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Transition Metal Catalyzed Polymerization of Butadiene in Supercritical CO_2

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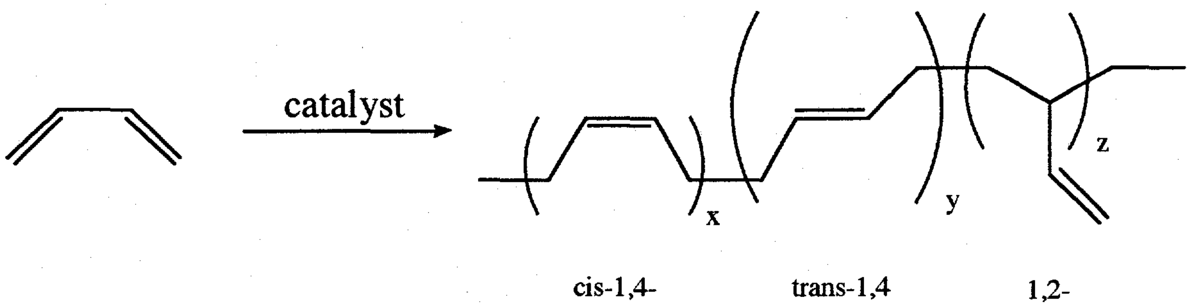
Introduction

A class of Ni(II) catalysts first synthesized by Dawans[1] and subsequently studied by Dawans and Tessyie[2], Taube[3] and others has been shown to stereoselectively catalyze the 1,4-polymerization of butadiene. The bottom figure shows the possible stereochemistries for individual butadiene units in polybutadiene.



The cis/trans ratios for polybutadiene observed using the polymerization catalyst $[(\pi\text{-allyl})Ni(CF_3CO_2)]_2$ **1** are solvent dependent. For example, polymerization of 1,3-butadiene with **1** in toluene at 25 C yielded 99% 1,4 linkages with a cis/trans ratio of 59/40 whereas reaction in heptane under similar conditions at 55 C resulted in 99% 1,4-linkages with a cis/trans ratio of 94/5[4]. In neat 1,3-butadiene at 55 C, a cis-trans ratio of 96/4 was reported. Although the reasons for the large difference in product stereochemistry for the reactions in toluene vs. heptane using **1** were unclear, we were intrigued that such a large change in the product stereochemistry could be effected by using reaction solvents of different polarities.

We have been investigating the use of supercritical CO_2 as an environmentally benign replacement solvent for conventional hydrocarbon and halocarbon solvents for a variety of chemical transformations. Above 31 C, CO2 enters a supercritical phase, where its physical

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[1] Dawans, F., Belgian Patent No. 719.790, (1969). Bourdauducq, P.; Dawans, F. J. Poly Sci: Pt A-1 (1972) 10, 2527.

[2] Marechal, J. C.; Dawans, F.; Teyssie, Ph. J. Poly Sci.: Pt A-1 (1970) 8, 1993. Dawans, F.; Marechal, J. C.; Teyssie, Ph. J. Organomet. Chem. (1971) 21, 259. Durand, J. P; Dawans, F.; Teyssie, Ph. J. Poly. Sci.: Pt A-1 (1970) 8, 979.

[3] Taube, R.; Wache, S. J. Organomet. Chem. (1992) 428, 431. Taube, R.; Schmidt, U.; Gehrke, J.P.; Bohme, P.; Langlotz, J.; Wache, S. Makromol. Chem., Macromol. Symp. (1993) 66, 245.

[4] Dawans, F., Belgian Patent No. 719.790, (1969). Taube, R.; Schmidt, U.; Gehrke, J.P.; Bohme, P.; Langlotz, J.; Wache, S. Makromol. Chem., Macromol. Symp. (1993) 66, 245.

properties are both liquid-like and gas-like. Importantly, the solvent properties such as dielectric constant for supercritical fluids can be varied by changing the pressure of the fluid.

