through 4 (Table I) are referred to as "open system reactions," and were carried out in a four-necked, 100 mL round-bottomed flask equipped with a nitrogen inlet tube, thermometer, condenser with a guard tube, septum inlet adapter, magnetic stirrer, and constant temperature bath. The flask was heated to 100°C under vacuum and was cooled to room temperature under dry nitrogen; 55 mL of n-heptane were added through the septum inlet. To this was added the organometallic portion of the catalyst, followed by the transition metal compound. The catalyst was digested for 15 min, and then monomer was introduced. Dry, high-purity nitrogen was bubbled through the mixture during the course of polymerization, and at the end, the reaction was terminated by pouring the mixture into 200 mL methanol. The solid polymer was separated, and a second fraction, if any, was recovered from the evaporation of solvent–methanol mixture. The polymer was purified by dissolution in hexane and reprecipitation with methanol. It was dried at room temperature under vacuum for 48 hr.

2. Polymerization 5 (Table I), referred to as a "closed system reaction," was carried out in a closed Aldrich sure-seal bottle (120 mL) equipped with a septum. The bottle was charged with 55 mL heptane and then capped with sure-seal after bubbling dry nitrogen through the solvent for 30 min. To this were added the organometallic and transition metal compound portions of the catalyst in the same sequence as before. The catalyst was digested for 15 min, and 1-hexene was introduced. The polymerization was carried out for 21 hr, and then the reaction mixture was poured into 200 mL of methanol. The solid polymer obtained was dissolved in hexane and was reprecipitated with methanol. It was dried at room temperature under vacuum for 48 hr.

TABLE 1
Polymerization of 1-Hexene in n-Heptane at 25°C

Reaction no.	Polymer no.	Monomer (g)	Catalyst (mole)	Al:V or Al:Ti (wt basis)	Time (hr)	Polymer yield (g)	Intrinsic viscosity (dL/g) hexane, 25°C	Solubility in CO_2 (g/L) 2500 psi, 32°C
I	1	10(0.1188)	$TiCl_4$ 0.001779 $AlEt_2Cl$ 0.00238	0.85	44	4.33	0.047	9.26
II	6 2	10	$TiCl_4$ 0.001776 $AlEt_3$ 0.00251	0.85	17	3.3 .3	3.58 0.26	0.80 6.56
III	3	10	$VOCl_3$ 0.000256 $AlEt_2Cl$ 0.00294	7.99	24	0.1	1.54	3.54
IV	4	10	$VOCl_3$ 0.0002565 $AlEt_3$ 0.0031	7.96	18	0.5	2.07	2.39
V	5	5	$TiCl_4$ 0.000888 $AlEt_3$ 0.00125	0.85	21	3.37	3.04	1.3

POLYMER CHARACTERIZATION

Intrinsic viscosities were measured in *n*-hexane at 25°C using a Cannon-Ubbelohde viscometer. MWDs were obtained by gel permeation chromatography (GPC). A Waters liquid chromatograph model 264 with a differential refractometer detector was used. Lichrogel PS40 and PS1 (E. Merck, Darmstadt, FRG) columns were used in series with tetrahydrofuran (THF) as the mobile phase. The flow rate was maintained at 1 mL/min, and a 50 µL polymer solution with varying concentration (individual concentrations are given in Fig. 2) was injected following filtration through a 5.0 µm filter. The chart recorder speed was 0.5 cm/min. The GPC chromatograms in Figure 2 represent the real scales.

DETERMINATION OF POLYMER SOLUBILITY IN DENSE CO_2

The detailed procedure for the solubility determination at elevated pressure has been previously described.[3,4]

RESULTS AND DISCUSSION

Table I shows the data on the polymerization conditions, polymer yield, intrinsic viscosity, and solubility in dense CO_2. The Al/V ratios ranging from 1 to 8 have been used in the copolymerization of ethylene with various 1-olefins.[5] In this work, a ratio of 8 was chosen since a ratio of 4 yielded only a negligible amount of polymer. The Al/Ti ratio of 0.85, however, was found to be the most effective for 1-hexene polymerization. This ratio produced better yields and higher molecular weight polymers compared to a ratio of 2.5, which has been widely used for ethylene and propylene polymerizations. A catalyst concentration of 4% based on monomer weight was found to be ideal. Polymerizations which were carried out in the open system generally gave lower yields compared to the closed system polymerization. The apparent reason for this was the loss of monomer from open system reactions caused by the continuous flow of nitrogen.

