

Investigation of Chiroptical Properties of Helical Copolymers with Aromatic Side Chains¹

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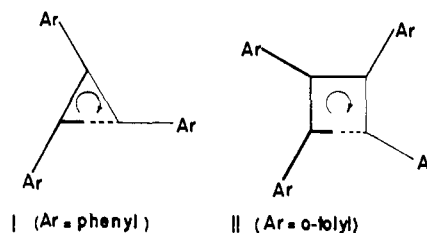
Abstract: Optical and chiroptical properties of the copolymers of styrene and *o*-methylstyrene with optically active α -olefins have been calculated with the DeVoe theory. A statistical distribution along a helical chain and a third neighbor interaction model was assumed. The results agree well with observed CD and uv spectra and confirm the predominant screw sense proposed on stereochemical grounds. The components of the absorptivity and CD tensor along and perpendicular to the helix axis are also given. Our calculations indicate for the first time that the DeVoe theory provides a useful method for the calculation of the CD of polymers.

Among the theories available for the calculation of optical and chiroptical properties of polymers^{3a} the theory of DeVoe^{3b} seems to be one of the most useful. Though derived by classical means, it has been shown to be equivalent to the time-dependent Hartree approximation in quantum mechanics.⁴ One of the prime advantages is the possibility of using empirical absorption data of the monomer analogs as input, including the *shape* of the polarizabilities. The theory gives directly circular dichroism instead of rotational strengths,^{3a} thus allowing a direct comparison with experimental spectra even in regions of overlapping transitions. Yet, in spite of the apparent potential of the method, no examples of the calculation of chiroptical properties of polymers have been published. The original calculations of the absorption spectrum of uracil crystals and the hypochromism of DNA by DeVoe himself⁵ are the only applications of the general method reported in the literature.

Stereoregular (coisotactic) copolymers of styrene or *o*-methylstyrene with optically active α -olefins⁶ seemed to be suitable models for the theory. They show a system of optically active bands between 35 and 55 kK due to the π -electron system of the aromatic chromophore only, no other chromophoric moiety being present which could absorb above 55 kK.^{6,7} The most interesting feature of the CD spectrum is the couplet between 49 and 55 kK which was attributed⁷ to the interactions between the aromatic side chains disposed along a helical chain with a predominant screw sense, a negative couplet⁸ indicating a right-handed screw sense.⁹

Calculations

In the present investigation it was assumed that the relative geometry of the phenyl (or *o*-tolyl) side groups was the same as in a right-handed helix of the corresponding homopolymers in the crystalline state. That is, a 3_1 helix with a 6.65 Å identity period for polystyrene¹⁰ (I) and a 4_1 helix with a 8.20 Å identity period



for poly-*o*-methylstyrene¹¹ (II). The right-handed screw sense was chosen because it is preferred for the isotactic homopolymer of (*R*)-3,7-dimethyl-1-octene^{12,13} which was used as the optically active comonomer. As this last homopolymer assumes in the crystalline state a 4_1 helix¹³ and polystyrene assumes a 3_1 helix, it was expected that this could affect the relative geometry of the phenyl groups in the copolymer. Therefore, calculations for the styrene copolymer were performed also for a 7_2 and 4_1 helix in which the phenyl groups form angles of 103 and 90°, respectively. With this assumption possible conformational irregularities in the copolymer are neglected. The CD due to interactions of the aromatic side chains in irregular sections of the polymer should be small relative to the CD from the ordered regions which we consider.

In the DeVoe theory it is assumed that the optical properties of each monomer are due to its electric and magnetic oscillators. The properties of an aggregate of such monomers are then obtained by assuming that the oscillators of different units are dynamically coupled to all order *via* electrostatic forces. The resulting equations^{3b} for electric and magnetic oscillators must be

(1) VI. Optically Active Hydrocarbon Polymers with Aromatic Side Chains. For paper V, see C. Carlini, F. Ciardelli, L. Lardicci, and R. Menicagli, *Makromol. Chem.*, in press.

