Fig. 1.—Rotatory dispersion of dimethyldibenzsuberone in isoöctane: ————— calculated; ● experimental. Two dots connected by a vertical line indicate two separate measurements at the same wave length.

phenomenon may be attributed to the formation of a twisted composite chromophore from the carbonyl and ethylenic (or other π-electronic) moieties; there are indications from ultraviolet spectral and optical rotatory dispersion[5] data that in the α-haloketones, chlorine, bromine and iodine may act in the same manner as the π-electronic groups. As has been noted previously,[6] such *inherently* twisted chromophores (*e.g.*, hexahelicene) will in general be associated with rotational strengths of greater orders of magnitude than are their more symmetric counterparts (*e.g.*, the carbonyl group in saturated ketones).

The above discussion has important implications for structural organic chemistry. It permits a generalization of the octant rule[7] to include β,γ-unsaturated ketones, although the theoretical principles involved are somewhat different than for the case of the saturated alkyl ketones. Moreover, because the contributions to the optical activity associated with the inherent asymmetry so outweigh those that can be attributed to asymmetrically disposed substituents, such as the ring methylene and alkyl groups, the sign of the Cotton effect of the long-wave length transition will be determined solely by the orientation of the unsaturated group with respect to the carbonyl chromophore.[8] In addition, because of the limitations placed on such orientations by the necessity of satisfying reasonable bond distances and bond angles, the handedness of twist (and hence the sign of the Cotton effect) can be correlated with the four far octants of the previously enunciated octant rule,[7] provided that the relative geometry of π-electronic system and carbonyl group is fixed, as in rigid molecules. Conversely, *conformations may be assigned to flexible molecules of this type on the basis of absolute configuration and Cotton effect curve.*

It is an important corollary to our work that for the type of compound under consideration the

shape of the partial rotatory dispersion curve is uniquely determined by the shape of the corresponding absorption curve. This means that in a compound such as that depicted in Fig. 1, where the electric dipole and magnetic dipole transition moments must be colinear, it should be possible to *construct the rotatory dispersion curve* (if the background rotation is not too large) *solely from a knowledge of the absorption curve.*[6,9] Our calculations on this point, indicated in Fig. 1, bear out our contentions.

In a later paper the theory will be discussed in detail and examples will be given which point up the utility of the generalized octant rule.

(9) A. Moscowitz, chapter 12 in ref. 5.

DEPARTMENT OF CHEMISTRY   KURT MISLOW
NEW YORK UNIVERSITY   M. A. W. GLASS
NEW YORK 53, N. Y.
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MINNESOTA   ALBERT MOSCOWITZ
MINNEAPOLIS 14, MINN.
DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY   CARL DJERASSI
STANFORD, CALIFORNIA
                 RECEIVED MAY 20, 1961

EQUILIBRIA BETWEEN LOW-MOLECULAR WEIGHT "LIVING" POLYMERS AND THEIR MONOMER[1]
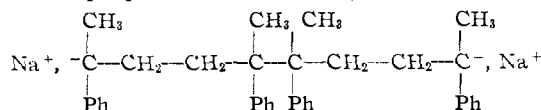
Sir:

Solutions of "living" polymers, *i.e.*, polymeric species retaining indefinitely their ability to grow,[2] must be in equilibrium with their monomer. For a high molecular weight material the equilibrium concentration of the monomer is independent of the degree of polymerization.[3,4] However, this is not the case for a low molecular weight polymer. For each monomer–"living" polymer system there is a minimum degree of polymerization n_0 such that $P_{no}{}^*$ may grow but not degrade.[5] The equilibrium concentration M_e is given, therefore, by the equation

$$k_p M_e \cdot \underset{n \geqslant n_0}{\Sigma P_n{}^*} = k_d \underset{n > n_0}{\Sigma P_n{}^*} \ i.e. \ M_e = K^{-1}(\underset{n > n_0}{\Sigma P_n{}^*})/(\underset{n \geqslant n_0}{\Sigma P_n{}^*})$$

where k_p and k_d are the rate constants of propagation and depropagation and K is the equilibrium constant of the polymerization, $P_n{}^* + M \rightleftarrows P_{n+1}{}^*$.

