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THE CONFIGURATIONAL STEREOCHEMISTRY OF ATACTIC VINYL HOMOPOLYMERS

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Summary: Atactic vinyl homopolymers, synthesized from non-dissymmetric monomers, are produced racemic or enantiomerically pure depending on the length of the polymer chain. The optical inactivity of high molecular weight samples of these polymers arises by a mechanism unknown in small molecules: intermolecular compensation of diastereomers.

Natta[1] pointed out that, ignoring end groups, an atactic vinyl homopolymer is chiral in contrast to its iso- and syndiotactic diastereomers. He suggested that bulk samples of such atactic polymers would be optically inactive because the individual chains would be internally compensated in addition to compensation among different chains[1,2]. Because the hypothesis of "internal compensation" is now understood to be inaccurate[3], and because recent discussions of polymer stereochemistry[4] have disregarded the chirality of atactic vinyl homopolymers, we have attempted to analyze the stereochemistry of these polymers in modern terms.

Bernoullian[5] statistics yield 2^{n-1} different configurational sequences for an atactic vinyl homopolymer of chain length n. The figure presents the average number of each diastereomeric chain in a sample containing 0.1 mole of polymer molecules as a function of the degree of polymerization n. Greater than 10^4 of each diastereomer will be produced for n less than 60. These samples will be conventionally racemic since the probability of finding enantiomeric pairs will be nearly unity. In contrast, for n greater than 70, the number ($\overline{N}_i$, figure) of each polymer diastereomer is far below that statistically necessary to assure the production of enantiomeric pairs. The sample produced will not be racemic, but will consist of a large number of enantiomerically pure diastereomers. This situation is unique in chemistry since symmetrical chemical events leading to nonpolymeric chiral molecules always produce racemic mixtures[6].

The samples containing the shorter chains described above must be optically inactive because they are racemic. In samples of higher degrees of polymerization, individual chiral diastereomers, whether containing equal numbers of opposite configurational centers or not[7], may exhibit nonzero rotations at various wavelengths. Nevertheless, the distribution of rotations from such an enormous number of distinct configurational arrays would likely be symmetrically disposed about zero, and a simple statistical argument predicts optical inactivity at all wavelengths for the bulk sample[8]. This cause of optical inactivity is unknown in small molecules but could fall under the general classification of cryptochirality[6].

The discussion above centers on stereochemical principle. The experimental observation of this hidden chirality depends on the availability of appropriate samples. At present, the separation of chiral vinyl homopolymers has been demonstrated only in conformationally rigid stereoregular polymers[9]. Such separations may be possible in conformationally rigid polymers even in the absence of stereoregularity[10,11].