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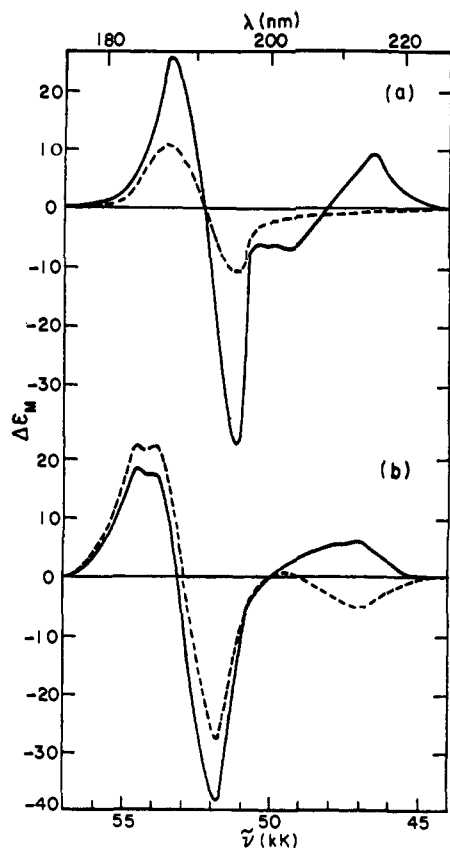
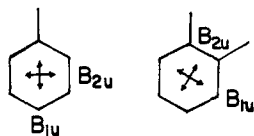


Figure 1. Calculated CD spectra for the AABB (full line) and ABAB (dashed line) tetramers: (a) *o*-methylstyrene in the 4_1 right-handed helix, (b) styrene in the 3_1 right-handed helix ($\Delta\epsilon_M$ is the $\Delta\epsilon$ based on one A unit).

evaluated for each frequency of interest. This was done with a Fortran program written for this purpose. In the present calculation magnetic oscillators were assumed to be absent, as we deal with the ${}^1A_{1g} \rightarrow {}^1E_{1u}$, ${}^1A_{1g} \rightarrow {}^1B_{1u}$, and ${}^1A_{1g} \rightarrow {}^1B_{2u}$ transitions of benzene only. Similarly, the static interaction of the monomeric chromophores with their environment was neglected. For the interaction of the oscillators with each other the point dipole approximation was chosen, with the oscillators placed in the middle of the chromophores. This is certainly a good assumption; the minimum distance between interacting oscillators is 6.5 \AA , and the polarizabilities of the individual chromophores correspond to circular disks of about 2.5-\AA diameter in the wavelength region of interest.

The imaginary part of the polarizability for the oscillators of the aromatic chromophores of the styrene and *o*-methylstyrene copolymer was obtained from the uv absorption spectra of toluene and *o*-xylene, respectively, taken in *n*-hexane.¹⁴ The real part was generated from the imaginary one by a Kronig-Kramers transformation. The direction of the oscillators is indicated below. The band corresponding to the ${}^1A_{1g} \rightarrow {}^1E_{1u}$



(14) "U.V. Atlas of Organic Compounds," Plenum Press, New York, N. Y.

transition of benzene¹⁵ was resolved into two perpendicular components along the directions of the ${}^1A_{1g} \rightarrow {}^1B_{1u}$ and ${}^1A_{1g} \rightarrow {}^1B_{2u}$ transitions, both components centered at the same frequency but with different dipole strengths. The difference was taken to be the dipole strength of the nearby ${}^1A_{1g} \rightarrow {}^1B_{1u}$ transition, assuming that this transition borrows its intensity from the parallel ${}^1A_{1g} \rightarrow {}^1E_{1u}$ component. To account for the remaining polarizability of the chromophores a spherical polarizability was put at the center of each phenyl ring, represented by three perpendicularly oriented damped oscillators with resonance frequencies of 80 kK and dipole strengths of 42 D^2 .