It was suggested[5] that $n_0 = 4$ for the system α-methylstyrene–poly-α-methylstyrene and this structure was proposed for the "living" tetramer

$$Na^+, \ \overset{CH_3}{\underset{Ph}{-\overset{|}{\underset{|}{C}}}}-CH_2-CH_2-\overset{CH_3}{\underset{Ph}{\overset{|}{\underset{|}{C}}}}-\overset{CH_3}{\underset{Ph}{\overset{|}{\underset{|}{C}}}}-CH_2-CH_2-\overset{CH_3}{\underset{Ph}{\overset{|}{\underset{|}{C}}}}{}^-, \ Na^+$$

To show that the action of metallic sodium on diluted THF solutions of α-methylstyrene produces *the* tetramer, and not a mixture of polymers of $\overline{DP} = 4$, we studied the monomer–tetramer equilibrium. Increasing amounts of the monomer were added to the tetramer solutions and the mixture

(5) C. Djerassi. "Optical Rotatory Dispersion," McGraw-Hill Book Co., New York, N. Y., 1960.
(6) W. Moffitt and A. Moscowitz, *J. Chem. Phys.*, 30, 648 (1959).
(7) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi. *J. Am. Chem. Soc.*, 83, August (1961). See also chapter 13 in ref. 5.
(8) K. Mislow and C. Djerassi, *J. Am. Chem. Soc.*, 82, 5247 (1960).

(2) M. Szwarc, *Nature*, 178, 1168 (1956); M. Szwarc, M. Levy and R. Milkovitch, *J. Am. Chem. Soc.*, 78, 2656 (1956).
(3) H. W. McCormick, *J. Polymer Sci.*, 25, 488 (1957).
(4) D. J. Worsfold and S. Bywater, *ibid.*, 26, 299 (1957).
(5) M. Szwarc. *Makromolekulare Chemie*, 35, 132 (1960).

then was kept at $0°$. After the system reached the state of equilibrium the "living" polymers were "killed" by adding a few drops of water and M_e then was determined by the ultraviolet absorption of α-methylstyrene. The pertinent results are given in Table I.

TABLE I

SYSTEM α-METHYLSTYRENE–"LIVING" α-METHYLSTYRENE "TETRAMER." EQUILIBRIUM ESTABLISHED AT $0°$ IN TETRAHYDROFURAN; COUNTER-ION IS Na^+

Concn. "living" ends = E_0	M_0	M_0/E_0	M_e
	I Series		
0.068	0.0464	0.68	0.0346
.068	.0920	1.35	.0675
.068	.186	2.73	.135
.068	.281	4.13	.209
.068	.372	5.47	.304
.068	.465	6.84	.366
.068	.789	11.60	.543
	II Series		
0.0606	0.0275	0.45	0.0212
.0613	.0470	0.77	.0332
.0564	.0541	0.96	.0414
.0599	.0843	1.41	.0624
.0640	.137	2.14	.0995
.0655	.165	2.52	.114
.0599	.188	3.14	.134
.0617	.312	5.06	.212
.0607	.409	6.74	.302
.0592	.572	9.66	.428
.0613	.594	9.89	.434
.0584	1.115	19.09	.644
.0143	0.394	27.6	.372
.0164	0.985	61.6	.715

For a constant initial tetramer concentration the plot of M_e versus the initial monomer concentration M_0 is shown by Fig. 1. The experimental curve goes through the origin proving that the original "living" polymers were indeed the tetramers. These equilibria eventually are established

$$T^* + M \rightleftarrows P_5^* \qquad K_1$$

$$P_5^* + M \rightleftarrows P_6^* \qquad K_2$$

$$P_6^* + M \rightleftarrows P_7^* \qquad K_3, \text{ etc.}$$
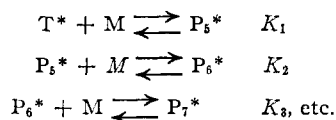
and for each experiment listed in Table I K_1 may be calculated if it is assumed that $K_1 = K_2 = K_3 = \ldots = K_\infty$. The relation[6]

