Notes

Comments on the Paper "Dynamic Processes of Optically Induced Birefringence of Azo Compounds in Amorphous Polymers below T_g" by O.-K. Song, C. H. Wang, and M. A. Pauley (*Macromolecules* 1997, *30*, 6913)

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In this paper published recently in *Macromolecules*,[1] the authors criticize some of our previously published data and their interpretation. The subject of investigation is the phenomenon of photoinduced orientation of azobenzene groups in polymeric materials. There are two main points of contention: the first is related to a power dependence or independence of rates of signal (birefringence) growth and relaxation; the second refers to the (in)dependence of signal growth on film thickness. We would like the have the opportunity to reply to this criticism.

Photoinduced birefringence in azo-containing polymers, having the azobenzene groups either bound or just dissolved in the polymer, is the subject of intense investigation in the literature, with a few hundreds of publications since 1987. The mechanism of inducing birefringence, involving photoisomerization and photoselection of orientation, is fairly well understood, as described by the authors of the above-mentioned paper and as reviewed by Dumont.[2] There are still many unknowns, and research into power and temperature dependence of the process is a very welcome addition to the literature. That some of the results may be contradictory is expected, and such discrepancies may actually be the source of progress. However, some of the discrepancies noted in the above paper could easily be explained.

Biexponential Description of the Signal Growth. Song et al. use the same biexponential equations previously used by us[3] to describe the growth of the signal when the laser is on and its decay after the laser has been turned off. The difference is that they use the equations to analyze the signal, while we used it to analyze the birefringence (which is approximately the square root of the signal). In agreement with their findings, we had also concluded that neither the growth of birefringence nor its decay could be described by single exponentials. Within the range of powers used, they note no change in the rate constants and they conclude that the rate is independent of the laser power. We do not question their results, however, we have actually used the power dependence of the writing rate to slow the process to a level where it can be spectroscopically monitored.[4] Using about a tenth of the laser power, the birefringence is photoinduced in about 20 min, instead of seconds, and the "order parameter" growth and decay curves follow the usual birefringence growth and relaxation behavior. Also, some other authors have published data showing a dependence of signal growth on light intensity. Hvilsted et al.[5] showed in their Figure 16 that not only the level of birefringence changes with the laser intensity, the time to achieve the saturation level (and, consequently, the rate constant of the process) is obviously different at different power levels. Even more convincing is a plot of the initial slope of the photoinduced phase difference which is shown to depend linearly on the light intensity.[6]

Power Dependence of the Signal Relaxation. Song et al. claim that in our first paper, published in 1992,[7] we asserted that the birefringence decay depends on the laser intensity. This is probably just a misunderstanding, since we did not assert such a thing, and Song et al. are right: while the laser is off there cannot be any power dependence. We believe that the misunderstanding may have arisen from their treatment of the relaxation curve. There is a residual long term birefringence present in polymer films of relatively high T_g's, which is described by the term E in the biexponential equations used by us and by them. Song et al. say that the E value can be minimized by the introduction of circularly polarized light, which affects the cis content. In fact, introducing circularly polarized light starts the whole photoisomerization process all over, but this time the only photoselection is along the laser direction. While the circularly polarized light is on, the process is much more complicated than just a thermal relaxation, and this is what we analyzed in our first paper,[7] the dependence of the time to "erase" the signal on the power of the circularly polarized laser. We would like to emphasize that this process is analogous to the photoinduced *orientation* process (signal growth, not signal relaxation); the only difference is the polarization of the light, and we did find that the process is dependent on the laser power, as we noted under the first heading.

Film Thickness Dependence. On this analysis, unfortunately, the comparison made is not proper. Song et al. used films of dissolved azobenzenes where the azobenzene concentration is 2 wt %. We[8] used homopolymers containing one azobenzene group per structural unit. Our equivalent concentration was over 80%. Obviously, with similar extinction coefficients, the absorbances in our samples were much higher than those presented in this paper (where the maximum absorbance was 2.312). In fact, with our homopolymers, any film thicker than about 400 nm is opaque; all the light is absorbed. Using our model,[8] a calculation of the phase shift for the absorbances analyzed in this paper shows that, indeed, for this range of thicknesses and

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absorbances, at this azobenzene concentration, there is minimal dependence on the laser power. This appears to be a classical case of comparing apples with oranges. Recent studies[9] of the rates and saturation levels as a function of the writing beam intensity indicate the existence of two types of behavior. The present model is certainly not adequate to explain all the results, and alternative models[6,10] will have to be considered.

Comment on the Cis Lifetime. One other point of contention throughout the paper is that the model proposed by us for photoinducing birefringence does not account for the presence of the cis isomer and is thus incorrect. The authors claim to have demonstrated that the cis lifetimes are long enough to exist during the whole process of orientation and relaxation. While we did not want to put too much emphasis on the interpretation of our biexponential description of the process, we believe that while the laser is on, a photostationary state is achieved, and it does contain a significant presence of the cis isomer (some 10% at least). When the laser is turned off, the cis isomers will isomerize to trans and in the process will reduce the photoinduced orientation by some heat dissipation and probably by their reorientation, as Song et al. mention. The rate of thermal isomerization is directly related to the rate of the "fast" relaxation process. We have actually measured it for our polymers in our working conditions.[11,12]

In conclusion, while the data published by Song et al. are a very useful addition to the knowledge of the azobenzene photoinduced orientation process, most of the criticism of our publications and of our interpretation is not warranted and is mainly based on misunderstanding.

References and Notes

(1) Song, O. K.; Wang, C. H.; Pauley, M. A. *Macromolecules* **1997**, *30*, 6913.
(2) Dumont, M. *Mol. Cryst. Liq. Cryst.* **1996**, *282*, 437.
(3) Ho, M. S.; Natansohn, A.; Rochon, P. *Macromolecules* **1995**, *28*, 6124.
(4) Natansohn, A.; Rochon, P.; Pezolet, M.; Audet, P.; Brown, D.; To, S. *Macromolecules* **1994**, *27*, 2580.
(5) Hvilsted, S.; Andruzzi, F.; Kulinna, C.; Siesler, H. W.; Ramanujam, P. *Macromolecules* **1995**, *28*, 2172.
(6) Pedersen, T. G.; Johansen, P. M. *Phys. Rev. Lett.* **1997**, *79*, 2470.
(7) Natansohn, A.; Rochon, P.; Gosselin, J.; Xie, S. *Macromolecules* **1992**, *25*, 2268.
(8) Rochon, P.; Bissonnette, D.; Natansohn, A.; Xie, S. *Appl. Opt.* **1993**, *32*, 7277.
(9) Labarthet, F. L.; Sourisseau, C. *New J. Chem.* **1997**, *21*, 879.
(10) Schonhoff, M.; Mertesdorf, M.; Losche, M. *J. Phys. Chem.* **1996**, *100*, 7558.
(11) Barrett, C.; Natansohn, A.; Rochon, P. *Macromolecules* **1994**, *27*, 4781.
(12) Barrett, C.; Natansohn, A.; Rochon, P. *Chem. Mater.* **1995**, *7*, 899.

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