The copolymers experimentally investigated⁷ contain 20 mol % of aromatic units (A) and 80 mol % of (*R*)-3,7-dimethyl-1-octene (B). We assumed a statistical distribution and a third-neighbor interaction model. The absorbance (or circular dichroism) per 1 mol of A of the A/B (1 : 4) copolymer, in the spectral range where B does not absorb and interactions between A and B units can be neglected, is then given by eq 1. K_i is

$$[K] = \frac{5}{4} \frac{1}{625} (K_{AAAA} + 8K_{AAAB} + 4K_{AABA} + 4K_{ABAA} + 48K_{AABB} + 32K_{ABAB} + 16K_{ABBA} + 256K_{ABBB}) \quad (1)$$

the absorbance (or circular dichroism) of the *i*th tetramer with different distributions of the units being specified by the subscripts only when they lead to different K values. The statistics therefore show that among the optically active tetramers those containing AA and ABA sequences are the most probable ones. The calculated CD curves for these tetramers are reported in Figure 1 for both the styrene and *o*-methylstyrene containing copolymers.

Results and Discussion

The uv and CD spectra of the copolymers calculated by using all terms of eq 1 are given in Figures 2 and 3, together with the experimental data. The single components of the absorptivity tensor for light polarized along and perpendicular to the helix axis, and for the CD tensor for light incident along these axes, are reported in Table I. They can be measured with stretched

Table I. The Components of the Absorptivity and Circular Dichroism Tensor Parallel and Perpendicular to the Helix Axis for the *o*-Methylstyrene Copolymer

Spectral region		ϵ_{\perp}	ϵ_{\parallel}	ϵ_{av}
B_{1u}	48 kK ^a	11,000	5,200	9,050
E_{1u}	52 kK	74,000	13,900	54,000
		$\Delta\epsilon_{\perp}$	$\Delta\epsilon_{\parallel}$	$\Delta\epsilon_{av}$
E_{1u}	51.2 kK	-36.1	+29.0	-14.4
	53.4 kK	+30.1	-26.9	+11.1

^a The frequencies refer to the position in the theoretical spectra from which the values were calculated; comparison with experiment should be made taking into account the red shift in the observed spectra (see Figure 2).

films, by flow orientation, or in crystals. For the styrene and *o*-methylstyrene copolymers the size and shape of the calculated couplets in the 54–50-kK region are in

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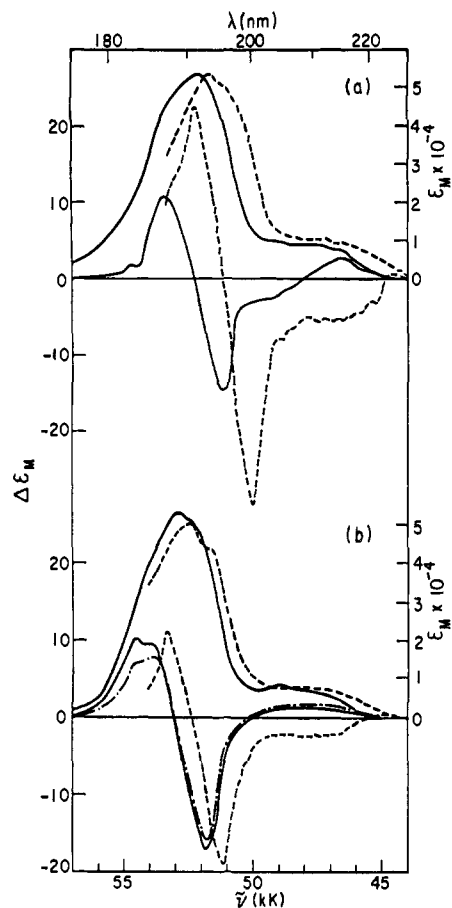


Figure 2. Uv (upper curves) and CD (lower curves) spectra between 57 and 44 kK of (a) the *o*-methylstyrene/(*R*)-3,7-dimethyl-1-octene and (b) the styrene/(*R*)-3,7-dimethyl-1-octene 1:4 copolymers: (---) experimental spectra in *n*-heptane at 27°, (—) spectra calculated according to eq 1 for the 4_1 (a) and 3_1 (b) helices of Figure 1. In b the calculated spectrum for a 7_2 helix is also given (---).

good agreement with the experimental ones. The right-handed screw sense proposed for these polymers on stereochemical grounds⁷ is thus nicely confirmed. Preliminary results for copolymers of 1-vinylnaphthalene with optically active 3,7-dimethyl-1-octene¹⁶ are in equally good agreement with the proposed conformation and observed CD.

