Cationic Polymerization of Vinyl and Cyclic Ethers in Supercritical and Liquid Carbon Dioxide

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Herein we report the utilization of liquid and supercritical carbon dioxide as a solvent/dispersing medium for conducting cationic polymerizations. Recent developments from our laboratories have shown that supercritical CO_2 is an excellent alternative to conventional aqueous and organic reaction media for both homogeneous[1-3] and heterogeneous[4-6] free-radical polymerizations. Specifically, supercritical carbon dioxide exhibits many solvent properties which make it an excellent choice as a reaction medium for polymerizations. These solvent properties, such as a large diffusion coefficient, low viscosity, and low solvent dielectric constant, are all functions of temperature and pressure and therefore can be easily and systematically controlled by adjusting reaction conditions. We suspect that the adjustable solvent power of supercritical carbon dioxide can be exploited as a method to enhance the integrity of growing carbocationic centers of propagating polymer chains.

It is well-known that the choice of solvent plays an important role in controlling the course of cationic polymerizations. Nonpolar solvents tend to suppress the formation of solvent-separated ion pairs in the propagating species, resulting in reduced activity and slower reaction rates. Polymer solubility is not a necessity for an acceptable reaction medium as many commercial cationic polymerizations are precipitation processes. Butyl rubber, a copolymer of isobutylene and a conjugated diene such as isoprene, is produced commercially in chloromethane at very low temperatures as a slurry polymerization.[7]

Previous work utilizing CO_2 as a reaction medium for cationic polymerizations is scarce. In 1960, Biddulph and Plesch reported the cationic polymerization of isobutylene in liquid carbon dioxide using either aluminum bromide or titanium tetrachloride as the catalyst at −50 °C and low pressures (>16 bar).[8] Their work demonstrated that liquid CO_2 could be used as a reaction medium for cationic polymerizations. In 1970, Fukui et al. reported in the patent literature an example of the cationic polymerization of ethyl vinyl ether in liquid CO_2 at room temperature. Molecular weights and spectroscopic analysis of the polymer product were not reported.[9]

Carbocationic polymerizations are an area of growing interest in polymer synthesis. Many types of monomers such as isobutylene, vinyl ethers, cyclic ethers, *N*-vinylcarbazole, *p*-alkoxystyrenes, oxiranes, and formaldehyde can be polymerized through cationic routes. For many years carbocationic polymerizations were believed to be uncontrollable processes dominated by chain transfer and termination due to the inherent instability of the propagating carbenium ion. However, since 1984 when Higashimura reported the first living cationic polymerization of isobutyl vinyl ether,[10] much work has been done in selecting the proper counteranion, temperature, and solvent conditions to allow for the living polymerization of many different monomer systems. Much of the work focused on the selection of a counteranion which was nucleophilic enough to stabilize the cation but still active enough to permit propagation.[11-13] In 1989, Higashimura[14] reported a new cationic polymerization system based on the use of a weak nucleophile and a Lewis base deactivator for the living polymerization of vinyl ethers at higher temperatures. This system employed ethylaluminum dichloride coupled with the adduct of acetic acid and isobutyl vinyl ether (IBVE) (**1**) as the initiator and Lewis base deactivators such as ethyl acetate. Cyclic ethers such as oxetanes or tetrahydrofuran may also be polymerized cationically via a ring-opening mechanism. Initiation occurs by cationation of the oxygen, and propagation proceeds through subsequent nucleophilic attack by other monomer molecules at the endocyclic α carbon in the tertiary oxonium ion. Numerous Lewis acid initiator systems are known to initiate the polymerization of these monomers.[15]

