

Reply to Comment on “Polydiacetylene macromolecules in solution: Electric field induced birefringence”

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It is obvious that neither the logarithmic terms can be cancelled nor—even if one considers the log terms as approximately negligible—is it allowed to equal

$$\frac{\langle 1/L \rangle}{\langle 1/L^3 \rangle} \neq \frac{\langle L \rangle^3}{\langle L \rangle} \quad (2)$$

Neglecting polydispersity the field free decay time would yield a rod length $L = 3.8 \mu\text{m}$. This value is not compatible with a “single chain rigid rod” picture, because it is much larger than a fully extended PDA chain of $P_w = 2400$.

A more quantitative estimate of the effect of polydispersity on the presented measurements is hardly possible as long as the exact chain length distribution is not known, even if the above mentioned equations were corrected. The assumption of a Gaussian chain length distribution for PDA is totally unrealistic. The distribution is highly unsymmetric and might be approximated (with still large errors) by a logarithmic normal distribution.

Furthermore, the authors state incorrectly that the measured field free decay time of PDA in the red solution necessarily rules out of the formation of a complex, aggregated structure formed by several PDA chains. Indeed, more complex structures could very well exhibit similar decay times. Dröscher and Smith⁴ measured nearly the same decay times for lamellar single crystals of ethylene oxide-propylene oxide triblock copolymers and interpreted their data in terms of a square lamellar crystal, the field free decay time which is given by⁵

$$\tau = \frac{4\sqrt{2}\eta_0 L^3}{9K_b T} \quad (3)$$

with L the side length of the square lamellar crystal, K_b , T the thermal energy, and η_0 the solvent viscosity.

For $\tau = 0.2$ s, as measured by Lim *et al.*,¹ the side length L is derived roughly as $L = 1.3 \mu\text{m}$.

To avoid misunderstandings, we do not believe that PDA form square lamellar crystals, but this example demonstrates that there are several models to interpret a single decay time and that the data presented are not unique for a rigid rod formation. It seems rather probable that a more complex, aggregated structure with a densely packed, highly oriented center and a few pending flexible ends could exhibit the measured rotational diffusion constant.

We formerly judged these aggregates to consist of 500–700 single chains.⁶ As Lim *et al.*³ have demonstrated, the size of these aggregates strongly depends on the concentration. Very recent static light scattering studies⁷ qualitatively confirmed this effect but still yielded aggregated structures composed of roughly 30 single chains at concentrations as small as 0.47×10^{-3} mg/ml.

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Reply to Comment on “Polydiacetylene macromolecules in solution: Electric field induced birefringence”

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In two recent papers,^{1,2} we used electric field induced birefringence, spectroscopy, and dynamic light scattering to investigate the conformational transition of polydiacetylene macromolecules in solution in toluene. Based on the experimental values obtained for the measured rotational and translational diffusion constants in the two phases, we concluded that the transition is from a rod conformation at low temperatures to a coil conformation ($T > 70^\circ\text{C}$). Based on the concentration independence of the data, in the dilute regime, we conclude that the transition is a single chain phenomenon.

Schmidt and Wegner^{3,4} criticized aspects of the measurements and analysis presented in these papers. They agree that in the high temperature phase the conformation is that of a coil. They also agree that the low temperature phase

is “highly oriented,” i.e., rod-like. They argue, however, that these rods exist only in aggregates and that the transition is driven by aggregation. The evidence we have presented, however, demonstrates that the conformational transition is a single chain phenomenon with subsequent aggregation being expected for long and relatively rigid rods in solution.