In this report, we present results of an investigation of the polymerization of 1,3-butadiene using **1** in supercritical CO_2. We conducted 1,3-butadiene polymerizations in CO_2 to determine whether or not we could systematically and predictably adjust the regiochemistry/stereochemistry of the polybutadiene product by varying the solution properties at different pressures. We also mention experiments with Co catalysts that are known to give 1,2-syndiotactic polybutadiene, and with a Pd catalyst system that is known to copolymerize olefins with CO to give perfectly alternating copolymers.

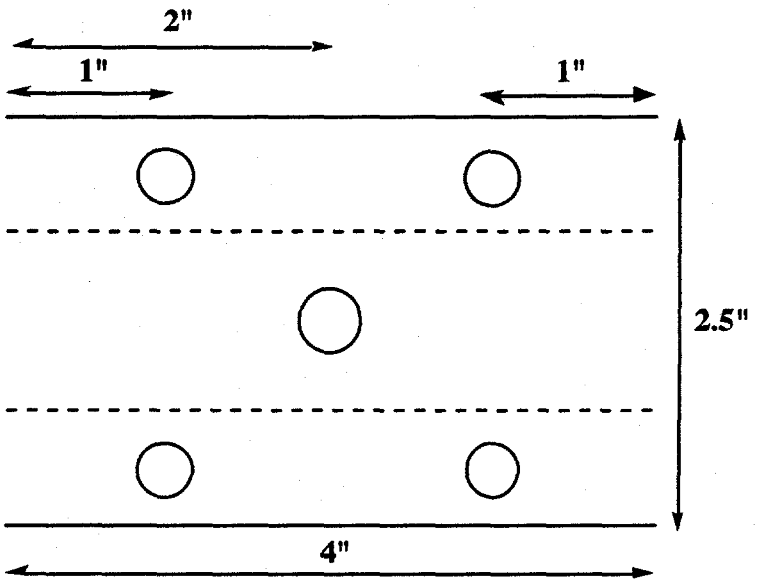
Experimental Hardware

The high pressures necessary to work with liquid liquid phase and supercritical phase CO2 solvent required the design and fabrication of metal reaction cells and a means to introduce the CO2 and pressurize the cell and heat the contents. The following drawings were used in the fabrication of the cell. Also is a schematic of the manifold constructed for these experiments.

HIGH PRESSURE 316-SS CELL

Sam Borkowky (a modified Dave Morgenstern Model)

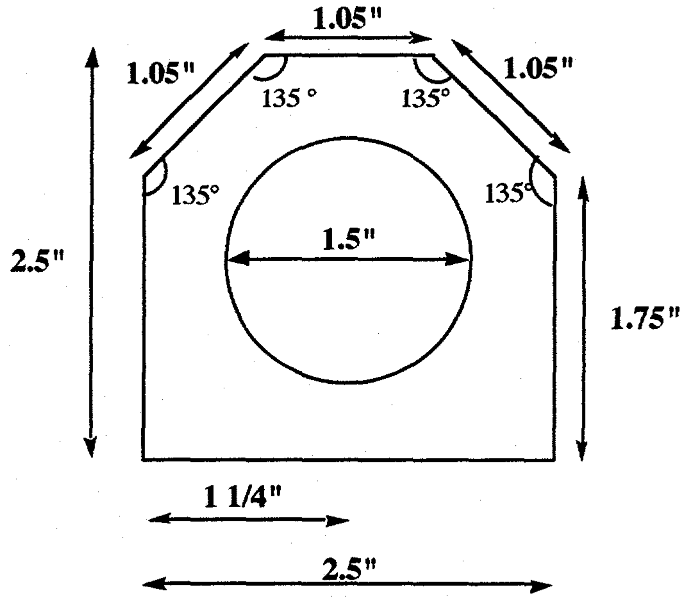
TOP VIEW



NOTES:
-316 SS
-All holes are 1/4" NPT
-All 1/4" holes are tapered
-center the holes
-Tolerance on length of cell: 1/8"
-Tolerance on hole distances: 0.01"

