Polymer Bulletin 32, 537–543 (1994)

Polymer Bulletin

Carbocationic polymerizations in supercritical carbon dioxide

I. Exploratory experiments with isobutylene

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Abstract

The first carbocationic polymerization of isobutylene (IB) in supercritical carbon dioxide ($SC{\cdot}CO_2$) has been accomplished. It was demonstrated that in CO_2 at 32.5 °C and ~120 bar the 2-chloro-2,4,4-trimethyl-pentane (TMPCl)/$SnCl_4$ and TMPCl/$TiCl_4$ initiating systems lead to ~30% IB conversion, and gave polyisobutylenes (PIB) with M_n~2000 and M_w/M_n~2.0. This is the highest temperature IB was ever polymerized to reasonably high molecular weight products. Polymerizations at 32.5 °C under similar but conventional (non-living) conditions in the absence of $SC{\cdot}CO_2$ would yield only very low molecular weight oligomers (~tetramers). The structure of the PIBs obtained in $SC{\cdot}CO_2$ is virtually identical to those obtained at much lower temperatures in conventional liquid-phase systems indicating the presence of chain transfer to monomer in both systems. In contrast to TMPCl initiated polymerizations, the 1,3-bis-(2-hydroxy-2-propyl)-5-tert-butylbenzene (HPBB) initiator in conjunction with BCl_3 and $SnCl_4$ yields only oligomers (M_n~500) in $SC{\cdot}CO_2$.

I. Introduction

In the course of our fundamental studies on carbocationic polymerizations ($C^{\oplus}Pzn$) we became interested in exploring the possibility of effecting $C^{\oplus}Pzn$ in $SC{\cdot}CO_2$. Incentives for this research came from our desire to find a new inexpensive, environmentally harmless solvent for $C^{\oplus}Pzn$ (these polymerizations are usually carried out in toxic chlorinated hydrocarbons, i.e., CH_3Cl, CH_2Cl_2) and to study $C^{\oplus}Pzn$ under heretofore unexplored conditions. Our exhaustive manual and computer-aided literature and patent search, including data-bases such as RAPRA, STN International, and CAS, failed to identify a single reference concerning $C^{\oplus}Pzn$ in $SC{\cdot}CO_2$ that is at temperatures higher than T_c = 31.1 °C, the critical temperature of CO_2.

While $SC{\cdot}CO_2$ has lately often been used as the solvent of choice for all sorts of extractions [1,2], much less experimentation was done to explore its use as a reaction medium [3-8]. Indeed very few studies have been published describing the use of $SC{\cdot}CO_2$ as a polymerization solvent, and those few that exist concern the free radical initiated polymerization of ethylene [9] styrene [10] acrylamide [11] and more recently, fluorinated acrylates [12].

Dearth of research in the latter field is somewhat surprising in view of the many unique and extremely useful solvent properties of $SC{\cdot}CO_2$ [1,2]: extremely rapid diffusion and low viscosity of $SC{\cdot}CO_2$ similar to those of gases [2,13], the ease and completeness of the removal and/or recirculation of CO_2 after polymerization, the possibility of controling the density of CO_2 by regulating the pressure or temperature or both (the solvent strength often associated with density can be increased or decreased ("tuned") by varying the pressure and temperature [1,4]), the possibility of further tuning of solvent power of CO_2 by the addition of small amounts (1-5%) of conventional cosolvents (i.e., methanol, acetonitrile, benzene, etc.) [14], the fact that $SC\cdot CO_2$ is known to dissolve materials soluble in polar (methylene chloride) and nonpolar (*n*-hexane) solvents [14], environmental neutrality (the same amount of CO_2 is removed from the atmosphere and is employed, is discharged after use), and last but not least, all this for a very low cost.

$SC\cdot CO_2$ can be readily obtained by heating CO_2 to or above its critical temperature (T_c) of 31.1 °C while maintaining or exceeding its critical pressure (P_c) of 74.8 bar [14]. A number of review and other publications concern the properties and handling of $SC\cdot CO_2$ [1,11,12-14].

This series of publications will focus on $C^{\oplus}Pzn$ carried out by the use of $SC\cdot CO_2$ as the polymerization medium. The present paper concerns experimental conditions and procedures, together with a description of corrosion-proof pressure equipment developed and found useful for carrying out $C^{\oplus}Pzns$ specifically that of (IB) polymerizations induced by Friedel-Crafts acids in $SC\cdot CO_2$, and the results of representative polymerizations coinitiated by BCl_3, $TiCl_4$ and $SnCl_4$. The polymerizability of IB in $SC\cdot CO_2$ has been demonstrated.

