Comments on: "The Heat Capacity of Poly(Oxymethylene) as a Function of Crystallinity"

S. Z. D. Cheng and Bernhard Wunderlich*

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12181, USA

Summary
It is shown that the heat capacities of semicrystalline poly(oxymethylene)s (POM) measured recently by Illers and published in this journal support, rather than refute, the existence of a "rigid, amorphous fraction". The former was suggested by Illers, the latter was our proposal (Suzuki et al.).

Introduction
In a recent note, communicated to us by Dr. Illers and printed in this Journal,[1] it was suggested that new measurements of heat capacity, C_p, on 50-80% semicrystalline poly(oxymethylene) (POM) did not support a conclusion made by us after an extensive literature search,[2] some new measurements,[3,4] and calculation of solid heat capacity from vibrational spectra[5] that there exists a "rigid amorphous" fraction in semicrystalline POM.[6] The rigid amorphous part of the polymer is defined by us as being not crystalline (as measured by heat of fusion), but possessing <u>above</u> the glass transition temperature, T_g (of the "mobile amorphous" part) still a C_p indicative of the solid state (vibrational motion only, continuous to the glassy C_p below T_g). In this note we would like to point out how this discrepancy can be resolved.

Discussion
As stated also in Ref. 1, in the measured region the liquid C_p data of Dr. Illers (440-513 K, 10 measurements)[1] and ours (430-540 K, 36 measurements)[4] agree well. At 440 K the two proposed linear equations for C_p differ by +1.4%; at the other limit of experimentation, 540 K, by -0.6%. We have compared also the semicrystalline data. In Fig. 1 our data are superimposed with the data of Illers[1] (heavy lines). The deviation of our data from the Illers average is +2±2%, well within the error limit (especially if one considers that the POM's used are slightly copolymerized and different samples have been used). Furthermore, a 1.2% lower heat of fusion for the crystallinity calculation was used for the two data sets. The critical data bank[2] comparison of measurements from many laboratories on over 100 different polymers commonly shows agreement to ±3%

* To whom offprint requests should be sent

for "acceptable" data. We deal here thus with an exceptionally "good" agreement. How is it then possible to come to such different conclusions?

Dr. Illers used no further information beyond his own measurements, in fact, disregarded the available literature data[2] on 100% crystalline POM as "questionable". Straight-line extrapolations with respect to temperature and crystallinity yielded then at about 300 K a 6% lower C_p for liquid POM than in Ref. 4 and a 20% lower C_p for 100% crystalline POM than in Ref. 5 (see Fig. 4 of Ref. 1). Such errors are outside common error limits for quality thermal analysis and are in need of explanation.

As already suggested above, our data on 100% crystalline POM rest mainly on direct measurements since POM is one of the rare polymers available in close to 100% crystallinity.[2] In addition, these heat capacities are supported by a discussion of the C_p calculated from the vibrational frequency spectrum. This calculation makes use of independent IR and Raman spectra and needs only one or two heat capacity fitting parameters in a temperature range where no crystallinity-dependence exists.[5] At 300 K the C_p calculation differs from the experiment by about -5%[5]. A -20% error would need a substantial increase in vibrational frequencies, completely against all present day knowledge. Analogous calculations and measurements on seven other linear polyoxides were not only successful, but also showed that on the basis of chemical structure all polyoxide heat capacities can be predicted within ± 5%. A -20% different C_p, as suggested by Illers,[1], would make POM an exceptional polymer.

The liquid POM C_p, in turn, was not just extrapolated by us to 200 K, but compared to other linear polyoxides which have a stable liquid phase down to 200 K.[4] The combined experimental data of eight different polyoxides could be used to derive a single equation which reproduces measurements on all these polymers ranging from 200 to 630 K to within ± 3%, making the 6% different extrapolated heat capacity of Illers suspect.

Conclusion
We think it is unlikely that the extrapolations as proposed by Illers[1] are correct. The difference is five times the accepted collective error (± 5%) established for all measured polyoxides. If one, in turn, accepts the values of Refs. 2 and 4, there is a need to assume a rigid amorphous fraction to account for the heat capacity of semicrystalline POM between the glass transition and melting.
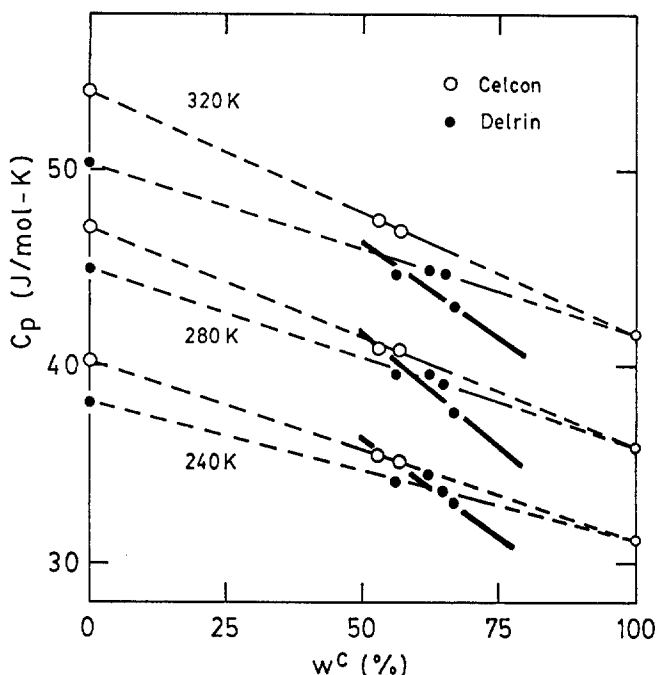
<u>Figure 1</u>   Heat capacity for semicrystalline POM as measured in Ref. 3, recommended data for 100% crystalline POM and attempted extrapolations to 0% crystallinity. The latter leads to too low heat capacity, i.e. suggests a rigid amorphous fraction. The heavy lines represent the average data of Illers at the same temperatures for a Delrin sample.

<u>References</u>

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