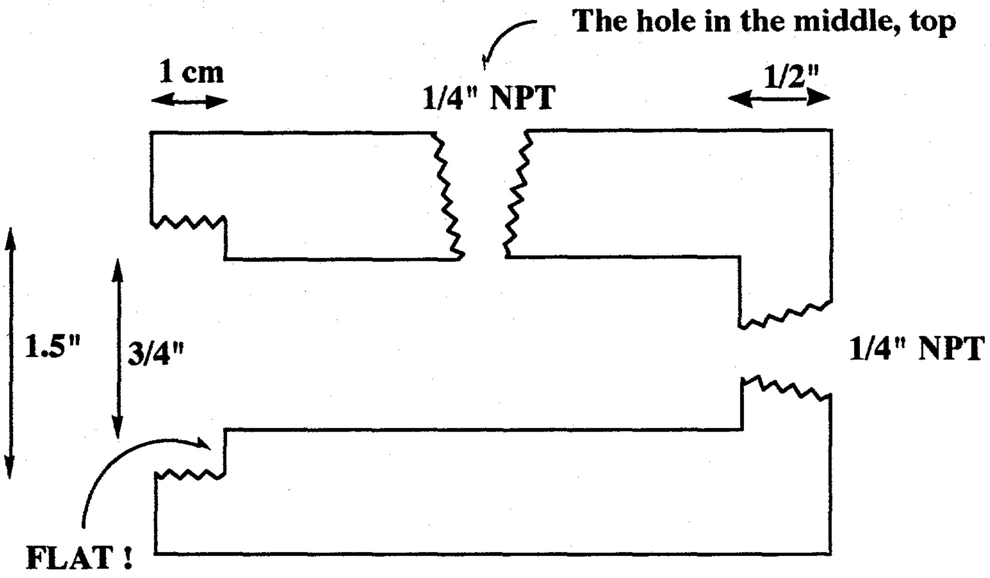
END VIEW

(window side)



NOTES:
-Center the holes
-Tolerances:
for the hole: 0.005"
For the length of the sides: 0.05 "
For the angles, 2 deg
Not critical that the 1.05" sides be perfectly flat

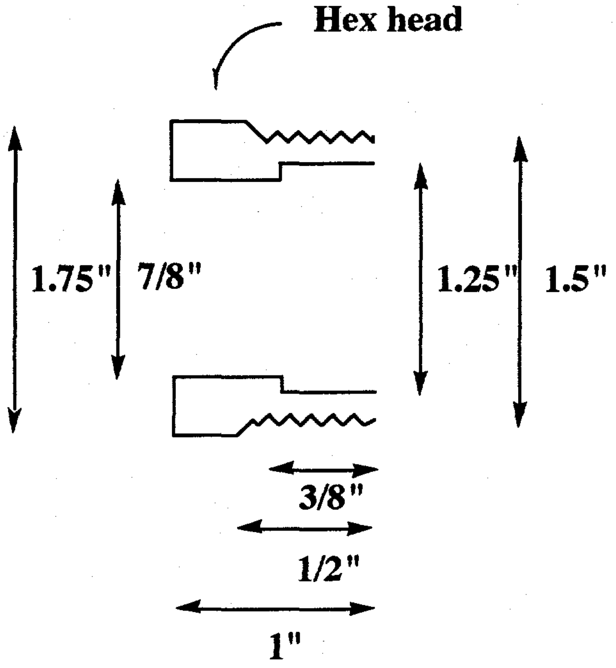
SIDE VIEW CUTAWAY



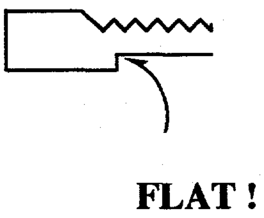
NOTES:
-316 SS
-Tolerances:
For the threaded hole on left: 0.005"
-Thread at discretion of machinist as long as it fits the gland on the next page.