As an initial step toward including the effect of polydispersity, we attempted to define average decay times from the data and proceeded with a simple analysis in which we included the effect of polydispersity on the ratio τ_t/τ_r . Schmidt and Wegner³ correctly point out that this treatment is not exact. We have developed a rigorous treatment of the decay of the birefringence $\Delta n(t)$:

$$\Delta n(t) = \int_0^\infty P(L) \Delta n(L, t) dL, \quad (1)$$

where $\Delta n(L, t)$ is the time-decaying birefringence for molecules of length L and $P(L)$ is the (normalized) length distribution. Thus, e.g., with a Gaussian distribution,

$$\Delta n(t) = \frac{\int_0^\infty \Delta n_0(L) \exp \left[-\frac{(L - \bar{L})^2}{2\sigma^2} \right] \exp \left[-t/\tau_R(L) \right] dL}{\int_0^\infty \exp \left[-\frac{(L - \bar{L})^2}{2\sigma^2} \right] dL}, \quad (2)$$

where $\Delta n_0(L) = [2\pi(\Delta\alpha')^2 E^2 / 15nk_B T]^2$, $\Delta\alpha'$ is the anisotropic polarizability per unit length, and all other quantities are defined in Ref. 1. The reader will note that this is *not* equivalent to averaging either the decay time τ_R or the decay rate $1/\tau_R$. Equation (2) implies fast relaxation for short rods and slow relaxation for long rods. Thus, the fit to the long time regime of Figs. 2 and 3 will undoubtedly overestimate the mean length. We have carried out a preliminary numerical analysis of the data using Eq. (2) and find good agreement. A more detailed study is underway. Because of the sensitivity of Eq. (1) to the shape of $P(L)$, we believe the

birefringence decay can be developed as an important method for determining $P(L)$.

Schmidt and Wegner argue that highly oriented aggregates with characteristic dimension of $1.3 \mu\text{m}$ would have a similar decay time. We see no way in which random aggregation of 500–700 macromolecules⁵ could lead to a highly oriented particle with dimensions comparable to the length of a single molecule!

Our conclusion is that the field induced birefringence data confirm the rod-coil transition as a single chain phenomenon. The cluster growth and aggregation which occur prior to gelation is the result of the rod-like conformation, but it is not the cause of the conformational change.

¹K. C. Lim, A. Kapitulnik, R. Zacher, and A. J. Heeger, *J. Chem. Phys.* **82**, 516 (1985).

²K. C. Lim and A. J. Heeger, *J. Chem. Phys.* **82**, 522 (1985).

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⁴M. Schmidt and G. Wegner, *J. Chem. Phys.* **84**, 1057 (1986).

⁵M. A. Müller, M. Schmidt, and G. Wegner, *Makromol. Chem.* **5**, 83 (1984).

Comment on: "Perturbation theory for a polymer chain with excluded volume interaction"

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Recently, Muthukumar and Nickel¹ published an article entitled "Perturbative theory of a polymer chain with excluded volume." It is a remarkable piece of work, extending at one stroke the three previously known terms of the series, which had taken some 30 years to obtain, to six. In addition they provide a proof that the mean square length $\langle R_N^2(w) \rangle$ is free of terms in $\log N$ to all orders. It is on this proof that we wish to comment. Though it is correct, it raises a small, but important question which deserves clarification.

In the proof, the authors employ a power counting argument to demonstrate that in three dimensions no graph contributing to order $n > 2$ can yield such logarithmic terms. An apparent counterexample is the graph shown in Fig. 1,

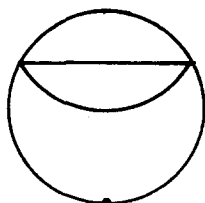


FIG. 1. A third order graph yielding terms in $\log N$.

which, as shown by Barrett and Domb,² is a third order graph yielding terms in $\log N$. If the proof is correct, why do Barrett and Domb find logarithms where Muthukumar and Nickel find none? The answer lies in the way the singular part of the propagators is handled. Barrett and Domb have replaced the propagator by a simpler nonsingular function which is asymptotically equal to it. The power counting argument is not valid in this case. On the other hand, Muthukumar and Nickel have simply subtracted propagators so that the singular parts cancel. This step is crucial as is made clear by the following elaboration of the proof:

If a graph contributes to order n , it may be described as having $2n - 3m - 1$ edges and m \odot configurations (Fig. 2): Each edge is represented by a simple propagator of the form

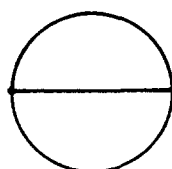


FIG. 2. \odot configuration.