II. Experimental Section

A. Materials

The synthesis and purification of 2-chloro-2,4,4-trimethyl-pentane (TMPCl) and 1,3-bis-(2-hydroxyl-2-propyl)-5-tert-butylbenzene (HPBB) have been described [15,18]. The source and purification of IB, BCl_3, $TiCl_4$, and CH_3Cl have been published [16, 17]. 2,6-di-tert--Butylpyridine (DtBP) and $SnCl_4$ (Aldrich) were used without further purification. CO_2 (Akron Oxygen and Supply Co.) was used as received (water content 32 ppm).

B. Polymerization equipment and procedures

Polymerizations were carried out in a 300 mL Parr Hasteloy C pressure reactor, surrounded by a flexible heating mantle, and equipped with a magnetically driven stirrer, a cooling coil, thermocouple, a gold faced inconel safety rupture disc designed for 5000 psi (~290 bar) burst pressure and two sapphire windows 180° apart. Figure 1 shows the essential elements of the reactor and the rest of the assembly used. The reactor temperature was regulated by a microprocessor-based, high precision temperature controller (Parr Co. 1670 series, ± 0.1 °C control and ± 0.001 °C reading).

Prior to experiment the reactor was purged with dry nitrogen at 110-120 °C for at least 4-5 hrs. The reactor was charged in a dry box under an atmosphere of dry nitrogen, with predetermined amounts of initiator (TMPCl or HPBB), IB, cosolvent, DtBP, and with a sealed glass ampoule (5 mL) containing the coinitiator ($SnCl_4$, BCl_3, $TiCl_4$). The ampoule was filled with the Friedel-Crafts acid or the initiating system (e.g.,TMPCl/$TiCl_4$) in the dry box under nitrogen, sealed, and stored ("aged") at -15 °C until use. TMPCl/$TiCl_4$ mixtures are deep red-orange at room temperature and turn light yellow at -15 °C. The color change is reversible. TMPCl/$SnCl_4$ systems are colorless. After charging the reactor and assembling the system, the reactor was heated to the desired temperature and pressurized with CO_2 by using an air driven gas booster (HASKEL, suction pressure 200 psi (~13 bar)).

Polymerizations were started by breaking the ampoule containing the Friedel-Crafts acid by pressurizing the reactor with CO_2. Figure 2 is a three-dimensional temperature-pressure-time profile of the first 70 minutes of a representative reaction. The three individual projections; temperature/time, pressure/time and temperature/ pressure, are combined and shown by the heavy line; the boundaries of the liquid, gaseous and $SC\cdot CO_2$ are also indicated. The vertical lines indicate the temperature/time projections. Preliminary experiments have shown that the ampoules break when the pressure reaches 25 ±5 bar (see arrow #1 on the pressure/time projection). The exact moment of the breaking of the ampoule can be heard (characteristic crushing noise) and is indicated by a sudden 6-10 °C temperature rise followed by quick decrease due to the intensive cooling (see

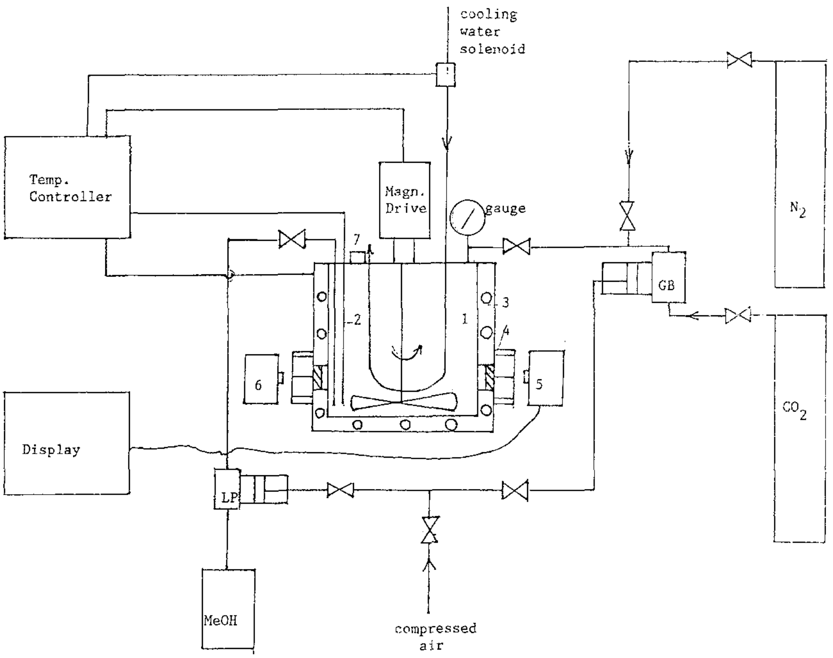

Figure 1. Equipment used for the polymerization of IB in $SCCO_2$, 1. Hasteloy C reactor, 2. Termistor, 3. Flexible heating mantle, 4. Sapphire windows, 5. Video camcorder, 6. Light source, GB = gas booster, LP = liquid pump, 7. Rupture disc.

