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Can Furfuryl Alcohol Generate Single-Crystalline Nanostructures by Thermal Polymerization?

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Furfuryl alcohol (FA) is the most important industrial furan commodity and one of the best representatives of a chemical derived from renewable resources.^[1,2] The materials obtained from its polymerization have been employed for decades as resins for metal casting, corrosion protection, polymer concretes, adhesives, etc.^[3] Apart from the obvious technological studies related to the properties and applications of these resins, the actual mechanisms leading to their complex macromolecular structure have also attracted considerable attention,^[1–3] culminating in a thorough investigation which unraveled most of their intricacies.^[4] The acid-catalyzed polymerization of FA proceeds basically through a stepwise linear growth of 2,5-furanmethylenes generated by the bimolecular condensation of the hydroxyl group with the hydrogen atom at the C5 position of the furan heterocycle. However, the ensuing oligomers are highly susceptible to losing their simple initial structure through two major mechanisms, which introduce 1) conjugated structures (and therefore deeply colored products), and 2) frequent branches (responsible for the subsequent crosslinking of the materials).^[4] Although the mechanisms of these major “side reactions” are known,^[4] their causes are intrinsic to the system itself (FA + acid) and, therefore, the structural alterations they induce are unavoidable. The thermal resinification of FA follows a very similar pathway. Thus, whereas the ideal FA polymer (PFA) should be a linear, colorless, thermoplastic poly(2,5-furanmethylenes), the real product is a blackish crosslinked solid possessing a very complex structure.

Zhao and co-workers recently published a report in this journal^[5] describing the “surfactant-templated polymerization” of FA at 180 °C for several hours in the presence of toluene and sodium dodecylbenzene sulfonate (SDBS) and claimed that “...single-crystalline PFA nanostructures with wirelike morphology were successfully synthesized”. This claim was based on 1) TEM, SAED, and HRTEM images of the “single-crystal nanowires”, 2) their wide-angle XRD spectrum, 3) their DR-IR spectrum, 4) their MALDI-TOF mass spectrum, and 5) their elemental analysis, which led the authors to state: “...to the best of our knowledge, it is the first report of single-crystalline 1D nanostructures of PFA”. Surprisingly, the authors did not cite the most relevant study of FA polymerization.^[4]

I wish to express serious doubts about their claim that these nanoobjects are in fact poly(furfuryl alcohol), and provide the following arguments to corroborate my stance:

What the authors call a *polymer* of FA is in fact a mixture of *oligomers* with DPs ranging from 6 to 10, judging from the mass spectrum S-3 provided in their Supporting Information. The pattern of this spectrum has no repetitive *m/z* peaks and suggests therefore a mixture of different structures with different molecular weights. This observation casts a major doubt about the capacity of such a mixture to crystallize, let alone to form monocrystals. The authors do not propose any structure for their PFA.

The DR-IR spectrum of the “single-crystalline PFA nanowires” (Figure 2 in the original article^[5]) is interpreted as reflecting the presence of furan rings, some of which are described as 2,5-disubstituted, CH₂ moieties, and OH end-groups. A carbonyl peak, claimed to arise from “the opening of some furan rings by acid-catalyzed electrophilic attack”, was also detected, but it is not clear why this point had any relevance in the system studied by Zhao and co-workers,^[5] which did not involve *any* acidic component, only FA, sodium dodecylbenzene sulfonate, and toluene. The evidence for the presence of furan moieties is dubious, because of the lack of the characteristic strong and sharp band around 1000 cm⁻¹ (ring breathing). Equally dubious is the claim related to 2,5-disubstituted rings because of the lack of the characteristic strong peak at ≈ 800 cm⁻¹. Conversely, the *strongest* band of that spectrum, incorrectly attributed to furan moieties by the authors, appears at ≈ 1170 cm⁻¹, suggesting a considerable contribution from *non-furanic* C–O-bearing moieties. Finally, the strong intensity of the OH band points to an abundance of hydroxyl groups, well above their simple presence as end groups, even for oligomers with DPs of 6–10.

The sentence “The elemental analysis shows that the C/H molar ratio of the products is 1.22, which is in good agreement with the MS results.” is unclear to me and, in any case, does not provide any supporting evidence related to the structure of the “single-crystalline PFA nanowires”.

Regrettably, the authors did not characterize their products by ¹H and ¹³C NMR spectroscopy. Given their low molecular weights, they should have been soluble in solvents such as CD₂Cl₂ and the ensuing spectra would have provided valuable information about their detailed structure.

I wish to make it quite clear that I am not questioning the veracity of the beautiful pictures shown in Figures 1, 4, and 5 of their article. What I am questioning is the fact that they are ascribed to poly(furfuryl alcohol), because I find no evidence in the paper relating those nanoarchitectures to an oligomeric furanic chemical structure derived from FA, which would be sufficiently *regular* to be able to generate one-dimensional single-crystalline polymer nanowires, as claimed repeatedly in the paper, from its title down. I am confident that anyone who has worked with FA will find it difficult to rationalize how a mixture of FA, solvent, and surfactant, heated at 180 °C for several hours in an autoclave, could give rise to macromolecules possessing the structural regularity required to form single crystals.

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