The red shifts in both experimental uv and CD spectra of the styrene and *o*-methylstyrene copolymers with respect to the monomeric analogs are only partially reproduced by the calculations. A slight hypochromism of about 3.5% is calculated for both copolymers. This result cannot be checked against experimental data, as the concentration of A units in the copolymers has been determined by nmr and is accurate only to 10–20%. The same uncertainty applies to the absolute values of the circular dichroism.

The calculated amplitude of the couplet is very similar for all copolymers (Figure 2), being 25 for *o*-methylstyrene in the 4_1 helix and 27 and 24 for styrene in the 3_1 and 7_2 helix, respectively. Neither changes of the rotational angle between interacting side chains from 120 to 90° nor differences in the directions of the oscillators on the individual chromophores affect markedly the amplitude of the couplet. The ratio of the negative CD

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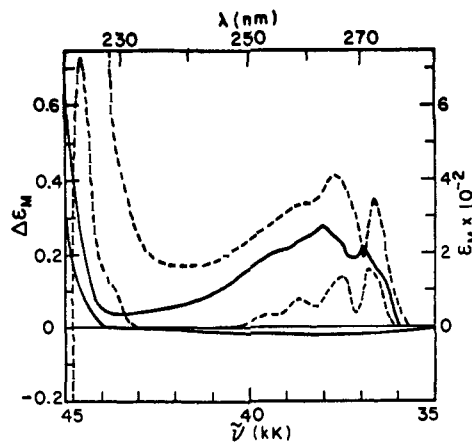


Figure 3. Uv (upper curves) and CD (lower curves) spectra between 45 and 35 kK of the *o*-methylstyrene/(*R*)-3,7-dimethyl-1-octene copolymer: (---) experimental spectra in *n*-heptane at 27°, (—) spectra calculated according to eq 1.

band to the positive CD band goes from 1.7 for the styrene copolymer (3_1 helix) to 1.3 for the *o*-methylstyrene copolymer; these figures agree within 1% with the experimental ones.

The observed CD for the *o*-methylstyrene copolymer is higher than that calculated. A likely explanation is that the distribution of the units is not strictly random, and the content of AA, ABA, and AAA sequences is higher than in eq 1. This would be in keeping with a certain tendency to block formation in the polymerization. As the same should be true for the styrene copolymer, its lower experimental CD with respect to the corresponding *o*-methylstyrene copolymer might be due to a lower predominance of the favored (right-handed) screw sense.⁷

In the region of the ${}^1A_{1g} \rightarrow {}^1B_{1u}$ electronic transition of benzene, the experimental CD shows a negative band with a small positive tail below 45 kK for both copolymers⁷ (Figures 2 and 3). The CD calculated for the *o*-methylstyrene copolymer is in substantial agreement with the sole exception of the intensity of the positive low-energy tail. The ratio of the negative peak to that of the negative couplet peak is also close to the observed magnitude of 1/5.5. These findings prove that the CD and uv spectra can be fully accounted for by the ${}^1A_{1g} \rightarrow {}^1E_{1u}$ and ${}^1A_{1g} \rightarrow {}^1B_{1u}$ electronic transitions in the 57- to 45-kK region. It also indicates for the first time that DeVoe theory permits the calculation of the correct CD of polymers and that it is likely to be useful for more complicated systems like nucleic acids or polypeptides.