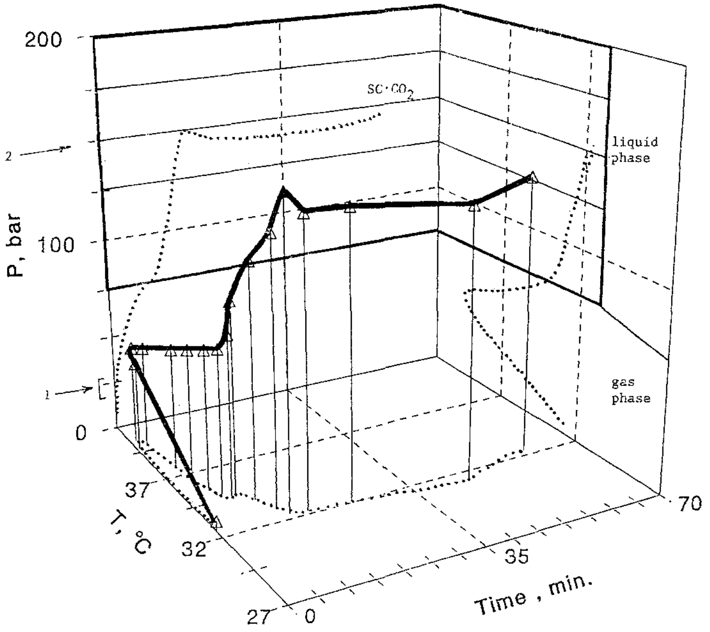

Figure 2. Temperature, pressure and time profile during the early stages of a representative polymerization.

temperature/time projection). This temperature increase is most likely due to the interaction between the Friedel-Crafts acid and CO_2, and to the excess internal energy of the compressed CO_2. The changes that occurred upon the crushing of the ampoule were observed visually and/or by videocamera. The pressure/temperature projection shows the phase behavior of the charge during pressurization of the reactor. The supercritical phase was reached directly from the gas phase without entering into the liquid region. As indicated by the temperature/pressure projection, as soon as the system became supercritical the pressure has increased sharply because of the high compressibility of the $SC{\cdot}CO_2$. After reaching the desired pressure, the CO_2 delivery was disconnected (arrow #2 on pressure/time projection).

Polymerizations were stopped by the addition of MeOH by using a high pressure liquid pump (HASKEL). During methanol addition (typically 8-10 mL) an increase of pressure (40-50 bar) and temperature was observed (6-7 °C).

After releasing the excess pressure, the PIB was dissolved in hexanes, filtered and precipitated from methanol twice and dried overnight in vacuum at 25 °C.

The M_n, and M_w/M_n were determined by GPC. The ^1H NMR spectra were obtained by the use of a 200 MHz NMR spectrometer (Varian) [18]. Details of the analytical procedures have been published [16,17].

III Results and Discussion

A. Interaction between Friedel-Crafts Acids and $SC{\cdot}CO_2$

We scoured the literature to information on interactions between Friedel-Crafts acids and $SC{\cdot}CO_2$. Surprisingly, again, our exhaustive literature and patent search (see above) revealed only one reference. Thus Tolley et al. studied by calorimetry the solvation of $TiCl_4$ and $SnCl_4$ by $SC{\cdot}CO_2$, and from a study of densities and heats of solvation concluded that the interaction between $SnCl_4$ plus $SC{\cdot}CO_2$ is stronger than that between $TiCl_4$ plus $SC{\cdot}CO_2$ [19].

The two windows in our reactor (see Figure 1) allowed to make visual and/or video-recorded observations of the changes that occurred in the reactor when the ampoule with the Friedel-Crafts acid was broken. Table 1 summarizes experimental conditions and observations. These observations may hold clues as to Friedel-Crafts acid/$SC{\cdot}CO_2$ interactions.

