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# A Response to the Comment on "Conformations and Rotational Barriers of Aromatic Polyesters" by Lautenschläger, Brickmann, van Ruiten, and Meier

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In this reply we formulate answers to the three comments made by Jung and Schürmann and hope to show that their approach is partly incorrect and does not lead to the "correct" values for the persistence lengths they are obviously after. As suggested by Jung and Schürmann (J&S) in their comment, we had indeed missed their second paper[1] at the time we wrote our paper. For this and for reasons of clarification we will refer to their first[2] *and* second[1] paper as well as to Jung's thesis[3] wherever appropriate.

We first make a comment on the purpose of the molecular dynamics (MD) simulations that we have presented in our paper.[4] We think it is clear in our paper that *we have not tried to put forward any value for the persistence length* of pHBA (or any other molecule) which we consider realistic. What we have discussed in section 4d of ref 4 is the problem of trying to simulate bulk or dissolved polymer chains (anyway not the chain in vacuum), i.e., the problems of finding a proper potential, the rejection by Jung and Schürmann of eq 1 in the regime they studied pHBA, and the necessity to rely upon more than one independent MD simulation when calculating proper dimensions.

**Ad. 1.** With respect to their remark 1, indeed we have not mentioned that the "0 ps" conformation has been omitted when calculating the average dimensions. In fact our simulation on pHBA was carried out at constant temperature (300 K), and the conformations involved in calculating the averages were those at 6, 12, 18, 24, 30, 36, 42, and 48 ps. The average and rms values for the dihedrals and valence angles involved (see ref 4) were calculated from the central 15 ester linkages for all 8 conformations individually. The 6- and 12-ps values for these averages and rms deviations were equal within statistical error to those at longer simulation times. Moreover, the total energy only fluctuated by a few kilocalories per mole over the time span of the simulation (6–48 ps). The end-to-end distance was calculated from

$$\langle r^2 \rangle = 2a[L - a - a\exp(-L/a)] \qquad (1)$$

by averaging over these eight conformations. Jung and Schürmann argue that the $\langle r^2 \rangle$ value as obtained by applying eq 1 is far too small. We obtained, however, the larger value of 94 Å when starting from a stretched conformation at 0 ps. Now Jung and Schürmann then state that 72 ps was needed to reach the "reference state" as they called it; to this concept we will reply under point 2, but at this point we can already say that (see also ref 4) some of the average and rms deviation of angles we obtained are *very similar* to those reported by Jung and Schürmann, indicating a (at least) partial similarity in potentials and overall dimensions. In this respect we recall that their torsional barriers are likely to be too large, as are those in the consistent valence force field.[4,5] The AMBER force field including the AMBER charges yields 8.6 kcal/mol (see ref 5) for the barrier in benzaldehyde, whereas the experimental value is just below 5 kcal/mol, a very significant difference at ambient temperatures. We stress that to our opinion a more careful look toward the potential parameter set and repeated simulations are at least required to obtain unambiguous and reliable results. Again, when we observed the problems with finding a proper torsional potential, we found we could not put forward any reliable value for, e.g., the persistence length.

**Ad. 2.** Jung and Schürmann's second paper[1] seems to contain some serious misconceptions. They have stated correctly that the applicability of the two equations derived from the Porod–Kratky model depends on the flexibility of the chains. They illustrated this by showing calculated values for three systems, *p*-PHB, *p*-BCO, and PETP. For all three cases they considered 30 repeat units, and it is PETP alone that yielded a persistence length based on eq 1 in reasonable agreement with that calculated from a RIS approach. We think their argumentation is incorrect for the following reasons.

The applicability of the equations following from the Porod–Kratky model[6] are questionable for the systems studied both by J&S and by ourselves since these equations have been derived from a wormlike chain model. This problem has already been discussed by Birshtein in 1974.[7]

Jung and Schürmann stated that a single chain that starts from a fully extended chain, during a molecular dynamics simulation, evolves to a collapsed coil by passing through a "reference molecular dynamics trajectory". In their comment to our paper they seem to identify this state with a state under Θ conditions. Although this might not be too obvious from their two publications, a better description can be found in Jung's thesis.[3] We quote from this thesis, page 35:[10] "Andererseits durchläuft eine Simulation auf dem Weg von der vollständig gestreckten Ausgangskonformation zu den unrealistisch stark zurückgefalteten Endzuständen einen bereich, in welchem die Konformationen denen am Θ-Punkt entsprechen....Mann kann den entsprechenden Teil der Trajektorie dadurch charakterisieren, daß in ihm die Persistenzlänge, welche sich mittels der Auswertung nach dem RIS-Modell ergibt, mit der nach dem Porod–Kratky-Modell sich ergebenden übereinstimmt. Das RIS-Modell berücksichtigt nämlich nur jeweils die Konformation einer Wiederholungseinheit und berechnet aus dieser die "ungestörten Dimensionen" eines Makromoleküls—also ohne ausgeschlossenes Volumen. Das Porod–Kratky-Modell betrachtet hingegen die Konformation der Kette als Ganzes und berücksichtigt somit das ausgeschlossene Volumen. Stimmen die aus diesen beiden Modellen resultierenden Persistenzlängen überein, so spielt der Effekt des ausgeschlossenen Volumens also keine Rolle und die Persistenzlänge entspricht derjenigen bei Θ-Punkt-Bedingungen." First of all, the statement that the Porod–Kratky model accounts for excluded volume is completely wrong.[6] Next, if the intermediate state would indeed correspond to Θ conditions, it has not been proven by J&S that the point in the dynamics simulation where the persistence length according to the RIS and the Porod–Kratky model, respectively, are identical corresponds to the Θ point. Moreover, both models will always yield the same persistence length when the chains can be described as wormlike chains; i.e., the persistence of the chain should be sufficiently high so that there are a large number of segments within a