HIGH PRESSURE CELL GLAND

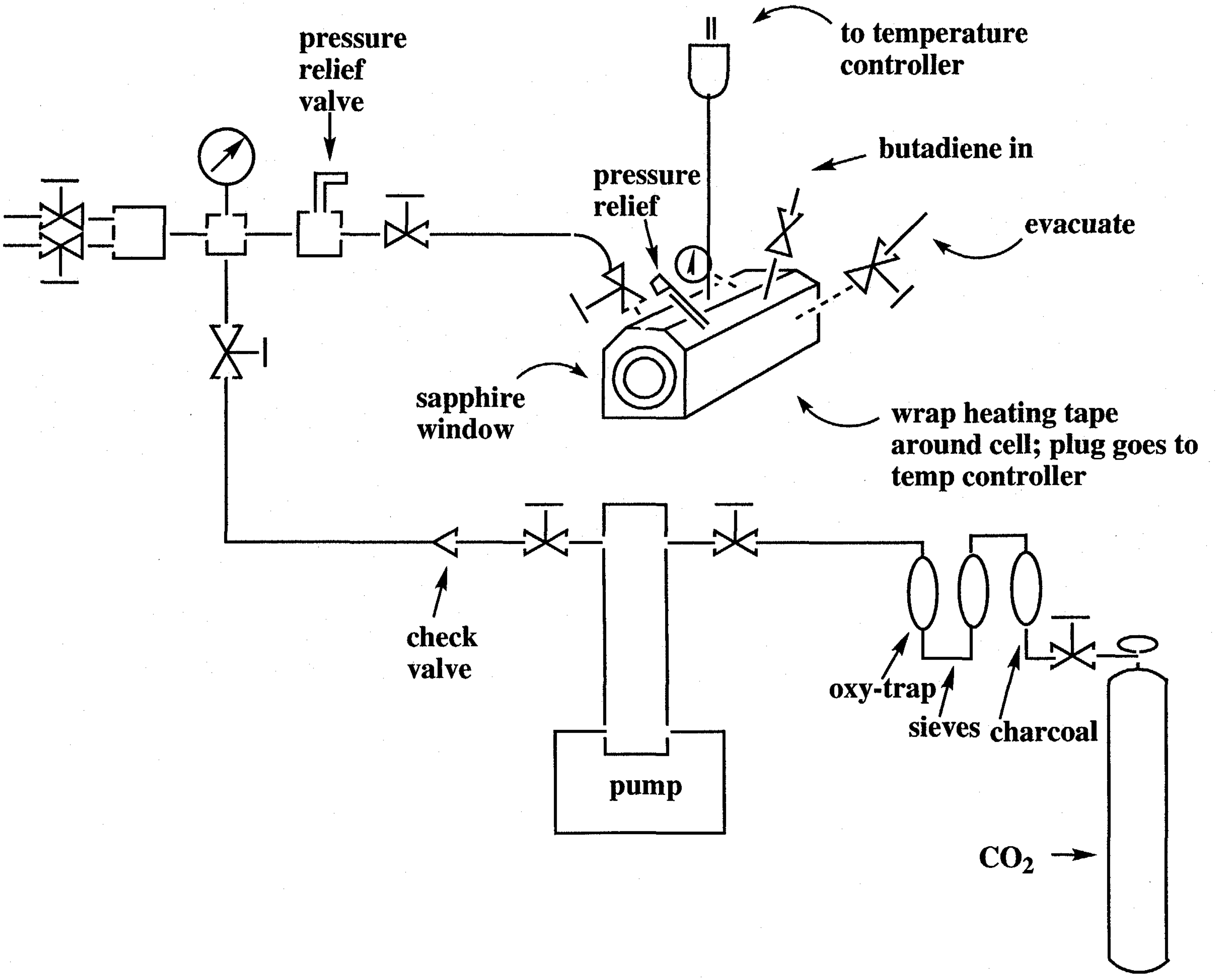
(Copied from David Morgenstern)



NOTES:
-316 SS
-Tolerances: 0.005".
-The thread of the gland is at the discretion of the machinist, as long as it fits the mating hole on the cell body on the left side of the side view cutaway



Schematic: Solvent, Pump, Manifold, View Cell



The schematic of the experimental apparatus shows a high purity CO2 tank connected to a series of traps which remove organics, residual water, and oxygen. This is connected to a pump and then to a high pressure stainless steel manifold. The high pressure cell is connected to the manifold via stainless steel tubing. Connections are made either with HIP fittings or swagelock. Fittings on the manifold are rated to at least 10,000 psi.