The solubility parameter of dense CO_2 at test conditions is approximately 6 hildebrand units. *n*-Pentane and *n*-hexane, with solubility parameters of 7 and 7.3 hildebrands, respectively, were found to be the most suitable screening solvents at atmospheric conditions. The poly-1-hexene samples were rubbery (I and IIb were viscous liquids) and completely dissolved in *n*-pentane and *n*-hexane. This suggests that the different catalysts used produced only amorphous polymers. Diethylether extraction, however, gave only a negligible amount of ether-soluble fraction.

n-Hexane was the chosen solvent for intrinsic viscosity measurements as it closely simulated dense CO_2 under atmospheric conditions and was also more suitable to work with than *n*-pentane. Figure 1 shows the plot of intrinsic viscosity vs. dense CO_2 solubility in poly-1-hexenes. It reflects a clear trend in decreasing solubility with increase in viscosity. The GPC curves showing MWD in all six polymer samples are presented in Figure 2. Polymers 1 and 2 show wide MWD with large amounts of low-molecular weight fractions. With the preferential extraction of such fractions, higher
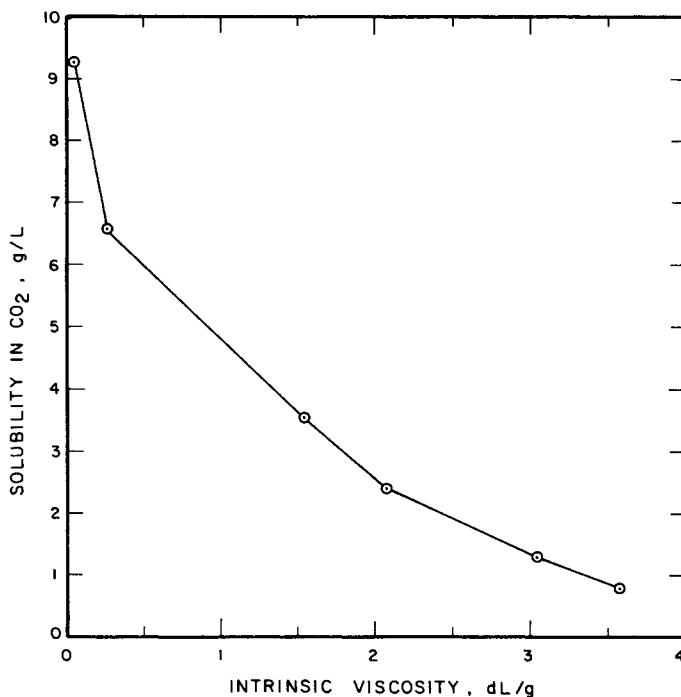
Fig. 1. Correlation between dense CO_2 solubility and intrinsic viscosity in poly-1-hexene.

solubility values may have resulted in these two cases. A closer look at Figure 2 and the data in Table I reveals that the solubilities of polymers 3–6 appear to be approximately proportional to the amount of low-molecular weight fractions present in the samples. The GPC data indicate the influence exerted by MWD of the sample on the solubility in dense CO_2. These observations also imply the need for narrow MWD polymers for dense CO_2 solubility measurements.

The poly-1-hexenes used for solubility measurements are likely to have different microstructures as these were prepared with various catalyst combinations. The effect of these microstructure differences on the solubility in dense CO_2 was not studied for two reasons. First, narrow MWD samples with comparable molecular weights could not be obtained from the various catalyst combinations used. Secondly, we considered our sample screening technique (of n-pentane solubility) to be adequate for the purpose of dense CO_2 solubility determinations.

In conclusion, amorphous poly-1-hexene samples of different intrinsic viscosities were synthesized using various Ziegler-Natta catalysts, and their solubility in dense CO_2 was studied. The influence of polymer MWD on dense CO_2 solubility measurements was found to be pronounced. Despite such an influence, wide molecular weight distribution samples of poly-1-hexene showed surprising correlation between intrinsic viscosity and dense CO_2 solubility.
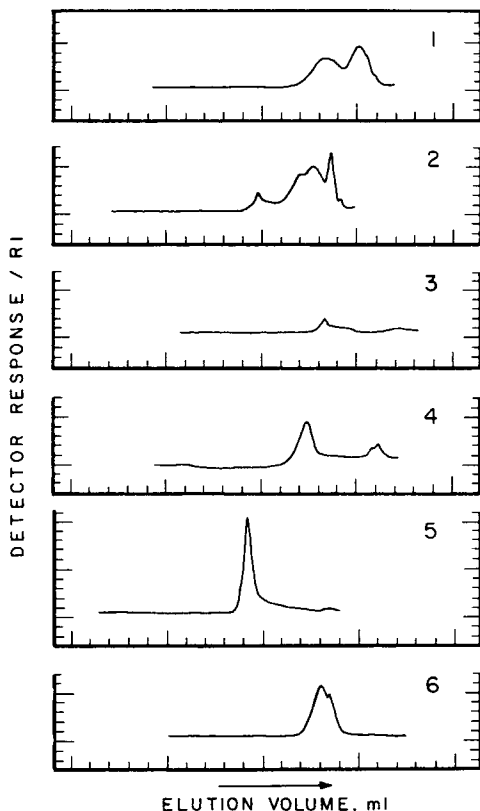
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Fig. 2. GPC chromatograms of poly-1-hexene samples in tetrahydrofuran at 25°C; polymer concentrations (g/100 ml) used were (1) 0.961, (2) 1.043, (3) 0.158, (4) 0.544, (5) 0.608, and (6) 0.567; chromatograms begin at injection point, and each division on x axis corresponds to 1 mL.

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