$$(M_0 - M_e)/E_0 = K_1 M_e/(1 - K_1 M_e)$$

is used in such calculations. The results, shown graphically in Fig. 2, demonstrate that the assumption of constant K's is unattainable. However, K_1 may be obtained by extrapolation to $M_0 = 0$ which leads to $K_1 = 4.9$ l./mole. Accepting this K_1 value and assuming now all the remaining K's equal to K_2 the apparent K_2 is calculated[7] as shown again in Fig. 2. The extrapolation gives $K_2 = 4.0$ l./mole. Similarly one calculates K_3 to be between 3.0-3.3 l./mole. For a large M_0 the plots of

(6) A. V. Tobolsky, J. Polymer Sci., 25, 220 (1957); A. V. Tobolsky and A. Eisenberg, J. Am. Chem. Soc., 81, 780 (1959).

(7) K_2 is calculated from the equation $K_2 = M_e^{-1} - \frac{1}{2}K_1$ $\left\{ \sqrt{1 + 4E_0/K_1 M_1 (M_0 - M_e)} - 1 \right\}$.
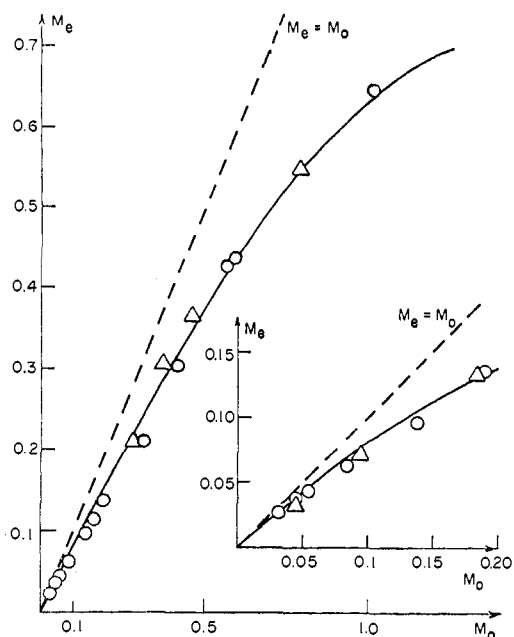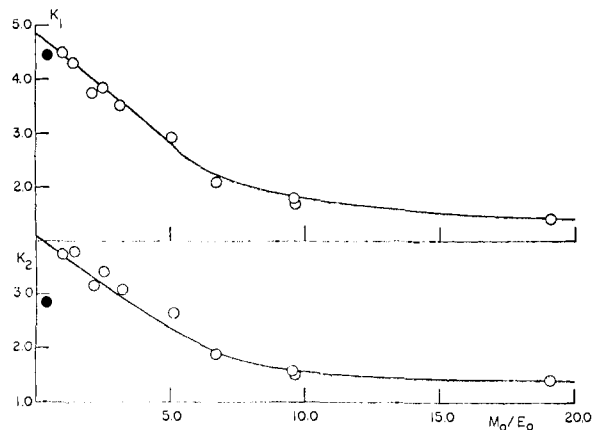

Fig. 1.

Fig. 2.

the apparent K_1's and K_2's approach asymptotically the same value of $K_\infty = 1.5$ l./mole, which agrees perfectly with those obtained from studies of equilibria involving high molecular weight polymers.[3,4]

The variations of K's value with n seems to indicate a dipole–dipole repulsion of the polymer ends. A good agreement is obtained between the observed and calculated K values if the C^-, Na^+ dipole moment is assumed to be 5 debyes.

DEPARTMENT OF CHEMISTRY   A. VRANCKEN
STATE UNIVERSITY COLLEGE OF   J. SMID
FORESTRY AT SYRACUSE UNIVERSITY
SYRACUSE 10, NEW YORK   M. SZWARC

6-METHYLENETETRACYCLINES.[1]   I.   A NEW CLASS OF TETRACYCLINE ANTIBIOTICS

Sir:

Of special interest during recent years have been tetracycline antibiotics with structural modifica-

(1) Alternatively, the 6,13-anhydrotetracyclines, cf. expression XIV.