Clarification of the Introduction to the Communication "New Polymerization Methodology: Synthesis of Thiophene-Based Poly(arylene ether ketone)s"

J. M. DeSimone* and V. V. Sheares

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

Received February 11, 1993
Revised Manuscript Received March 1, 1993

Recently we reported on a new polymerization methodology which employed thienyl–phenyl ether bond formation as the polymer-forming reaction in the step-growth polymerization of bis(5-chlorothienyl-2) ketone and 4,4′-isopropylidenediphenol which has general applicability to the synthesis of *heterocyclic* poly(ether ketone)s and poly(ether sulfone)s.[1] In the Introduction to our communication, we attempted to summarize the large body of literature on the commercially available, *phenylene-based* systems in a few sentences. We stated that "Hergenrother reported that high molar mass poly(arylene ether ketone)s could only be obtained with activated dichloro monomers having a 1:1 ketone to halide ratio, such as with 1,4-bis(4-chlorobenzoyl)benzene...". Hergenrother correctly observes that bis(4-chlorophenyl) ketone (4-CPK), having only a 1:2 ketone to chlorine ratio, can indeed be polymerized to high molar mass with certain, very reactive bisphenols, namely, 9,9-bis(4-hydroxyphenyl)fluorene (9,9-HPF).[2] Our paper, however, focused on commercially available polymer systems, especially those based on 4,4′-isopropylidenediphenol (BPA). (We did not even attempt to polymerize our thiophene analog of 4-CPK with the rather esoteric bisphenol that Hergenrother cites.) Therefore, in our summation[1] of Hergenrother's work on conventional, phenylene-based systems,[2] we may have, therefore, oversimplified the reactivity of dichloro monomers, but our statements were intended to focus on polymers made using BPA.

We never stated in our communication that "(Hergenrother's) paper contained a statement that was later retracted in the same paper". Our reference footnote 11 simply stated that "...(Hergenrother) retracted the *high molar mass nature...*" of a polymer made from 4-CPK and BPA. Our footnote attempted to summarize Hergenrother's[2] text:

"The 4-CPK/9,9-HPF polymer in Table 5 was obtained in high molecular weight form (η_{inh} = 1.02 dL/g) whereas problems were encountered in preparing high molecular weight polymer from the reaction of 4-CPK and BPA. In the first attempt, a relatively high molecular weight 4-CPK/BPA polymer (η_{inh} = 0.58 dL/g, see Table 3) was obtained. In five additional attempts using monomers from the same source and identical reaction conditions, only low molecular weight polymers were obtained."

Our summary was not intended to overstate the conclusions of Hergenrother[2] but to emphasize that problems are often encountered when one tries to make a high molar mass polymer from 4-CPK and BPA. If one were to simply look at Hergenrother's Table 3,[2] one would conclude that it is straightforward to obtain a high molar mass polymer with 4-CPK and BPA since this data point is not qualified in the table as being nonreproducible. Indeed, the reviewer of our communication assumed that the polymerization of 4-CPK and BPA was straightforward and cited Hergenrother's Table 3[2] as evidence for this. This is why we added the footnote to our revision.

It could be argued that the word retracted was misleading, since it implies a change of mind about something. In fact, we thought the authors' statement about the experimental results[2] did indicate a change of mind on their part. It appears, however, from their latest communication, that seemingly positive results from only *one out of six* experiments does not warrant speculation on our part[1] and, moreover, was justifiably published[2] along with "scientifically valid" data without qualification. We disagree on both points.

From our own experience, the polymerization of 4-CPK and BPA to high molar mass polymer is not straightforward, which has also been observed by others.[3–6] It is our position that the variables that influence the reaction mechanism and kinetics of these less reactive, bishalides have not yet been fully identified and thoroughly explained. Furthermore, our recent work using time-of-flight secondary ion mass spectrometry (TOF-SIMS)[7] indicates that the nature of these problems for the *phenylene-based* systems is clearly related to side reactions from the competing $S_{RN}1$ pathway with the less reactive, dichloro monomers, as first described by Percec[8] and Mohanty.[9]

References and Notes

(1) DeSimone, J. M.; Sheares, V. V. *Macromolecules* **1992**, *25*, 4235.
(2) Hergenrother, P. M.; Jensen, B. J.; Havens, S. J. *Polymer* **1988**, *29*, 358.
(3) Atwood, T. E.; Barr, D. A.; King, T.; Newton, A. B.; Rose, J. B. *Polymer* **1977**, *18*, 359.
(4) Atwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R. J.; Rose, J. B.; Stanliland, P. A. *Polymer* **1981**, *22*, 1096.
(5) Mohanty, D. K.; McGrath, J. E. In *Advances in Polymer Synthesis*; Culbertson, B. M., McGrath, J. E., Eds.; Plenum Press: New York, 1985; Vol. 31, p 113.
(6) Mani, R. S.; Zimmerman, B.; Bhatnagar, A.; Mohanty, D. K. *Polymer* **1993**, *34*, 171.
(7) Sheares, V. V.; DeSimone, J. M., unpublished results, manuscript in preparation.
(8) Percec, V.; Clough, R. S.; Rinaldi, P. L.; Litman, V. E. *Macromolecules* **1991**, *24*, 5889.
(9) Mani, R. S.; Mohanty, D. K. *Proc. Am. Chem. Soc. (Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.)* **1991**, *65*, 247.

0024-9297/93/2226-2642$04.00/0