Macromolecules **1996,** *29,* 495−496

Synthesis of Poly(2,6-dimethylphenylene oxide) in Carbon Dioxide

K. K. Kapellen, C. D. Mistele, and J. M. DeSimone*

CB #3290, Venable and Kenan Laboratories, Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599

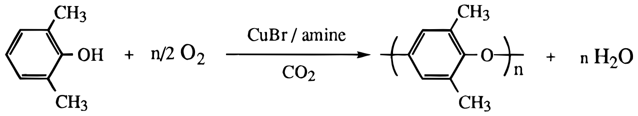
Received August 31, 1995
Revised Manuscript Received October 27, 1995

Herein we report the synthesis of poly(2,6-dimethylphenylene oxide) via oxidative coupling in a carbon dioxide reaction medium. Recently, the utilization of carbon dioxide as a medium for polymerization reactions has attracted significant interest.[1] For example, CO$_2$ has been successfully employed as a continuous phase in homogeneous free-radical polymerizations,[2−4] heterogeneous free-radical polymerizations,[5−11] cationic polymerizations,[12] and ring-opening methathesis polymerizations.[13] The advantages of carbon dioxide as a reaction medium include the ease with which the polymer can be separated from the reaction medium and the powdery form in which the polymer can be obtained. Furthermore, the density and the viscosity of carbon dioxide can be tuned over a large range due to the compressibility of CO$_2$, particularly in the supercritical phase.[3]

Poly(phenylene oxide)s are mainly synthesized via the oxidative coupling polymerization of 2,6-di- and 2,3,6-trisubstituted phenols.[14] The most common of these processes is performed using 2,6-dimethylphenol as monomer and a catalyst system which includes a copper halide, an amine, and oxygen (either neat or mixed with nitrogen or air). Oxygen is usually passed through the reaction solution during the course of the reaction.[15−19] Other catalyst systems based on cobalt or manganese have also been shown to catalyze the polymerization of phenols.[14,20,21] All of these processes are solvent intensive as they are performed in organic solvents like toluene, benzene, halogenated hydrocarbons, and dimethyl sulfoxide or in biphasic systems (toluene/water; chloroform/water) and are precipitated into a nonsolvent such as methanol to isolate the polymer.[16,17,22−25] The use of carbon dioxide as the reaction medium for the synthesis of poly(phenylene oxide)s would eliminate the need for utilizing organic solvents in the manufacture of this commercially important polymer.

Using a catalyst system based on copper bromide, an amine, and oxygen, we demonstrate the synthesis of poly(2,6-dimethylphenylene oxide) via oxidative coupling utilizing carbon dioxide as the reaction medium (Scheme 1). The reactions were performed in a 10-mL high-pressure Hasteloy reactor by adding a carbon dioxide/oxygen mixture to 2,6-dimethylphenol and copper bromide. The carbon dioxide and oxygen were completely miscible, and the polymerization was started by addition of the amine.[26] The reaction conditions (i.e., temperature, amine type, and the addition of a stabilizer) were varied systematically in order to optimize the yields and the molecular weights of the resultant poly(phenylene oxide)s.

Scheme 1. Synthesis of Poly(2,6-dimethylphenylene oxide) in CO$_2$



Poly(phenylene oxide), like most polymers, is insoluble in carbon dioxide, but it can be plasticized by CO$_2$, depressing the T_g by 30 °C at 62 bar.[27] Using the technologies developed in our laboratories for the stabilization of heterogeneous free-radical polymerizations, we postulated that the addition of an appropriate amphiphilic block copolymer would stabilize the growing polymer in the form of a colloid which could lead to higher molecular weights and yields.[8] An ideal stabilizer for the synthesis of poly(phenylene oxide) in CO$_2$ would therefore contain a CO$_2$-soluble segment and a CO$_2$-insoluble segment which is miscible with poly(phenylene oxide). Polymers which have been found to be very soluble in CO$_2$ include fluoropolymers, such as poly(1,1-dihydroperfluorooctyl acrylate) (PFOA), and siloxanes, such as poly(dimethylsiloxane) (PDMS). One polymer which is totally miscible with poly(phenylene oxide) is polystyrene; therefore block or random copolymers of styrene and 1,1-dihydroperfluorooctyl acrylate (FOA) or dimethylsiloxane were envisioned to be likely candidates for the stabilization of poly(phenylene oxide) in CO$_2$.[28]

Two different types of amines can be used for the synthesis of poly(phenylene oxide) in CO$_2$—low molar mass amines and polymeric, CO$_2$-soluble amines. Two different polymeric amines have been investigated for use in the synthesis of poly(phenylene oxide) in CO$_2$. The polymeric amines, copolymers of FOA and an amine, were themselves synthesized via homogeneous free-radical solution copolymerizations in CO$_2$ using AIBN as the initiator.[2,26] Both copolymers, poly(2-(dimethylamino)ethyl acrylate-*co*-FOA) [poly(DMEAE-*co*-FOA)] and poly(4-vinylpyridine-*co*-FOA) [poly(4VP-*co*-FOA)] are soluble in CO$_2$ because of their high fluorine content. These polymeric amines could also act as stabilizers as well to aid in the solubilization of the catalyst.