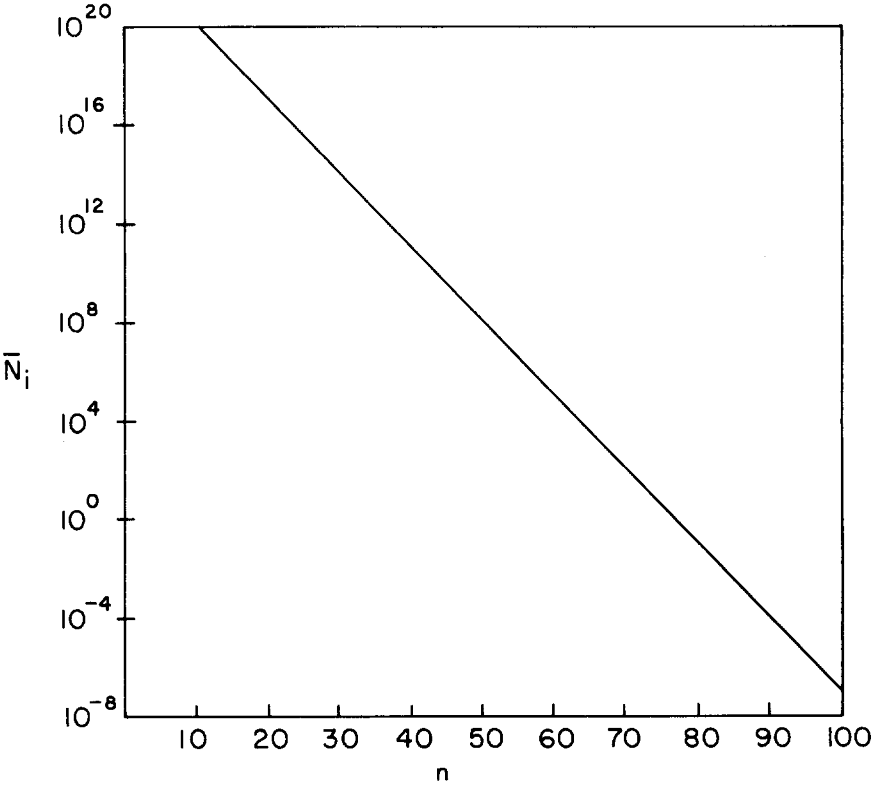

Figure: Plot showing the average number of each diastereomer ($\bar{N}_i$) for various degrees of polymerization (n) for a 0.1 mole sample.

References

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2. The hypothesis of internal compensation derives from the additivity principle of J. H. van't Hoff. See discussion and reference therein in: T. M. Lowry, "Optical Rotary Power", Dover Publ., N.Y., 1964, p. 274ff.

3. For discussion of the problems with the idea of internal compensation see: C.R. Noller, Science, 102, 508(1945); K. Mislow, ibid., 112, 26(1950). For a more extensive treatment see: W. Kauzmann, F. B. Clough, and I. Tobias, Tetrahedron, 13, 57(1961).

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6. K. Mislow and P. Bickart, Israel J. Chem., 15, 1(1977).

7. P. L. Luisi, G. Montagnoli and M. Zandomeneghi, Gazz. Chim. Ital., 97, 222(1967). Leading references to the theoretical connection between optical activity and structure in polymers may be found in: H. DeVoe, J. Chem. Phys., 43, 3199(1965); W. Hug, F. Ciardelli and I. Tinoco, Jr., J. Amer. Chem. Soc., 96, 3407(1974); E. Charney, "The Molecular Basis of Optical Activity", Wiley, N.Y., 1979, Ch. 8, is a general treatment of this subject. "Biophysical Chemistry, Part II", by C. R. Cantor and P. R. Schimmel, W. H. Freeman and Company, San Francisco, Calif., 1980, pp. 416-421.

8. The complete diastereomer population has a zero rotation because it is racemic. The rotations of individual diastereomers in the complete population are distributed about zero with a standard deviation, σ_d. The rotation from a series of random samples, each consisting of N molecules, will also be distributed about zero, the true population mean, with a standard deviation, $\sigma_s = \sigma_d/\sqrt{N}$. For a 0.1 mole sample, $\sqrt{N} \sim 10^{11}$, and σ_s is vanishingly small, for any conceivable value of σ_d.

9. For leading references see: Y. Okamoto, K. Suzuki, T. Kitayama, H. Yuki, H. Kageyama, K. Miki, N. Tanaka and N. Kasai, J. Amer. Chem. Soc., 104, 4618(1982) and references to earlier work on this system. For related research in other polymers and leading references see also: A. J. M. van Beijnen, R. J. M. Nolte, A. J. Naaktgeboren, J. W. Zwikker, W. Drenth and A. M. F. Hazemans, Macromol., 16, 1679(1983).

10. In the light of the discussion above we see that the first attempt to produce an optically active atactic vinyl homopolymer using asymmetric initiators or asymmetric pendant groups could not cause asymmetric induction in the main chain because the diastereomeric chains were already produced enantiomerically pure in a symmetrical environment. Indeed, perfect asymmetric induction in each monomer addition (i.e. 100% configurational excess) would produce the achiral isotactic polymer (ignoring end groups)! See: C. S. Marvel, R. L. Frank and E. Prill, J. Amer. Chem. Soc., 65, 1647(1943); C. S. Marvel and C. G. Overberger, ibid, 68, 2106(1946).

11. We are grateful to Herman Mark for encouraging us to develop these ideas, to Herbert Morawetz for his helpful criticism, and to Ernest Loebl for his useful comments concerning reference 8.

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