In regard to the two experiments (at 85 and 120 bar) with BCl_3, there was no visible change when the BCl_3-filled ampoule broke, i.e., the charge ($SC{\cdot}CO_2$ solution) remained homogeneous and colorless. According to this observation there is no (or very little)

Table 1. Visual observation of Reactor Content (see text)

Friedel-Crafts Acid	Conditions		Observations upon breaking the Friedel-Crafts acid Containing Ampoule
	T, °C	P,bar	
BCl_3	36	85	No change, reactor content remains homogeneous and transparent
		120	- " -
$TiCl_4$	36	75	Brown precipitate forms; it prevails and disappears upon MeOH addition or by decreasing the pressure
		100	- " -
$SnCl_4$	36	80	see text
		120	- " -

complexation between BCl_3 and SC•CO_2, or if complex(es) do form they are colorless and soluble in SC•CO_2.

In contrast, as soon as the ampoule with $TiCl_4$ was broken, a copious dark brown precipitate appeared which may be partially soluble in SC•CO_2. The brown precipitate (complex ?) disappeared upon CH_3OH introduction or by releasing the pressure to atmospheric.

When the ampoule containing the $SnCl_4$ broke, an opaque liquid phase formed (may be $SnCl_4$ in liquid CO_2) and was present for 5-10 mins; after this period the charge became homogeneous and transparent in ~1 min.

B. Polymerization of Isobutylene

As a result of considerable orienting experimentation, conditions were developed for the convenient polymerization of IB in SC•CO_2 by the use of Friedel-Crafts acids. Briefly, the reactor is filled with the desired reagents, SC•CO_2 is produced, and the polymerization is initiated by breaking the ampoule containing the Friedel-Crafts acid or, preferentially, the aged initiator/Friedel-Craft acid mixtures (see Experimental). Table 2 shows the specific conditions employed and results obtained in four series of polymerizations effected by the use of various Friedel-Crafts acid-based initiating systems.

Table 2. Polymerization of IB in SC•CO_2 ([TMPCl] = 0.001 mole, total volume 300 mL)

			Conditions				Results			
Exp	T	P	Friedel-Crafts acid	Aging of TMPCl/ Friedel-Crafts acids	CH_3Cl	IB	Time	Conv.*	M_n	M_w/M_n
	°C	bar	mole	days	mL	mole	hrs	%	g/mole	
Experiments with TMPCl/$TiCl_4$**										
1	36	100	0.027	20	14	0.15	3.5	~10	1000	1.5
2	32.5	125	0.027	23	13	0.15	24	~23	1200	1.9
3	32.5	125	0.027	2	15	0.36	4	~9	2000	2.3
4	32.5	125	0.027	6	15	0.36	23	~25	2200	2.2
5	32.5	122	0.036	9	15	0.36	3.6	~14	2000	2.2
6	32.5	113	0.036	13	14	0.36	22	~22	2300	2.7
Experiments with TMPCl/$SnCl_4$										
7	36	100	0.017	1	-	0.15	2	~7	1050	3.4
8	36	125	0.017	4	10	0.15	3	~30	1300	3.1
9	36	135	0.025	1	10	0.15	6	~35	1700	1.7
10	36	90	0.025	5	10	0.15	23	~30	2500	2.1
11	32.5	115	0.034	7	15	0.15	22	~30	1500	1.6
12***	32.5	85	0.020	-	10	0.15	23	<1	-	-
Experiments with HPBB/$SnCl_4$										
13	36	75	0.020	-	-	0.1	2	~9	<500	
14	36	110	0.020	-	-	0.1	3	~10	<500	
Experiments with HPBB/BCl_3										
15	36	80	0.020	-	-	0.1	1.0	~5	<500	
16	36	90	0.020	-	-	0.2	1.5	~5	<500	
17	36	75	0.020	-	-	0.2	2.5	~8	<500	

*Minimum values, minute losses due to incomplete product recovery from the reactor

**The charge also contained 8.5 x 10^{-4} mole D*t*BP

***Control experiment carried out in the absence of TMPCl

The TMPCl/TiCl$_4$ system (First series, Expts 1-6) readily induces IB polymerizations in SC•CO$_2$ (PIB forms in 3.5-4 hrs) and conversions reach 23-25% after about a day of stirring. The Mn`s increase 10-20% during this time period while the MWD do not change within what is considered to be experimental variation ($M_w/M_n$=2.0-2.5). The $M_n$`s doubled by increasing the IB concentration from 0.15 to 0.36 mole (compare Expts 1,2 with 3-6). Increasing the TiCl$_4$ concentration from 0.027 to 0.036 mole accelerated the rate of polymerization somewhat (from ~9% in 4hrs to ~14 % in 3.6 hrs, see Expts 3 and 5) but otherwise did not affect the final results.