The first section in Table 1 shows the results of the reactions performed with the polymeric amines in comparison to the reactions performed with the corresponding low molar mass amines.[29] The polymeric amines did not lead to higher yields and molecular weights as expected, but they stabilized the polymer in the CO$_2$ solution, as a milky dispersion was observed during the course of the reaction. In reactions without any stabilization, the polymer precipitated and did not disperse in CO$_2$.

In an attempt to obtain better stabilization of the growing polymer in CO$_2$, surfactants based on FOA and styrene have been examined.[9] The second section of Table 1 shows the results of three reactions involving PFOA, a block copolymer of styrene and FOA, and a random copolymer of styrene and FOA as stabilizers.[30] The addition of PS-*b*-PFOA leads to a higher yield and a higher molecular weight of the product in comparison to the other reactions. Although the addition of PS-*co*-PFOA leads to higher yields, the molecular weight of the product is very low. Conversely, the molecular weight is increased by the addition of PFOA, but the yield decreases. However, block copolymers of styrene and FOA seem to be effective stabilizers for the synthesis of poly(phenylene oxide) in CO$_2$ as they increase both yield and molecular weight. The role of the PS-*b*-PFOA stabilizer concentration was also investigated. As shown in the third section of Table 1, the highest

---

* Author to whom correspondence should be addressed.

0024-9297/96/2229-0495$12.00/0

Table 1. Results for the Synthesis of Poly(phenylene oxide) in CO_2 at 345 bar for 20 h Using a Copper:Amine:Monomer Ratio of 1:22:75

amine	stabilizer	stabilizer concn (wt/vol %)	temp (°C)	M_n ($\times 10^{-3}$)	MWD	yield (%)
pyridine			40	4.1	2.3	45
VP-*co*-FOA			40	2.9	3.9	18
DMEA			40	0.9	5.1	38
DMEA-*co*-FOA			40	2.1	2.3	44
pyridine			40	6.1	1.6	67
pyridine	PFOA	2.8	40	8.7	1.6	50
pyridine	PS-*b*-PFOA	2.8	40	17.2	5.8	74
pyridine	PS-*co*-PFOA	2.8	40	3.0	2.8	83
pyridine[a]	PS-*b*-PFOA	0	40	6.1	1.6	67
pyridine[a]	PS-*b*-PFOA	0.4	40	5.8	2.4	35
pyridine[a]	PS-*b*-PFOA	2.8	40	17.2	5.8	74
pyridine[a]	PS-*b*-PFOA	4.1	40	7.1	2.8	86
DBA			25	2.8	2.6	43
DBA			40	3.4	2.5	31
DMEA-*co*-FOA			25	1.6	2.5	16
DMEA-*co*-FOA			40	2.1	2.3	44
pyridine	PS-*b*-PFOA	2.8	25	1.8	4.2	56
pyridine	PS-*b*-PFOA	2.8	40	17.2	5.8	74

[a] Cu:amine:monomer = 1:44:75.

yield was obtained with of 4.1 wt/vol %, whereas the highest molecular weight was obtained with 2.8 wt/vol % PS-*b*-PFOA.

The temperature used for the synthesis of poly(phenylene oxide) in CO_2 also had an effect on molecular weights and yields of the resultant polymer as demonstrated in the last section of Table 1. Increasing the reaction temperature from room temperature to 40 °C resulted in an increase in the molecular weights of the product, especially when PS-*b*-PFOA was added as the stabilizer. A higher yield was also obtained at higher temperatures, which was also observed in the reaction where a polymeric amine was utilized. The higher solubility of the stabilizer and polymeric amine at the higher temperature is an important factor. In conventional systems, higher temperatures increase quinone formation and thus decrease yield and molecular weight.

It is common in this type of polymerization to get competition between C−O coupling leading to polymer formation and C−C coupling leading to 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone. The quinone byproduct was present in all the polymerizations, as could be seen by the crude yellow-orange polymer, but it was removed during the workup to give an off-white, tan polymer. The workup consisted of dissolution of the polymer in toluene, filtration, and precipitation into methanol. NMR analysis showed that the methanol-soluble portion was composed of PPO oligomers and the 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone.