Using previously known initiating systems,[14,15] we demonstrate that vinyl ethers and oxetanes can be polymerized through cationic routes in carbon dioxide. Control experiments were conducted in conventional liquid solvents: cyclohexane and methylene chloride were used as the solvents for the polymerization of vinyl ethers and oxetanes, respectively. Polymerizations with carbon dioxide as the solvent were conducted in a high-pressure reactor[16] constructed of Hastelloy B-22. Monomer and initiator were kept separate using a Hastelloy dish located in the reactor to prevent mixing of reagents prior to addition of carbon dioxide.[18] Ethylaluminum dichloride was used in both the absence and presence of **1** to initiate the polymerization of vinyl ethers (Scheme 1), and boron trifluoride/tetrahydrofuran complex was used to initiate the polymerization of oxetanes (Scheme 2). After a predetermined time, carbon dioxide was slowly vented and the polymerizations were terminated with sodium ethoxide in the case of the vinyl ethers and aqueous sodium hydroxide in the case of the oxetanes. Polymer structures were confirmed using ^1H NMR, ^{13}C NMR, and FTIR to confirm that carbon dioxide was not incorporated into the polymer chain as has been reported for certain systems.[17] Particularly, no carbonyl stretches were seen in the IR spectra and no carbonyl signals could be discerned from ^{13}C NMR. Molar masses were determined by gel permeation chromatography using polystyrene standards.[18]

Polymerization of Vinyl Ethers. Results for polymerizations of IBVE are shown in Table 1. Polymerizations of isobutyl vinyl ether were homogeneous throughout the course of the reaction in cyclohexane. However, reactions run in carbon dioxide began homogeneous but became heterogeneous as the polymer formed and precipitated. Polymerizations of isobutyl vinyl ether carried out in the absence of initiator **1** (employing adventitious water as the initator) in both cyclohexane and carbon dioxide resulted in polymers with high molar masses and broad molecular weight distributions (MWD), as expected.[14] However, polymerization in the presence of initiator **1** yield polymers with predictable molar masses and narrower molecular weight distributions. Particularly, polymerization with **1** in cyclohexane gave a polymer with very narrow MWD and a number-average molar mass proportional to the

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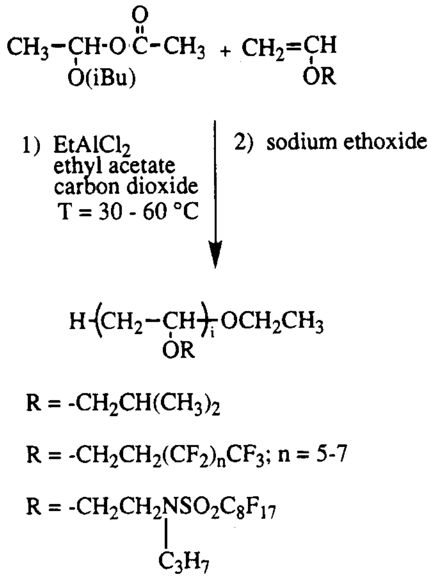
Scheme 1. Polymerization of Vinyl Ethers



Scheme 2. Polymerization of Oxetanes

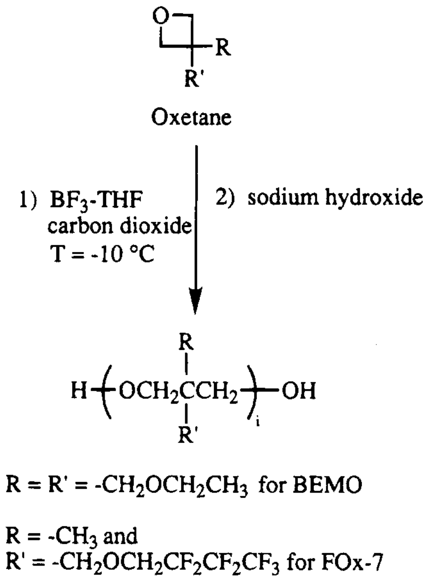


Table 1. Results for Polymerizations of IBVE[a]

solvent	initiator	temp (°C)	M_n ($\times 10^{-3}$)	MWD	yield (%)
cyclohexane	$EtAlCl_2$	40	107	1.5	80
CO_2	$EtAlCl_2$	40	152	4.0	87
cyclohexane	$1/EtAlCl_2$	40	7	1.2	44
CO_2	$1/EtAlCl_2$	40	7	1.8	91
CO_2	$1/EtAlCl_2$	40	23	3.9	87
CO_2	$1/EtAlCl_2$	60	36	9.4	92

[a] Reaction time = 12 h. CO_2 pressure = 345 bar. [Monomer] = 9.2×10^{-1} M. M_n determined by GPC using polystyrene standards.[18]

percent conversion for the targeted molar mass. Molecular weight control was maintained in carbon dioxide; however, MWD's typically broadened slightly for polymerizations in carbon dioxide, presumably due to precipitation of the polymer during the course of the reaction and continued propagation in the precipitated phase. This also would account for the increase in polydispersity with increasing molar mass. Molecular weight control in carbon dioxide was lost at temperatures above 40 °C. This phenomenon could be due to both increased rates of chain transfer to monomer at higher temperatures and a decrease in the density of carbon dioxide, resulting in faster precipitation of the polymer.