According to ^{1}H NMR spectroscopy (to be discussed in Part II of this series) the structure of the PIB`s produced by the TMPCl/TiCl$_4$ system in SC•CO$_2$ is similar to "conventional" PIB, i.e., the chain ends contain unsaturations (largely $-CH_2-C(CH_3)=CH_2$ groups) which suggests that the molecular weight determining event is deprotonation leading to chain transfer to monomer.

Similar experiments and results have also been obtained with the TMPCl/SnCl$_4$ combination (Second Series, Expts 7-12). The beneficial effect of using a polar cosolvent, CH$_3$Cl, is seen by comparing the results obtained in Expts 7 and 8. Evidently a relatively small amount (~3 vol%) of CH$_3$Cl strongly increases the yield and M_n, and somewhat narrows the MWD. Increasing the polymerization time from 3 to 23 hrs (Expts 8-10) does not effect the conversion (30-35%) but increases the M_n from 1300 to 2500. The very low (~1%) conversion obtained in the absence of TMPCl initiator (Expt 12) indicates that the effect of moisture (the ubiquitous initiator in conventional polymerizations) is negligible under our conditions in SC•CO$_2$.

According to ^{1}H NMR spectroscopy the products contained significant quantities of $-CH_2-C(CH_3)=CH_2$ endgroups indicating chain transfer to monomer (see also above).

As shown by the data in the lower part of Table 2 (Third and Fourth Series, Expts 13-17), experiments have also been carried out with the HPBB/SnCl$_4$ and HPBB/BCl$_3$ systems under various conditions in the absence of CH$_3$Cl. These runs gave very low (5-10%) conversions and the M_n of the product remained in the oligomer range. ^{1}H NMR spectroscopy of these oligomers showed a large concentration of terminal unsaturation which is evidence for chain transfer. The low conversions and concurrent low molecular weights may be due to the very low solubility of the aromatic initiator in SC•CO$_2$ [20].

It is of interest to contemplate the differences in molecular weights obtained at the same temperature in SC•CO$_2$ and in similar conventional liquid-phase systems. We submit that IB polymerizations effected by TMPCl/TiCl$_4$ or TMPCl/SnCl$_4$ in SC•CO$_2$ in the 32.5-36 °C range yield much higher M_n`s than those obtainable with similar reagents and reagent concentrations under conventional conditions (e.g., H$_2$O/TiCl$_4$ initiating system, CH$_2$Cl$_2$ diluent). Thus a simple linear extrapolation of the best molecular weight data in the literature generated with the H$_2$O/TiCl$_4$ system in CH$_2$Cl$_2$ in the +18 to -91 °C temperature range [21] indicates that the M_n of PIB that would arise in the 32.5-36 °C range in such a conventional liquid-phase polymerization would be ~200 g/mole (trimer-tetramer range). In contrast, according to the data shown in Table 2, it is not difficult to produce PIBs with M_n=2000-2300 g/mole in the 32.5-36 °C range in SC•CO$_2$.

IV Conclusions

The polymerization of IB in SC•CO$_2$ by the use of Friedel-Crafts acid-based initiating systems has been demonstrated. Thus TMPCl/TiCl$_4$ and TMPCl/SnCl$_4$ combinations gave 25-35% conversions, and PIBs in the M_n=2000-2300 g/mole range with M_w/M_n= 2-3. In contrast to these IB polymerizations effected in SC•CO$_2$ in the 32.5-36 °C range, those carried out at about the same temperature but under conventional conditions and similar reagents in polar diluent (i.e., with TiCl$_4$ in CH$_2$Cl$_2$) and reagents concentrations, would yield molecular weights lower by an order of magnitude. The lack of effect of time on conversion and molecular weight may be due to our being close to the ceiling temperature

(T_{ceil}=50 °C) [22]. The structures of PIBs obtained in SC·CO_2 under various conditions and those prepared in conventional (non-living) condensed-phase systems, are virtually identical (the spectra and their interpretation are given in the subsequent paper of this series). According to this evidence the overall mechanism of the critical molecular weight-determining events (i.e.,initiation, propagation, chain transfer, termination) operating in both systems, are also the same.

Acknowledgement

This material is based upon work supported by the National Science Foundation under Grant CTS-93-10398.

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Accepted February 28, 1994 K