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persistence length (formally, for a wormlike chain this number is infinite).[6,7]

It can be easily shown that the statement concerning the existence of an intermediate state that corresponds to a Θ state is not true in general. In fact, during the molecular dynamics simulation backfolding of the chain will most likely start at the chain ends which can indeed be observed from our simulations on PET (see Figure 23 of ref 4). Such a situation will never lead to a Θ state in the subsequent steps of the MD, though it might be very well possible that the persistence lengths as calculated according to the RIS and Porod–Kratky models will become equal. Actually the application of both the Porod–Kratky and RIS models for calculating persistence lengths is pretty useless since the chains in Figure 23 of ref 4 show a bimodal distribution of persistence lengths (one being due to the coiled end and the other being related to the extended central part of chain). Moreover, the reference state for which J&S calculated the persistence length and which corresponds to the situation for which $l_{\mathrm{pers}}(\mathrm{RIS}) = l_{\mathrm{pers}}(w)$, is a state at one particular time (53 ps for *p*-BCO and 109 ps for *p*-PHB) in the simulation. However, J&S calculated $l_{\mathrm{pers}}(\mathrm{RIS})$ from the time *span* 72–109 ps for *p*-PHB and 37–53 ps for *p*-BCO (see Table V in their second paper). With respect to PETP we are not able to make any detailed comments because, as J&S say, the chain backfolds already after 32 ps and they have not mentioned over what time span they have calculated the relevant averages. The backfolding is due to the unscreened attractive long-range interactions, and consequently this situation in principle does not refer to the Θ state. Screening of the long-range interactions can overcome this difficulty.[8] According to Jung's thesis, for PETP the relevant averages over angles were calculated from 1280 conformations in a 32-ps time interval. This implies that this interval either started at the 0-ps conformation in order to avoid averaging over conformations from the backfolded regime that starts at 32 ps in their MO simulation, which inevitably leads to too long a persistence length, or if not from 0 ps on the averaging involves conformations in the backfolded regime (beyond 32 ps in their MO simulation).

Finally, as to Jung and Schürmann's remark on the fair comparison of their calculated value with experiment, a wrong combination of short- and long-range interaction potentials can fortuitously lead to a "correct" result. Moreover, the authors of ref 9 for instance, a paper explicitly referred to by Jung and Schürmann, have reported on a *co*polymer and explictly stated in the abstract already that they have worked in a good solvent and that the second virial coefficient was always positive; i.e., the polymer chains were never under Θ conditions which Jung and Schürmann say to simulate. What about the hydrogen bond formation between the polymer and the solvent employed, i.e., 3,5-bis(trifluoromethyl)phenol?

**Ad. 3.** Jung and Schürmann criticize our statement that it is necessary to include interchain interactions to calculate the persistence length of liquid-crystalline polymers: "This is of course not necessary if we are interested in the rectalinearity of a single polymer chain...". Our remark that one should model bulk material originated from the findings that the potentials employed in both studies[1,2,4] tend to give too flexible molecules, even though the torsional potentials are too high. This was a point Jung and Schürmann *have completely neglected* in their studies although it is certainly one of the most important ingredients in these calculations. A better approach how to model these torsional potentials in the aromatic polyesters correctly is about to appear.[5] We have to stress that the persistence length might be substantially different in bulk polymer as compared to the polymer in solution. What precise approach to take will heavily depend on the objective of the study.

The statement by Jung and Schürmann that "it is widely accepted that the mean conformations in the isotropic bulk phase correspond to those in the isotropic Θ solution" is basically true, but this evidently does not justify the link they make by saying that "the dimensions evaluated by us from simulations in vacuo correspond to the Θ-state".

With regard to Jung and Schürmann's final remark, we stress that the search for a correct potential and the request for reliable (statistically acceptable) simulations are not "academic" but are at the basis of reliable computations. Further arguments with respect to the comparison with experimental data can be found in the above.

## References and Notes

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(10) English translation of the part cited from Jung's thesis: "On the other hand, a dynamics simulation starting off from a fully extended chain and evolving toward an unrealistically strong backfolded final state passes through a regime where the conformations are similar to those under Θ conditions....One can characterize the relevant part of the trajectory from the condition that in this part the persistence length, as calculated from the RIS model, equals the value as obtained from the Porod–Kratky model. The RIS model involves taking account of the conformation of single repeat units and subsequently calculates the "unperturbed dimensions" of a macromolecule—i.e., without excluded volume. The Porod–Kratky model thereagainst considers the conformation of the entire chain and therefore accounts for the excluded volume. If the persistence lengths as calculated from these two models agree, the effect of excluded volume is unimportant and the persistence length corresponds to that under Θ conditions."

**Registry No.** pHBA (homopolymer), 30729-36-3; pHBA (SRU), 26099-71-8.