Experimental Procedure

Catalyst **1** was synthesized via a procedure by Dawans[5] and stored under N_2 in a glove box. For a typical polymerization, **1** was weighed into an ampoule which was flame sealed under vacuum. The ampoule and a stir bar were placed into a high pressure SS reaction vessel equipped with a sapphire viewing window, a pressure gauge, a pressure release valve, thermocouple, and inlet and outlet valves. Heating tape was wrapped around the cell and the cell was weighed. An alumina column was connected to the cell, after which the cell and column were evacuated. Dry butadiene (sieves) was then either passed through the alumina to remove the inhibitor and transferred as a liquid to the cell, or was condensed from the gas phase into the cell. The cell was reweighed to obtain the weight of butadiene by difference and the apparatus was heated to the desired temperature. CO_2 was then added, and at a pressure of about 800 psi, the ampoule imploded releasing the catalyst. The cell was then filled with CO_2 to the desired pressure and stirred. Temperature equilibration of the reaction mixture was rapid (< 1 min). After an apppropriate time, heating was stopped and the cell was cooled to ambient T. The volatiles were vented and the cell was reweighed to obtain a yield. The polybutadiene product was analyzed via both NMR and IR spectroscopy.

For experiments in conventional solvents, a modified procedure was employed where butadiene was first added to a previously dried and evacuated cell and a saturated solution of the catalyst in the appropriate reaction solvent was added to the cell via syringe through a septum attached to the valve on the cell.

All reactions were run in batch mode as described in the procedure above. Since the product was difficult to remove, cells were completely dismantled for cleaning for each run. Cells were cleaned with acetone, Alconox and water, and rinsed with distilled water prior to reassembly. For all of the above reactions, the catalyst was never completely dissolved and it is difficult to estimate how much was dissolved, however it was clear that most of the catalyst remained undissolved. The ampoule containing the catalyst did not break in a predictable fashion, and if the major portion of the body remained intact with the catalyst inside, the polymer grew inside the ampoule and was completely insoluble (these experiments were of no value). As polymer was

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[5] Dawans, F., Belgian Patent No. 719.790, (1969)

formed, it was visible in the cell by viewing through the sapphire window. Runs were allowed to run for at least a day, as there was no polymer visible for reaction times of just a few hours.

Results and Discussion

The following table summarizes relevant data for the polymerization of butadiene with **1**. In addition to experiments in CO2 at various pressures, we repeated experiments in conventional solvents for comparison with literature data. The results we obtained in toluene and hexane (entries 2 and 3 in the following table) were in accord with the literature.

entry	solvent	C_4H_8/Ni	pressure	temp C	time	yield	% cis	% trans
1	neat			55			68	32
2	toluene	860		55	48h		69	31
3	heptane	1200		55	44h	85%	93	7
4	CO_2	790	1100	55	54h	76%	77	23
5	CO_2	725	2000	55	48h	78%	85	15
6	CO_2	800	3000	55	45h	75%	83	17

The cis-trans ratios were calculated from 13C NMR[6] spectra of the soluble product fraction (the uncrosslinked fraction). As an example, the 13C spectrum (chloroform-d, 3 sec delay, 75 MHz for 13C, 55C, resealable Young tube) for the product of run 4 is shown. The aliphatic peaks at 27.2 ppm (cis-1,4) and 32.6 ppm (trans-1,4) were integrated to determine the cis/trans ratio.

The IR of cis and trans 1,4- polybutadiene and 1,2-polybutadiene is well known[7]. We attempted IR analysis of the insoluble crosslinked products obtained from these reactions but the interpretation was complicated due to interfering peaks.

The data for run 4 as compared to runs 5 and 6 suggest that there is a small effect on the stereochemistry as pressure is changed. The cis/trans ratio increases from 77/23 at 1000 psi to 83/17 to 3000 psi. In addition to the small change in stereoselectivity, we discovered that the amount of insoluble crosslinked product increased with increasing pressure. Experimentally, although polymerizations at pressures up to about 5000 psi were conducted, we discovered that we were limited pressures not exceeding 3000 psi since we were unable to recover enough soluble product at higher pressures for NMR analysis. In addition, in my hands, cell leakage was also a problem at higher pressures.