For the styrene copolymer the agreement between calculated and observed CD in the B_{1u} region is less good. In this region the sum in eq 1 contains terms of different sign (see Figure 1); therefore, deviations from a random distribution are more critical than in the couplet region. Even if preliminary calculations show that A units separated by more than 3 B units can still interact to give a sizable CD in the 55–45-kK region, their statistical weight is too low to give substantial variation of the CD obtained with the third neighbor approximation. Calculations with different dihedral angles between the aromatic rings and the helical main chain have shown a strong dependence of the CD in the 50–45-kK region on this parameter; this could be responsible for the above discrepancy. In this respect

the geometry of the aromatic units in the *o*-methylstyrene copolymer can be more safely based on X-ray data.¹¹

In our calculations the contribution to the CD from the perturbation of each aromatic chromophore by the chiral surrounding has been explicitly neglected (which also implies $\Delta\epsilon_A = K_{ABBB} = 0$ in eq 1). For the ${}^1A_{1g} \rightarrow {}^1B_{2u}$ transition this is not a valid assumption because of the very low dipole strength of this transition. In ac-

cordance with this, the calculated CD is very small, and the observed CD therefore must be due to the local site symmetry of each aromatic chromophore.¹⁷

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Catalytic Properties of Metal Phosphides. I. Qualitative Assay of Catalytic Properties¹

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Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850, and Contribution No. 2052 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. Received November 13, 1973

Abstract: Preparation of transition metal phosphides supported on alumina was effected by deposition of metal complexes or organometallic compounds on alumina followed by hydrogen reduction and then reaction with phosphine at $\sim 200^\circ$. A variety of catalytic reactions was utilized to probe the surface chemistry of these phosphides. In the H_2 -1-butene reaction, phosphorus introduction onto the metal surface changed the reaction course from hydrogenation to isomerization. With ruthenium phosphide surfaces, there was a relatively selective inter-action of acetylene and hydrogen to give ethylene. Yet under these same conditions ethylene and hydrogen reacted quite exothermally to give ethane. Acetylene and acetylene plus hydrogen appear to give a surface template of considerable stability; this template then appears to direct the chemical reaction. The acetylene-hydrogen produced template may be primarily σ -bonded vinyl groups which pyrolyze to acetylene and hydrogen (and ethane). Acetylene reacts with the metal phosphide surface in a complex fashion as indicated by the flash pyrolysis products from acetylene treated phosphide. These products include methane, ethane, acetylene, monovinylacetylene, butenes, pentenes, and benzene. The presence of benzene in high concentration in the acetylene reaction suggests multicenter surface sites while the lack of activity of the phosphides for butene hydrogenation indicates that the size and extent of surface metal clusters are quite small.

A systematic chemical and physical investigation of the catalytic properties of transition metal phosphides has been initiated. Preliminary studies comprise a probing of the active surface sites in phosphides through a variety of catalytic reactions. This first report presents the procedure for preparation of the metal phosphides on an alumina support and a qualitative comparison of the catalytic properties of the phosphide with the parent metal and in some instances with the metal sulfide. For further comparisons, metal antimonides were prepared and catalytically assayed.

Selection of the phosphides for detailed catalytic studies is based on two major considerations. Firstly, phosphides are a structurally diverse group although a ubiquitous feature in metal-rich phases is a trigonal prismatic M_3P polyhedron.⁴⁻⁶ Catenation of phos-

phorus atoms arises in the phosphorus-rich phases where phosphorus chains run through the structure.⁴⁻⁶ Physical properties range from metallic to near-insulator like in character.⁴⁻⁶ Because there are gross structural and electronic similarities to sulfides, a need to compare catalytic properties of phosphides and sulfides was anticipated. Secondly, an especially attractive feature of phosphides stems from a crude and perhaps invalid analogy to the importance of phosphorus ligands in homogeneous catalysis.⁷⁻¹² Phosphine and phosphite ligands are a common element in catalytically active discrete coordination complexes. These ligands through electronic and steric effects and through their lability play a critical role in enhancing the $16 \rightleftharpoons 18$ electron traverse^{10,11} for the metal complex, a traverse that is the essential feature for "oxidative addition-reductive elimination" steps involving organic substrates.⁷⁻¹² The "ligand lability" feature cannot be important in the

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