Table 2. Results for Polymerizations of BEMO[a]

solvent	initiator	temp (°C)	M_n ($\times 10^{-3}$)	MWD	yield (%)
methylene chloride	BF_3	−10	14.6	1.9	71
carbon dioxide	BF_3	−10	8.0	2.7	67
carbon dioxide	BF_3/BDO	−10	7.0	1.6	43

[a] BDO = butanediol. Reaction time = 4 h. CO_2 pressure = 290 bar. [Initiator] = 2.9×10^{-2} M. [Monomer] = 1.15 M. M_n determined by GPC using polystyrene standards.[18]

Two vinyl ethers bearing fluorinated side chains were also polymerized in carbon dioxide (see Scheme 1), using ethylaluminum dichloride in the absence of initiator **1**. The polymerizations began homogeneous and remained so throughout the course of the reactions, as expected of fluorinated polymers.[1,2] One sample of the polymer bearing the fluorinated sulfonamide side chain demonstrated a $M_n = 4.5 \times 10^3$ and a polydispersity of 1.6. The narrow molecular weight distribution for this sample suggests that the broad molar mass distribution of the poly(IBVE) made in CO_2 is due to the heterogeneous nature of the synthesis of hydrocarbon polymers in CO_2. No molecular weight data were available for the other polymer samples due to inherent solubility problems. Yields were typically around 40%.

Polymerization of Cyclic Ethers. Control polymerizations of bis(ethoxymethyl)oxetane (BEMO) were conducted in methylene chloride at −10 °C (Table 2). As with isobutyl vinyl ether in cyclohexane, the polymerization of BEMO remained homogeneous throughout the course of the reaction in methylene chloride; however, polymerizations in carbon dioxide began homogeneous and then became heterogeneous as the polymer precipitated. Yields and molecular weight control were similar between polymers made in methylene chloride and carbon dioxide, but molecular weight distributions were slightly broader for polymers synthesized in carbon dioxide. Again this may be attributed to the heterogeneous nature of the reactions conducted in carbon dioxide versus methylene chloride. Polymer structures were again confirmed by ^1H NMR and FTIR.

A fluorinated oxetane, 3-methyl-3′-[(1,1-dihydroheptafluorobutoxy)methyl]oxetane (FOx-7), was studied as a possible candidate for homogeneous cationic polymerizations in carbon dioxide. A control experiment of the polymerization using Freon-113 as the solvent and boron trifluoride tetrahydrofuranate with trifluoroethanol as the initiator at −10 °C yielded a polymer with a M_n of 3.9×10^4 and a MWD of 1.7 in 70% yield. Polymerization of FOx-7 in carbon dioxide at 0 °C and 289 bar resulted in a polymer with a M_n of 2.0×10^4 and a MWD of 2.0 in 77% yield. The polymer was very soluble in Freon-113 and liquid carbon dioxide (remaining homogeneous throughout the polymerization), while it was partially soluble in acetone and THF and mostly insoluble in chloroform.

To summarize, we have successfully polymerized vinyl ethers and oxetanes cationically in carbon dioxide. These processes become heterogeneous using hydrocarbon vinyl ethers and oxetanes but high molar mass and high conversions can still be achieved. Homogeneous cationic polymerizations are also possible with fluorocarbon-based alkyl vinyl ether and oxetane monomers. Polymerization occurs without incorporation of carbon dioxide into the polymer backbone for the systems employed herein.

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Supplementary Material Available: Experimental methods of the polymerizations in supercritical and liquid carbon dioxide, NMR data, a figure of the Hastelloy B-22 high-pressure reactor, and tables of reaction conditions and results of polymerizations of various compounds (4 pages). Ordering information is given on any current masthead page.

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(18) See the supplemental section for further details.

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