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[6] Bovey, F.A.; Jelinske, L. W. Chain Structure and Conformation of Macromolecules, Academic Press, 1982.

[7] Bovey, F.A.; Jelinske, L. W. Chain Structure and Conformation of Macromolecules, Academic Press, 1982.

Obs Freq	75.4664000
SW +/-	8500.0
oboffset	126400.0000
RCVR gain	1600
dcplFreq	300.1345000
irrfreq	4500.0000
DEC Attn	115
temp K	300
No. Scans	5000
No. Points	32768
Last Delay	3.00e+01
Line Brdng	1.00
Nucleus	C13
Sequence	1Pulse carbon
Filename	EXP37 SB repeat
Acq. Time	1.93e+00
Scale	19
Amplitude	0.70

mostly soluble

6/8/95

Expt 37

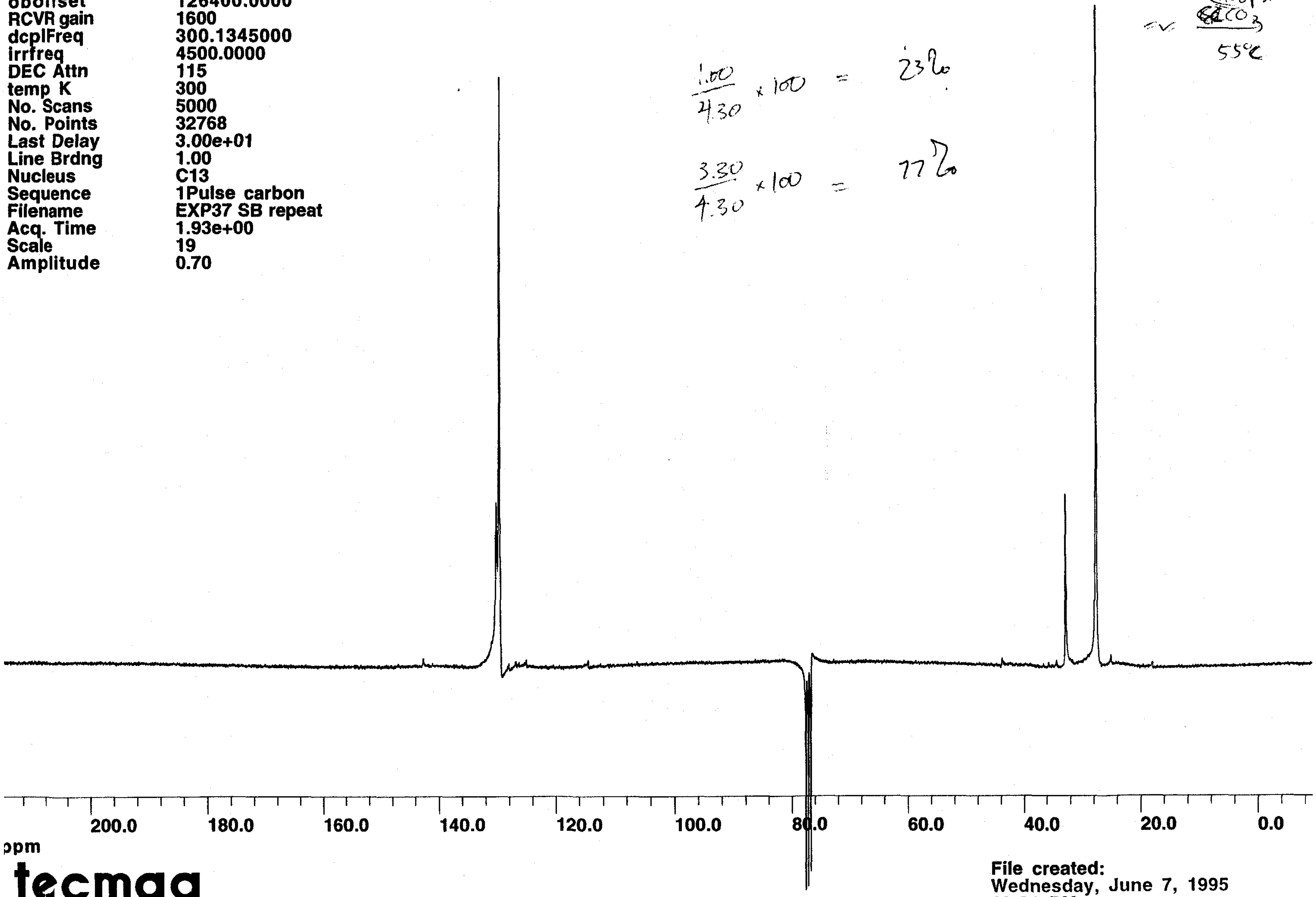
(1100psi)