In summary, we have described the successful synthesis of poly(phenylene oxide) via oxidative coupling in CO_2. The reactions resulted in yields as high as 83% and molecular weights as high as 1.7×10^4 g/mol. It was found that the addition of a stabilizer facilitated the synthesis of poly(phenylene oxide) in CO_2. An effective stabilizer for this reaction was found to be a block copolymer of polystyrene and PFOA. Continuing experiments are focusing on different catalyst systems and their formation and stability in CO_2, including the use of drying agents. Purification processes involving supercritical carbon dioxide are also being investigated.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation (Presidential Fellowship, J.M.D.: 1993−1997) and from the Consortium on Polymeric Materials Synthesis and Processing in CO_2 at UNC, which is sponsored by the National Science Foundation, the Environmental Protection Agency, DuPont, Hoechst Celanese, Air Products and Chemicals, B.F. Goodrich, Eastman Chemical, Bayer, Xerox, and General Electric. We also thank Isco Corp. for the donation of a syringe pump.

Supporting Information Available: Synthetic procedures and characterization results (^{1}H-NMR, ^{13}C-NMR, DSC, TG/DTA) for PPO-25 (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Shaffer, K. A.; DeSimone, J. M. *Trends Polym. Sci.* **1995**, *3*, 146−153.
(2) DeSimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science* **1992**, *257*, 945−947.
(3) Guan, Z.; Combes, J. R.; Menceloglu, Y. Z.; DeSimone, J. M. *Macromolecules* **1993**, *26*, 2663−2669.
(4) Romack, T. J.; Combes, J. R.; DeSimone, J. M. *Macromolecules* **1995**, *28*, 1724−1726.
(5) Fukui, K., et al. U.S. Patent 3 522 228, 1970.
(6) Hagiwara, M.; Mitsui, H.; Machi, S.; Kagiya, T. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 603−608.
(7) Sertage, W. G., et al. Canadian Patent 1 274 942, 1986.
(8) DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. J.; Combes, J. R. *Science* **1994**, *265*, 356−359.
(9) Guan, Z.; DeSimone, J. M. *Macromolecules* **1994**, *27*, 5527−5532.
(10) Adamsky, F. A.; Beckman, E. J. *Macromolecules* **1994**, *27*, 312−314.
(11) Romack, T. J.; Maury, E. E.; DeSimone, J. M. *Macromolecules* **1995**, *28*, 912−915.
(12) Clark, M. R.; DeSimone, J. M. *Macromolecules* **1995**, *28*, 3002−3004.
(13) Mistele, C. D.; Thorp, H. H.; DeSimone, J. M. *J. Macromol. Sci.*, in press.
(14) Aycock, D.; Abolis, V.; White, D. *Encyclopedia of Polymer Science and Engineering*; Wiley-Interscience: New York, 1988; Vol. 13, pp 1−30.
(15) Hay, A. S. *J. Polym. Sci.* **1962**, *58*, 581−591.
(16) Nakashio, S.; Nakagawa. I. U.S. Patent 3 573 257, 1971.
(17) Bennet, J. G.; Cooper, G. D. U.S. Patent 3 639 656, 1972.
(18) Cooper, G. D.; Schraga, I. U.S. Patent 4 035 357, 1977.
(19) Bennet, J. G.; Cooper, G. D. U.S. Patent 4 092 294, 1978.
(20) Olander, W. K. U.S. Patent 3 956 069, 1976.
(21) Banucci, E. G.; Olander, W. K. U.S. Patent 4 110 312, 1978.
(22) White, D. M. *Macromolecules* **1979**, *12*, 1008−1010.
(23) Hay, A. S.; Dana, D. E. *J. Polym. Sci., Polym. Chem.* **1989**, *27*, 837−880.
(24) Brandt, H., et al. U.S. Patent 4 696 996, 1987.
(25) Dautenhahn, P. C.; Lim, P. K. *Ind. Eng. Chem. Res.* **1992**, *31*, 463−469.
(26) See Supporting Information for further details.
(27) Hand, Y. P.; Lampron, S.; O'Neil, M. L. *J. Polym. Sci., Polym. Phys.* **1994**, *32*, 2549−2553.
(28) The PS−PFOA stabilizers are soluble in CO_2. Polystyrene is thermodynamically miscible with poly(phenylene oxide), so the PS segment is presumed to anchor to the growing poly(phenylene oxide) particles in the CO_2 solution.
(29) The molar masses were determined by gel permeation chromatography (GPC) in toluene using polystyrene as a standard.
(30) The molar mass/composition of PS-*b*-PFOA was 4.5×10^3 g/mol PS and 24.5×10^3 g/mol PFOA, and the random copolymer PS-*co*-PFOA consisted of 46.3% styrene and 53.7% FOA.

MA951299M