scCO$_2$ ✓

55°C

$\frac{1.00}{4.30} \times 100 = 23\%$

$\frac{3.30}{4.30} \times 100 = 77\%$



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Additional Experiments

The polymerization of butadiene to 1,2-syndiotactic polybutadiene using a variety of cobalt catalysts has been reported by Ashitaka[8] and Porri[9]. The Ashitaka catalyst mixtures were complex and consisted of a cobalt salt such as Co(acac)3, an alkylaluminum (such as Al(ibu)3), CS2, and a small amount of water. Several attempts at polymerizing butadiene using Ashitaka catalyst mixtures in CO2 afforded no polymer product.

We synthesized (η3-C8H13)(C4H6)Co **2** according to the Porri procedure. This catalyst was difficult to handle as it crystallized when cooled to dry ice/acetone temperatures, but oiled when warmed. For a butadiene polymerization in CH2Cl2 using **2**, we were able to obtain a white solid product which we assumed was a polymer product. Attempts to polymerize butadiene in CO2 with **2** were unsuccessful.

The low-pressure polymerization of olefins and CO to give perfectely alternating copolymers under is as area of recent interest.[10] A copolymer of this type has been obtained in CO2 solvent.[11] Some of us have reported the alternating copolymerization of hexadiene and CO with a complex SHELL catalyst mixture (palladium acetate, nickel perchlorate hexahydrate, napthaquinono) in chloroform.[12] For comparison purposes, we attempted to polymerize hexadiene with CO using the SHELL catalyst mixture in CO2 solvent but were unable to recover polymer product.

Conclusions

Although we were unsuccessful in obtaining polybutadiene products with a selection of cobalt catalysts. we have successfully polymerized butadiene to polybutadiene with nickel catalyst [(π-allyl)Ni(CF_3CO_2)]$_2$ **1** in CO2. The polymerization of butadiene with **1** in CO2 gives a highly cis-1,4 polymer, and the cis/trans ratio may be affected slightly with reaction pressure. There is a pressure effect on the percent of insoluble crosslinked polybutadiene product, where the fraction increases with increasing pressure. We have not quantified the amounts of soluble and insoluble product, and do not understand the origin of this effect.

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[8] Ashitaka, H.; Ishikawa, H.; Ueno, H. J. Poly Sci.: Poly. Chem Ed. (1983), 21, 1853. Ashitaka, H.; Jinda, K., Ueno, H. J. Poly Sci.: Poly Chem Ed. (1983) 21, 1951. Ashitaka, H.; Inaishi, K.; Ueno, H. J. Poly Sci.: Poly Chem. Ed. (1983) 21, 1973. Ashitaka, H.; Jinda, K.; Ueno, H. J. Poly Sci.: Poly Chem Ed. (1983) 21, 1989.

[9] Ricci, G.; Italia, S.; Porri, L. Poly. Comm. (1988) 29, 305.

[10] Sen, A.; Lai, T-W., J. Am. Chem. Soc. 1982, 104, 3520. Drent, E., van Broekhoven, J. A. M.; Doyle, M. J. J. Organomet. Chem. 1991, 417, 235.

[11] Brookhart, M.; Rix, F. R.; DeSimone, J. M.; Barborak, J. C. J. Am. Chem. Soc. 1992, 114, 5894.

[12] Borkowsky, S. L.; Waymouth, R.M. Macromolecules submitted 1996.